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Corrosion inhibition of some metals using lawsonia extract

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Abstract

The aqueous extract of the leaves of henna (lawsonia) is tested as corrosion inhibitor of C-steel, nickel and zinc in acidic, neutral and alkaline solutions, using the polarization technique. It was found that the extract acts as a good corrosion inhibitor for the three tested electrodes in all tested media. The inhibition efficiency increases as the added concentration of extract is increased. The degree of inhibition depends on the nature of metal and the type of the medium. For C-steel and nickel, the inhibition efficiency increases in the order: alkaline < neutral < acid, while in the case of zinc it increases in the order: acid < alkaline < neutral. The extract acts as a mixed inhibitor. The inhibitive action of the extract is discussed in view of adsorption of lawsonia molecules on the metal surface. It was found that this adsorption follows Langmuir adsorption isotherm in all tested systems. The formation of complex between metal cations and lawsone is also proposed as additional inhibition mechanism of C-steel and nickel corrosion.

Keywords: Natural products; Lawsonia; Corrosion inhibitor

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1. Introduction

One of the methods used to reduce the rate of metal corrosion is the addition of inhibitors. Many metals and alloys which used in different human activities are susceptible to different mechanisms of corrosion due to their exposure to different corrosive media. Among these, C-steel, nickel and zinc are very important. One of the methods used to reduce the rate of metallic corrosion is addition of inhibitors. Many studies have been carried out to find suitable compounds to be used as corrosion inhibitors for these metals in different aqueous solutions. These studies reported that there are a number of organic and inorganic compounds which can do that for the corrosion of steel [1–3], nickel [4,5] and zinc [6–8]. Many works were conducted to examine some naturally occurring substances as corrosion inhibitors for different metals in various environments [9–15].

The aim of the present work is to find a naturally occurring, cheap and environmentally safe substance that could be used for inhibiting the corrosion of C-steel, nickel and zinc. The use of such substances will establish, simultaneously, the economic and environmental goals. Lawsonia (henna) is cultivated in Africa and Asia for medicinal and dyeing purposes. The aqueous extract of its leaves, give a stable dyeing which is found on the nails of Egyptian mummies and must be of the oldest cosmetics still in use. Therefore, the aqueous extract of lawsonia leaves is tested as an inhibitor for the corrosion of steel, nickel and zinc in acidic, alkaline and neutral media. Potentiostatic polarization technique is used in this work, for evaluation of the inhibition efficiency.

2. Experimental

C-steel of type L-52, pure nickel and pure zinc were used in the present work. For potentiostatic experiments, a cylindrical rod of each was embedded in araldite leaving an exposed bottom area of $1.0\,cm^2$, and used as working electrode. Each working electrode was polished with different grades of emery papers, degreased with acetone and rinsed with distilled water, before its immersion in the test solution.

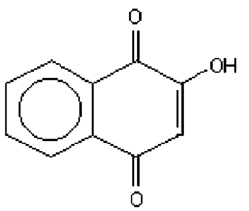
Potentiostatic polarization studies were carried out using EG&G model 363 Potentiostat/Galvanostat. Three-compartment cell with a saturated calomel reference electrode (SCE) and a platinum foil auxiliary electrode was used. For potentiodynamic experiments, the working electrode was held at the potential of hydrogen evolution for 10 min before the starting of the potential sweep, to get rid of any pre-immersion oxide film whice may be present on the surface. The electrode was then disconnected from the potentiostat, gently shaken in the solution to release the hydrogen bubbles attached to its surface and left in the test solution until the attainment of its steady state potential. Once the electrode acquires its steady state potential it reconnected to the potentiostat for the polarization experiment procedure. The inhibition efficiency IE was calculated using the following equation:

$$\mathrm{IE} = [(I - I_\mathrm{i})/I] \times 100$$

where I and I_i are the corrosion rates in free and inhibited solutions, respectively.

All chemicals used for preparing the test solutions were of analytical grade and the experiments were carried out at room temperature, 30 ± 1 °C.

The powder of the crushed leaves is extracted in boiled water for 20 min. After filtration, the water was evaporated from the extract. The solid residue was used for preparation of the tested concentrations of lawsonia. It was reported that lawsonia leaves contain soluble matter, lawsone (2-Hydroxy-1,4-naphthoquinone), resin and tannin, coumarins, gallic acid and sterols [16]. Lawsone amounts to 1.02% in the leaves [17]. The coloring matter is quinone.



