

The Corrosion Inhibition of The Carbon Steel structure and Oil Pipelines in 1M H₂SO₄ by Expired Chlorhexidine and Rhuvex, Drugs

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المخلص

تُعاني المعادن من التآكل بواسطة الموائع المحيطة بها، مما يتسبب في خسائر اقتصادية كبيرة، وأثاراً بيئية سيئة خاصة في أنابيب النفط، أو خزاناته، ولذا كان الاهتمام بإيجاد مواد رخيصة، وصدقية لها، يمكنها مقاومة التآكل، ومن المواد المستخدمة بكثرة، وأثبتت فاعليتها الأدوية المنتهية الصلاحية، نظراً لغناها بالمواد الكيميائية ذات المجموعات الوظيفية القطبية والتي لها القدرة على الامتصاص على سطح المعدن، أو أنابيب النفط، ومن الأدوية المنتهية الصلاحية التي استعملت في هذه الورقة البحثية، كلوروهكسيداتين، والرهوفكس، وتتبع تثبيط التآكل بطريقة فقد الوزن، وبالطريقة الجهدية.

وقد بينت النتائج أن الكلوروهكسيداتين أكثر كفاءة من الـ رهوفكس سواء بطريقة فقد الوزن، أو بالطريقة الجهدية، وأن الـ رهوفكس أكثر ثباتاً عند ارتفاع درجات الحرارة، وأكدت ذلك منحنيات أرهينوس، والحالة الانتقالية، وحساب طاقة التنشيط، والتغير في المحتوى الحراري، والتغير في الإنتروبي، وبينت الطريقة الجهدية مدى تغير الجهد مع الزمن لكل تركيز من تركيزات الدواء المنتهي الصلاحية لمدة ساعتين، وأنه يزداد الجهد بزيادة التركيز مما يدل على قدرة عالية للمثبط بالاتصاق بالمعدن.

الكلمات المفتاحية: مثبطات التآكل، الصلب الكربوني، أنابيب النفط، أدوية منتهية الصلاحية، الطريقة الجهدية.

Abstract

Metals suffer from corrosion by the surrounding fluids, which causes great economic losses and bad environmental effects, especially in oil pipelines or reservoirs. Therefore, attention was paid to finding cheap and environmentally friendly materials that can resist and reduce corrosion. Among the widely used materials, expired medicines have proven their effectiveness due to their richness in chemicals with Polar functional groups that have the ability to be adsorbed on the surface of the metal or oil pipelines, and the expired drugs that were used in this research paper are Chlorhexidine (Ch.) and Rhuvex (Rh.), and corrosion inhibition is tracked by the method of loss of balance and by the voltage method.

The results showed that (Ch.) is more efficient than (Rh), whether by weight loss method or by the Potentiometric method, and that (Rh.) is more stable at high temperatures, and this was confirmed by the Arrhenius curves, state and transition, activation energy calculation, change in enthalpy and change in entropy, and the potentiometric method showed the extent of voltage change with time for each A concentration of expired drug concentrations for two hours, and that the voltage increases with increasing concentration, which indicates a high ability of the inhibitor to adsorb to the metal.

Keywords: Corrosion Inhibitors, Carbon Steel, Oil Pipelines, Expired Drugs, Potentiometric Method.

1. INTRODUCTION

Corrosion is defined as the interaction of a metal with its surrounding environment of gases and liquids. Expired drugs are good fluids for corrosion and are used as corrosion inhibitors (CI). To limit the interaction of the metal with its environment. Therefore, drugs or chemical compounds are considered environmentally friendly alternatives as (CI) for use in various industrial and biological applications. Not only this issue, the cost of re-equipment eroding in the industry negatively affects the economy.

