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Electrochemical Corrosion Inhibition of Mild Steel in Hydrochloric Acid Medium Using the Antidiabetic Drug Janumet as Inhibitor

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Abstract: **The inhibiting effect of Janumet in 1 M HCl on the corrosion of mild steel was studied by potentiodynamic polarization (PDP), Scanning Electron Microscopy (SEM) and Fourier Transform Infrared Spectroscopy (FTIR) techniques. The results of potentiodynamic polarization showed that corrosion current density, i_{corr}, decreases with increasing the concentration of organic inhibitors indicating a decrease in the corrosion rate as well as an increase in the inhibition efficiency of mild steel. The drug act as mixed type inhibitors, they retarded both cathodic and anodic reaction. The adsorption of Janumet on the carbon steel surface obeys Langmuir adsorption isotherm. Results from SEM and FTIR measurements confirmed well this behaviour.**

Keywords: **Mild steel , HCl, Corrosion inhibition, Potentiodynamic polarization.**

1. INTRODUCTION

Inhibitors are generally used in the industrial process to control metal dissolution, especially in acid environment [1]. Most of the efficient inhibitors used in industry are the organic compounds such as drugs which possess at least one functional group, which is considered as the active center for the adsorption process. Several researchers have made an attempt to study the inhibiting action of various drugs on the corrosion of aluminium, its alloys, and composites in acid and alkaline media [2- 8]. Most drugs have multiple bonds in their molecules which mainly contain nitrogen and sulphur atoms through which they are adsorbed on the metal surface. Compounds with functional groups containing oxygen, nitrogen and sulphur have ability to form complexes with iron. Drugs have been reported to act as effective inhibitors to the surface of steel by means of their competitive adsorption through the surface complex formation (4 -9). Little seems to be published concerning the corrosion inhibition of mild steel using Janumet drug.

A tablet of Janumet contains two drugs: Sitagliptin phosphate monohydrate (Januvia), an orally active inhibitor of dipeptidyl peptidase-4 enzyme and metformin hydrochloride. Metformin hydrochloride (or Glucophage) is chemically not related to any other class of oral antidiabetic agents. Janumet is used in the management of type II diabetes only and it belongs to the incretin therapies. The drug stimulates the beta cells of the islets of Langerhans in the pancreas to release insulin that helps decrease blood glucose levels in the body. Two prescription Janumet drugs that are taken after meals are Janumet tablets and Janumet XR tablets (extended-release). Janumet tablet is taken twice daily while Janumet XR is taken once daily. It was Janumet tablets and not the extended-release form that were used in this study. Each tablet of this drug contains 50 mg sitagliptin phosphate monohydrate as free base and 1000 mg metformin hydrochloride and the tablets are red, capsule-shaped, film-coated tablets with “577” debossed on one side. The chemical structures of sitagliptin phosphate monohydrate and metformin hydrochloride are shown below.

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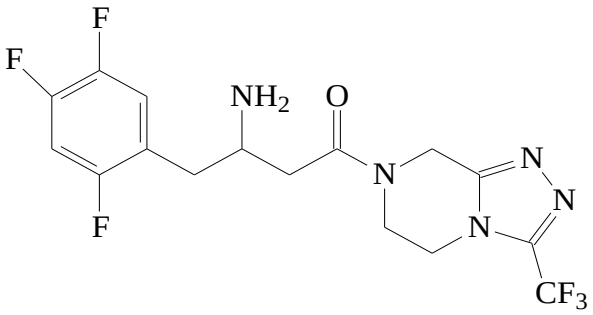
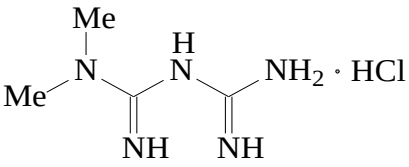


