

## Expired Dulcolax Drug as Corrosion Inhibitor for Low Carbon Steel in Acidic Environment

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Dulcolax is a common laxative medicine, and Dulcolax is one of the most well-known. Bisacodyl medicines increase peristaltic contractions by exerting a parasympathetic effect on the mucosal sensory neurons. It was utilized for pre-and postoperative constipation, as well as situations that required defecation facilitation. Dulcolax is frequently used in our homes and maybe left unattended after its expiration date, posing a risk to children and the environment. The expired or unused Dulcolax medicinal medicine was used as a nontoxic green corrosion inhibitor of mild steel used in the production of petroleum pipelines in a 1.0 M hydrochloric acid corrosive environment in the current study. Estimates were made using chemical, analytical, and electrochemical methods. The impact of drug concentration and reaction temperature on the outcome was investigated. Corrosion inhibition rose as concentration increased and reduced as temperature increased. The inhibition could be caused to drug components adsorbing and adhering to the steel surface. The Langmuir isotherm model was found to govern adsorption. The expired medications are mixed-type inhibitors, mostly cathodic, according to potentiodynamic polarization data. The expired Dulcolax medicine boosts polarization resistance and inhibition performance by adsorbing on the metal/electrolyte interface, according to an EIS investigation. In the absence and presence of expired pharmacological inhibitors, AAS was utilized as an analytical approach to determine the ferric ions concentration in the corrosive environment. All of the evidence points to the plausibility of utilizing and applying Expired Dulcolax as a non-toxic green inhibitor for steel.

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**Keywords:** Expired drugs; Dulcolax; Bisacodyl; non-toxic inhibitor; Potentiodynamic; EIS, AAS; green inhibitors.

## 1. INTRODUCTION

Dulcolax is a stimulant laxative prescription medicine that is made up of chemical organic compounds. Dulcolax stimulates bowel movement by acting directly on the colon [1-3]. It's often used to treat occasional and chronic constipation, as well as neurogenic bowel dysfunction, and as part of bowel preparation for medical exams like colonoscopies. Triphenylmethane was used to make bisacodyl. Because of its structural resemblance to phenolphthalein, it was first employed as a laxative in 1953. Dulcolax works by causing peristalsis, or colon contractions, by stimulating intestinal nerve cells. It also acts as a contact laxative, increasing fluid and salt excretion. Dulcolax has a negligible effect on the small intestine. Colonic evacuation is mostly promoted by stimulant laxatives [1-3].

Bisacodyl or Dulcolax the famous laxative drugs widely spread in our homes and may be left after the expiry date, which poses a danger to both the children and the environment. In general, medicinal drugs are one of the most popular chemicals and the most prevalent as it was used daily in our homes and on an ongoing basis. Environmental and health accidents were recorded due to the accumulation of unused and expired medicinal drugs, which caused the death of 78,000 people per year, including 2,000 children per year. Expired medicines are disposed of in some countries by leaving them in holes outside the cities in the desert, which leads to the arrival of these expired medicinal drugs materials to the groundwater. It causes groundwater to be polluted with these medicinal substances. All these problems drew the attention and interest of Reda Abdel Hameed to search for new applications for expired drugs and drugs, as he used some of them as metal corrosion inhibitors and published the first scientific research on the use of drugs as metal corrosion inhibitors in 2009, then followed by the second research in the same field in 2011.[4,5]. From 2009 to the present, intensive research investigations on the use of expired prescription pharmaceuticals as corrosion inhibitors for some metals and alloys have been ongoing. For the first time, expired ranitidine medicinal medicines were employed as non-toxic corrosion inhibitors for aluminum in sulfuric acid solution [4], and expired ranitidine medicinal medications were also used as corrosion inhibitors for steel in hydrochloric acid [5]. These findings have prompted some scientists to study and analyze a variety of expired medicinal materials as corrosion inhibitors for metals and alloys. In addition, unused prescription medications have been studied for their ability to stop the corrosion of carbon steel in a variety of corrosive conditions [6-17].

Environmentally friendly and potentially non-toxic corrosion inhibitors, also known as green corrosion inhibitors, have been developed over the last decade as a result of research work in the field of corrosion inhibition [18-46]. Recently expired medications are being used to address solid waste accumulation issues as well as to introduce a potential nontoxic inhibitor to conserve energy. The overall cost of preparing or sailing chemical corrosion inhibitors accounts for around 7% of the total revenue spent on the corrosion inhibition of metals and alloys in industrial applications [4-17].

Because of green chemistry, the use of expired drugs in the form of inhibitors are helpful in many ways, like a) avoiding the toxic effect of the same nature inhibitors to human, b) using drugs that can save the energy and organic solvent used in the synthesis of corrosion inhibitors c) use of drugs as inhibitors leave no waste materials and finally d) this use avoids the accumulation of drugs waste and I turn to reduce the danger on child and groundwater. Due to these reasons, expired drugs can be

considered green inhibitors. The drug obtained directly from the laboratory and is used as inhibitors is a clean process with almost minimal waste and these inhibitors further used in their pharmacological extent is safe both for human beings & environment. In corrosion, oxidation of metals takes place mainly due to the environment. But these corrosion products can be achieved at the cost of metal lattice, which is a waste of natural resources & finances. However, control of corrosion of steel is technically important as well as economically & environmentally. This makes hard & useful metal a corrosive element having a hazardous effect on the environment. Uncontrolled damage by corrosion can cause high-cost maintenance and protection for materials.

