Green Approach to Corrosion Inhibition on Mild Steel in Acidic Media by the Expired Sulpha Drug

L.P. Chaudhari[1], S. N. Patel[2,*]

[1, 2] PG and Research Department of Chemistry,S.P.D.M. College, Shirpur, Dist. Dhule, Maharashtra, India*

ABSTRACT

The inhibiting effect of expired Bactrim drug on the corrosion of mild steel in 2 M HCl was studied by Gravimetric method, potentiodynamic polarization, electrochemical impedance spectroscopy (EIS), scanning electron microscopy (SEM), energy dispersion spectroscopy (EDS) and FTIR techniques. Maximum inhibition efficiency occurs 400ppm Inhibitor concentration for 4 hour time of immersion at 303^{o}K.adsorption process is follows. Results obtain from various methods are in good agreement to each other. El-Awardy adsorption isotherm. Adsorption is spontaneous and exothermic. Use of expired Bactrim drug is economically beneficial as well as safe to environment.

Keywords- Mild Steel, expired drug, potentiodynamic polarization, EIS, FTIR

1. INTRODUCTION

Corrosion is defined as loss in the useful properties of materials due to attack of surrounding on the surface of materials. Corrosion is a principal process assuming an important role in economics and safety especially for metals. The utilization of inhibitors is one of the best methods for protection corrosion of metals especially in acidic media. Technological and financial considerations may sometimes favour the addition of inhibitors to reduce the corrosion rate [1-4]. Mild steel is an important material which finds wide applications in industry due to its excellent mechanical properties and low cost. It is extensively used in various industries as construction material for chemical reactors, heat exchanger and boiler systems, storage tanks, and oil and gas transport pipelines. During such activities, inhibited hydrochloric acid is widely used in pickling, descaling, cleaning agents and stimulation of oil wells in order to increase oil and gas flow. Hence inhibition of corrosion of mild steel is a matter of theoretical as well as practical importance [5-8].

Most well-known inhibitors are organic compounds containing nitrogen (N-heterocyclic), sulphur, long carbon chain or aromatic and oxygen atoms. The use of drugs offers interesting possibilities for corrosion inhibition due to the presence of heteroatoms in their structures, and they are of particular interest because of their safe use. But fresh drug cannot be used as inhibitor because some of them are too expensive compare to the conventionally used organic inhibitors[9-13]. Expired / unused drug can be good alternative instead of using fresh drug as inhibitor. In most of the cases, people dispose the unused expireddrug through waste basket or toilet flush through which the drug can be exposed to sunlight, oxygen, moisture or extreme temperature leading to an uncontrolled degradation which can potentially generate toxic waste products. The use expired drug can be helpful to reduce the disposal costs of expired drugs as well as to avoid the environmental pollution[14-18].

In this study expired Bactrim drug is used as corrosion inhibitor for mild steel in acidic media. Thus research would give an effective, non-hazardous and green alternative to toxic corrosion inhibitors.

2. EXPERIMENTAL

2.1. MATERIAL

2.1.1MILD STEEL SAMPLE PREPARATION

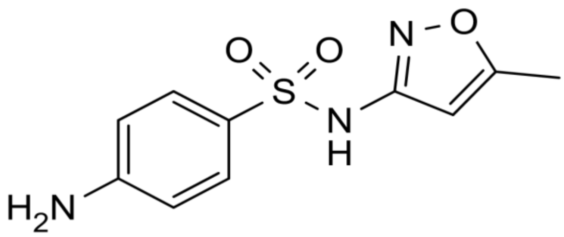
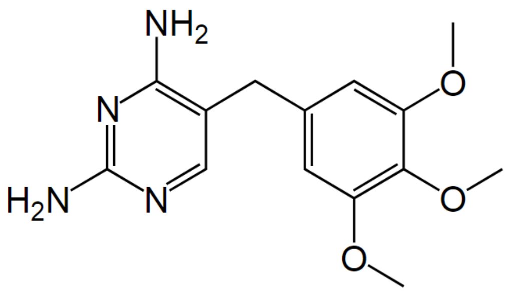
Mild steel (MS) coupons (composition: 0.041% C , 0.009% S, 0.011% P 0.1% Mn, 0.01% Si 0.06% Al and balanced Fe). of size 3x3x0.051 cm is press cut from the commercially available mild steel sheet. Each coupons is polished with different grades (upto to 1200 grade) of abrasive emery paper and degreased with acetone washed with double distilled water were used for the present study. Electrochemical measurements were carried out on a 6 cm long coupon with exposed area of 2 cm^2 and remaining portion was covered with commercially available lacquers.

2.1.2 INHIBITORS

Bactrim pill is White, Round and has been identified as

Generic Name: Sulfamethoxazole/Trimethoprim[400 mg / 80 mg]

Bactrim is used in the treatment of skin infection ,urinary tract infection bacterial infection sinusitis etc.

