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Chemical and Electrochemical Studies on Expired Lioresal Drugs as Corrosion Inhibitors for Carbon Steel in Sulfuric Acid

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ABSTRACT

Lioresal is a muscle relaxer and an antispasmodic agent, known as Lioresal. The active ingredient is β-(Aminomethyl)-p-chlorohydrocinnamic acid, a racemic mixture of the R,(-) and S, (+) isomers. It affects directly the spinal cord with adverse effects including drowsiness, dizziness, weakness, fatigue, headache, trouble sleeping, nausea and vomiting, urinary retention, or constipation. Therefore, the accumulation of expired or unused Lioresal in our home is so dangerous and harmful for our children. The present work introduces an idea for using expired Lioresal as a corrosion inhibitor for steel in 1.0 M H2SO4. The effect of both concentration and temperature were studied. The inhibition efficiency was found to increase with concentration and decreased with rising temperature. Chemical, electrochemical, and analytical techniques, namely, gravimetric, thermometric, gasometric, acidimetric, AAS, and potentiodynamic polarization were used to evaluate the inhibition action of the expired Lioresal drugs. The inhibition performance is due to the adsorption and adhesion of drugs constituent molecules on the steel surface. The adsorption was found to obey Langmuir isotherm. The surface area available for the anodic dissolution of iron and cathodic hydrogen evolution process diminishes without changing the reaction mechanism. The values of $E_{corr.}$ readings slowly decrease to negative values, showing that these inhibitors are mixed-type inhibitors mainly cathodic inhibitors. The data obtained from different techniques are in good agreement with each other. Electrochemical and analytical Techniques are efficient and accurate in the determination of the corrosion rate and inhibition performance of expired drugs in an aqueous medium.

1. INTRODUCTION

Lioresal medicinal drugs is a muscle relaxers and an antispasmodic agent. Lioresal is given intrathecally directly into the spinal cord or orally by mouth. Lioresal is used to treat muscle pain, spasms, and stiffness in people with multiple sclerosis or spinal cord injury or disease. Lioresal is primarily used for the treatment of spastic movement disorders, especially in instances of spinal cord injury, cerebral palsy, and multiple sclerosis.[1-3] Its use in people with stroke or Parkinson's disease is not recommended.[1-3] Lioresal has also been used for the treatment of alcohol use disorder but evidence from a systematic review conducted in 2018 shows that the evidence of its use as a first-line intervention remains uncertain [32, 49]. Common side effects include sleepiness, weakness, and dizziness [32, 49]. For the mentioned reasons the Lioresal medicinal drugs is dangerous to be left in the environment after the expired date and the accumulation of expired Lioresal medicinal drugs in our homes is dangerous for children. The Lioresal drugs contains promise functional groups which are amino, carboxylic, p-substituted phenyl, and heteroatoms help in the using it as corrosion inhibitor for steel in aqueous acidic environment in addition its have good solubility in that environment. The carbon steel used in the manufacturing of petroleum tanks and petroleum pipeline so addition of inhibitor is important to protect steel from corrosion. The inhibitors considered the best method for protecting of steel pipeline from the inside area from the corrosive petroleum mixture containing corrosive ions like sulfate, chloride, and water mixed with petroleum. The present work introduces an idea for using and application of the expired Lioresal medicinal drug as a corrosion inhibitor for carbon steel in an aqueous acidic environment. Corrosion control of metals and alloys is so important and attractive field for more than 2000 scientists and researchers in the last decade [4-20]. Corrosion inhibitors are the best way to protect steel pipelines boilers and tanks from acidic, alkaline, and aqueous corrosive environments [4-20]. Organic corrosion inhibitors containing nitrogen, sulfur, oxygen, and heteroatoms are widely used for inhibition of steel in different corrosive media [21-26]. The using and applications of the expired drugs as corrosion inhibitors were traced Liok to the 2009's when Reda Abdel Hameed use the expired ranitidine as inhibitor for corrosion of aluminum in hydrochloric acid [27]. In 2011's Reda Abdel Hameed also used expired ranitidine medicinal drugs as inhibitor for carbon steel in acidic environment [28]. Further scientific efforts followed up the Reda Abdel Hameed idea for using and applications of expired drugs materials as corrosion inhibitors for metals and alloys in different corrosive media [29-31]. As a result of the environmental prohibitions and the toxicity of traditional inhibitors, there was an urgent need to use environmentally friendly corrosion inhibitors (green inhibitors). Plastic waste recycling products have been used as green inhibitors for metal corrosion in different media [32-39]. Many reported expired medicines were also used as non-toxic and environmentally friendly corrosion inhibitors [40-47]. The reported expired medicinal drugs that were used as corrosion inhibitors for metals and alloys are the following drugs: expired megavit drugs, expired co-amoxiclav, expired, indomethacin therapeutics, expired voltaren drugs, expired diclofenac, expired phenytoin sodium drug, expired vitamin B6, Omeprazole and expired paracetamol medicinal drugs namely [40-48].