The nontoxic expired drugs act as green and eco-friendly corrosion inhibitors, nontoxic for humans at very low concentrations. Analytical and electroanalytical are rated as more efficient accurate and effective materials, largely used for the estimation and the evaluation of any kind of materials and products which used and studied as corrosion inhibitors for metals and alloys in many different aqueous corrosive environments, like acids, alkaline, and aqueous salts [27-46]. Expired Bisacodyl or Dulcolax was employed as a non-toxic green corrosion inhibitor for carbon steel alloy used in the manufacturing of petroleum pipelines in this study. The corrosion inhibition efficiency of the used expired Dulcolax medicine was evaluated using chemical, analytical, and electrochemical techniques. Expired drug concentrations and reaction temperature were also investigated. The behavior of adsorption and the mechanism of inhibition were also investigated and addressed. The medications Bisacodyl or Dulcolax were used to treat constipation or bowel irregularity, according to a review of the literature [1-3]. It hasn't been linked to elevated serum enzymes during treatment or clinically obvious liver injury with jaundice. Bisacodyl is a stimulant laxative made from a synthetic pyridinyl methylene-diacetate ester derivative [1-3]. Its chemical structure contains efficient functional groups which are nitrogen heterocyclic pyridinyl, two-terminal ester groups, and aromatic benzene rings as a chemical formula with the addition of drug formulation additive (excipients materials: natural surfactants, colloidal materials, flavors, and salts). Dulcolax tablets contain 5 mg Bisacodyl mixed with excipients (Surfactants, salts, and colloidal materials as additives). Its chemical structure and drug constituents make Dulcolax or Bisacodyl drugs highly promising as corrosion inhibitors.

## 2. EXPERIMENTAL AND METHODS

### 2.1. Materials and Test Solution

Corrosion inhibition tests were carried out on carbon steel coupons with a composition similar to that of the steel used in the production of petroleum pipelines. As seen in table 1, it is a compound.

In 1.0 M hydrochloric acid, the corrosive electrolytic solution is employed. Diluted analytical grade 37 percent hydrochloric acid (made by spectrum reagents and chemicals pvt. Ltd) and distilled water are used to make this. The inhibitor concentration (Dulcolax tablets in the solution is 100, 200, 300, 400, and 500 ppm). The Dulcolax tablets are used in the expired form after the expired date by one month, it is taken from our homes as a product of Delpharm Reims- France. Marketing authorization holder Sanofi-Aventis Deutschland GmbH. It is white to off-white crystalline powder in which particles

have a diameter smaller than 50 microns. It has molecular formula  $C_{22}H_{19}NO_4$  and its IUPAC name is [4-[(4-acetyloxyphenyl)-pyridin-2-ylmethyl]phenyl] acetate. It is partially soluble in water and alkaline solvents but easily soluble in acids, alcohol, and propylene glycol. The inhibitor solution was prepared in the present study by refluxing the crashed tablets powder with ethanol for 3 h. The combination was cooled to room temperature and filtered, and the resulting filtrate was utilized as an inhibitor solution at the concentrations of 100, 200, 300, 400, and 500 ppm, respectively. Figure 1 depicts the chemical and three-dimensional structure of Dulcolax pharmaceutical medications. For electrochemical tests, rectangular specimens with a dimension of 5.0 x 1.0 x 0.1cm were utilized, whereas, for other research, rectangular specimens with an exposed surface area of 1 cm<sup>2</sup> were employed. To remove scales and oxide, samples were cleaned using emery paper of 400, 600, and 800 grit. To remove any organic contamination on the surface, it was cleaned with acetone (solvent). The samples were dried at room temperature and kept in moisture-free desiccators until they were needed again.

**Table 1.** The gravimetric composition of the mild steel materials, which was used as metal substrate in the present study.

The Elements	Manganese	Silicon	Zn	S	Phosphorous	Carbon	Iron
Its composition Weight (%)	0.517	0.201	0.56	0.009	0.007	0.157	The rest component

## 2.2. Weight loss Measurements (Chemical Studies)

Low carbon steel materials coupons were scraped away using various grades of emery sheets, which were cut into the specified dimension of 4.0 x 2.0 x 0.2. For additional cleaning, it was placed in an acetone bath for ten minutes. It was then washed and dried using a gentle towel. With the use of a four-digit analytical balance, weight measurements were taken. These carbon steel coupons were immersed in various concentrations of expired Dulcolax drugs (100, 200, 300, 400, and 500 ppm) in a 1.0 M hydrochloric acid solution for 7 hours at temperatures ranging from 303 to 333 degrees Celsius. The trials were repeated three times to ensure that the data and computations were consistent. Following that, the average weight loss was calculated. Freshly made expired medication solution was used for each new reading. The calculations used to investigate the inhibition parameters are listed below.