Sulfamethoxazole Synonyms • 3-(p-Aminophenylsulfonamido)-5-methylisoxazole • 3-Sulfanilamido-5-methylisoxazole • 4-Amino-N-(5-methyl-3-isoxazolyl)benzenesulfonamide	
Trimethoprim Synonyms • 2,4-Diamino-5-(3,4,5-trimethoxybenzyl)pyrimidine • 5-[(3,4,5-Trimethoxyphenyl)methyl]-2,4-pyrimidinediamine	

Drug was purchased from medicine shop and used without further purification after the six months of the date of expiry. Different concentrations of expired Bactrim drug were prepared by diluting appropriate volume of 1000 ppm stock solution.

2.1.3. AGGRESSIVE SOLUTION

The aggressive solution (2M HCl) was prepared by dilution of Analytical Grade 35.5 % HCl with double-distilled water.

2.2 Procedure

2.2.1 Gravimetrc method.

Gravimetrc measurements were carried out in glass beakers containing 100 mL solution without and withdifferent concentrations of expired drug inhibitor (100 to 500 ppm) in 2 M HCl solutions for different time of immersion(2,4,6,10,16 and 24 hrs.). Experiments were carried out in triplicates and average value of weight loss is reported. Temperature dependence of the inhibition efficiency was studied in the temperature range 303, 313, 323 and 333 K using equitron stirred water bath

2.2.2 Electrochemical method

Three-electrode glass cell assembly with platinum wire as a counter electrode, a saturated calomel electrode (SCE) as a reference electrode and MS specimen (exposed area 2 cm2), were used as working electrode for electrochemical study. All electrochemical measurements were carried out using Gamry Instruments Interface 1010T model at 303 K. temperatures. Echem Analyst 7.06 Software installed in a laptop was used for fitting data. After establishment of the open circuit potential, potentiodynamic polarization curves were obtained with a scan rate of 1 mVs-1 in the potential range from -150 to +150 mV. Corrosion current density (icorr) values were obtained by Tafel extrapolation method. A time interval of 30 min was given for each experiment to attain the steady-state open-circuit potential. The EIS measurements were carried out in a frequency range from 20 kHz to 0.1 Hz with amplitude of 10 mV. Electrochemical Impedance Spectroscopy (EIS) used to provide information about the kinetics of the electrochemical processes at the mild steel/acid interface.

2.2.3 SURFACE ANALYSIS

2.2.3a SEM-EDX ANALYSIS

Mild steel coupons were immersed in 2 M HCl in the absence (blank) and presence of 400 ppm (optimum concentration) of expired bactrim solution at 303 °K for 4 hours.Comparative study of was carried outusing scanningelectron microscopy (SEM) and energy dispersive x-rayspectroscopic analysis (EDX).

2.2.3b. FOURIER TRANSFORM INFRARED SPECTROSCOPIC ANALYSIS

FTIRanalysis is carried out to identify the characteristic adsorption peaks ofinhibitor molecules on the mild steel electrode surface using a FT-IR (IR Affinity 1), Shimadzu, Japan

3. RESULTS AND DISCUSSION

3.1GRAVIMETRC METHOD

Corrosion rate, degree of surface coverage (θ) and inhibition efficiency (% IE) calculated from weight loss using following equations.

The corrosion rate (CR) was computed from the following equation:

$$\mathrm{CR(mm\ per\ year)} = \frac{87.6W}{atD} \qquad \textbf{(1)}$$

where

$W$is the average weight loss of MS coupons, a represents the total surface area of one MS coupon, t is the immersion time and D is the density of MS in g cm$^{-3.}$

The surface coverage (θ) is calculated as follows:

$$\text{surface coverage } (\theta) = 1 - \left(\frac{\mathrm{CR}}{inh_{CR}}\right) \qquad \textbf{(2)}$$

Where CR and ^{inh}CR are the corrosion rates of MS in the absence and presence of the inhibitors respectively. The inhibition efficiency (% IE) is calculated as follows:

$$\text{Inhibition efficiency (\% IE)} = \text{surface coverage } (\theta)\ X\ 100 \qquad \textbf{(3)}$$

3.1.1 Effect of inhibitor concentration and time of immersion

From Table 1 and Figure 1 it is clear that for expired Bactrim as corrosion inhibitor inhibition efficiency increases with increase in concentration of inhibitor. Inhibition efficiency increases with increase in time up to 4 hrs. then start decrease as shown in fig 1.[19]

Table 1. Inhibition efficiency on mild steel of the inhibitor in 2 M HCl for various immersion and Time in different concentrations