The aim of the present work is to study the effect of expired Lioresal medicinal drugs as ecofriendly and save corrosion inhibitor for carbon steel used in the manufacturer of the petroleum pipeline in 1.0 M H2SO4 acidic environment. Chemical and analytical techniques were used to evaluate the inhibition action of the expired Lioresal medicinal drugs. Effects of drugs dose and temperature were also studied.

2. EXPERIMENTAL

2.1. Materials and Test Solution

The corrosive solution prepared in this study is aggressive 1.0 M sulfuric acid of 0.0 pH, which prepared from analytical grade 98 % H2SO4(Sigma Aldrich) prepared by dilution with double-distilled water and titrated against 1.0 N Na_2CO_3, then diluted to appropriate required pH. Each experiment was performed in aerated stagnant solutions and was repeated at least three times under the same conditions to check the reproducibility and the average of the three replicated values was used for processing of the data. The gravimetric composition of steel materials employed in this study is given in Table 1. It is similar to the composition of the carbon steel used by manufacturer of petroleum pipelines.

Table 1. Gravimetric composition of the used steel materials

Element	**Mn**	**Si**	**S**	**P**	**C**	**Fe**
Composition Weight (%)	0.517	0.201	0.009	0.007	0.157	About 99 %

Lioresal (Lio) tablets medicinal drug is taken from our home as a product of NOVARTIS Pharmaceutical Manufacturing Company(NOVARTIS Pharma AG - Saphad), was used as inhibitor in the form of tablets after expired date by 6 months. It is used as green corrosion inhibitor for steel in the present study. Lioresal is a white (or off-white) mostly odorless crystalline powder, with a molecular weight of 213.66 g/mol. It is slightly soluble in water, very slightly soluble in methanol, and insoluble in chloroform . The active ingredient is: β-(Aminomethyl)-p-chlorohydrocinnamic acid a racemic mixture of the R,(-) and S, (+) isomers. One tablet contains 10mg Lioresal. Each Lioresal tablet contains 61mg Wheat starch (containing gluten). One 10mg tablet contains no more than 6.1 micrograms of gluten. Its chemical structure and composition are given in figure 1.

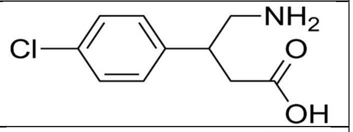
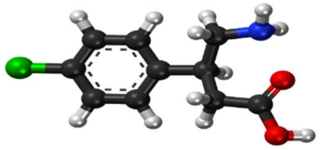
Drug name	Lioresal (Lio)
Molecular Formula	$C_{10}H_{12}ClNO_2$
Drug IUPAC name	β-(4-chlorophenyl)-γ-aminobutyric acid (β-(4-chlorophenyl)-GABA)
Chemical Structure Formula	
3 D Structure Formula	

Figure. 1. Structure and composition of Lioresal Drugs (used as inhibitor)

2.2. Gravimetric studies

The gravimetric method is widely used because it has the advantage of being simple and does not require a complex equipment or procedures. All the experiments were done three times and the recorded data was taken to the medium value with (± 0.1) error. In this study, two types of gravimetric tests were carried out, namely the weight loss measurement and the dosing of the metal passed in solution by atomic absorption spectroscopy.

2.2.1. Weight Loss Measurement

The technique is based on determining the weight loss (WL) of a sample (coupon) of the surface (S) immersed for a time (t) in the aggressive solution. The tests are performed in 100 ml glass vials in non-aerated medium, at room temperature. The immersion time is 8 h, the iron samples are undergoing cleaning with distilled water, degreasing with acetone and drying before and after the immersion. The determination of the corrosion rate W was made from the following relation [21-26]:

$$W = \frac{mi - mf}{St} \qquad (1)$$

where W ($mg.cm^{-2}.h^{-1}$) is the corrosion rate, m_i (mg) and m_f (mg) are the mass before and after exposure to test solution, respectively, S (cm^2): is the surface of area of specimen, t (h): is the immersion time. Regarding the inhibitory efficiency I.E.% and the surface coverage (θ), which represents the part of the metal surface covered by the inhibitors molecules, were calculated according to the following equations [21-26]:

$$\%\ I.E = ([W^o - W]/W^o) \times 100 \qquad (2)$$

$$\theta = ([W^o - W]/W^o) \qquad (3)$$

where W^o and W represent the corrosion rates in the absence and presence of the inhibitors, respectively.