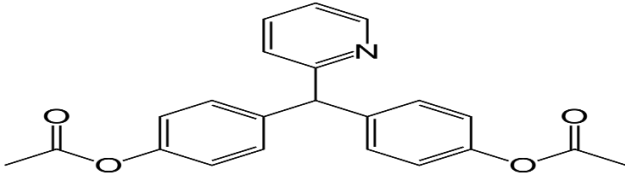
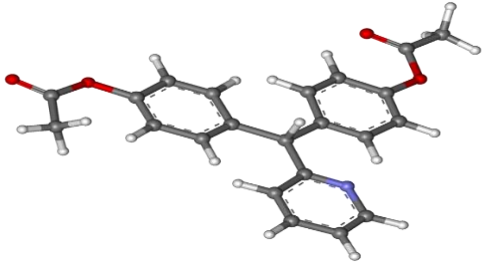
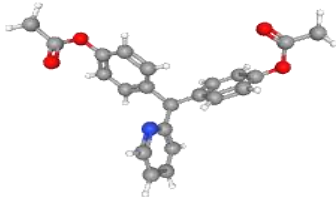
The following equation [21-26] was used to compute corrosion inhibition efficiency (percent I.E.) based on weight/mass loss (mg) in the presence (M) and absence (M<sub>0</sub>) of the corrosion inhibitor [21-26]:

$$\% \text{ I.E.} = [ ( M_0 - M ) / M_0 ] \times 100 \quad (1)$$

The following equation was used to calculate the corrosion rate:

$$CR = 87.6 \times [ ( \Delta M / ( A \times t \times \rho ) ] \quad (2)$$

Where CR stands for corrosion rate in mm/year, M stands for weight/mass loss of low carbon steel (mg), A stands for the exposed surface area of the examined coupon in cm<sup>2</sup>, t stands for exposure time (hr), and  $\rho$  stands for the mild steel density in g/cm<sup>3</sup>

Drug name	Dulcolax ( DULC)
Molecular Formula	C <sub>22</sub> H <sub>19</sub> NO <sub>4</sub>
Drug name (IUPAC)	4- [(4-Acetyloxyphenyl) – pyridine -2- yl methyl ] phenyl] acetate.
Chemical Formula (structural)	
Ball and Stick Model	
3 D Structure Formula	

**Figure 1.** Structure and composition of Dulcolax (DULC) Drugs (used as inhibitor)

The surface covering fraction was computed using the following equation [21-26]:

$$\theta = [(M_0 - M) / M_0] \quad (3)$$

The surface coverage values acquired from the weight loss approach were graphically fitted into various isotherms, with the best fit determined by the regression coefficient value with the highest value.

### 2.3. Atomic absorption AAS, Measurements (Analytical Studies)

The content quantity of iron ions in the solutions containing corrosive materials in the occurrence and no occurrence (the absence and the presence) of medicinal drugs materials in an expired form which studied as corrosion inhibitors investigated by the atomic absorption spectroscopy (AAS). The concentration of ferric ions, which passed in the corrosive solution, has been estimated and measured by

using the Varian Spectra AA 220 atomic absorption spectroscopy. The procedure adopted to find the concentration was that we dissolved the corrosive medium by aqua regia [34, 35].

#### 2.4. Gasometrical Measurements (Analytical Studies)

The development of the corrosion process and the corrosion reaction was estimated using the volumetric method by measuring the volume of evolved hydrogen due to corrosion at a different time interval. The used steel metal sample was immersed in a corrosive solution in a Büchner flask. The used flask was then sealed with a rubber bung, and rubber tubing was linked to the bottom of an inverted measuring cylinder, which was placed above a basin, via its hose barb protruding through its neck. Distilled water was used to fill both the cylinder and the basin. The evolved hydrogen propels the distilled water step by step into the cylinder, where it is collected at the top and its volume monitored over time [34, 35]. This technique was carried out with and without various concentrations of the tested inhibitors.

#### 2.5. Potentiodynamic polarization measurements. (Electrochemical Studies)

For all electrochemical measurements, the experiments are made using the radiometer analytical, Volta master (PGZ301, DYNAMIC ELS VOLTAMMETRY). A counter electrode made of platinum wire is used. A reference electrode is made of calomel so that it is standard and all potential is attributed to it. In addition, a cylindrical electrode (1 cm<sup>2</sup> in area) is made of steel as a working electrode. It is abraded and cleaned using 600, 1000, 1200, 1500, and 2000 grade silicon carbide abrasive papers. Then it is washed with distilled water and degreased with ethyl alcohol, then cleaned with water and dried to be ready to work as a working electrode it was used immediately. This procedure was done before each experiment. The working electrode was dipped in the corrosion solutions for 50 min. The electrical scanning is done at a scan rate of 1 mV/sec. The inhibition efficiency % I.E. was calculated using the following mathematical equation [21-26].

$$\% \text{ IE} = \left( \frac{I - I_0}{I} \right) \times 100 \quad (4)$$

Where  $I$  and  $I_0$  are the corrosion current densities in the absence of inhibitors and in the presence of inhibitors, respectively. The corrosion potential ( $E_{\text{corr}}$ ), corrosion current ( $I_{\text{corr}}$ ), and Tafel constants ( $a$  &  $c$ ) were computed and tabulated using the values of the cathodic and anodic Tafel slopes obtained from the Tafel plot.