Lawsone

3. Results and discussion

3.1. C-steel

Fig. 1 represents the anodic and cathodic polarization curves of C-steel in 0.1 M HCl solutions devoid of and containing different concentrations of lawsonia (L) extract. Inspection of the figure reveals that the presence of lawsonia extract shifts the anodic curves toward the noble direction and the cathodic curves toward active direction. This behavior suggests the inhibitive effect of the additive. The straight

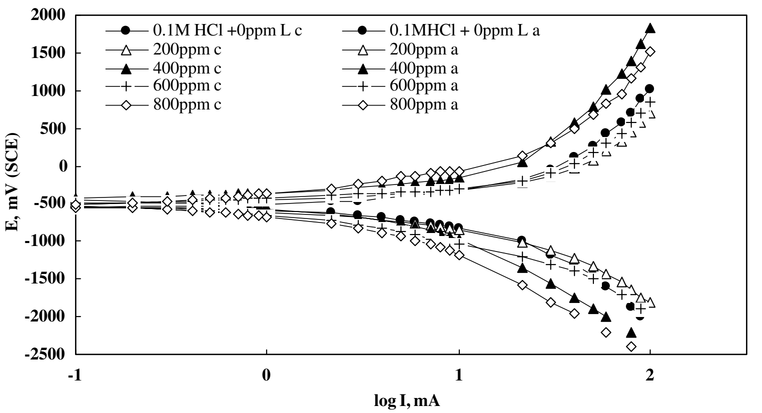


Fig. 1. Anodic and cathodic polarization curves of C-steel in 0.1 M HCl solutions containing different concentrations of (L).

lines which extended along more than one decade of $\log I$, from 0 to about 1.5, were taken as Tafel lines which were used for determination of the corrosion parameters.

The electrochemical parameters of C-steel corrosion in free and inhibited 0.1 M HCl solutions, which are obtained from Fig. 1, are given in Table 1. Inspection of Table 1 reveals that as the concentration of (L) is increased the corrosion potential shifts toward a more noble direction. Moreover, the corrosion current decreases markedly in the presence of (L), and the magnitude of such an effect increases with increasing (L) concentration. These results show the inhibitive action of the extract to corrosion of C-steel in the acidic medium. The calculated values of inhibition efficiencies, IE, in Table 1 indicate the high performance of lawsonia extract as an inhibitor for acid corrosion of C-steel. Moreover, it could be seen that the inhibition efficiency increases with increasing extract concentration.

Further inspection of Table 1 reveals that the values of anodic and cathodic Tafel constants are markedly changed in the presence of lawsonia extract. This result reflects the effect of the extract on both anodic and cathodic reactions. Therefore, it could be concluded that lawsonia extract acts as a mixed inhibitor.

The observed inhibitive action of lawsonia extract could be due to the adsorption of its molecules on the steel surface making a barrier for charge and mass transfer between the metal and the environment. As the concentration of extract is increased, the fraction of steel surface covered by the adsorbed molecules (θ) increases leading to higher inhibition efficiency. Because of such direct relation between the inhibition efficiency IE and (θ), the latter could be estimated using the relation: (θ) = IE/100. For testing the adsorption isotherm obeyed by this system, a graphic relation

Table 1
Electrochemical parameters of C-steel corrosion in different media devoid of and containing different concentrations of (L)

Medium	β_a (mV/decade)	$-\beta_c$ (mV/decade)	E_{corr} (mV)	I_{corr} (mA)	IE (%)
0.1 M HCl+					
0 ppm (L)	360	380	−565	1.9522	–
200 ppm (L)	180	240	−530	0.6309	68.37
400 ppm (L)	160	200	−521	0.2238	88.78
600 ppm (L)	100	190	−511	0.1412	92.92
800 ppm (L)	180	160	−518	0.0841	95.78
3.5% NaCl+					
0 ppm (L)	180	490	−578	0.1166	–
200 ppm (L)	110	360	−550	0.0398	65.85
400 ppm (L)	70	330	−535	0.0223	80.80
600 ppm (L)	80	300	−530	0.0167	85.60
800 ppm (L)	70	330	−520	0.0104	91.01
0.1 M NaOH+					
0 ppm (L)	1360	560	−520	0.1778	–
200 ppm (L)	1140	500	−548	0.1166	34.43
400 ppm (L)	1020	510	−521	0.0859	51.69
600 ppm (L)	980	500	−540	0.0656	63.11
800 ppm (L)	780	470	−480	0.0304	69.56