The use of expired drugs as (CI) is a low-cost, cost-effective, and environmentally friendly alternative to the high-cost corrosion process. For example, used an expired Tramadol (ETr) as (CI) for (MS) in 1M HCl solution^[1], an expired Imocam drug molecule was used as corrosion inhibitor with good (MS) in 1M HCl^[2], an expired three kinds of Cephalosporins were used as (CI) for carbon steel (CS) in 0.1M H₂SO₄^[3], an expired tenoxicam drug was used as (CI) for (CS) in 0.5M HCl at different concentrations^[4], there are different sorts of medications (Antibacterial, Antifungal, Antibiotic, Anti-malarial, Analgesic, Anti-depressant, Anti-hypertensive, Antihistamine) have been viably energetic as plausible (CI) for diminishing the impact of consumption on compounds and metals^[5], an expired Ceftazidime (the antibiotic) was used as (CI) for Cu metal in 1M HCl^[6], an Expired Etoricoxib was used as an environment-friendly (CI) for (CS) in 0.5M H₃PO₄ solution^[7], Imidazole drugs Omeprazole (OMP), and its by-products Omeprazole Sulfide (OMP-1), and Omeprazole Sulfonate (OMP-2) on Q235 were used as (CI) for steel in 1M

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HCl^[8], an expired anti-biotic, Cefdinir (CDR) was used as (CI), this study includes anti-corrosion performance of CDR molecule against corrosion of (MS) in HCl medium^[9], an expired Tetracycline drug was used as (CI) for (CS) alloy (ck45) in 1M HCl solution^[10], an expired Thioridazine HCl (TH), an antipsychotic drug, was used as against corrosion on (MS) in 1M HCl^[11], medications such as (Antibacterial, Antifungal, Antibiotic, Anti-malarial, Analgesic, Anti-depressant, Anti-hypertensive, Antihistamine) have been viably energetic as (CI) for metals and compounds^[12], Tiazofurin, as a new corrosion inhibitor, was evaluated using weight loss measurements, electrochemical methods, and other techniques, for steel in acid medium^[13], an expired Herbal drug was evaluated of the corrosion inhibition performance of (CS) in a 1M HCl solution^[14].

Drugs used as (CI) for numerous metals and alloys in HCl, H₂SO₄, NaCl, H₃PO₄, HNO₃, and OH-based electrolytes. Because of their complex molecular structure, they provide good corrosion inhibitors, they effectively inhibit corrosion by adsorbing on the metallic surface mainly following the Langmuir adsorption isotherm^[15], an expired Dioxopromethaxine HCl (DPZ) and Promethazine HCl (PZ) were used as (CI) for Cu in 0.5M H₂SO₄ solution. The electrochemical method results, and topography information indicated that corrosion inhibition ability of PZ outshines DPZ, the suppression efficiency was high to 96.98% and 93.43%, respectively^[16], an expired Chlorhexidine digluconate was used as (CI) for (CS) electrode in aerated stagnant water and diesel emulsion solution^[17], an expired Perphenazine (PPZ) and Chlorpromazine HCl (CPZ), drugs, were used as (CI) for Cu in 0.5M H₂SO₄ solution which formed co-adsorbed on the copper surface, due to its contain N, S multiple active sites so they can play a certain (CI) for Cu in H₂SO₄ solution^[18], an expired (Acarbose, Voglibose and Miglitol) anti-diabetic drugs were used as (CI) for (MS) in 700 ppm NaCl solution^[19], an expired Pioglitazone (PGZ) drug used as (CI) for (MS) corrosion in 1N HCl solution^[20], an expired drug Metformin was evaluated for its corrosion inhibition performance in a simulated acidizing environment (15% HCl) solution^[21], an expired Dexamethasone drug (DM) was evaluated for its (CI) for (MS) corrosion in 2 M HCl solution^[22], an expired Tramadol drug (TR) used as green (CI) for (Al) corrosion was proven in 1M HCl solution^[23].

Cysteine amino acid was used as an effective green corrosion inhibitor, due to the similarity of structural between d-Penicillamine (PA) drug and cysteine, it is expected PA also acts as a green corrosion inhibitor, then describe the corrosion inhibition ability of PA and l-Cysteine (Cys) on the (MS) in 1M HCl solution^[24], an expired Rabeprazolesodium, Domperidone, and Benfotiamine drugs are the corrosion inhibition ability, on (MS) specimens were immersed 5 days with and without drug molecule in 3.5 wt% medium film formed on MS surface^[25], an expired Cephapirin drug used as (CI) for (CS) in 2M HCl^[26], an expired Rosuvastatin drug was used as (CI) for steel in 1M HCl and 0.5M H₂SO₄ solutions^[27], an expired drug Paracetamol as (CI) for (CS) in 0.5 M H₂SO₄ and 1M HCl have been examined by cyclic voltammetry^[28].

