Application of expired Co-amoxiclav medicinal drugs for corrosion inhibition of steel alloys used in petroleum industry in acidic environment

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Abstract

Co-amoxiclav medicinal drug is one of the famous antibiotics used for the treatment of several bacterial infections. Large quantities of expired Co-amoxiclav accumulated worldwide in the environment making continuous hazards for biological systems and causing pollution for underground water when disposed in the environment. The present research introduces the idea for the application of expired Co-amoxiclav ampoules in the corrosion inhibition of steel alloys in an aqueous acid environment, namely 1.0 M H₂SO₄. Expired Co-amoxiclav ampoules were used to control the corrosion of steel alloys in this aqueous acid environment. Techniques such as gravimetric, atomic absorption spectroscopy (AAS), acidimetric, gasometric, and thermometric technique were employed in the present study. The effects of drug concentrations, reaction temperature, and pH on the corrosion inhibition efficiency were studied. Adsorption studies indicate that it obeys the Langmuir adsorption isotherm. The techniques used are in good agreement with each other ($\pm 2\%$) and indicate that expired Co-amoxiclav drug can be used as potential nontoxic green corrosion inhibitor for steel in industrial field at low pH. The Co-amoxiclav antibacterial drug is considered as a multifunction green corrosion inhibitor for steel in the petroleum field.

Keywords: steel, Co-amoxiclav, green inhibitors, gravimetric, thermometric, AAS, acidimetric.

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Introduction

The worldwide use of medicinal drugs is dramatically increasing with a continuous increase in population and with continuous increases of the environmental pollution as more diseases appear every day. As a result, large quantities of expired drugs accumulate in our homes and in the environment, which is a hazard for both human health and environment as they reach the underground water. Co-amoxiclav is a famous antibiotic used for the treatment of many bacterial infections. It is a chemical mixture of amoxicillin and potassium salt of clavulanic acid. Co-amoxiclav is widespread in our homes, so it is dangerous to be left in the environment after it expires, since it is harmful to the children. Generally, drugs are among the most famous chemical materials for daily and continuous use in our homes. Expired drugs are considered as dangerous materials in the environment as they cause the death of more than 2000 children every year. In some countries expired drugs were disposed into holes in a desert thus leading to the pollution of underground waters by harmful materials. All these observations took the attention of Reda Abdel Hameed to search for new applications for expired drugs. The use of expired drugs as corrosion inhibitors for metals was introduced by Reda Abdel Hameed in 2009 and 2011 [1, 2] when he used expired ranitidine drugs as eco-friendly potential non-toxic corrosion inhibitors for aluminum in sulfuric acid solution. His works attracted the attention of other scientists who studied many expired drugs as corrosion inhibitors. Further, the research of unused drugs has been focused on corrosion inhibition of carbon steel in various corrosive media [3–7]. In the past decade, scientific efforts in the field of corrosion inhibition were focused on eco-friendly and potentially non-toxic corrosion inhibitors known as green corrosion inhibitors. The most recent efforts are the use of expired drugs to solve not only the problem of solid waste accumulations but also to introduce a potential nontoxic inhibitor to save energy, money consumed in the preparing or sailing a chemical corrosion inhibitor, since about 7% of the total income were consumed for the corrosion inhibition of metals and alloys in industrial fields [8–12]. From the green chemistry point of view, the use of expired drugs as inhibitors helps one to 1) avoid the toxic effect of some inhibitors to humans; 2) save the energy and organic solvents used in the synthesis of corrosion inhibitors; 3) prevent waste accumulation by using drugs as inhibitors; 4) avoid the accumulation of drug waste which is dangerous to the children and groundwater. So the expired drugs considered as green inhibitors, because there is not any waste for the process of using drugs as inhibitors as it was taken directly from the drug market to the laboratory where they are used in their pharmacological form which is safe for humans and the environment in very small doses. Corrosion is a process of oxidation of metals by the environment, leading to corrosion products and destruction of the metal lattice. This phenomenon results in a terrible waste of both natural resources and money. So the corrosion control of steel is of technical, economical, and environmental importance. As steel is corroded, it changes from a hard and useful metal to a corrosion product which is hazardous to the environment, so the corrosion control of steel is also considered as a green process. The damage by corrosion results in high costs for maintenance