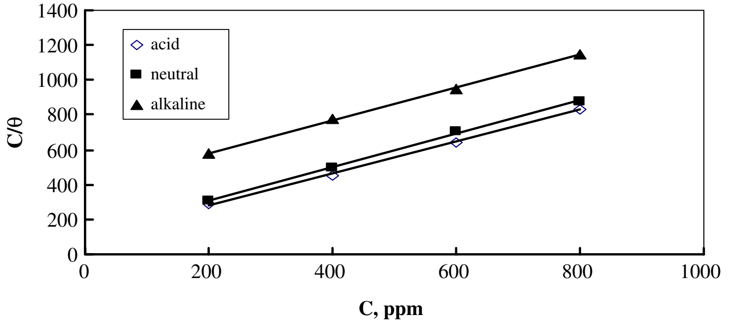


Fig. 2. Adsorption isotherm of lawsonia on C-steel surface in different media.

between the extract concentration C and C/θ is drawn and represented in Fig. 2. Straight line with almost unit slope was obtained indicating that the system follows Langmuir adsorption isotherm. This result indicates that there are no interaction forces between the adsorbed molecules.

The anodic and cathodic polarization curves of C-steel in 3.5% NaCl solutions devoid of and containing different concentrations of (L) extract were obtained (not shown). The electrochemical parameters which are obtained from these curves are given in Table 1. Inspection of the table reveals that the corrosion potential shifts toward less negative values and the corrosion current decreases on addition of increasing concentrations of (L) extract. The effect of (L) extract on both the corrosion potential and current increases as the concentration of (L) extract is increased. These results indicate that (L) extract acts as a good inhibitor for the corrosion of C-steel in neutral medium. Moreover, the data of Table 1 show that both anodic and cathodic Tafel constants change markedly on addition of (L) extract, indicating that it acts as a mixed inhibitor. Fig. 2 illustrates that the adsorption of (L) extract compounds on C-steel surface in neutral medium follows Langmuir adsorption isotherm.

Further inspection of Table 1 reveals that, (L) extract acts as a good inhibitor for the corrosion of C-steel in 0.1 M NaOH solution. Moreover, the addition of (L) extract changes both the anodic and cathodic Tafel constants suggesting the mixed behavior of its inhibition action. The data in Table 1 also show that the inhibitive effect of lawsonia extract on C-steel corrosion depends on the type of medium. Thus, the inhibition efficiency decreases in the following order: acid > neutral > alkaline. Fig. 2 shows that the adsorption of the compounds contained in (L) extract on C-steel surface in alkaline medium, follows Langmuir adsorption isotherm.

3.2. Nickel

The anodic and cathodic polarization curves of nickel in 0.1 M HCl solutions devoid of and containing different concentrations of lawsonia extract are represented in Fig. 3. The straight Tafel lines begin at point corresponding to $\log I$ value of -1.5 and extend up to about 1.0. Inspection of the figure reveals the inhibiting effect of

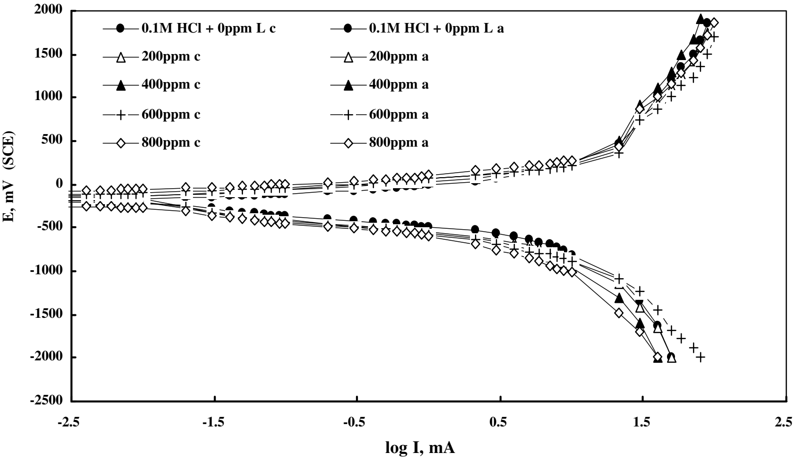


Fig. 3. Anodic and cathodic polarization curves of Nickel in 0.1 M HCl solutions devoid of and containing different concentrations of (L).

the extract. Thus, the anodic curves are shifted toward the anodic side whereas the cathodic ones are shifted toward the cathodic side, upon increasing the added extract concentration.