5.25% NaOCl, 0.2% chlorhexidine gluconate, and chlorinated soda with KOH used as (CI) on the surface of stainless-steel^[29].

In this work an expired Chlorhexidine (Ch.) and Rhuvex (Rh.) drugs (Paracetamol or acetaminophen) were used as (CI) for

(CS) in 1M H₂SO₄ solution has been studied by weight loss measurements and potentiometric method.

2. EXPERIMENTAL

2.1. Materials and Chemicals:

The (CS) sample with the following chemical composition, (wt%): C (0.200g), Si (0.003g), Mn (0.35g), P (0.02g) and Fe (Rest). The piece area was $1.23 \times 10^{-3} \text{ m}^2$. The sample was embedded in a glass tube of just larger diameter than the sample. Epoxy resin (supplied from Ciba Co.) was used to stick the sample to the glass tube. Surface of (CS) electrode was mechanically rub off using sand papers, in different grades, for example 1200 grade, before used. The tests were used 1M H₂SO₄ (supplied from Sigma-Aldrich) with the addition of various concentrations of an expired drugs (100-400) ppm. All the test solutions were prepared from analytical chemistry grade chemical reagents prepared using distilled water, and used without further pure cation. For each hold, a freshly prepared solution was used. Temperature of solutions was thermostatically controlled at desired value, and all chemical material high purity about 99%^[30].

2.2 Apparatus:

All Potentiometric measurements were made at $25 \pm 1^\circ \text{C}$ with an Orion (Model 720) pH/mV meter (Fisher scientific). Double junction Ag/AgCl reference electrode was used with digital multimeter (TMT480012). All chemicals were of analytical reagent grade unless otherwise stated and distilled water was used throughout. Testing was performed using dielectrode electrochemical cell with a volume of 250 ml. The working electrode was made of the (CS) with an exposed to solution area of 0.00123 m^2 , the reference electrode was Ag/AgCl electrode, The inhibitors were added into the test solution. The current recorder by m A, the potential mV, and the time by min. The inhibitor measurements, the potential vs time dependences of (CS) in the H₂SO₄ 1M solution without and with the addition of an expired drugs as inhibitors were recorded.

2.3 Tools and working method:

Voltage and current multimeter device, a glass beaker with a capacity of 250 ml, 1M H₂SO₄ acid titrated with Na₂CO₃ of accurate concentration, Ag /AgCl as a reference electrode prepared by dipping two silver electrodes in a 1M solution of HCl and passing a direct current between them from a 1.5 Volt battery, and the working electrode is (CS) electrode.

2.4 Cell preparation:

The cell consists of two electrodes, one of which is the silver electrode Ag/ AgCl electrode as a reference electrode, while the working electrode is (CS) electrode, an area immersed in acid $1.23 \times 10^{-3} \text{ m}^2$. Voltage (mV) and current (mA) are measured every ten minutes for 2 hours, during which corrosion of (CS) takes place in the presence of 1M H₂SO₄ acid. Voltage, current and time are measured in the presence of different concentrations of (Ch.) and (Rh.) the expired drugs were used as (CI) at concentrations of 100, 200, 300, 400, ppm and for a 2 hour for each concentration.

2.5. Weight loss measurements:

Experiments were performed with different concentrations of the inhibitors. The immersion time for the weight loss is 2 h at

25 °C. The results of the weight loss experiments are the mean of three runs, each with a fresh specimen and 100 ml of fresh acid solution. The inhibition efficiency $IE_w\%$ and $IE_e\%$ were calculated.