and protection of the materials used. In the previous works [13, 14], expired paracetamol and expired Indomethacin were studied as corrosion inhibitors for steel in an acid sodium chloride-containing corrosive environment using chemical and electrochemical techniques. Analytical and electroanalytical methods are highly effective and widely used for the evaluation of numerous materials as corrosion inhibitors for metals and alloys in many different aqueous corrosive environments containing acids, alkali, and aqueous salts [15–30]. In the present work, five different analytical techniques were used to estimate the expired ampules of Co-amoxiclav medicinal drug as a green corrosion inhibitor for steel alloy in 1.0 M sulfuric acid corrosive environment. The effect of expired drug concentration, reaction temperature, and pH on the corrosion inhibition efficiency was studied. A survey of literature shows that Co-amoxiclav is a combination consisting of amoxicillin, a β -lactam antibiotic, and potassium clavulanate, a β -lactamase inhibitor. It is specifically used for otitis media, strep throat, pneumonia, cellulitis, urinary tract infections, and animal bites. It is taken by mouth or by injection into a vein. Many branded products indicate their strength as the quantity of amoxicillin. Co-amoxiclav 250, for example, contains 250 mg of amoxicillin and 125 mg potassium salt of clavulanic acid [31, 32]. From the literature, we can conclude that the expired Co-amoxiclav drug is highly promising as a corrosion inhibitor for steel in an acid environment.

2. Experimental

2.1. Materials and Test Solution

The corrosive solution used in this study is 1.0 M sulfuric acid with pH 0.0. It was prepared from analytical grade 98% H_2SO_4 (Sigma Aldrich) by dilution with double-distilled water and titrated against 1.0 M Na_2CO_3 , then diluted to the 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 further data processing. The mass composition of the steel material employed in this study is given in Table 1. It is similar to the composition of the carbon steel used in the manufacturer of petroleum pipelines.

Table 1. Gravimetric composition of the steel material used.

Element	Manganese	Silicon	Sulphur	Phosphorus	Carbon	Fe
Composition Weight (%)	0.517	0.201	0.009	0.007	0.157	Rest

Co-amoxiclav drug taken from our home as a product of Glaxo Smith Kline (GSK) company, UK, was used as the inhibitor in the form of ampules 6 months after the expiration date. It was used as a green corrosion inhibitor for steel in the present study and its chemical structure and composition are given in Figure 1.

Drug constituent name	Content of each constituent	Drug chemical structure
Amoxicillin	250 mg
The potassium salt of clavulanic acid	125 mg	

Figure 1. Structure and chemical composition of Co-amoxiclav drug.

2.2. Gravimetric studies

The gravimetric method is widely used because it has the advantage of being simple and does not require complex equipment or procedures. All the experiments were done three times and the recorded data was taken to the mean value with (± 0.1) error. In this study, two types of gravimetric tests were carried out, namely the measurement of the weight loss and the amount 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) with a surface (S) immersed for a time (t) in the corrosive solution. The tests are performed in 100 ml glass vials in a non-aerated medium, at room temperature. The immersion time is 8 h. The steel samples undergo cleaning with distilled water, degreasing with acetone, and drying before and after the immersion. The corrosion rate W was determined from the following relation (1):

$$W = \frac{m_i - m_f}{St} \quad (1)$$

Where: W ($\text{mg} \cdot \text{cm}^{-2} \cdot \text{h}^{-1}$) is the corrosion rate; m_i (mg) and m_f (mg) are the mass before and after exposure to the test solution, respectively; S (cm^2) is the specimen's surface area; and t (h) is the immersion time. The inhibitory efficiency $IE\%$ and the surface coverage (θ), which represents the part of the metal surface covered by the inhibitor molecules, were calculated by to the following equations:

$$IE\% = \left(\frac{[W^0 - W]}{W^0} \right) \cdot 100 \quad (2)$$

$$\theta = \left(\frac{[W^0 - W]}{W^0} \right) \quad (3)$$

Where W^0 and W represent the corrosion rates in the absence and presence of the inhibitor, respectively.

2.2.2. Atomic Absorption Spectroscopy (AAS) measurements

The amount of iron ions in the corrosive solutions in the absence and presence of the drug used as the corrosion inhibitor was determined by atomic absorption spectroscopy (AAS). The concentration of the ferrous ions passed into the solution was determined using a Varian Spectra AA 220 atomic absorption spectroscope. To determine the concentrations of iron ions in the corrosive solution both when the inhibitor was absent and present, we diluted the corrosive medium with *aqua regia* [13].