Polarization curves similar to those in Fig. 3 were also obtained for nickel in both neutral and alkaline solutions. The electrochemical parameters of nickel corrosion in different free and inhibited solutions are determined, from the polarization curves, and given in Table 2. Inspection of Table 2 reveals that the addition of lawsonia extract shifts the corrosion potential toward less active direction and decreases markedly the corrosion rate of nickel in all tested solutions. These results suggest the inhibitive effect of lawsonia extract toward nickel corrosion in different media. The inhibition efficiency increases as the added concentration of the extract is increased. For all the added concentrations of lawsonia extract, the inhibition efficiency decreases in the following order: acid > neutral > alkaline.

Further inspection of Table 2 reveals that the addition of lawsonia extract changes slightly both anodic and cathodic Tafel constants of nickel in acidic and neutral solutions. On the other hand both Tafel constants in the alkaline medium are markedly changed. This result suggests the mixing behavior of the extract.

The adsorption behavior of lawsonia extract is illustrated in Fig. 4 which represents the plot of C/θ against inhibitor concentration C. Straight lines with almost unit slopes are obtained suggesting that the adsorption of lawsonia extract on nickel surface follows Langmuir adsorption isotherm, in all tested media.

3.3. Zinc

The anodic and cathodic polarization curves of zinc in 0.1 M HCl solutions devoid of and containing different concentrations of lawsonia extract are represented

Table 2
Electrochemical parameters of corrosion of Nickel in different media devoid of and containing different concentrations of inhibitor (L)

Medium	β_a (mV/decade)	$-\beta_c$ (mV/decade)	E_{corr} (mV)	I_{corr} (mA)	IE%
0.1 M HCl+					
0.0 ppm (L)	330	490	−230	0.7356	–
200 ppm (L)	290	400	−210	0.2928	60.18
400 ppm (L)	270	420	−200	0.2154	70.71
600 ppm (L)	230	370	−200	0.1258	82.88
800 ppm (L)	220	370	−180	0.0825	88.77
3.5% NaCl+					
0.0 ppm (L)	210	490	−190	0.0316	–
200 ppm (L)	200	480	−160	0.0158	50.0
400 ppm (L)	200	470	−110	0.0116	63.12
600 ppm (L)	200	460	−109	0.0079	74.88
800 ppm (L)	200	480	−70	0.0054	82.88
0.1 M NaOH+					
0.0 ppm (L)	1140	640	−495	0.2818	–
200 ppm (L)	500	340	−420	0.1584	43.76
400 ppm (L)	410	300	−490	0.1166	63.12
600 ppm (L)	430	280	−497	0.0926	67.13
800 ppm (L)	510	270	−630	0.0735	73.91

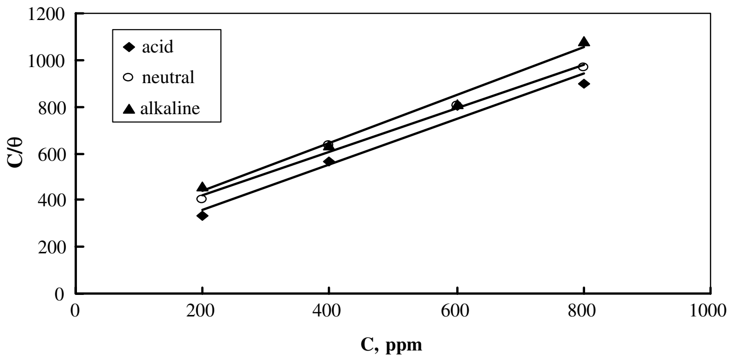


Fig. 4. Adsorption isotherm of lawsonia extract on nickel surface in different media.

in Fig. 5. Similar curves were also obtained for zinc in 0.1 M solutions of NaCl and NaOH (not shown). The straight Tafel lines start at about $\log I$ of 0.5 and extend beyond 1.5. The electrochemical parameters which are determined from the polarization curves are given in Table 3.