Weight loss calculations are comprehensive corrosion tests for laboratory and field. Also, they help us to make a quantitative estimate of amount of corrosion. The corrosion behaviour of the metal in an aqueous environment is describe by the extent to which it dissolves in the water solution.

Calculated the weight of a specimen before and after precipitate and applying the following equation:

$$W = \frac{m1 - m2}{At} \text{ ----- (1)}$$

where $m1$ and $m2$ – the mass of the sample before and after testing, respectively, g ; A – area of the sample, m^2 ; t – exposure time, hours.

$$IE_w\% = \frac{W_0 - W}{W_0} \times 100 \text{ ----- (2)}$$

where W_0 and W – corrosion rate of (CS) in test solution without and with inhibitors, respectively.

All Potentiometric measurements were made at $25 \pm 1^\circ C$ with an Orion (Model 720) pH/mV meter (Fisher scientific). Double junction Ag/AgCl reference electrode was used with digital multimeter (TMT480012). All chemicals were of analytical reagent grade unless otherwise stated and distilled water was used throughout. Testing was performed using dielectrode electrochemical cell with a volume of 250 ml. The working electrode was made of (CS) with an exposed to solution area of $0.00123 m^2$, the inhibitor was added into the test solution, the effect of inhibition IE_e was determined by the formula:

$$IE_e = \frac{I_0 - I_{inh}}{I_0} \times 100 \text{ ----- (3)}$$

where I_0 and I_{inh} – corrosion current density of steel in test solution without, and with inhibitor, respectively, the current recorder by mA, the potential mV, and the time by min.

Expired drug measurements, the potential vs time dependences of (CS) in the $1M H_2SO_4$ solution without and with the addition of drugs inhibitors were recorded.

2.6. Preparation of expired drug solution

The structure, nomenclature, molar mass, & molecular formula of expired drugs one liter stock solution (1000 ppm) of an investigated antibiotic, as tablets, was prepared by dissolving an accurately weighed quantity (1g) in (1L) of doubly distilled H_2O , and then the desired concentrations (100 - 400) ppm are obtained by diluting the stock solution with the desired volume of distilled H_2O . The corrosive solution, $1M H_2SO_4$ was prepared by diluting of high-grade H_2SO_4 (98 % w, $d=1.84 g/ml$, $M. wt.= 98 g/mol.$) with distilled water and dilute to up to $1M$ then titrate with $1M Na_2CO_3$ standard solution to obtain exact $1M H_2SO_4$ at suitable indicator.

(CS) sample has area $1.23 \times 10^{-3} m^2$ was placed in $1M H_2SO_4$ in a beaker devoid of, and with distinct quantities of the drugs for 2 hours at 298-323 K. Then they washed, desiccated, weighed after 10 min and measure the current and potential.

3. RESULTS

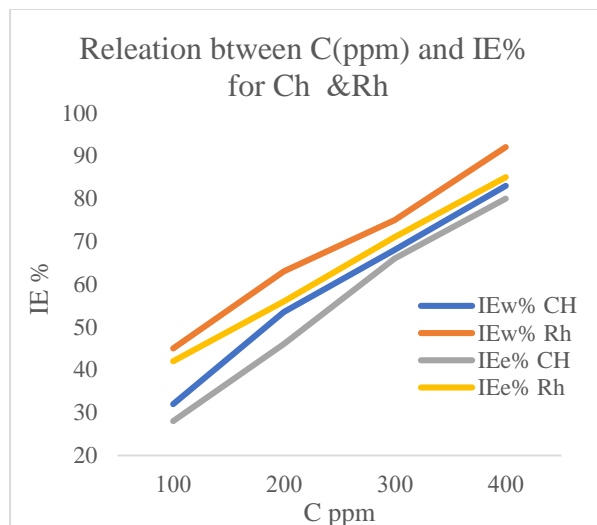


Fig.1. Effect of (Ch.&Rh.) expired drugs concentrations (ppm) in corrosion $IE_w\%$ of (CS) in $1M H_2SO_4$ solution.