2.2.2. Atomic absorption Spectroscopy (AAS) measurements

Quantification of iron ions contents in corrosive solutions in the absence and presence of the used drugs as corrosion inhibitors was determined by atomic absorption spectroscopy(AAS). Concentration of the ferric ions passed into solution has been performed by using Varian Spectra AA 220 atomic absorption spectroscopy. In order to determine the concentrations of iron ions within corrosive solution both when the inhibitor was absent and present, we dissolved the corrosive medium by aqua regia [45-47].

2.3. Gasometrical Measurements (Hydrogen Evolution Measurements)

The progress of the corrosion reaction was determined by volumetric measurement of the evolved hydrogen. The metal sample was put in a Büchner flask containing the test solution. The flask is sealed with a rubber bung, and from its hose barb protruding from its neck, rubber tubing is connected to the bottom of an inverted measuring cylinder which is fitted above a basin. The cylinder and the basin are filled with distilled water. The evolved hydrogen gradually displaces the distilled water and is collected at the top inside the cylinder, and its volume is measured directly with time [46,47]. The experiment is done in the absence and presence of different concentrations of the tested inhibitor.

2.4. Thermometric measurements

The carbon steel sheet was press cut 2 x2 x 0..1 cm with chemical composition as mentioned in table 1. The measurements were carried out in a Dolvacpyrex flask cover with sheet of aluminum foil. The reaction vessel consists of 50 ml of the acid test solution put into the flask covered with sheets of aluminum foil, corked with a Check temp digital thermometer in place. The metal coupon was introduced into the corrosive solution and quickly covered. Thermometric measurements depend on measuring the temperature variation during the reaction of a metal with test piece with a definite volume of a corroding solution [45-46]. The variation of temperature of the system was monitored with time and the reaction number (RN) is defined as [45-46].

$$\mathbf{RN\ (^0C/min.) = (T_m - T_i) / t_m} \qquad (4)$$

Where T_m and T_i are the maximum and initial temperature respectively, t_m is the time in minutes taken to attain the maximum temperature.

2.5. Acidimetric Measurements

Each experiments were preceded by evaluation for the pH of the prepared solution by a standard BT-500 model pH meter (Germany). The pH was checked for the five concentrations 100, 200, 300,400, and 500 ppm pre and post dipping in the checked solution for 5 hrs. The %IE computed by implementing in the next equation.

$$\mathbf{\%\ I.\ E = 1\ (\ [\Delta H^+]_{inh} / [\Delta H^+]_{uninhi})\ x\ 100} \qquad (5)$$

Where ΔH^+ inh. and ΔH^+ uninhi. are changes in H^+ concentration with and without of the inhibitor, respectively [45-46].

2.6. Measurements of Electrochemical Potentiodynamic Polarization

Electrochemical techniques were utilized to perform the inhibitor's corrosive assessments, which was one of the ways used to evaluate this inhibitor. These tests were carried out with the help of a Potentiostat/Galvanostat (PGSTAT302N) that was tested with Auto lab (NOVA) software, allowing for effective dynamic scanning of coupons via the use of an electrochemical cell, which traditionally consists of three electrodes, to form an encapsulated corrosion cell. The reference electrode was silver/silver chloride (Ag/AgCl), the counter electrode was platinum, the active electrode was carbon iron, and the conduction was done in series. It should be noted that the materials used in the construction of the working electrode are the same as those used in all other measurements [21-25].

3. RESULTS AND DISCUSSION

Lioresal medicinal drugs known as Lioresal is a medication used to treat muscle spasticity such as from a spinal cord injury or multiple sclerosis[1-3]. It may also be used for hiccups and muscle spasms near the end of life. It is taken by mouth or by delivery into the spinal canal. It is believed to work by decreasing levels of certain neurotransmitters. The active ingredient is: β-(Aminomethyl)-p-chlorohydrocinnamic acid (Lioresal), a racemic mixture of the R,(-) and S, (+) isomers. One tablet contains 10mg Lioresal in addition of excipient with known effect: Each Lioresal tablet contains 61mg Wheat starch (containing gluten). One 10mg tablet contains no more than 6.1 micrograms of gluten[1-3].

The chemical composition and constituents of Lioresal tablets makes it highly promise green corrosion inhibitor. In the present work five different analytical techniques were used to evaluate the expired Lioresal drugs as green corrosion inhibitor for steel alloy in 1.0 M sulfuric acid corrosive environment, effect of expired drugs concentrations, reaction temperature, and pH on the corrosion inhibition efficiency were studied. Simple analytical techniques were used in estimation of the corrosion rate and ferrous ion determination in the presence and absence of Lioresal drugs as green corrosion inhibitors in acidic environment of 1.0 M H2SO4 solution. In the present research effect of inhibitor concentration, pH, and temperatures were studied, different techniques were also used in this study are, gravimetric, thermometric, gasometrical, acidimetric, and atomic absorption spectroscopy (AAS) as analytical techniques. The used Lioresal drugs as green inhibitor is symbolized here as LIO. The studied concentrations are 100,200,300,400and 500 ppm.