		Time of Immersion (hour)											
	Inhibitor Conc (ppm)	2		4		6		10		16		24	
		CR	% IE	CR	% IE	CR	% IE	CR	% IE	CR	% IE	CR	% IE
303 ^{0}K	Blank	4.257	---	13.264	---	18.995	---	13.755	---	46.136	---	33.923	---
	100	2.947	30.77	7.369	44.44	9.825	48.27	7.401	46.19	25.954	43.74	21.505	36.60
	200	2.620	38.46	6.222	53.09	9.279	51.14	6.484	52.85	24.562	46.76	18.886	44.33
	300	2.292	46.15	5.240	60.49	7.642	59.77	5.639	59.00	22.188	51.91	16.675	50.84
	400	1.965	53.85	4.257	67.90	7.205	62.06	5.174	62.38	21.123	54.21	15.938	53.02
	500	1.965	53.85	4.585	65.43	7.423	60.92	5.436	60.47	21.451	53.50	16.320	51.89

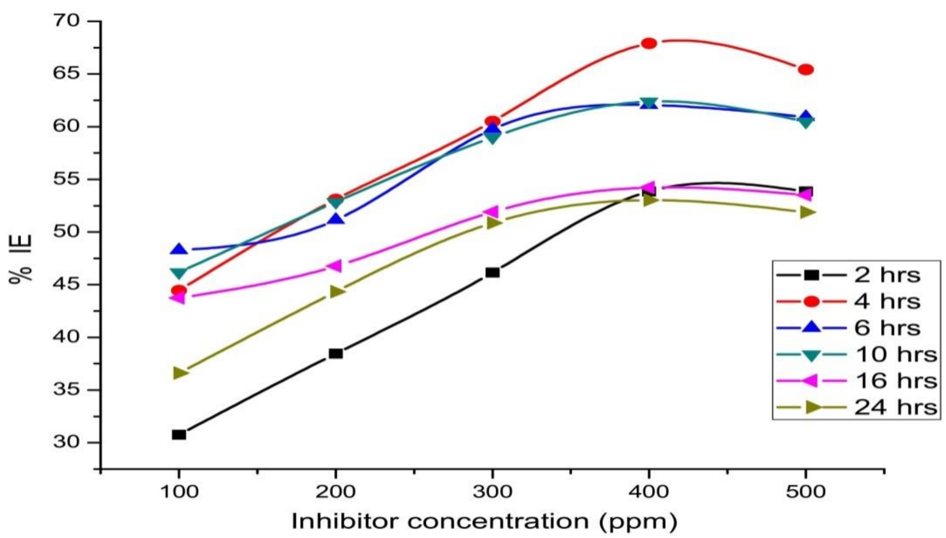


Figure 1.Variation of inhibition efficiency with concentrations of expired bactrimin 2 M HCl for the different Time of immersion at 303K

3.1.1 Effect of Tempearure

Effect of Temperature was studied in the temperature range 303Kto 343 K for 4 hour immersion time in 2M HCl and various concentration of expired bactrim. The data is summarised in table 2. From the data it is concluded that that Corrosion rate increases with increase in temperature while inhibition efficiency decreases with increase in temperature due to desorption of inhibitor (fig.2)[20-21].

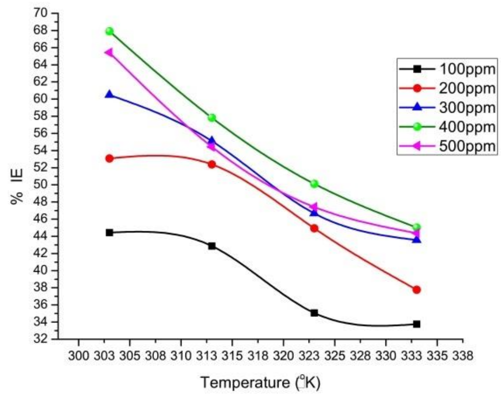


Fig2. Variation of inhibition efficiency with Temperature for the different concentrations of expired bactrim in 2 M HCl

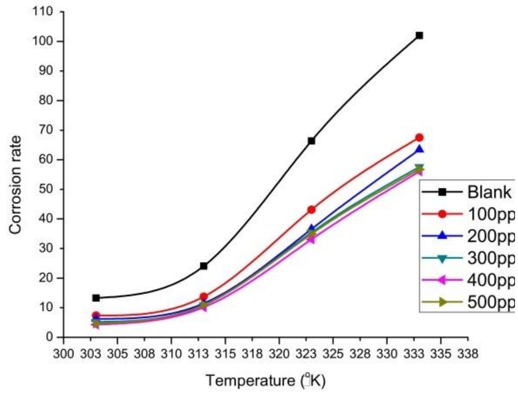


Fig2b. Variation in Corrosion rate with Temperature for the different concentrations of expired bactrim in 2 M HCl