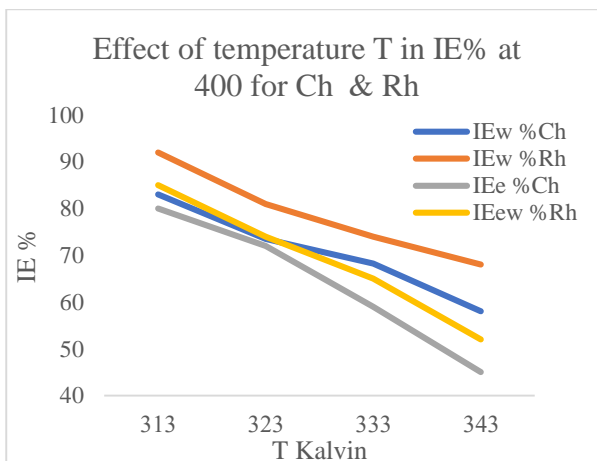


Fig.2. Effect of T Kalvin in IE% at 400 ppm for (Ch. & Rh.) expired drugs.

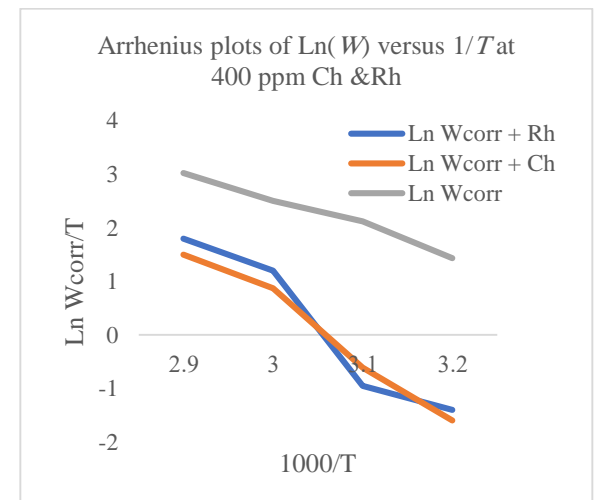


Fig.3. Arrhenius plots of Ln(W) vs 1/T at 400 ppm of (Ch. & Rh.) expired drugs.

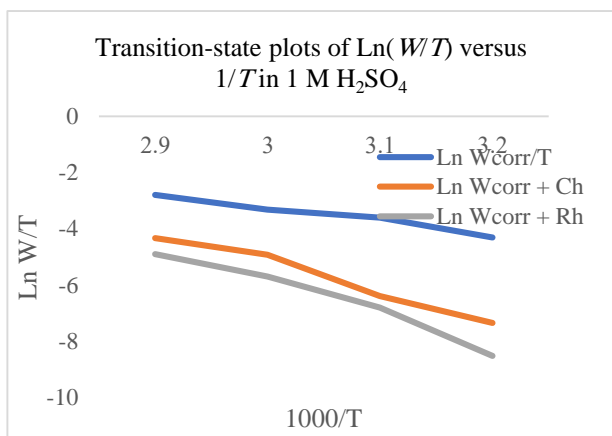


Fig.4. Transition-state plots of $\ln(W/T)$ vs $1/T$ in $1M H_2SO_4$ in absence and presence of 400 ppm concentrations of (Ch. & Rh.) expired drugs.

Table 1. Shows that, E_a , ΔH°_{ads} , and ΔS°_{ads} for the corrosion of (CS) in $1M H_2SO_4$ in the absence and presence of (Ch. & Rh.) expired drugs.

	E_a (kJ/mol)	ΔH°_{ads} (kJ/mol)	ΔS°_{ads} (J/mol.K)
Blank	44.06	41.3	- 41.8
Ch.	85.9	83.3	-83.69
Rh.	82.6	81.4	-82.1