3.1 Gravimetric Measurements

3.1.1. Effect of Concentrations

Gravimetric techniques were used in determination of the corrosion rate and corrosion inhibition efficiency %I.E of expired Lioresal drugs for the various concentrations of LIO inhibitor after 7 hours of immersion of steel coupon in sulfuric acid corrosive environment of different pH (pH 1,2, and 3). The values of corrosion rate (W) and corrosion inhibition efficiency %I.E are given in table 2. And figures 2. According to gravimetric results the weight loss and consequently the corrosion rate decreases and inhibition efficiency increases by adding the expired Lioresal drugs (LIO) green inhibitor and this behavior was increased by increasing the LIO inhibitor concentrations. It's clear that the inhibition efficiency increase as the inhibitor concentration increases to attain 96 % at 500 ppm. The inhibitory efficiency % I.E and the surface coverage (θ), which represents the part of the metal surface covered by the inhibitors molecules, were calculated according to equations 2 and 3 mentioned in experimental part. Inspection of table 2 reveals that; the values of inhibition efficiency increase with increasing concentration of drug and decreased by lowering pH of the medium. Figure 2 reveals that by increasing the concentrations of expired LIO drugs, the weight loss of carbon steel samples are reduced this clarified that the occurrence of these compounds lowered the dissolution of iron in 1.0 M H2SO4 solution indicating that these drugs act as inhibitors. The relation between weight loss with time in uninhibited and inhibited 1.0 M H2SO4 is linear This illustrates that the absence of insoluble surface films during corrosion. In this case, the inhibitors are first adsorbed onto the metal surface and thereafter impede corrosion either by merely blocking the reaction sites (anodic and cathodic) or by altering the mechanism of the anodic and cathodic partial processes, [21-26]. The maximum inhibition efficiency obtained using 500 ppm of expired Lioresal drugs is 96% which is higher when it compared by the obtained efficiency in the cited references (previous works) [46-47]. this observation may be due to the presence small amount of starch (containing gluten) as additives in the Lioresal drugs which act as promoter and enhance the inhibition efficiency.

3.1.2. Effect of temperature

To elucidate the mechanism of inhibition and to determine the kinetic parameters of the corrosion process gravimetric (weight loss) measurements was performed at different temperatures e.g., 303,313,323,333K. The effect of temperature on the percentage inhibition efficiency of steel in the presence of the inhibitor is graphically represented in figure 3. It is obvious that the values of %I.E decreased with increase in temperature, leading to the conclusion that the protective film of these compounds formed on the steel surface is less stable at higher temperature; which may be due to the desorption of some adsorbed molecules from the surface of the steel at higher temperature due to which greater area of the metal is exposed to the acidic environment [21-26]. All the experiments were done three times and the recorded data was taken to the medium value with (± 0.1) error.

Table 2. Effect of concentration of the LIO drugs on the corrosion parameters of steel in H2SO4 solution of different pH obtained from weight loss measurements at 303 k.

	pH = 1			pH = 2			pH = 3		
Expired drugs Concentrations (ppm)	**W mg cm^{-2} hr^{-1}**	**I.E. %**	**θ**	**W mg cm^{-2} hr^{-1}**	**I.E. %**	**θ**	**W mg cm^{-2} hr^{-1}**	**I.E. %**	**θ**
Blank	9.00	-	-	7.8	-	-	6.9	-	-
100	0.90	90.0	0.90	0.72	91	0.91	0.6	91.3	0.913
200	0.88	90.2	0.902	0.68	91.3	0.913	0.5	92.7	0.927
300	0.85	90.5	0.905	0.65	91.7	0.917	0.43	93.9	0.939
400	0.80	91.1	0.911	0.6	92.3	0.923	0.32	95.5	0.955
500	0.70	92.2	0.922	0.57	93.5	0.935	0.29	95.9	0.959

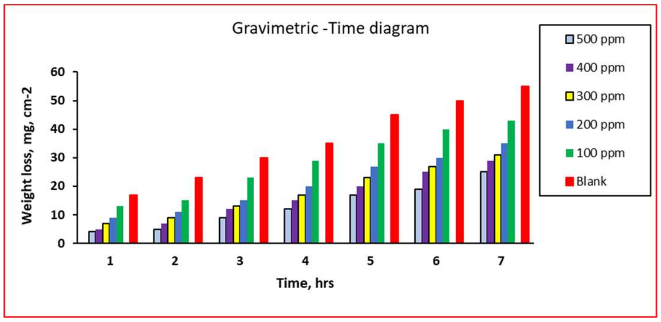


Figure 2. Weight loss of steel as a function in time in 1.0 M H2SO4 in absence and presence of expired LIO drugs as green inhibitor for steel corrosion.