Inspection of Table 3 reveals that the addition of lawsonia extract shifts the corrosion potential of zinc toward less active direction and decreases the corrosion current in all tested media. These results suggest the inhibitive effect of the extract toward zinc corrosion in different media. The inhibition efficiency increases as the

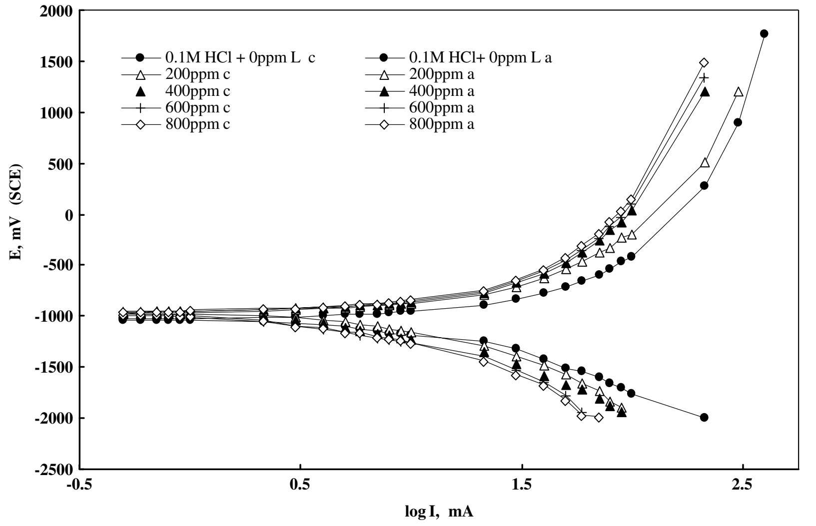


Fig. 5. Anodic and cathodic polarization curves of Zinc in 0.1 M HCl solutions containing different concentrations of (L).

Table 3
Electrochemical parameters of corrosion of Zinc in different media devoid of and containing different concentrations of inhibitor (L)

Medium	β_a (mV/decade)	$-\beta_c$ (mV/decade)	E_{corr} (mV)	I_{corr} (mA)	IE%
0.1 M HCl+					
0 ppm (L)	150	290	−1036	2.8183	_
200 ppm (L)	130	180	−980	1.5848	43.76
400 ppm (L)	130	230	−980	1.1657	58.63
600 ppm (L)	90	240	−975	0.7356	73.89
800 ppm (L)	95	190	−975	0.671	76.19
3.5% NaCl+					
0 ppm (L)	65	290	−1053	0.1711	_
200 ppm (L)	60	460	−1009	0.0304	82.22
400 ppm (L)	60	450	−1010	0.0251	85.32
600 ppm (L)	70	420	−1025	0.0177	89.61
800 ppm (L)	70	440	−957	0.0112	93.44
0.1 M NaOH+					
0.0 ppm (L)	2350	500	−1330	1.8475	_
200 ppm (L)	850	450	−1275	0.9523	47.91
400 ppm (L)	950	500	−1218	0.8577	53.35
600 ppm (L)	850	375	−1169	0.5734	68.96
800 ppm (L)	1100	350	−1195	0.4264	76.92

concentration of the added extract is increased. Moreover, the addition of the extract changes both anodic and cathodic Tafel constants and thus it is considered as a mixed inhibitor.

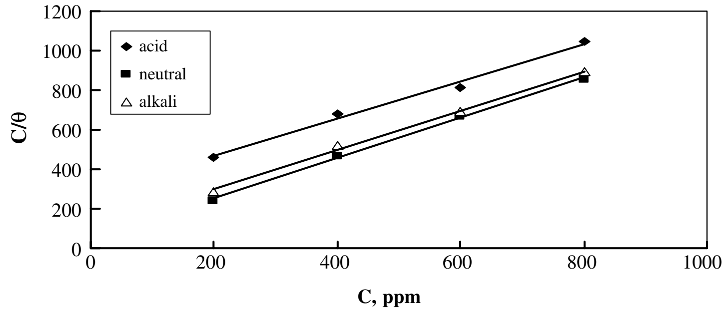


Fig. 6. Adsorption isotherm of lawsonia extract on zinc surface in different media.

It is of interest to note in Table 3 that the inhibition efficiency of lawsonia extract toward zinc corrosion depends on the nature of the corrosive medium and decreases in the order: neutral > alkaline > acid. This media dependence behavior is quite different from that observed above for the corrosion of C-steel and nickel.

Plotting of inhibitor concentration (C) against C/θ gives straight lines with almost unit slopes for all tested media (Fig. 6), indicating that the adsorption of the extract on zinc surface follows Langmuir adsorption isotherm.