Table 2. Inhibition efficiency on mild steel of the inhibitor in 2 M HCl for range of temperature in different concentrations

Temperature (°K)								
Inhibitor Concentration(ppm)	303		313		323		333	
	CR	%IE	CR	%IE	CR	%IE	CR	%IE
Blank	13.279	---	24.098	---	66.393	---	101.967	---
100	7.377	44.44	13.770	42.86	43.115	35.06	67.541	33.76
200	6.230	53.09	11.475	52.38	36.557	44.94	63.443	37.78
300	5.246	60.49	10.820	55.10	35.410	46.67	57.541	43.57
400	4.262	67.90	10.164	57.82	33.115	50.12	56.066	45.02
500	4.590	65.43	10.984	54.42	34.918	47.41	56.721	44.37

3.1.4. ADSORPTION ISOTHERM

Adsorption isotherms are usually used to describe the adsorption process.

Attempts are made to fit the most frequently used isotherms such as Langmuir, Freundlich, Temkin, El-Awardy, Flory-Huggins and frumkin adsorption isotherms.The experimental data have been then fitted into the modified form of Langmuir isotherm known as El-

Awadyisotherm which can appropriately represent the adsorption behavior ofthe inhibitor onto the metal surface. El-Awady isotherm is given by

$\log(\Theta/1\text{-}\Theta) = \log K + y \log C$ **(4)**

where,

y is number of inhibitor molecules occupying one active site.

Θ (IE/100) is the surface coverage. C is the concentration,

K is the constant related to the equilibrium constant of adsorption process.

$K_{ads}=K^{1/y}$ and y represent the number

of inhibitor molecules occupying a given site. The values of

1/y calculated from El-Awady model is given in Table 3. And figure

Table 3. Adsorption parameter derived from El-Awadyadsorption isotherms for Mild steel corrosion at different temperature

K_{ads}	1/y	ΔG^0_{ads}(kJ/ppm)	R^2
0.0067	1.4697	-12609	0.9678
0.0055	2.317	-13125	0.9781
0.0026	2.2941	-14974	0.9614
0.0015	2.7871	-16467	0.9656

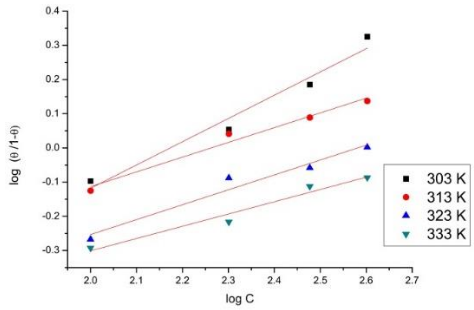


Figure 3. El-Awadyisotherm for the adsorption of Expired Bactrim drug on mild steel surface

From adsorption isotherm (Figure 3) and data obtain (Table 3) it suggest that the valye 1/y obtained were more than unity which indicates that each molecule of expired drug inhibitor involved in the adsorption process was attached to more than one active site on the metal surface.

Kads value decreases as temperature increases indicates that adsorption is not favoured at high temperature . Larger values of the Kads implied more efficient adsorption and hence better IE.

Relation between the equilibrium constant for the adsorption process (Kads) and standard free energy of adsorptionΔGads given as

$\Delta G^0_{ads} = -RT \ln(55.5\, K_{ads})$ **(5)**

Where, 55.5 is the concentration of water in solution in mol L

and R is the universal gas constant.

T is the absolute temperature

Adsorption process is spontaneous since values of ΔG^0_{ads} isnegative. Generally, values of

ΔG^0_{ads} up to - 20 kJ/mol are associated with the physisorption while those around−40 kJ/mol^{-1} or larger negative are associated with chemisorption. In current ΔG^0_{ads} values are less than −20 kJ/mol, indicates physisorption[22-23].

3.1.5. THERMODYNAMIC ACTIVATION PARAMETERS

Thermodynamic parameters of adsorption play an important role to undestnad the mechanism of adsorption process of the metal surface. The adsorption heat (ΔH^0_{ads}) calculated using the van't Hoff equation:

$$\ln K_{ads} = -\Delta H^0_{ads}/RT + \text{Constant} \qquad (6)$$

where, $(-\Delta H^0_{ads}/R)$ is the slope of the straight-line $\ln K_{ads}$ vs 1/T(fig 4),

R is the gas constant and T is the absolute temperature. The entropy of adsorption ΔSads was determine using Basic thermodynamic equation as Follows:

$$\Delta \text{Gads} = \Delta \text{Hads} - T\Delta \text{Sads} \qquad (7)$$

The enthalpy of adsorption (ΔHads) can be calculated from the rearranged Gibbs-Helmholtz equation

$$\frac{\Delta \text{Gads}}{T} = \frac{\Delta \text{Hads}}{T} + K \qquad (8)$$

The Plot ofΔGads/T verses 1/T gave a straight line with a slope of ΔHads as shown in **fig5.**