3.3. Potentiometric results

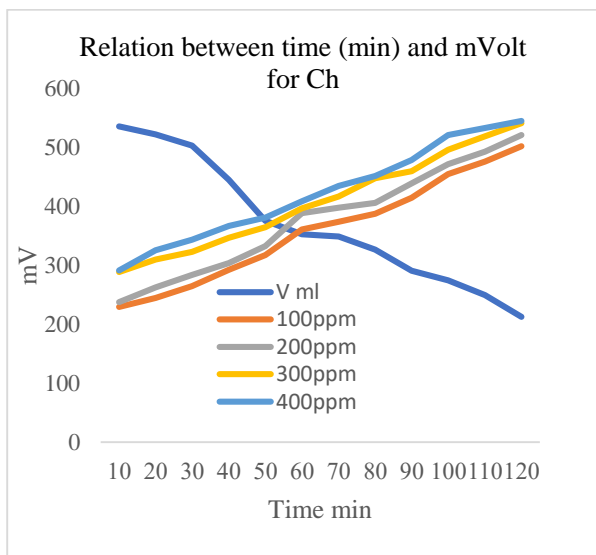


Fig. 5. Relation between time (min) and ml Volt at different concentration of expired (Ch.) drug.

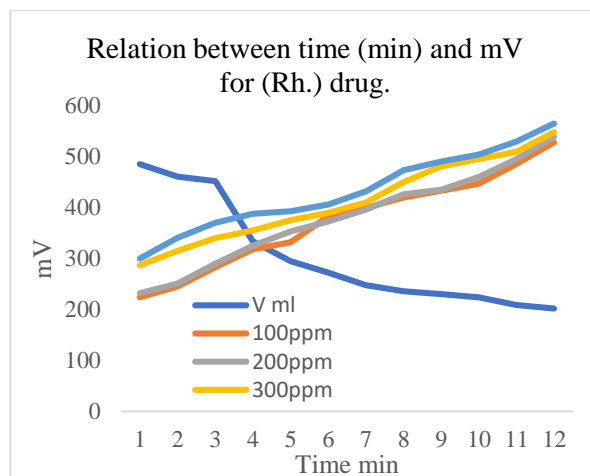


Fig.6. Relation between mV and log I/A of an expired (Rh.) drug.

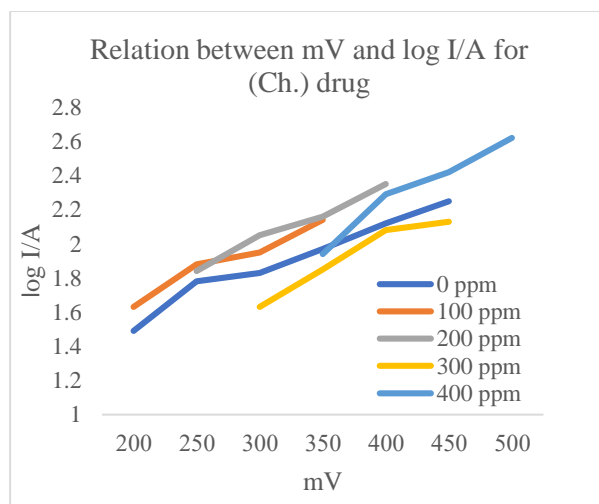


Fig.7. Relation between mV and log I/A of (Ch.) drug.

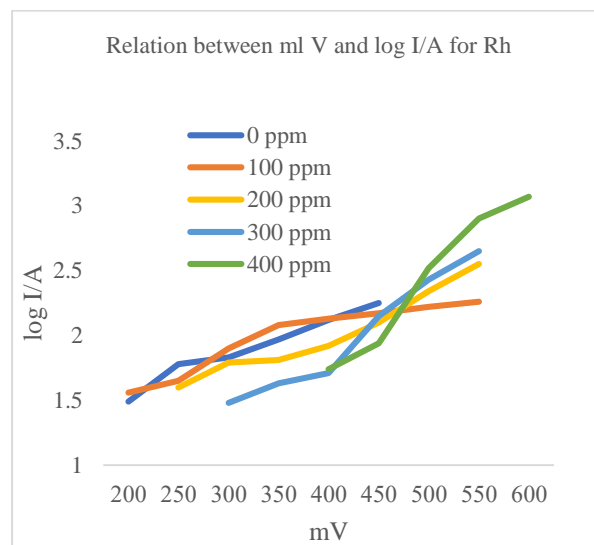
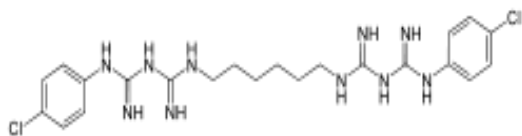


Fig.8. Relation between time (min) and mV at different concentration expired (Rh).