Sitagliptin phosphate monohydrate



Metformin hydrochloride

Metformin causes a buildup of lactic acid in the blood (lactic acidosis) as a rare but serious side effect and this can cause death. Pancreatitis, an inflammation of the pancreas that can be characterized by necrosis in and around the pancreas, has been reported as a serious side effect of sitagliptin and other DPP-4 inhibitors as a result of which the U.S. package insert a warning for this effect. Therefore both the two drugs contained in Janumet have side effect of serious concern. This also forms part of the reason why this study was carried out to investigate some other outlet for the drug. Janumet drug contains heteroatoms (ten nitrogen, seven fluorine and one oxygen atom) as reactive centers through which they can adsorb readily on the metal surface hence their suitability for the study. For these reasons, the objective of the present work is to investigate the corrosion inhibition of mild steel in weakly acid solutions, using Janumet by electrochemical, Scanning Electron Microscopy (SEM) and Fourier Transform Infrared Spectroscopy (FTIR) techniques

2. MATERIAL AND METHODS

2.1 Materials:

The sheets of mild steel used for this study were obtained from the Novara group Limited England. Each sheet was 0.4 mm in thickness and were mechanically pressed cut into 1.5 cm × 1.5 cm coupons. The coupons were degreased by washing in absolute ethanol, dried in acetone and stored in moisture free desiccators before use [9]. Analar grade reagents were used. These included concentrated hydrochloric acid, ethanol and silver nitrate

2.2 Methods:

2.2.1 Potentiodynamic Polarisation:

Thepotentiodynamic current-potential curves were recordedby changing the electrode potential, E_{corr} automatically with a scan rate 0.33 mV s-1 from a low potential of -800 to -300 mV (SCE). Before each run, the working electrode wasimmersed in the test solution for 30 minute until a steady state was achieved. The linear Tafel segments of the anodic and cathodic curves obtained were extrapolated to corrosion potential to obtain the corrosion current densities (i_{corr}) . The inhibition efficiency (I%) and degree of surface coveragewas evaluated from the measured i_{corr} values using equation 1 and 2 [10]:

$$\%I = \frac{i^0_{Corr} - i_{Corr}}{i^0_{Corr}} \times \frac{100}{1} \qquad 1$$

$$\theta = \frac{i^0_{Corr} - i_{Corr}}{i^0_{Corr}} \qquad 2$$

where i^0_{Corr} and i_{Corr} are the uninhibited and inhibited corrosion current densities, respectively.

The corrosion rate was evaluated using equation 3 [11]:

Corrosion rate (mm/year) = (i_{corr} x M_W)/ (F x n x D) 3

where F is the Faraday constant (96485 $C.mole^{-1}.S^{-1}$), D is the density of metal($g.cm^{-3}$), n is the number of electrons involved in the reaction (in moles ofelectrons per mole of metal corroded), M_w is the molecular weight ($g.mole^{-1}$) and i_{corr} is the corrosion current density ($A.cm^{-2}$).

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2.2.2 FTIR analysis:

FTIR analysis of the Janumet and those of the corrosion products (in the absence and presence of the inhibitor) were carried out using Cary-630 Agilent Fourier transform infra-red spectrophotometer. The analysis was carried out by scanning the sample through a wave number range of 650 to 4000cm^{-1}.

2.2.3 Scanning electron microscopy studies:

A scanning electron microscope (SEM) model JSM-5600 LV, was used to analyze the morphology of the mild steelsurface without and with inhibitor added. The sample was mounted on a metal stub and sputtered with gold in order to make the sample conductive, and the images were taken at an accelerating voltage of 10 kV using different magnifications.

3. RESULTS AND DISCUSSIONS

3.1 Electrochemical study:

Figure 1 show the cathodic and anodic polarization curves for mild steel corrosion in 0.1 M HCl in the absence and the presence of different concentrations of Janumet. It is noted that the addition of increasing concentrations of the drug accompaniment by a parallel shift for each of cathodic and anodic polarization curves towards the areas with lowcurrent densities. This shift in cathodic and anodiccurves show that the drug under study acts as a mixed inhibitor to control both the cathodic and anodic reactions. Polarization data deduced from the plots which include corrosion potential ($E_{cor}r$) and corrosion current (I_{corr}.) are presented in Table 1. Also in Table 1 are the values of inhibition efficiencies (IE %), degree of surface coverage (Θ) corrosion rates (CR) for mild steel in absence and presence of different concentrations of the drug calculated using equations 1, 2 and 3. From the results it can be seen that E_{corr} shifted to more negative values .The corrosion current vary slightly with concentration which suggest that Januvia blocks the actives sites for cathodic and anodic reaction, thereby protecting the metal against corrosion [12].