#### 2.6. Electrochemical Impedance measurements (Electrochemical Studies)

The electrochemical experiments were carried out using a three-electrode assembly that included calomel as a reference electrode, platinum wire as a counter electrode, and carbon steel specimens with an exposed surface area of 1 cm<sup>2</sup> as a working electrode. At an open circuit potential, impedance responses were tested (frequency range: 10-100 KHz, 5mV amplitude). All of the measurements and experiments were carried out at room temperature, in a motionless or unstirred environment.

Charge-transfer resistance, represented as  $R_p$  in the Nyquist plots' impedance data, was used to calculate the inhibitory efficiency.

The inhibition efficiency was calculated using charge-transfer resistance, which was designated as  $R_{ct}$  in the Nyquist plots' impedance data was calculated from the following equation[21-26]:

$$\% IE = [(R_{ct0} - R_{ct}) / R_{ct0}] \times 100 \quad (5)$$

The charge transfer resistance with inhibitor is  $R_{ct}$ , while the charge transfer resistance without inhibitor is  $R_{ct0}$ .

### 3. RESULTS AND DISCUSSION

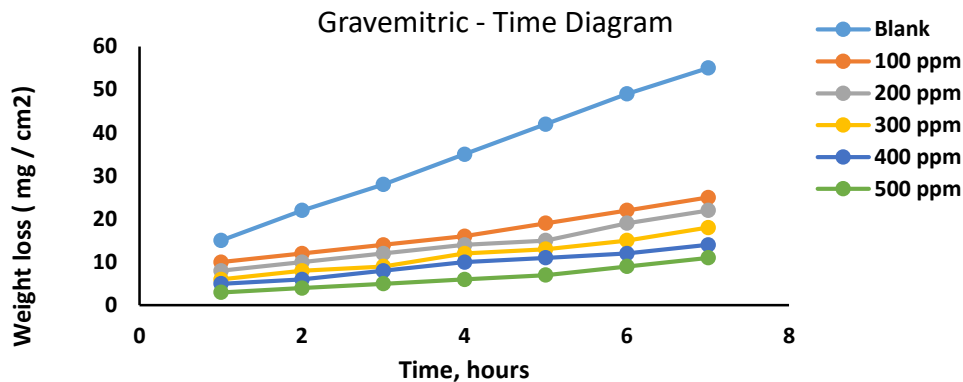
#### 3.1. Weight loss measurements (Chemical studies)

##### 3.1.1. Effect of inhibitor concentration.

The used inhibitor is expired Dulcolax medicinal drugs symbolized here as DULC, five different concentrations were used which are, 100,200, 300, 400, and 500pp. the corrosive environment is 1.0 M HCl solution. The weight of steel samples before and after immersion in the corrosive environment without and with inhibitor for 7 hours is taken as an average of three readings. The mass loss calculated was used in the calculation of corrosion rate, surface coverage  $\theta$ , and corrosion inhibition efficiency. The results of the weight loss measurements are tabulated in table 2. The expired DULC inhibitor act as a good corrosion inhibitor for steel in a 1.0 M HCl acidic corrosive environment. The corrosion rate increased dramatically by increasing the time of immersion but decreased by increasing inhibitor concentration. The corrosion inhibition efficiency increases with an increase in the drug inhibitor concentration (figure 2).

**Table 2.** shows weight loss statistics and characteristics for low carbon steel corrosion in 1.0 M HCl with and without expired DULC medication as an inhibitor at 303 k.

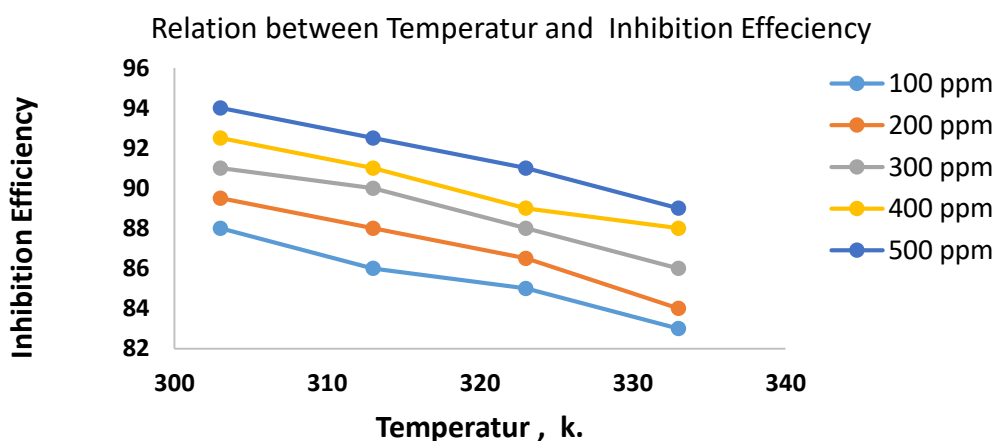
Inhibitor	The used Concentration (ppm)	The Rate of Corrosion (mmpy x 10 <sup>-3</sup> )	The surface coverage ( $\theta$ )	The values of Corrosion Inhibition Efficiency (% I.E.)
Blank	Free	9.7		
Expired Dulcolax medicinal drug DULC	100	1.7	0.824	82.4
	200	1.4	0.855	85.5
	300	1.2	0.876	87.6
	400	0.9	0.907	90.7
	500	0.8	0.9175	91.8