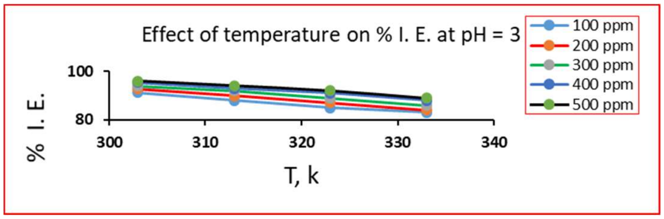


Figure 3. Effect of temperature on % I.E for steel in 1.0 M H2SO4 in the presence of different concentrations of the expired LIO drugs as green inhibitor, data from weight loss at pH = 3.

3. 1.3. Atomic Absorption Spectroscopy(AAS)

Atomic absorption spectroscopy (AAS) produce considerable simplification of procedures for the analysis of aqueous, acidic, or basic solutions, and thereby contribute to a reduction in costs. The industrial application of atomic absorption for routine analysis is divided into four areas: (1) the incoming inspection of all raw materials, (2) production testing, (3) final inspection of all products, and (4) environmental analysis. For rapid analysis during the production process atomic absorption is mainly of indirect value because, as the sequential character of the technique, it cannot be used for complete steel or slag analysis in a two to three-minute period [46,47]. AAS was used for corrosion rate prediction in different media, acidic, basic, and neutral based on fundamental chemistry of the solubility of the corrosion products. The AAS method was applied to the determination of Fe ions in mineral waters and natural waters [45-47]. The iron ions released into solution due to corrosion were detected directly by atomic absorption spectroscopy and their concentration was determined using a calibration curve. The corrosion of the iron samples in solution was accelerated by high salinity, lowering pH, the presence of chloride ions, and temperatures [45-47]. Iron corrosion is a complex process that occurs when iron is exposed to oxygen and humidity and is exacerbated by the presence of chloride ions. The deterioration of iron structures or other components can be costly to society and can be evaluated by following the properties of the corroding material [46]. In the present study the ferrous ions Fe^{+2} concentrations result due to corrosion of steel by acidic H2SO4 of different pH were determined by atomic absorption spectroscopy(AAS). The concentrations of the ions passed into solution has been performed by using AAS in order to determine the concentrations of ferrous ions within corrosive solution both when the green inhibitor was absent and present. The data of AAS are listed in table 3 and figure 4 which shows that the ferrous ion Fe^{+2} concentrations in the corrosive medium were decreased by increasing inhibitor concentration and increased by lowering pH of the solution. Here ferrous ions concentration taken as a function of corrosion rate consequently as the ferrous ions in the solution increases the corrosion rate increases and vice versa. All process is influenced by adding inhibitor. The data in table 3 agree well with results obtained by gravimetric (weight loss) method so that, the tow gravimetric techniques are in good agreement to each other to indicate that, the addition of expired (LIO) drugs inhibit the corrosion of steel in acidic environment and it decreases the iron dissolution process (ferrous ion concentration Fe^{+2}) in this environment at lower pH values.

Table 3. Effect of pH and inhibitor concentrations on ferrous ion concentrations as result of AAS technique

Sample	**Inhibitor Concentration (ppm)**	**Ferrous ion concentrations [Fe^{+2}], ppm**		
		pH = 1	**pH = 2**	**pH = 3**
Blank	**Free**	131	123	109
Expired Lioresal	100	61	49	43
	200	53	39	35
	300	49	31	29
	400	39	25	19
	500	27	19	17

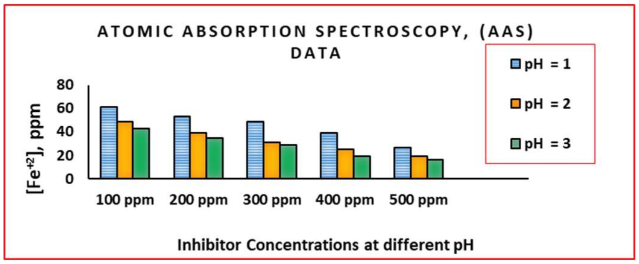


Figure 4. Effect of expired drugs(LIO) inhibitor concentrations on the ferrous ion concentration [Fe^{+2}] in the presence of 1.0 M H2SO4 , data obtained from atomic Absorption Spectroscopy(AAS) at different pH.