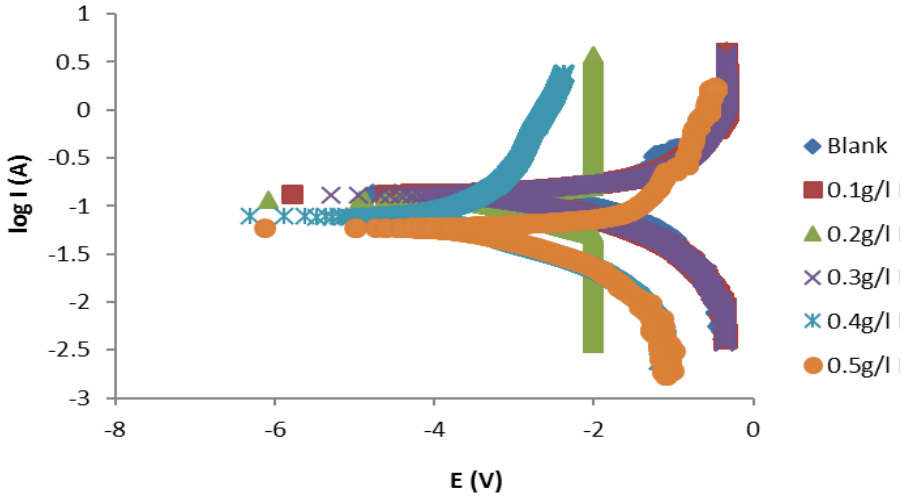

Fig. 1. Polarization curve for the corrosion of mild steel in 1.0 M HCl in the presence and absence of various concentration of Janumet at 303K

Table 1.: Polarization data for the corrosion of Mild steel in 0.1 M HCl in the absence and presence of Janumetat 303 K

Conc.(g/l)	E_{corr}(mV)	Icorr (µA)	θ	IE %	CR
Blank	-856.24	1163.02		-	0.042204
0.1	-871.84	525.64	0.5480	54.80	0.019075
0.2	-934.76	315.57	0.7287	72.87	0.011451
0.3	-962.11	281.00	0.7584	75.84	0.010197
0.4	-993.75	199.47	0.8285	82.85	0.007238
0.5	-1015.33	131.02	0.8873	88.73	0.004754

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3.2 Thermodynamic/adsorption study:

The degree of surface coverage at various concentration of the studied drug was tested with different isotherm equations such as Freundlich, Temkim, El-Awady and Langmuir and correlation coefficients (R^2) were used to determine best fit which was obtained with the Langmuir adsorption isotherm. Figure 2 presents Langmuir isotherm for the adsorption of Janumet on mild steel surface at 303 K. From the figure it can be observe that a plot of C/θ versus C gives a straight line confirming that the inhibitor obeyed Langmuir adsorption isotherm. This result supports the conclusion that maximum inhibition corresponds to the formation of an adsorbed layer of the inhibitor on the active sites of the metal surface.