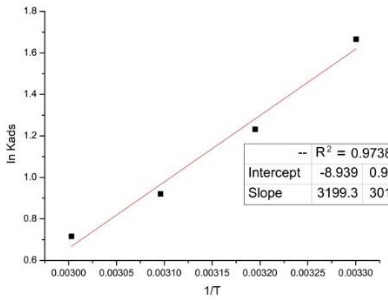


Figure4. Plot of lnKads versus 1/T

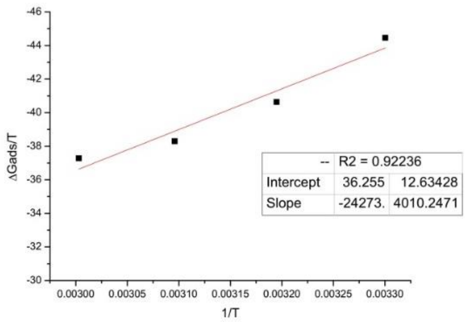


Figure 5. Plot of ΔGads/T verses 1/T

The value of the enthalpy and entropy of adsorption calculated by Van't Hoff equation , Basic Thermodynamic equation and Gibbs–Helmholtz relations are in good agreement.

Negative sign of enthalpy of adsorption indicates that adsorption is exothermic. The positive value of ΔSads can be attributed to the increase in the solvent entropy[24-26].

Table4. calculated value of the enthalpy and entropy of adsorption

	ΔHads	ΔSads
Van't Half Equation	-26599	40.932
Basic Thermodynamic equation	-23954	35.25
Gibbs- Helmholtz Equation	-24277	---

3.2. ELECTROCHEMICAL MEASUREMENTS
3.2.1. POTENTIODYNAMIC POLARIZATION

Electrochemical parameters such as corrosion potential (Ecorr), corrosion current density (Icorr), tafel constants (βa and βc), , Inhibition Efficiency (%IE) are obtained by the tafel extrapolation method (fig 6).

The inhibition efficiency (% IE) was calculated using the following equation (9) and represented in table 5.

$$\% \text{ IE} = 1 - \frac{\text{Icorr}}{\text{I}^0\text{corr}} \text{X } 100 \qquad (9)$$

Where I^0corr and Icorr are the corrosion current density in the absence and presence of the inhibitor respectively.

Table 5. Electrochemical parameters from Tafel polarization Curves for the dissolution of mild steel in absence and presence of various concentrations of inhibitor at 303K

Concentration (ppm)	Ecorr(mV)	βc mV/decade	βa (mV/decade)	Icorr (µA/cm2)	%IE	Corrosion Rate(mpy)
Blank	-536	131.7	71.8	2510	0	618.2
100	-550	120.1	67.7	2100	16.33466	470.5
200	-549	126.5	71.6	1220	51.39442	273.8
300	-545	132.4	66	304	87.88845	68.16
400	-552	128.3	61.7	141	94.38247	31.55
500	-538	134.4	70.7	226	90.99602	50.64

From Table 5 it isobserved thatt the values of βc for inhibited test specimens showed more prominent change as compared to value of βa, with respect to value of Tafel slopes (βcand βa) of uninhibited solution. This suggests that the expired Bactrim dug predominantly affect the mechanism of cathodic hydrogen evolution. control of cathodic reaction also supported due to slight shift in Ecorr value towards negative direction in presence of inhibitor as compared to in blank solution.Since the displacement in Ecorr is less than 85 mV suggest the Mixed mode of inhibition [27-28]

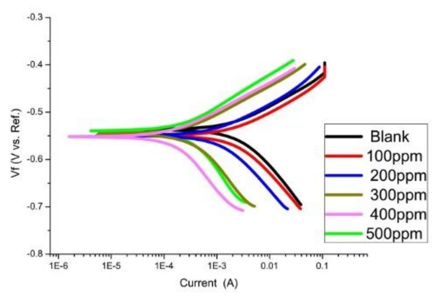


Figure6. Tafel polarization Curves for the dissolution of mild steel in absence and presence of various concentrations of inhibitor at 303K

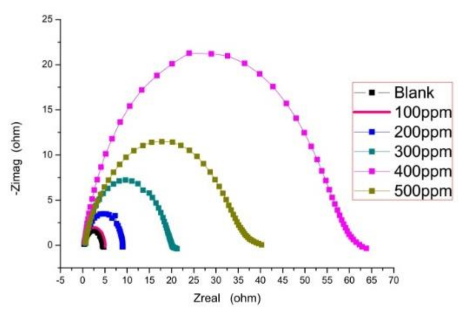


Figure7 Nyquist plot for mild steel in absence and presence of various concentrations of inhibitor at 303K

3.2.2Electrochemical Impedance Spectroscopy (EIS)

Nyquist plots in the absence and presence of different concentrations of expired Bactrim inhibitor at 303 K are shown in Fig. 7.