2.3. Acidimetric Measurements

Each experiment was preceded by estimating the pH of the prepared solution by a standard BT-500 model pH meter (Germany). The pH was checked for five concentrations, namely 50, 100, 150, 200, 250, and 300 ppm, pre and post-dipping in the tested solution for 5 hrs. The $IE\%$ value was computed by the following equation:

$$IE\% = \left(1 - \frac{[\Delta H_{inh}^+]}{[\Delta H_{uninh}^+]} \right) \cdot 100 \quad (4)$$

Where ΔH_{inh}^+ and ΔH_{uninh}^+ are the changes in H^+ concentration with and without the inhibitor, respectively [33].

2.4. 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 was sealed with a rubber bung, and from its hose barb protruding from its neck, rubber tubing was connected to the bottom of an inverted measuring cylinder which was fitted above a basin. The cylinder and the basin were filled with distilled water. The evolved hydrogen gradually displaced distilled water and was collected at the top inside the cylinder, then its volume was measured directly over time [17]. The experiment was performed in the absence and presence of various concentrations of the tested inhibitor.

2.5. Thermometric measurements

Carbon steel sheet with a chemical composition mentioned in Table 1 was press cut into 2x2x0.1 cm samples. The measurements were carried out in a Dolvacpyrex flask covered with an aluminum foil sheet and corked with a check temp digital thermometer in place. The reaction vessel contained 50 ml of the acid test solution. The metal coupon was introduced into the corrosive solution and quickly closed. Thermometric measurements depend on measuring the temperature variation during the reaction of a metal with a test piece with a definite volume of a corrosive solution [13, 17]. The variation of temperature in the system with time was monitored and the reaction number (*RN*) was determined as [13, 17]

$$RN(^{\circ}C/min) = (T_m - T_i) / t_m \quad (5)$$

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.

3. Results and Discussion

Analytical techniques were used to estimate the corrosion rate and determine ferrous ion in the presence and absence of Co-amoxiclav drug as a green corrosion inhibitor in the acid environment of 1.0 M H_2SO_4 solution. In the present research, the effects of inhibitor concentration, pH, and temperature were studied. Various techniques used in this study include gravimetric, thermometric, gasometrical, acidimetric, and atomic absorption spectroscopy (AAS) analytical techniques. The Co-amoxiclav drug green inhibitor is designated here as CO-AMOX. The studied concentrations are 50, 100, 150, 200, 250, and 300 ppm.

3.1 Gravimetric Measurements

3.1.1. Effect of Concentration

Gravimetric techniques were used in the determination of the corrosion rate and corrosion inhibition efficiency *IE*% of expired Co-amoxiclav drug at various concentrations of CO-AMOX inhibitor after 7 hours of immersion of steel coupon in the sulfuric acid corrosive environment with various pH (pH 1, 2, and 3). The values of corrosion rate (*W*) and corrosion inhibition efficiency *IE*% are given in Table 2 and Figure 2. According to gravimetric results, the weight loss and consequently the corrosion rate decreases and inhibition efficiency increases upon addition of expired CO-AMOX green inhibitor, and this behavior increases with an increase in the CO-AMOX inhibitor concentration. It is clear that the inhibition efficiency increases as the inhibitor concentration increases to attain 96 % at 300 ppm. The inhibition efficiency *IE*% and the surface coverage (θ), which represents the part of the metal surface covered by the inhibitor molecules, were calculated according to Equations 2 and 3 mentioned in the Experimental section. Inspection of Table 2 reveals that the values of inhibition efficiency increase with increasing concentration of the drug and decreased with a decrease in the medium pH. Figure 2 reveals that with an increase in the CO-AMOX

concentration, the weight loss of carbon steel samples is reduced. This indicates that the presence of these compounds lowered the dissolution of iron in 1.0 M H_2SO_4 solution indicating that these drugs act as inhibitors. The variation of weight loss with time in uninhibited and inhibited 1.0 M H_2SO_4 is linear, which implies 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 [32]. The maximum inhibition efficiency obtained using 300 ppm of expired Co-amoxiclav drugs is 96% which is higher than the efficiency obtained in the cited previous works [13, 14]. This observation may be due to the presence of small amount of potassium iodide as an additive in the Co-amoxiclav drugs which acts as a promoter for organic drug molecules, as mentioned elsewhere [13, 26] that the presence of inorganic salts has a synergistic effect on the corrosion 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 were performed at various temperatures, namely, 303, 313, 323, and 333 K. 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 $IE\%$ decrease with an 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 steel surface at higher temperature due to which a greater area of the metal is exposed to the acid environment [36–39]. All the experiments were done three times and the recorded data was reported as the mean value with ($\pm 0.1\%$) error.