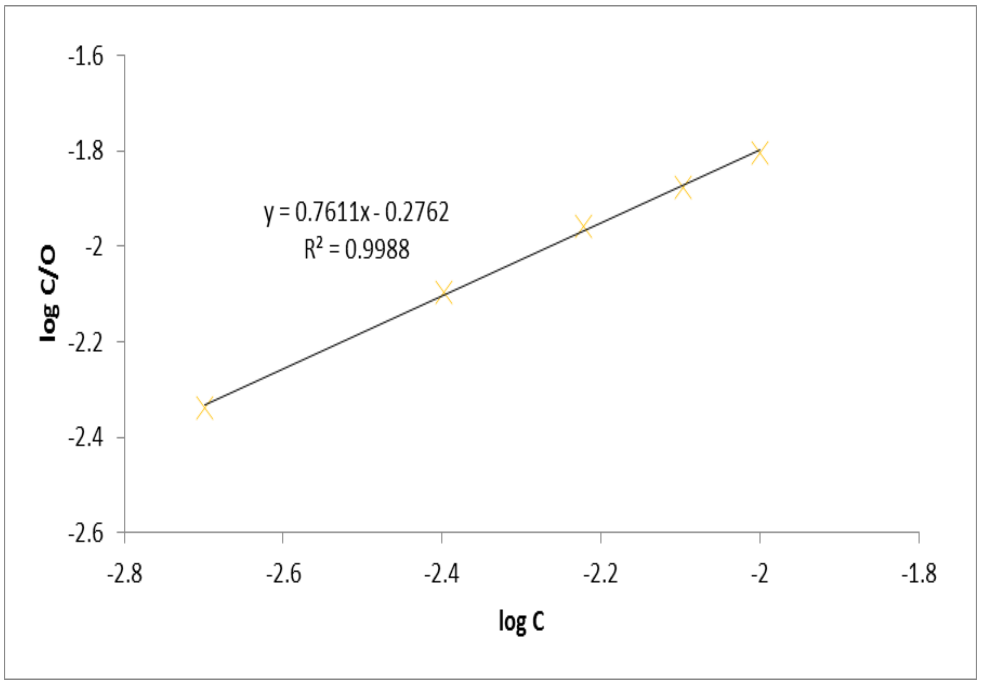

Fig. 2: Langmuir isotherm for the adsorption of Janumet on mild steel surface at 303 K

It is also significant to note that the value of the adsorption equilibrium constant obtained from the intercept of the adsorption isotherm is related to the free energy of adsorption according to the equation [9]

$$\Delta G^{o}_{ads} = -2.303RTlog(55.5K_{ads}) \quad 4$$

The standard Gibbs' free energy calculated from equation 3 was found to be - 28.0452 kJ/mol. Negative ΔG_{ads} values indicate spontaneity of the adsorption process [13]. Generally, ΔG_{ads} values with magnitude much less than 40 kJ mol^{-1} have typically been correlated with the electrostatic interactions between organic molecules and charged metal surface (physisorption), whilst those of magnitude in the order of 40 kJ mol^{-1} and above are associated with charge sharing or transfer from the organic molecules to the metal surface (chemisorption) [9]. Hence the adsorption of Janumet is said to be spontaneous and follows the mechanism of physical adsorption.

3.3 Fourier Transform Infrared Spectroscopy (FTIR) study:

The FTIR spectrum of Janumet is shown in Figure 3 while Figure 4 showed the FTIR spectrum of the corrosion product of mild steel when Janumet was used as an inhibitor. Frequencies and peaks of absorption from the spectrum are presented in Table 2. From the results obtained, the =C-H bend in an alkene at 759cm^{-1} was shifted to 854cm^{-1}, C-O stretch at 1050cm^{-1} and 1210cm^{-1} were shifted to 1092cm^{-1} and 1209cm^{-1} respectively, C-C stretch in ring at 1442cm^{-1} was shifted to 1443cm^{-1}, N-H bend at 1616cm^{-1} was shifted to 1614cm^{-1} and O-H stretch at 3416cm^{-1} was shifted to 3405cm^{-1}. The shift in the frequencies indicates that there is interaction between the mild steel and the inhibitor [11]. On the other hand, C=O stretch at 1722cm^{-1} and O-H stretch at 2935cm^{-1}were missing suggesting that these bond were used for adsorption of the inhibitor onto the surface of the mild steel.

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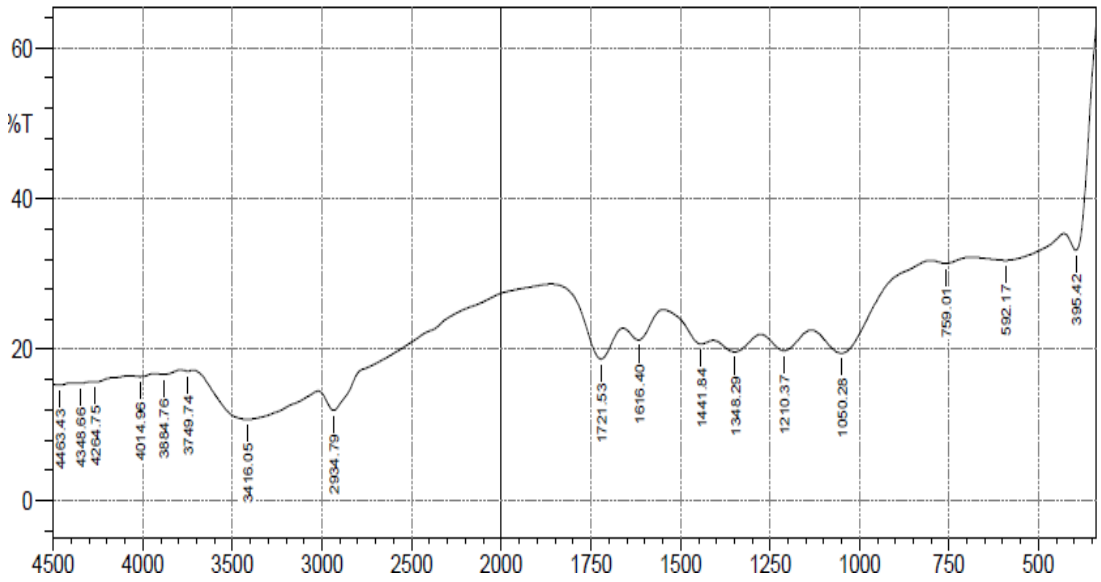