**Figure 2.** Mild steel weight loss in mg vs. time in 1.0 M HCl corrosive solution in the absence and presence of expired DULC medications as a potential nontoxic (green) corrosion inhibitor

3.1.2. Effect of temperature.

Figure 3 depicts the relationship between temperature and corrosion inhibition efficiency. For the samples with varying concentrations, a temperature range of 303K-333K was used with a 7-hour immersion time. It can be shown that as the temperature rises, the inhibition efficiency diminishes. This could be due to increased solution agitation shifting the adsorption-desorption equilibrium towards the desorption of adsorbed inhibitors. The ability of the inhibitor to be adsorbed on the metal surface may be reduced as a result of this, as well as the roughening of the metal surface due to increased corrosion. This demonstrates that adsorption is a physical process. The inhibitory efficiency diminishes as the temperature rises, possibly because the amount of adsorbed molecules on the carbon steel surface reduces [21-26].



**Figure 3.** Effect of temperature on steel percent I.E. in 1.0 M HCl in the presence of various doses of expired DULC medicines as a green inhibitor, data from weight loss measurements.



3.2. Atomic absorption spectroscopy measurements (AAS) (Analytical studies)

Atomic absorption spectroscopy measurements is simple and accurate techniques used in measurements of many metal cations in aqueous, acidic, and alkaline solution. AAS techniques of many advantages, as it is simple, low cost, high speed, and can be applied in both scientific and industrial applications. Atomic absorption has many applications in the industrial and environmental field, it is used for raw materials inspection, product evaluation, final product inspection, and environmental analysis. AAS is considered as an indirect measurement, as the concentration of iron ions in the corrosive solution which results from the corrosion of steel in an acidic environment was measured. The ferric ions released in the solution were measured directly using atomic absorption spectroscopy techniques. Corrosion of steel structures or other components can be costly to society, and the qualities of the corroding material can be assessed [33, 34]. The ferric ions  $Fe^{+2}$  concentrations that occur from steel corrosion in an acidic HCl corrosive environment were determined using atomic absorption spectroscopy in this work. The AAS data are provided in table 3, and an examination of this data revealed that raising the inhibitor concentration decreased the ferric ion concentration in the corrosive solution. In the present study, ferric ions were taken as a function of the corrosion rate, which means the increase of the ferric ion concentration accompanied by an increase in the corrosion rate and vice versa. The process of corrosion and ferric ion concentration is influenced by adding expired drug inhibitors. The data in table 3, which was obtained from AAS, are in good agreement with the data obtained from weight loss as chemical techniques. This means that both analytical and chemical measurements prove the good inhibition action of Expired DULC medicinal drugs and the drug inhibits the steel corrosion in an acidic environment.

**Table 3.** Shows the effect of expired drug DULC inhibitor concentrations on ferric ions concentrations as a consequence of the AAS technique (data taken at 303-333 k).

Inhibitor	Inhibitor Concentration	Concentrations of Ferric ions [ $Fe^{+3}$ ], ppm			
		303 k	313 k	323 k	333 k
Blank	Free	125	136	142	151
Expired Dulcolax medicinal drug DULC	100 ppm	28	43	51	62
	200 ppm	25	39	46	54
	300 ppm	21	31	41	49
	400 ppm	17	24	33	42
	500 ppm	11	14	27	38

3.3. Gasometrical measurement Hydrogen Evolution Method ( Analytical Studies)

The gasometrical or hydrogen evolution measurement was based on measuring the volume of the evolved hydrogen at different time intervals. When the steel or any active metals placed in an acidic environment upon the electrochemical reactivity series the more active metal like iron replace hydrogen of the acid, the hydrogen was evolved in the form of hydrogen gas. The evolved hydrogen was measured

using a gasometric system and used for calculation of corrosion inhibition efficiency % I.E. The gasometrical technique was utilized in this work to evaluate expired Dulcolax medical medications as green steel inhibitors in a 1.0 M HCl acidic environment. In the absence and presence of different concentrations of expired DULC medicines as a green inhibitor, 100, 200, 300, 400, and 500 ppm, the volume of hydrogen evolved during the corrosion reaction of iron with acidic 1.0 M HCl medium was measured with time at room temperature (30 0C). The following equation [34, 35] was used to compute the inhibitory efficiency:

$$\% \text{ I.E} = [ 1 - ( V_{\text{inh.}} / V_{\text{free}}) ] \times 100 \tag{6}$$

Where  $V_{\text{inh}}$  denotes the volume of hydrogen gas evolved by an inhibited solution and  $V_{\text{free}}$  denotes the volume of hydrogen gas developed by an uncontrolled solution. Table 4 shows the evolved hydrogen volumes and inhibition efficiency at various doses of the employed green inhibitor, DULC. As the inhibitor concentration is increased, the efficiency of inhibition improves. This suggests that the pharmacological inhibitor chemicals are effective carbon steel inhibitors in a 1.0 M HCl acidic environment [34, 35].