Table 2. Effect of concentration of CO-AMOX drugs on the corrosion parameters of steel in H_2SO_4 solution with various pH obtained from the weight loss measurements at 303 K.

Expired drugs concentration, ppm	pH=1		pH=2		pH=3	
	$IE\%$	θ	$IE\%$	θ	$IE\%$	θ
Free (blank)	–	–	–	–	–	–
50	87	0.87	88	0.88	90	0.90
100	89	0.89	90	0.90	91	0.91
150	90.5	0.905	92	0.92	93	0.93
200	91.6	0.916	93	0.93	94	0.94
250	93.1	0.931	94.1	0.94	95	0.95
300	93.7	0.947	95.2	0.952	96	0.96

Figure 2. Weight loss of steel as a function of time in 1.0 M H_2SO_4 in the absence and in the presence of expired CO-AMOX drugs as green inhibitor for steel corrosion.

Figure 3. Effect of temperature on $IE\%$ for steel corrosion in 1.0 M H_2SO_4 in the presence of various concentrations of expired CO-AMOX drugs as a green inhibitor. Weight loss data obtained at $\text{pH}=3$.

3. 2. Atomic Absorption Spectroscopy (AAS)

Atomic absorption spectroscopy (AAS) produces considerable simplification of procedures for the analysis of aqueous, acidic, or basic solutions, and thereby contributes 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 two to three minutes [13, 35]. AAS was used for corrosion rate prediction in various media, acidic, basic, and neutral based on fundamental chemistry of the solubility of

corrosion products. The AAS method was applied to the determination of Fe ions in mineral waters and natural waters [13, 35]. The iron ions released into the solution due to corrosion were detected directly by atomic absorption spectroscopy and their concentration was determined using a calibration curve. The corrosion of iron samples in solution was accelerated by high salinity, lowering pH, the presence of chloride ions, and temperature [13]. 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 [13]. In the present study, the concentration of ferrous ions Fe^{+2} formed due to corrosion of steel by acidic H_2SO_4 with various pH were determined by atomic absorption spectroscopy (AAS). The concentrations of ferrous ions passed into the corrosive solution were determined by using AAS both when the green inhibitor was absent and present. The data of AAS are listed in Table 3 and Figure 4 showing that the concentration of ferrous ion Fe^{+2} in the corrosive medium decreased with an increase in the inhibitor concentration and increased upon lowering the solution pH. Here the ferrous ions concentration is taken as a function of corrosion rate since the concentration of ferrous ions in the solution increases as the corrosion rate increases and *vice versa*. The process is affected upon adding the inhibitor. The data in Table 3 agree well with results obtained by the gravimetric method, so the two techniques are in good agreement with each other to indicate that the addition of expired (CO-AMOX) drugs inhibit the corrosion of steel in an acid 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 obtained by the AAS technique.

Sample	Inhibitor concentration, ppm	Concentrations of ferrous ions [Fe^{+2}], ppm		
		pH=1	pH=2	pH=3
Blank	Free	131	123	111
	50	41	27	23
	100	38	23	16
	150	29	19	13
	200	23	15	8
	250	16	9	6
Expired Co-amoxiclav	300	13	7	4

Figure 4. Effect of expired drugs (CO-AMOX) inhibitor concentrations on the ferrous ion concentration $[Fe^{+2}]$ in the presence of 1.0 M H_2SO_4 . The data were obtained by atomic Absorption Spectroscopy (AAS) at various pH.

3.3. Acidimetric measurements

The pH was measured for the five inhibitor concentrations 50, 100, 150, 200, 250, and 300 ppm pre and post-dipping in the tested solution for 7 h, where $[H^+]$ was computed in each case.

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

$$W \text{ (mole} \cdot \text{dm}^{-3} \cdot \text{cm}^{-2} \cdot \text{h}^{-1}) = \frac{\Delta H^+}{At} \quad (6)$$

Where ΔH^+ is the variation between the first and last concentration of H^+ ; a is the surface area of the coupon in cm^2 ; and t is the time in h. The $IE\%$ was computed utilizing the next equation:

$$IE\% = 1 - \left(\frac{[\Delta H_{inh}^+]}{[\Delta H_{uninh}^+]} \right) \cdot 100 \quad (7)$$

Where ΔH_{inh}^+ and ΔH^+ are changes in H^+ concentration with and without the CO-AMOX inhibitor, respectively.