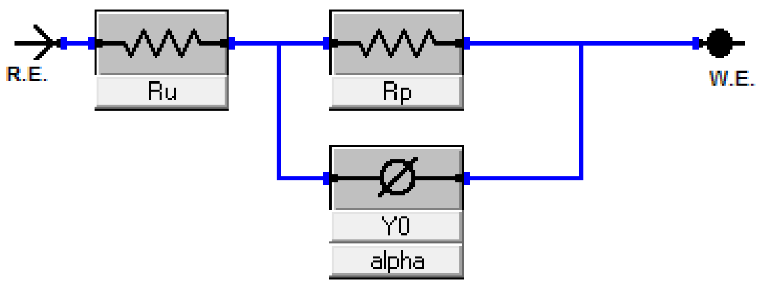


Figure 8. electrical equivalent circuit model used to fit the impedance measurements

In a Model

Ru represents solution resistance

Rp represents the polarization resistance

Y0 represents CPE coefficient

Alpha (α) represents CPE exponent (phase shift) which is a measures of surface homogeneity.

The double layer capacitance (*C*dl) was calculated from the following equation**(10)**.$\boldsymbol{C_{dl}= Y0(\omega_{max})^{\alpha-1}}$ **(10)**

Table 6. Impedence data for for mild steel in absence and presence of various concentrations of inhibitor at 303K

Inhibitor Concentration	Rp	Y0	Alpha (α)	Cdl (mF cm2)	%IE
blank	4.238	8.87E-04	0.833	27.9E-05	---
100	4.817	6.31E-04	0.853	22.9E-05	12.01993
200	8.687	4.54E-04	0.838	15.4E-05	51.21446
300	19.44	2.70E-04	0.829	8.95E-05	78.19959
400	61.03	3.05E-04	0.765	7.89E-05	93.05587
500	36.05	3.84E-04	0.753	9.25E-05	88.24411

where, $\omega_{max} = 2\pi\ f_{max}$ (f_{max}represents the maximum frequency at which the imaginary component of the impedance has a maximum value).

The inhibition efficiency (%IE) of the inhibitor has been found out from the charge transfer resistance values using the following equation **(11).**

$$\%\ \mathrm{IE} = 1 - \frac{Rp^0}{Rp^{inh}} \mathrm{X}\ 100 \qquad \mathbf{(11)}$$

Where$Rp^{inh}$and $Rp^0$are the values of charge transfer resistance in presence and absence of inhibitor in 2M HCl respectively.Results obtained are reported in table 4

The data shown in Table 5 reveal that The decreases in *C*dl value on increasing the concentration of the inhibitors indicates increase in the thickness of the electrical double layer, also the value of *Rp* increases with increase in concentration of inhibitors confirms adsorption of inhibitor molecules at the metal/solution interface .

Inhibition efficiency values obtain from potentiodynamic polarization and Electrochemical Impedance Spectroscopy are in a good agreement.[29-30]

3.2.3 SURFACE ANALYSIS

3.2.3 Surface analysis

Fig. 9 (a and b) shows the SEM images of the mild steel surface after immersion in 2 M HCl, for a period of 6 h, in absence (fig9 a) and presence (fig 9b) of 400ppm solution, respectively.

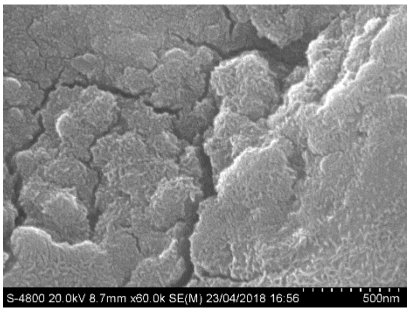
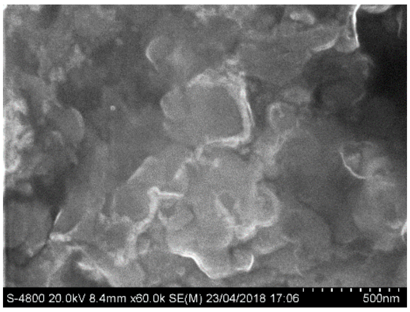
	

Figure9a. Mild Steel in 2M HCl	Figur9b. Mild Steel in 400 ppm expired bactrim

The SEM micrographs show that the surface of mild steel is highly damaged in the blank solution compare to surface in the presence of the inhibitor)). These results indicate that the inhibitor molecules hinder the dissolution of carbon steel by formation of a protective film on the steel surface.