**Table 4.** Shows the hydrogen volumes and percentage inhibition efficiency for steel corrosion in an acidic H2SO4 solution with and without various concentrations of expired DULC medication at 303 k.

Sample	Expired drugs Concentrations ppm	The Volume of hydrogen gas (ml/ cm <sup>3</sup> )	I.E %
Blank	Free	56	-
Expired Dulcolax medicinal drug <b>DULC</b>	100 ppm	12	78.5
	200 ppm	10	82.1
	300ppm	7	87.5
	400 ppm	6	89.3
	500 ppm	5	91.0

### 3.4. Potentiodynamic Polarization Measurements ( Electrochemical studies)

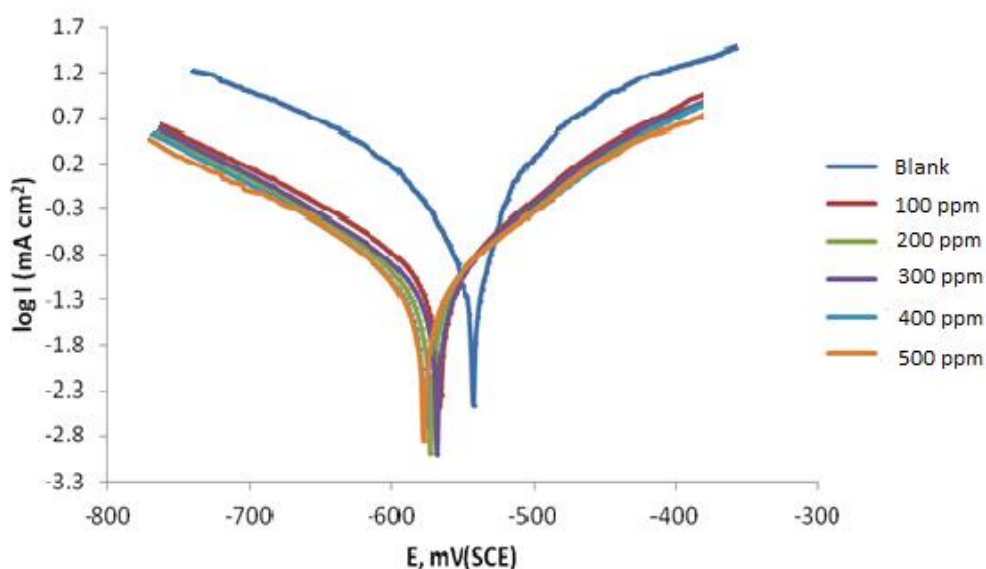
The characteristic elements of the corrosion inhibition process that produces a change in the anodic/cathodic process are studied using potentiodynamic polarization curves. Table 5 lists the parameters that were estimated. The expired medicine has been observed to have great biocompatibility, nontoxicity, and the ability to create a coating on the surface.

Inhibitors can change the process by slowing down the rate of corrosion. The corrosion current density and corrosion potential are determined by the point where the anodic and cathodic curves intersect.  $E_{\text{corr}}$  shifts towards value in the presence of an inhibitor when compared to blank, but no definitive change has been detected (Figure 4). As a result, the expired medications work as a combined inhibitor with a cathodic effect.  $I_{\text{corr}}$  values fell as drug inhibitor concentrations increased, implying that

in the presence of inhibitors, electrochemical processes are hampered by the creation of a shield on the low carbon steel surface [21-26].

**Table 5:** Potentiodynamic parameters for low carbon steel corrosion in 1.0 M HCl at 303 k with and without varying doses of expired DULC medication as an inhibitor.

Inhibitors	Conc., ppm	-E <sub>corr</sub> mV (SCE)	I <sub>corr</sub> mA cm <sup>-2</sup>	β <sub>a</sub> mVdec <sup>-1</sup>	β <sub>c</sub> mVdec <sup>-1</sup>	% I.E.	θ
Blank	Free	485	1.2	102	121	Free	Free
Expired Dulcolax medicinal drug DULC	100	531	0.22	121	139	81.6	0.816
	200	546	0.18	129	145	85.0	0.850
	300	549	0.13	138	151	89.1	0.891
	400	549	0.10	143	159	91.7	0.917
	500	553	0.09	148	163	92.5	0.925



**Figure 4.** Steel potentiodynamic polarization curves at 30 °C in 1.0 M HCl solution with various doses of expired DULC pharmacological inhibitor.