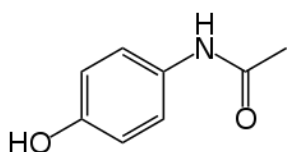
4. DISCUSSION

3.1. Chlorhexidine (Ch.) structure



N''''1,6-Hexanediyldis[N'-(4-chlorophenyl)(imidodicarbonimidic diamide)]

3.2. Rhuvex drug structure



Paracetamol or acetaminophen (N-(4-hydroxyphenyl)acetamide)

Chemical drugs (drugs) were used as (CI) of metal or steel corrosion is one of the most effective,

green corrosion, environmentally friendly, and cheap things, this is due to its composition diversity, complex structures and large surface area. The effective different functional groups in the drug molecules provide good coverage and protection for the surface. To explain how the drug molecules act as (CI) where the drug molecules provide excellent surface coverage and protection as its molecules contain many electrons rich centers such as polar functional groups and aromatic rings through which they adsorb and act effectively as excellent corrosion inhibitors. The use of chemical drugs (drugs) as inhibitors of metal corrosion as explain [32]. The corrosion rate and $IE_w\%$ for (CS) in 1M H_2SO_4 solution at 25°C in the absence and presence of (Ch.& Rh.) drugs are given in **Fig.1**. As the (Ch.&Rh.) an expired drugs increases in concentration; the corrosion rate decreases. In other words, the $IE_w\%$ of (Ch.&Rh.) expired drugs increases with the increase of its concentration to attain 92%.

In Fig.1. Shows that, as the concentration of inhibitors increases the $IE_w\%$ also increases, due to the numbers of molecules were adsorbed on the surface of (CS), also increases.

In Fig.2. Shows that as increase in temperature decrease the efficiency due to increase the kinetic energy of molecules of drugs adsorbed, then decrease the numbers of molecules were adsorbed on the surface of (CS). It clearly indicates that temperature mainly influences the desorption of adsorbed inhibitor on the (CS) surface. As the concentration of inhibitors increases and $IE_w\%$ also increases, but when the temperature increases the inhibitor efficiency decreases this is because at a high temperature, the hydrogen evolution increases on the metal surface and desorption of the thin film takes place and so inhibitor efficiency decreases. When the temperature increases the corrosion rate is increased linearly, it is clearly indicates that temperature mainly influences the desorption of adsorbed inhibitor on the metal surface.

In Fig.3. Shows the relation between $1/T$ and $\ln(W)$ as Arrhenius equation (4) to calculate the activation energy (E_a)

for the corrosion of (CS) in the absence and presence of 400 ppm concentrations of (Ch. & Rh.), Arrhenius-type equation:

$$W_{corr} = A e^{\frac{-E_a}{RT}} \text{ --- (4)}$$

where (E_a) is the activation corrosion energy; R is the universal gas constant; A is the Arrhenius pre- exponential factor, T is the absolute temperature and W_{corr} is corrosion rate, and from Arrhenius plots for the corrosion rate of (CS) in 1M H_2SO_4 , the values of E_a were evaluated from the slope of $\ln W$ versus $1/T$ plots.

In Fig. 4. Shows the relation between $1/T$ and $\ln(W/T)$ for (Ch. & Rh.) expired drugs, in 1M H_2SO_4 to calculate, the enthalpy of activation (ΔH^*) and the entropy of activation (ΔS^*) for the corrosion of (CS) in H_2SO_4 may be estimated using the transition-state equation:

$$W_{corr} = \frac{K_B T}{h} \exp\left(\frac{\Delta S^*}{R}\right) \exp\left(-\frac{\Delta H^*}{RT}\right) \text{ --- (5)}$$

Where, k_B is the Boltzmann's constant and h is the Planck's constant. A plot of $\ln(W/T)$ versus $1/T$, straight lines was obtained with a slope of $-\Delta H^*$ and from the intercepts of $\log(W/T)$ -axis, ΔS^* values were calculated.