Energy Dispersive Spectroscopy

The energy dispersive x-ray analysis (EDX) technique was used to find the element composition of the surface of the mild steel sample from fig10a, 10b and 10c in the presence and absence of inhibitor in 2M HCl solution after 6h immersion is given in table 8.

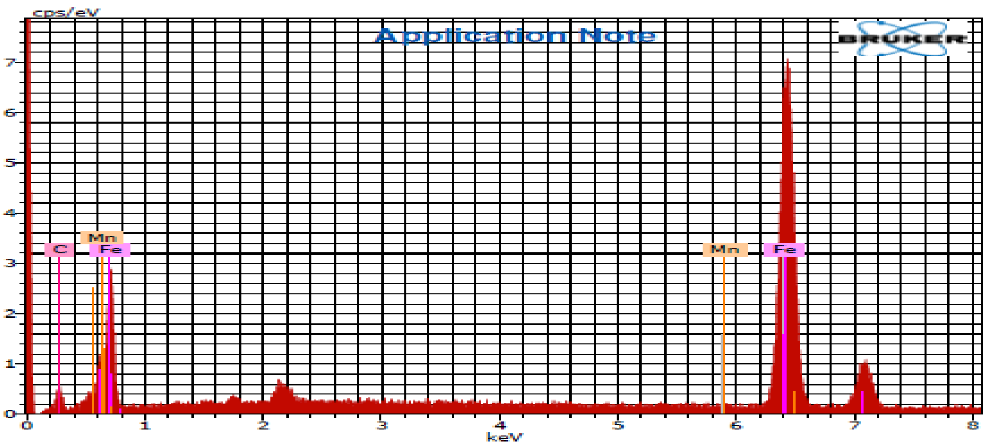


Fig. 10a: Polished Mild Steel

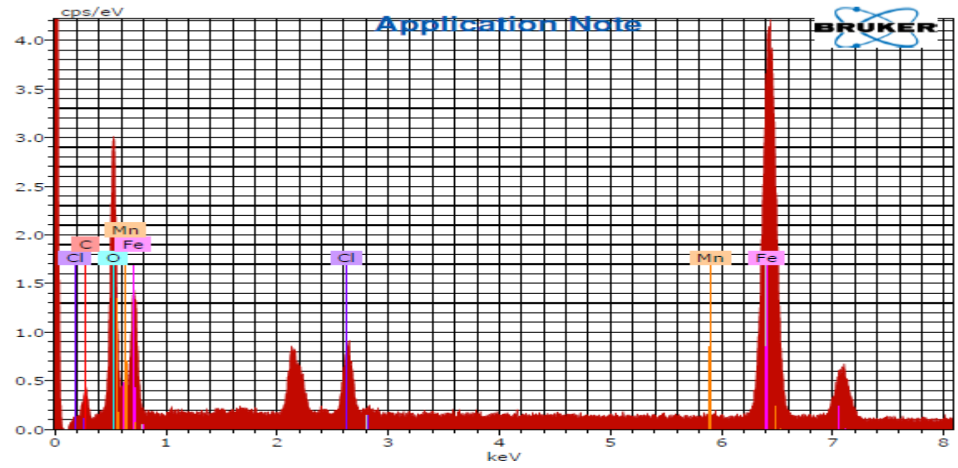


Fig. 10b. Mild Steel in 2M HCl

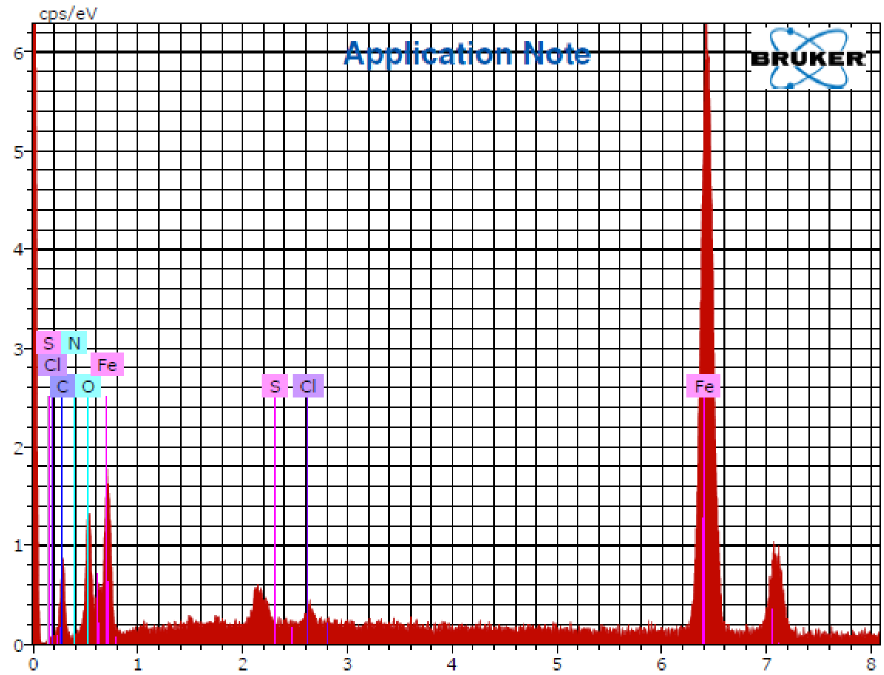


Fig. 10c. Mild Steel in 400 ppm expired bactrim

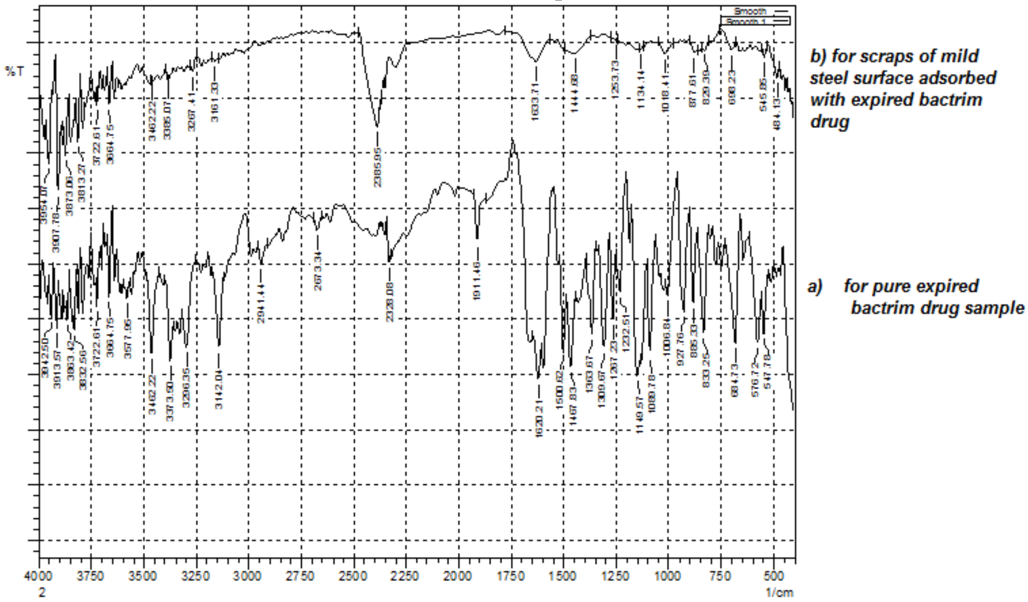
Table7. Element composition (Atomic %) of Mild steel sample in the presence and absence of inhibitor in 2M HCl solution after 6h immersion at 25 °C .

Inhibitors / Elements	Fe	Mn	C	O	N	S	Cl
Mild Steel (polished)	61.21	1.03	37.75	----	---	---	---
Mild Steel in 2M HCl	30.61	0.27	20.54	48.07	---	---	0.52
Mild Steel in 400 ppm expired bactrim	38.13	---	26.58	40.49	0.73	0.12	0.42

From table 7 we conclude that that Peaks for nitrogen (N) and Sulphur (S) are observed in presence of inhibitor which were absent in blank solution evident that protective layer is of expired bactrimdrug.Also the per cent atomic content of Oxygen and Chlorine is lower in presence of inhibitor solution as compared to blank solution suggest the protection of metal surface by the film of inhibitor. [31-32]