Fig 3: FTIR spectra of Janumet

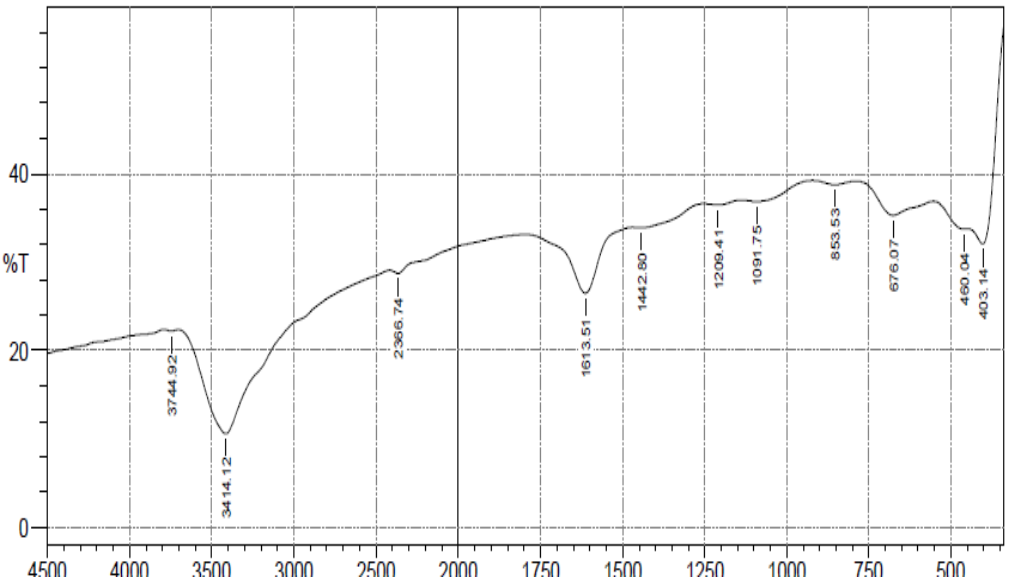

Fig. 4.:FTIR spectra of corrosion product from the corrosion of mild steel when 0.5g/l of Janumet was used as an inhibitor in 0.1M HCl.

Table 2.: Frequencies and peaks of FTIR adsorption by Janumetand the corrosion product of mild steel in HCl

Janumet		**Corrosion Product**		
Frequency of FTIR	**Area**	**Frequency of FTIR**	**Area**	**Assignment**
759.01	56.74	853.53	54.42	=C-H Bend
1050.28	196.25	1091.75	90.10	C-O Stretch
1210.37	92.15	1209.41	50.15	C-O Stretch
1441.84	87.52	1442.8	99.00	C-C stretch (in ring)
1616.40	71.75	1613.51	160.22	N-H bend
1721.53	126.75	-	-	C=O Stretch
2934.79	791.10	-	-	O-H Stretch
3416.05	620.64	3414.12	880.10	O-H Stretch

3.4 Scanning Electron Microscope (SEM):

Surface of polished mild steel specimens immersed in 0.1M HCl in the presence and absence of Jamumet was examined using SEM. When a blank determination was conducted, the metal's surface was corroded with etched grain boundaries and other corrosion products were also noticed as seen in the Fig.6. The micrograph reveals that the surface is strongly damaged in the absence of inhibitor (active corrosion). But in the presence of inhibitor, the micrograph reveals that there is decrease in the corrosion sites and pits over the surface of the mild steel (Fig.7). This is due to the formation of adsorption layer of inhibitor on the metal surface. From these observations we can say that the inhibitor gives a good inhibition effect for the mild steel and thus confirms the results obtained from electrochemical and FTIR method.