3.4. Mechanism of inhibition

The obtained results indicated that lawsonia extract performs a good inhibition for the corrosion of C-steel, nickel and zinc in acidic, neutral and alkaline solutions. Except for zinc metal, the inhibition efficiency increases as the acidity of the corrosive medium is increased. For zinc metal, the highest inhibition efficiency is obtained in neutral solution.

The main components of lawsonia extract are hydroxy aromatic compounds such as tannin and lawsone. The inhibitive action of tannin was attributed to the formation of a passivating layer of tannates on the metal surface [18,19]. Tannins are also known to form complex compounds with different metal cations, especially in the basic media. For this reason they are used in the manufacture of anti-rusting paints and coating. Therefore, formation of tannins complexes may be responsible for the observed inhibition in the alkaline medium.

The other constituent of the extract is lawsone which is present in a relatively higher amount. Lawsone molecule is a ligand that can chelate with various metal cations forming complex compounds. Therefore, the formation of insoluble complex compounds, by combination of the metal cations and the lawsone molecules adsorbed on the metal surface, is a probable interpretation of the observed inhibition action of lawsone. A substantial support for the formation of metal complex is often obtained by conductometric titration [20]. Such procedures were conducted, in the present work, to confirm the formation of metal complexes. Thus, the lawsonia extract was titrated, in separated experiments, by $FeCl_2$, $NiCl_2$ and $ZnCl_2$, in solutions

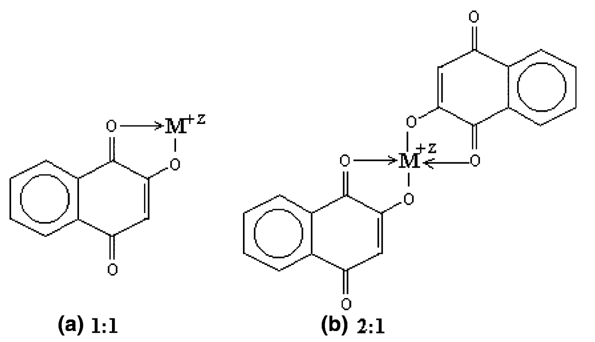


Fig. 7. Forms of M-lawsonia complexes. **M** is Fe, Ni or Zn.

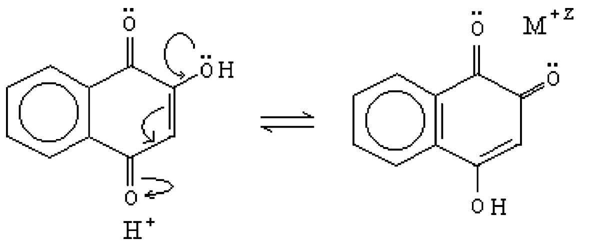


Fig. 8. Forms of lawsone due to electron delocalization.

with different pH values. The obtained results showed the formation of metal complexes with stoichiometric ratios of 1:1 and 2:1 as shown in Fig. 7.

In the acidic medium, delocalization of the lone pair of electrons on hydroxyl group takes place resulting in the rearrangement shown in Fig. 8. Such a rearrangement, in the presence of metal cations, enhances the complex formation reaction. This could be the reason for the observed high inhibition efficiencies in the acidic medium for C-steel and nickel. On the other hand, inhibition of zinc did not show the same behavior, may be due to the low stability of zinc complexes. The stability of complex compound depends on the value of *e*/*r*, where *e* is the effective charge and *r* is the ionic radius of the metal cation [21]. In such manner, the value of *e*/*r* decreases in the order; $Fe^{+2} > Ni^{+2} > Zn^{+2}$. This sequence is in agreement with that of the inhibition efficiency of lawsonia in the acidic medium. However, the inhibition of zinc is higher in the other media. It could be concluded that the inhibition of zinc by lawsone is established by adsorption rather than complex formation.

4. Conclusions

1. The extract of lawsonia leaves acts as a good inhibitor for the corrosion of C-steel, nickel and zinc in acidic, neutral and alkaline media.

2. Lawsonia extract is a mixed inhibitor and its molecules are adsorbed on both anodic and cathodic sites at the metal surface.
3. The adsorption of lawsonia molecules on metal surfaces follows Langmuir adsorption isotherm.
4. Lawsonia inhibit C-steel and nickel corrosion also by forming stable and insoluble complexes.

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