3.1.4. Gasometrical technique (Hydrogen Evolution Method)

Gasometrical techniques based on measuring of the evolved hydrogen gas with time in the absence and presence of inhibitors in acidic environment. Gasometrical technique (hydrogen evolution method) was used for evaluation of the expired Lioresal, LIO as green corrosion inhibitors for carbon steel alloy in acidified sulfuric acid solution of different lower pH (pH 1, 2, and 3). Iron metal is an active metal of higher oxidation potential so it replaces the hydrogen of acid easily giving metal salt and the hydrogen evolved in the form of gas.

The volume of hydrogen evolved during the corrosion reaction of iron acidic H2SO4 medium in the absence and presence of different concentrations of the expired LIO drugs as green inhibitor, 100, 200, 300, 400, and 500 ppm. was measured with time at room temperature (30 ^{0}C). The inhibition efficiency was calculated using the following equation [45-47].

$$\mathbf{I.E} = [\,1 - (V_{inh.} / V_{free})]\ \times\ 100 \qquad (6)$$

where, V_{inh} is the volume of hydrogen gas evolved for inhibited solution and V_{free} for the uninhibited solution. The values of evolved hydrogen volumes and inhibition efficiencies at different concentrations of the used green inhibitor, LIO, are shown in table 4. The inhibition efficiency increase with increasing the inhibitor concentration. which indicate that the drug inhibitor compounds act as a good inhibitor for carbon steel in H2SO4 acidic environment [46].

Table 4. Hydrogen volumes and the percentage inhibition efficiency for the steel corrosion in acidic H2SO4 solution of different pH with and without different concentrations of the expired LIO drug at room temperature.

	pH = 1		**pH = 2**		**pH = 3**	
Expired drugs Concentrations (ppm)	**Volume of hydrogen (ml/ cm^2)**	**I.E %**	**Volume of hydrogen (ml/ cm^2)**	**I.E %**	**Volume of hydrogen (ml/ cm^2)**	**I.E %**
Blank	56	-	49	-	38	-
100	10	82.1	8	83.7	5	86.8
200	8	85.7	6	87.7	4.5	88.2
300	7	87.5	5	89.7	3.5	90.8
400	6	89.3	4	91.8	2.0	94.7
500	5	91.0	3	93.8	1.8	95.3

3.1.5. Thermometric Measurements

Reaction number (RN) values are known as a relative measure of retardation of the dissolution process [45-47]. The extent of corrosion inhibition can have expressed in terms of the percentage reduction in reaction number (% RR) given by the following equation [45-47].

$$\%\mathbf{RR} = \frac{\text{RN uninhibited} - \text{R inhibited}}{\text{RN uninhibited}} \times 100 \qquad \textbf{(7)}$$

The thermometric parameters and inhibition efficiency are summarized in table 5. The inhibition efficiency and t_m increase by increasing inhibitor concentrations. The inhibition efficiency and time delay (Δt_m) of the used inhibitor decrease with increasing the pH value in the following order: pH 3 > pH 2 > pH 1 . This order similar that obtained from both weight loss and gasometrical techniques.

Table (5). Thermometric parameters for the steel corrosion in acidic H2SO4 solution of different pH in presence of 500 ppm of the expired Lioresal drugs, LIO, green inhibitor.

Thermometric Parameters	**DOMPY** H2SO4 of pH = 1 With expired Lioresal medicinal drugs used as inhibitor	**DOMPY** H2SO4 of pH = 2 With expired Lioresal medicinal drugs used as inhibitor	**DOMPY** H2SO4 of pH = 3 With expired Lioresal medicinal drugs used as inhibitor
T_m, ^0C	45	42	38
t_m, min.	332	381	397
RN, ^0C/min.	0.0451	0.0314	0.0201
% RR	91	93	95
Δt_m	265	353	371

Table 6 values of %I. E for acidimetric method for expired Lioresal medicinal drugs used as corrosion inhibitor for steel in 1.0 M H2SO4 at 303K.

	pH = 1			**pH = 2**			**pH = 3**		
Expired drugs Concentrations (mg/L)	**ΔH^+ x 10^4**	**θ**	**%I.E**	**ΔH^+ x 10^4**	**θ**	**%I.E**	**ΔH^+ x 10^4**	**θ**	**%I.E**
Blank	96	-	-	89	-	-	82		
100	19	0.80	80.2	16	0.82	82.0	14	0.82	82.9
200	15	0.844	84.4	13	0.85	85	11	0.86	86.6
300	13	0.865	86.5	10	0.89	89	8	0.90	90.2
400	10	0.896	89.6	8	0.91	91	6	0.92	92.7
500	9	0.06	90.6	7	0.92	92	4	0.95	95

3.1.6. Acidimetric measurements

The pH was checked for the five concentrations 100, 200, 300, 400 and 500 (ppm) pre and post dipping in the checked solution for 7 hrs. where [H^+], was computed in each case.