The values of surface coverage (θ) were computed utilizing the following equation [31]:

$$\theta = 1 - \left(\frac{[\Delta H_{inh}^+]}{[\Delta H_{uninh}^+]} \right) \quad (8)$$

As shown in Table 4, the values of corrosion inhibition efficiency and surface coverage increased with increasing concentration of CO-AMOX inhibitor due to a decrease in the hydrogen ion concentration in the medium as the inhibitor molecule acts as a ligand for protons in acidic media.

Table 4. Values of *IE*% for the acidimetric method for expired Co-amoxiclav inhibitor in 1.0 M H₂SO₄ at 303 K.

Expired drugs concentrations ppm	pH=1			pH=2			pH=3		
	$[\Delta\text{H}^+]\cdot 10^4$	θ	<i>IE</i> %	$[\Delta\text{H}^+]\cdot 10^4$	θ	<i>IE</i> %	$[\Delta\text{H}^+]\cdot 10^4$	θ	<i>IE</i> %
Blank	96	–	–	89	–	–	82	–	–
50	20	0.79	79	16	0.82	82	13	0.84	84
100	17	0.823	82	13	0.85	85	11	0.86	86
150	13	0.86	86	10	0.89	89	8	0.9	90
200	11	0.885	88.5	8	0.91	91	6	0.93	93
250	10	0.895	89.5	7	0.92	92	5	0.94	94
300	8	0.917	91.7	6	0.93	93	4	0.95	95

3.4. Gasometrical technique (Hydrogen Evolution Method)

Gasometric techniques are based on measuring the evolved hydrogen gas with time in the absence and presence of inhibitors in an acid environment. The gasometric technique (hydrogen evolution method) was used for evaluation of the expired Co-amoxiclav as a green corrosion inhibitor for carbon steel in an acidified sulfuric acid solution with various pH (pH 1, 2, and 3). Iron is an active metal of higher oxidation potential so it replaces the hydrogen of acid easily giving a metal salt and hydrogen is evolved in the form of gas. The volume of hydrogen evolved during the corrosion reaction of iron in an acidic H₂SO₄ medium in the absence and presence of various concentrations of expired CO-AMOX green inhibitor, 50, 100, 150, 200, 250, and 300 ppm, was measured as a function of time at room temperature (30°C). The inhibition efficiency was calculated using the following equation [17]:

$$IE\% = \left[1 - \frac{V_{\text{inh}}}{V_{\text{free}}} \right] \cdot 100 \quad (9)$$

Where V_{inh} is the volume of hydrogen gas evolved for the inhibited solution and V_{free} for the uninhibited solution. The values of evolved hydrogen volumes and inhibition efficiencies at various concentrations of CO-AMOX inhibitor are shown in Table 5. The inhibition efficiency increases with increasing inhibitor concentration, which indicates that the drug inhibitor compounds act as a good inhibitor for carbon steel in the H₂SO₄ acid environment.

3.5. Thermometric Measurements

Reaction number (*RN*) values are known as a relative measure of retardation of the dissolution process [13]. The extent of corrosion inhibition can be expressed in terms of the percentage reduction in reaction number (%*RR*) given by the following equation [13].

$$\%RR = \frac{RN_{\text{uninhibited}} - RN_{\text{inhibited}}}{RN_{\text{uninhibited}}} \cdot 100 \quad (10)$$

The thermometric parameters and inhibition efficiency are summarized in Table 6. The inhibition efficiency and t_m increase with an increase in the inhibitor concentrations. The inhibition efficiency and time delay (Δt_m) of the inhibitor decrease with increasing pH in the following order: pH 3 > pH 2 > pH 1. This order is similar to that obtained from both weight loss and gasometrical techniques.

Table 5. Hydrogen volumes and the percentage inhibition efficiency for steel corrosion in acidic H_2SO_4 solution with various pH with and without various concentrations of expired CO-AMOX drug at room temperature after 7 hrs.

Expired drugs concentrations, ppm	pH=1		pH=2		pH=3	
	Volume of hydrogen (ml/cm ²)	IE%	Volume of hydrogen (ml/cm ²)	IE%	Volume of hydrogen (ml/cm ²)	IE%
Blank	56	–	49	–	38	–
50	13	76.8	11	77.5	8	78.9
100	12	78.5	9	81.6	6	84.2
150	10	82.1	8	83.7	5	86.8
200	7	87.5	5	89.7	3.5	90.8
250	6	89.3	4	91.8	2.0	94.7
300	5	91.0	3	93.8	1.8	95.3

Table 6. Thermometric parameters for the steel corrosion in acidic H_2SO_4 solutions with various pH in the presence of 300 ppm of expired Co-amoxiclav drugs, CO-AMOX, green inhibitor.