3.3b. Fourier transform infrared spectroscopic analysis

The FTIR spectra of expired Bactrim drug and scrapings from the inhibitor films on the surface of mild steel specimens is shown below.



Almost all the peaks observed for the surface film of the scraps the mild steel surface as that peaks obtain for expired Bactrim drug, which means that most of the functional groups of inhibitor also present in the adsorbed surface film. Moreover, some of the peaks for the Adsorbed film diminished or even vanished. By observing spectra it is concluded that –NH stretching(3462.22 cm^{-1}), $–NH_2$(2385.95 cm^{-1}) S=O (1018-1134 cm^{-1}) these functional groups are directly involved in metal-inhibitor interactions.[33]

Conclusions

Expired Bactrim drug acts as a good inhibitor for the corrosion of mild steel in 2 M HCl. The inhibition efficiency of drug increases with increase in concentration. Inhibition efficiency decreases with decrease in temperature. Adsorption process is spontaneous and exothermic, accompanied by an increase of entropy and follows El-Awardy adsorption isotherm. Potentiodynamic polarization curves reveals that Expired Bactrim drug is a mixed-type but predominantly cathodicinhibitor. Formation of the protective film of inhibitor on the mild steel was confirmed by surface analysis techniques (SEM–**EDXS** and FT-IR).

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