The corrosion rate (W) of steel samples was computed utilizing the next equation:

$$\mathbf{W}\ (\text{mole dm}^{-3}\ \text{cm}^{-2}\ \text{h}^{-1}) = \mathbf{\Delta H^+ / At} \qquad \textbf{(8)}$$

Where [Δ H^+] is the variation between the first and last concentration of H^+, A the surface area of coupon in cm^2 and t, the time in hrs. The %I.E was computed utilizing the next equation [45-47]:

$$\%I.E = 1- \left([\Delta H^{+}]_{inh} \ / \ [\Delta H^{+}]_{uninh} \right) \ x \ 100 \qquad (9)$$

Where ΔH^{+}_{inh} and ΔH^{+} are changes in H^{+} concentration with and without the presence of green inhibitor, LIO, respectively.

The values of surface coverage (**θ**), was computed utilizing the next equation: [46]

$$\theta = 1- \left([\Delta H^{+}]_{inh} \ / \ [\Delta H^{+}]_{uninh} \right) \qquad (10)$$

As shown from the table 6 the values of corrosion inhibition efficiency and surface coverage were increased with increasing the concentration of green inhibitor LIO, due to decreasing of the hydrogen ion concentrations in the medium as inhibitor molecule act as a ligand for protons in acidic media[46,47].

3.1.7. Electrochemical Potentiodynamic Polarization Measurements (EPDP)

Figure 5. illustrates the polarization curves for carbon steel electrodes in 1.0 M H2SO4 solution with and without different concentrations(100-500 ppm) from the expired Lioresal (Lio) drugs which were used as corrosion inhibitors for carbon steel in 1.0M sulfuric acid. The electrochemical corrosion parameters such as the values of cathodic (β_c) and anodic (β_a)Tafel slopes were determined from the linear region of the polarization curves. , The values of corrosion current density (I_{corr}) were computed from the intersection of the anodic and cathodic lines with the corrosion potential ($E_{corr.}$). Inspection of Table 1. It is concluded that the values of anodic (β_a) and cathodic (β_c) Tafel slopes are approximately changed slightly proving that these compounds acted as mixed inhibitors.

Without changing the reaction mechanism, the surface area available for the anodic dissolution of iron and cathodic hydrogen evolution process diminishes. $E_{corr.}$ readings slowly decrease to negative values, showing that these inhibitors are mixed type inhibitors mainly anodic inhibitors [47,48]. The values of $I_{corr.}$ drop, and therefore the values of IE's increase, showing that these compounds have an inhibitory impact on carbon steel corrosion in a 1.0M H2SO4 solution corrosive environment.

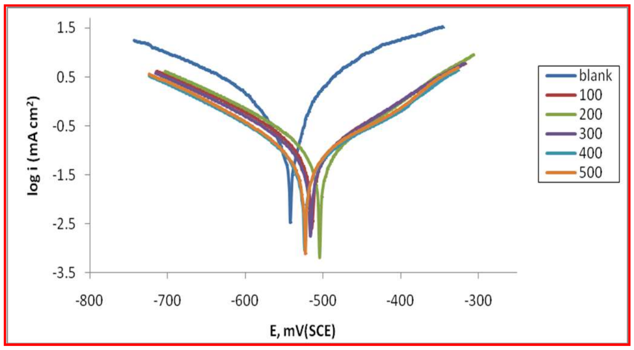


Figure 5. The polarization curves of carbon steel in 1.0M H2SO4 solution containing different concentrations in ppm (100-500 ppm) of the expired Lioresal (Lio) inhibitor.

The inhibition efficiency is given from the following equation [23-25]:

$$\%IE = 1- \ (I_{inh} / I_{uninh}) \ x \ 100 \qquad (11)$$

Where: I_{uninh} and I_{inh} ae the corrosion current densities in the absence and presence of inhibitor respectively.

Table7. The electrochemical corrosion parameters were obtained from the polarization measurements for the carbon steel in a 1.0 M H2SO4 solution containing different concentrations of expired Lioresal (Lio) inhibitor.