Thermometric Parameters	CO-AMOX H_2SO_4 with pH=1 with expired Co-amoxiclav inhibitor	CO-AMOX H_2SO_4 with pH=2 with expired Co-amoxiclav inhibitor	CO-AMOX H_2SO_4 with pH=3 with expired Co-amoxiclav inhibitor
T_m , °C	41	39	36
t_m , min.	315	360	370
RN , °C/min.	0.035	0.025	0.016
%RR	91	93	96
Δt_m	293	341	362

3.6. Adsorption Isotherm

The process of adsorption is mainly affected by the charge, metal surface nature, electronic characteristic of the metal surface, the temperature of the reaction, the presence of electron withdrawing or electron-donating groups in the derivatives, the electrochemical potential at the solution interface, solvent adsorption, and others ionic species [41]. Many reported works and reviews proved that the corrosion inhibition of metals is mainly due to the adsorption of inhibitor molecules on a metal surface and the adsorption behavior obeys many adsorption isotherm models [41–46]. In the present work, gravimetric data was used to find out the values of surface coverage (θ) at various drug concentrations to explain the best-fit isotherm for the adsorption process. The results are best fitted by the Langmuir adsorption isotherm according to the following equation [40]:

$$\frac{C_{\text{inh}}}{\theta} = \frac{1}{K_{\text{ads}}} + C_{\text{inh}} \quad (11)$$

Where, K_{ads} and C_{inh} are the equilibrium constant of the adsorption process and the inhibitor concentration, respectively [40].

Plotting C_{inh}/θ versus C_{inh} gave a straight line, as shown in Figure 5. The straight line with approximately unit slope value has an intercept of $1/K$. The standard free energy of adsorption ΔG_{ads}^0 is calculated using the equation:

$$K_{\text{ads}} = \frac{1}{55.5} \exp\left(\frac{-\Delta G}{RT}\right) \quad (12)$$

Where K_{ads} is the adsorption equilibrium constant, 55.5 is the concentration 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}^0 is -36.5 kJ/mol. The negative value of ΔG_{ads}^0 indicates that the adsorption process of drug molecules on the metal surface is spontaneous [40]. On the other hand, the obtained value is smaller than the threshold value of -40 kJ/mol required for chemical adsorption which indicates that the mechanism of adsorption is physical [26–40]. It is generally accepted that the expired drug compounds studied inhibit the corrosion process by adsorbing its constituent molecules at the metal/solution interface. Also, it is believed that the formation of a solid organic molecule complex with the metal atom has received considerable attention [41–46].

Figure 5. Langmuir adsorption isotherm model for steel in 1.0 M H₂SO₄ solution at 30°C.

Conclusions

1. Co-amoxiclav is considered as a green corrosion inhibitor as it is a nontoxic inhibitor to human especially at very low concentrations, also, prevention of steel from corrosion is of environmental importance, as corrosion is a terrible waste of both natural resources and money.
2. The corrosion inhibition efficiency increases with an increase in the CO-AMOX inhibitor concentration and reaches 96% at 300 ppm. At the same time, the concentration of Fe⁺² ions decreases.
3. The inhibition is due to the adsorption of drug molecules on the steel surface, which obeys the Langmuir adsorption isotherm model.
4. AAS data show that the concentration of ferrous ion Fe⁺² decreased with an increase in inhibitor concentration and increased upon lowering the pH of the solution.
5. Results of the acidimetric method indicate that the hydrogen ion concentrations decreased in the inhibited medium as the inhibitor molecule acts as a ligand for protons in an acid environment.
6. The volume of hydrogen evolved during the corrosion reaction of steel in acidic H₂SO₄ medium decreased upon increasing expired CO-AMOX inhibitor concentration which may be due to control of the hydrogen evolution reaction by the inhibitor compounds.
7. The reduction in the reaction number and time delay (Δt_m) of the expired CO-AMOX inhibitor decreases with increasing pH in the following order: pH 3 > pH 2 > pH 1.
8. The data obtained from different analytical techniques are in good agreement with each other to within ($\pm 1\%$) to indicate that the addition of expired Co-amoxiclav drugs inhibit the corrosion of steel in the acid environment and decrease the iron dissolution process in this environment. So expired Co-amoxiclav drugs act as a green corrosion inhibitor.

9. Co-amoxiclav as an antibacterial drug is considered as a multifunction green corrosion inhibitor for steel used in the petroleum field.

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