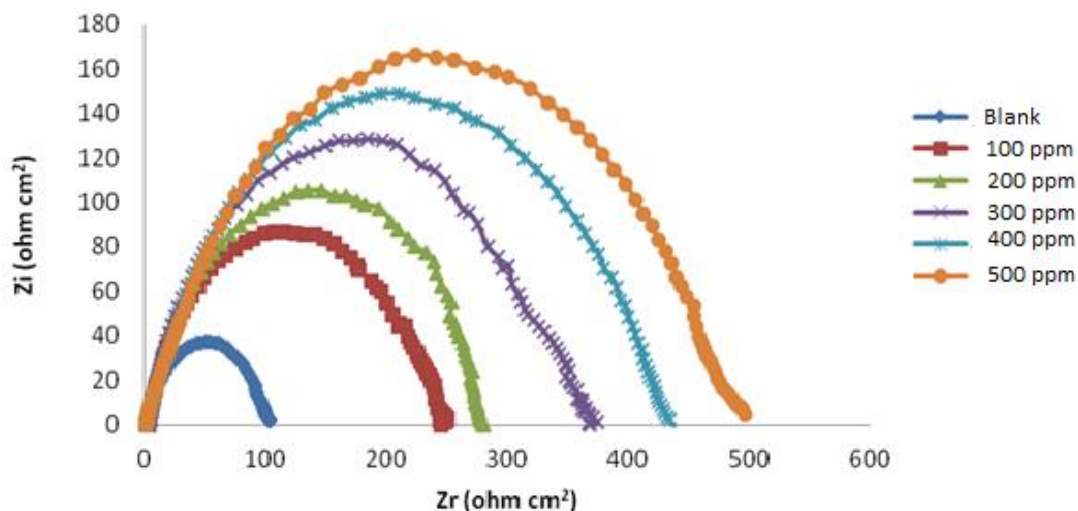
3.5. Electrochemical Impedance Spectroscopy, EIS, (Electrochemical studies)

Electrochemical impedance spectroscopy, or EIS, is a very precise technique that aids in the understanding of corrosion and inhibitory mechanisms. Electrochemical impedance spectroscopy was used to investigate corrosion inhibition with and without inhibitor at varied concentrations of expired medicines inhibitor (EIS). The values obtained for the characteristic parameters connected to the impedance diagrams are listed in Table 5. R<sub>ct</sub>, a measure of electron transmission across a contact, is

found to be inversely proportional to corrosion rate. The semicircle fitting approach was used to get the electrochemical impedance parameters. A single time constant is represented by a perfect semicircle in Nyquist plots. Impedance measurements reveal surface resistance and capacitance, as well as a substance's suitability as a corrosion inhibitor and the nature of the inhibition process. The frequency dispersion of interfacial impedance, which is related to non-homogeneity of the surface and roughness of the metal, is blamed for deviations from perfect circular forms [21-26]. In our study, the layout obtained was not a complete semicircle. This could be related to the insertion of an inhibitor that induces a complete semicircle distraction. Single semicircles are shifted concurrently with the real impedance of the x-axis in the Nyquist plot (Figure 5). The impedances rose as the concentrations of expired drugs increased. Furthermore, for all concentrations, the impedance profiles remained unchanged. Inhibitors can change the process by slowing down the rate of corrosion. Furthermore, because of the inhibitor corrosion, it can be determined that the rate-controlling mechanism is a reaction-controlled mechanism. With an increase in inhibitor concentration,  $R_{ct}$  values rise. As a result, the corrosion response is predominantly controlled by the charge transfer mechanism. Furthermore, a drop in  $C_{dl}$  values with an increase in inhibitor concentration is owing to the inhibitor's increased surface coverage. An increase in inhibition efficiency is the cause of this. The decrease in  $C_{dl}$  value could be due to a lower local dielectric constant and/or a thicker electric double layer on the carbon steel surface[21-26].

**Table 6.** shows the electrochemical impedance parameters of low carbon steel corrosion in 1.0 M HCl with and without various doses of expired DULC medication as an inhibitor at 303 k.

Sample	Inhibitor concentration ppm	R1 (Ohm/cm <sup>2</sup> )	Rct (Ohm/cm <sup>2</sup> )	Cdl μF cm <sup>-2</sup>	% I.E.	θ
Blank	Free	1.7	18.5	1.6	Free	Free
Expired Dulcolax medicinal drug DULC	100	9.9	145	10.5	87.2	0.872
	200	10.7	175	10.7	89.4	0.894
	300	11.5	220	11.6	91.5	0.915
	400	12.8	250	11.9	92.6	0.926
	500	12.9	280	12.5	93	0.93



**Figure 5.** Nyquist plots for a carbon steel electrode in 1.0 M HCl at 300°C with varied doses of expired DULC pharmaceuticals as a green inhibitor.

### 3.6. Adsorption isotherm

The nature of the mild steel metal surface and its charge contributes to the adsorption process as well as to the electronic characteristics of metal surfaces. This is also related to ionic species, the temperature of the corrosion process, adsorption of elements, and electrochemical potential.