Inhibitor Sample	**Inhibitor concentrations ppm**	**$-E_{corr}$ mV**	**I_{corr} mA cm^{-2}**	**β_a $mVdec^{-1}$**	**β_c $mVdec^{-1}$**	**% IE**	**θ**
Blank	Free	492	1.9	89	102	--	--
Expired Lioresal (Lio) inhibitor	100	513	0.3	105	117	84.2	0.842
	200	519	0.2	109	125	89.5	0.895
	300	527	0.17	115	129	91.1	0.911
	400	539	0.13	125	137	93.2	0.932
	500	543	0.10	129	141	94.7	0.947

3.1.8.The Adsorption Isotherm Model

The charge and nature of the metal surface, electrical features of the metal surface, adsorption of solvent and other ionic species, temperature of the corrosion reaction, and the electrochemical potential at the solution-interface all play a role in the adsorption process. In the derivatives, the presence of electro repelling or electro donating groups. Gravimetric measurement is used to find out the values of surface coverage (θ) at different drug concentrations to explain the best fit isotherm for the adsorption process. The results are best fitted by Langmuir adsorption isotherm according to the following equation [21-26]:

$$C_i / \theta \quad = \quad 1/ K_{ads} + C_i \qquad (12)$$

where, K and C are the equilibrium constant of adsorption process and the drug concentration, respectively [21-26].
Plotting C/θ versus C gave straight line, as shown in figure The straight line with approximately unit slope value has an intercept of 1/K. The standard free energy of adsorption $\Delta G°_{ads}$ is calculated using the equation [21-30]:

$$K_{ads} = 1/55.5 \exp \left(-\Delta G_{ads} / RT\right) \qquad (13)$$

Where K_{ads} is the adsorption equilibrium constant, 55.5 is the dose of water in the bulk of solution in mole/liter, T is the absolute temperature and R is the gas constant. The calculated value of ΔG_{ads} is -36.47 kJ/mol. The negative value of $\Delta G°_{ads}$ indicates that the adsorption process of drug molecules on the metal surface is spontaneous [21-26]. On the other hand, the obtained value is less than the threshold value of -40 kJ/mol required for chemical adsorption, which indicates that the mechanism of adsorption is a physical [21-26]. It is generally accepted that the studied expired drug, compound inhibit the corrosion process by adsorbing at the metal/solution interface. In addition, it is believed that the formation of a solid organic molecule complex with the metal atom has received considerable attention [21-26].

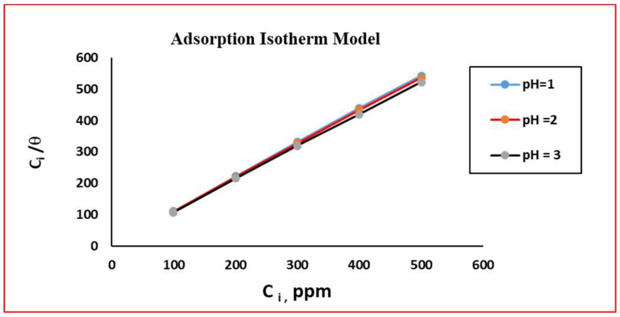


Figure 6. Langmuir adsorption isotherm for carbon steel in 1.0 M H2SO4 inhibited by the used expired LIO inhibitor at 30ºC.

4. CONCLUSIONS

Expired Lioresal medicinal drugs considered as green corrosion inhibitor as it is a nontoxic inhibitor to human specially at very low concentrations, in addition, prevention of the steel from corrosion is of environmental importance, as corrosion a terrible waste of both natural resources and money. The corrosion inhibition efficiency increase by increasing LIO inhibitor concentrations reach to 96 % at 500 ppm. As soon as the Fe^{+2} ion decreases.

The data of AAS show that the ferrous ion Fe^{+2} concentrations were decreased by increasing inhibitor concentration and increased by lowering pH of the solution. The volume of hydrogen evolved during the corrosion reaction of steel in acidic H2SO4 medium was decreased by increasing expired LIO inhibitor concentrations which may due to inhibitor compounds control the hydrogen evolution reaction. The reduction in the reaction number and time delay (Δt_m) of the expired LIO inhibitor decrease with increasing the pH value in the following order: pH 3 > pH 2 > pH 1. Results of acidimetric method indicate that the hydrogen ion concentrations decreased in the inhibited medium as inhibitor molecule act as a ligand for protons in acidic environment.

The surface area available for the anodic dissolution of iron and cathodic hydrogen evolution process diminishes without changing the reaction mechanism. The values of $E_{corr.}$ readings slowly decrease to negative values, showing that these inhibitors are mixed type inhibitors mainly cathodic inhibitors. The values of $I_{corr.}$ drop, and therefore the values of IE's increase, showing that these compounds have an inhibitory impact on carbon steel corrosion in a 1.0M H2SO4 solution corrosive environment.

The data obtained from different analytical techniques are in good agreement to each other with (±2) to indicate that the addition of expired Lioresal, (Lio) drugs inhibit the corrosion of steel in acidic environment and decrease the iron dissolution process in this environment. So expired Lioresal, LIO, drugs act as green corrosion inhibitor. The inhibition due to adsorption and adhesion of expired Lioresal, (Lio) drugs molecules and its constituent's additives on the metal surface by chemisorption mechanism, the adsorption was found to obey Langmuir isotherm.

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