The data was collected in **Table.1** indicate that the addition of (Ch. & Rh.) leads to an increase in the activation E_a and ΔH^* to values greater than that of the free solution. Moreover, the average difference value of the $E_a - \Delta H^*$ is 2.6 kJ/mol which is approximately equal to the value of RT (2.63 kJ/mol) at the average temperature (238 K) of the domain studied. This result agrees that the corrosion process is a unimolecular reaction as described by the known equation of perfect gas [31].

$$E_a - \Delta H^* = RT \text{ --- (6)}$$

It is pointed out in the literature that positive sign of the enthalpies reflects the endothermic nature of the (CS) dissolution process, the presence of inhibitors tested reveals that the corrosion process becomes more and more endothermic when compared to blank.

The activation energies are $E^*_a = 44 \text{ kJ mol}^{-1}$, $E^*_a = 85.9 \text{ kJ mol}^{-1}$ for Ch., and 82.6 kJ mol^{-1} for Rh were the activation energies in the absence and presence of drugs, respectively. The low value of the activation energy (less than 80 kJ mol^{-1}) indicate physical adsorption of the drugs molecules on metal surface.

The decrease of % IE with temperature is explained by the adsorption of an organic adsorbate on the surface of a metal is regarded as a substitutional adsorption process between the organic compound in the aqueous phase, org_{aq} , and the water molecules adsorbed on the electrode surface H_2O_{suf} .

Large and negative values of entropies show that the activated complex in the rate determining step represents an association rather than a dissociation step, meaning that a decrease in disordering takes place on going from reactants to the activated complex.

The activity of specific cations and anions can measure potentiometry with ion-selective microelectrodes at the solid/liquid interface from the solution side. Anodic and cathodic components of corrosion processes change the

concentration of H^+ , OH^- in local solution, ions of the supporting electrolyte, and metal cations [33].

In Fig. 5,6. shows that the voltage during the corrosion process without adding (Ch & Rh.) expired drugs, which is used as a corrosion inhibitor in steel in the presence of H_2SO_4 , we find that the voltage decreases with the increase in corrosion processes, and with the increase of time the voltage decreases to increase the formation of a layer of oxide that increases the conductivity of the solution. Then the voltage decreases between the working electrode and the reference electrode,

while the voltage increases when (Ch & Rh.) were added as a result of adsorption of the drug on the surface of (CS), which makes a protective layer between the steel and the solution, and it increases gradually with increasing time until two hours, and the voltage increases as the concentration of expired (Ch & Rh.) increases from a concentration of 100 ppm to 400 ppm.

In Fig. 7,8. Shows the relationship between the voltage and the logarithm of the current density, which is the current intensity in A/m^2 . We note that the current density is higher when the solution is without an inhibitor (0 ppm), then it decreases as the concentration of the inhibitor increases at the same voltage, for example at a voltage of 400 mV, we find that the density decreases. The current increases with the concentration of the inhibitor, although it generally increases with the increase in the voltage, because the current generally increases with the increase in the voltage. It is noted here that the voltage increase is delayed at a concentration of 100 ppm and its decrease with time may be due to the fact that the layer formed at this concentration did not adhere sufficiently or because the drug contained more than one compound (three compounds) that were not all of the same degree of efficiency in the process of adsorption or inhibition corrosion process, but it began to increase its efficiency by increasing the concentration up to 400 ppm.

5. CONCLUSION

(Ch.) drug is more efficient than (Rh.) drug, by weight loss method or by the voltage method, that (Rh.) is more stable at high temperatures, this was confirmed by the Arrhenius curves, state, transition, activation energy calculation, change in enthalpy, the change of entropy, and the Potentiometric method showed the extent of voltage change with time for each A concentration of expired drug concentrations for two hours, that the voltage increases with increasing concentration, which indicates a high ability of the inhibitor to stick to the metal.

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