To describe the best-fit isotherm for the adsorption process, mass loss measurement is utilized to determine the values of surface coverage ( $\theta$ ) at various drug doses. The Langmuir adsorption isotherm [21-26] is the best fit for the results.

$$C_i / \theta = 1 / K_{\text{ads}} + C_i \quad (7)$$

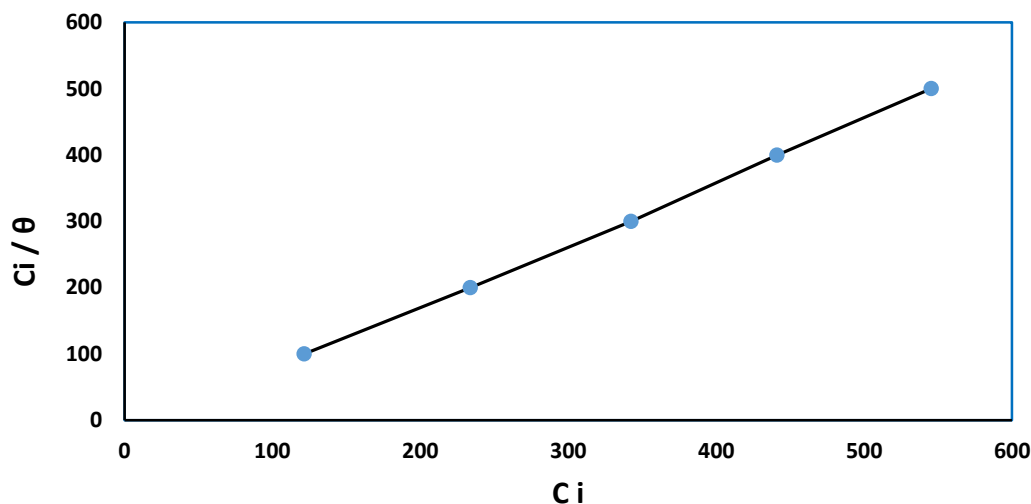
Where  $K$  and  $C$  are the adsorption process's equilibrium constants and the drug concentration, respectively [21-26].

As seen in figure 6, plotting  $C/\theta$  vs  $C$  yielded a straight line. The intercept of a straight line with a nearly unit slope value is  $1/K$ . The equation for calculating the standard free energy of adsorption  $\Delta G^\circ_{\text{ads}}$  is:

$$K_{\text{ads}} = 1/55.5 \exp (-\Delta G_{\text{ads}} / RT) \quad (8)$$

Where  $K_{\text{ads}}$  is the adsorption equilibrium constant, 55.5 is the mole/liter water dose in the bulk of the solution,  $T$  is the absolute temperature, and  $R$  is the gas constant.  $\Delta G_{\text{ads}}$  have a computed value of -33.65 kJ/mol. The fact that  $\Delta G_{\text{ads}}$  is negative implies that drug molecules adsorb spontaneously on the metal surface [21-26]. The obtained value, on the other hand, is less than the -40 kJ/mol threshold value necessary for chemical adsorption, indicating that the adsorption mechanism is physical [21-26].

It's widely assumed that the investigated expired medication, compound, inhibits corrosion by adsorbing at the metal/solution contact. Furthermore, the development of a solid organic molecule complex with the metal atom is thought to have gotten a lot of attention [21-26].



**Figure 6.** Carbon steel Langmuir adsorption isotherm in 1.0 M HCl inhibited by the used expired DULC drug inhibitor at 30°C.

#### 4. CONCLUSION

The following conclusions were reached based on the experimental findings and theoretical calculations:

1- The Dulcolax (DULC) expired medicines act as possible nontoxic (green) corrosion inhibitors. It is safe for people, especially at the very low quantities utilized, yet it has a significant technical, economic, and environmental influence on steel materials.

2- It was discovered that increasing the DULC concentration increased the corrosion inhibition efficiency until it reached 92 percent inhibition efficiency at 500 ppm from the expired Dulcolax (DULC) prescription medications. The amounts of ferric ions ( $Fe^{+3}$ ) were reduced by increasing the inhibitor concentration, as evidenced by atomic absorption spectroscopy (AAS) data.

3- The volume of hydrogen gas produced by mild steel corrosion in an acidic environment was observed to decrease as the concentrations of the expired prescription drug Dulcolax increased (DULC). This means that the medication molecules are in charge of controlling and inhibiting the corrosion and hydrogen evolution processes.

4- The Potentodynamic polarization data shows that the values of corrosion potential ( $E_{corr}$ ) are steadily changing to the negative region (negative values), indicating that the utilized expired medical medications Dulcolax (DULC) are inhibited in a mixed-type manner, but in a cathodic region.

5- The electrochemical Impedance spectroscopy (EIS) data shows that the size of the semicircle grows in proportion to the inhibitor concentration, indicating that the charge transfer mechanism is the primary governing factor in the steel dissolution process.

6- It was established that the process of mild steel corrosion inhibition was caused by the adsorption and adherence of inhibitor particles (drug components) to the steel surface, where they created an inert protective coating.

7- The development of a single layer of drug Dulcolax (DULC) molecules on the surface of

the mild steel metal was discovered to follow the Langmuir adsorption curves.

8- All of the results agreed that it was possible to use expired prescription medications like Dulcolax (DULC) as mild steel inhibitors in an acid medium.

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