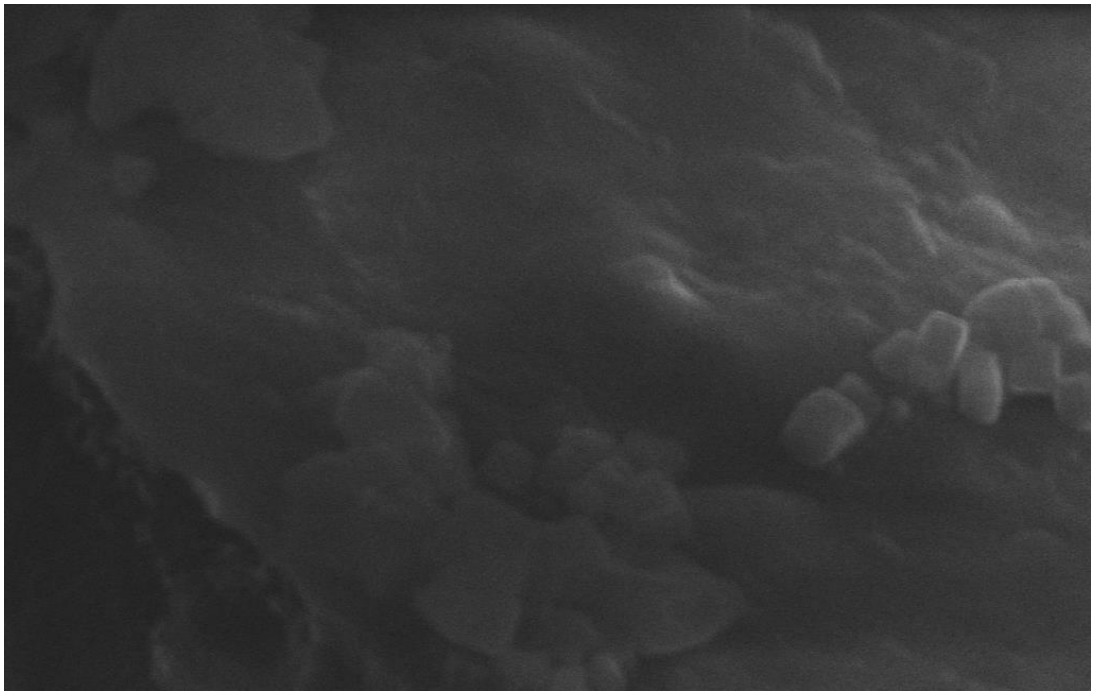

Fig. 5: SEM of mild steel metal

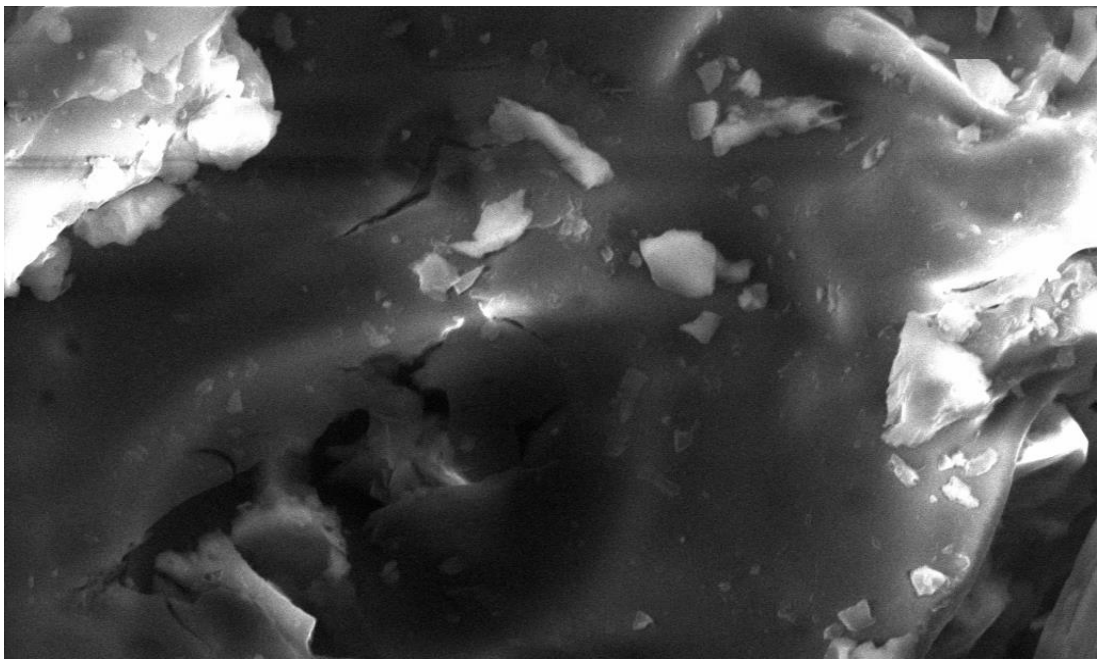

Fig. 6: SEM of mild steel exposed to 0.1Mhydrochloricacid in the absence of 0.5 g / L Janumet

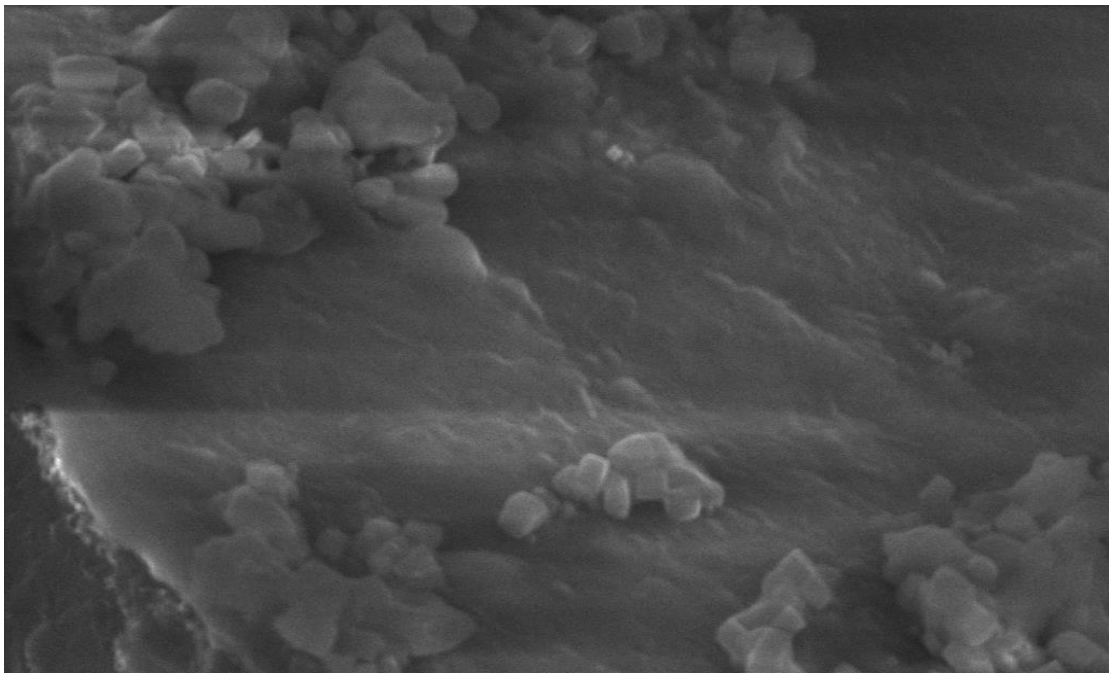

Fig 7: SEM of mild steel exposed to 0.1 M hydrochloric acid in the presence of 0.5 g / L Janumet

4. CONCLUSION

From the research, it can be concluded that Janumet acted as a good inhibitor for mild steel in HCl medium. The inhibitor acted as mixed inhibitor and maximum efficiency (%) attains an optimum value of 0.5 g/ L. the adsorption of inhibitor was consistent with Langmuir isotherm. SEM, and FTIR results all indicate that the corrosion reaction was inhibited by adsorption of the drug on the corroding mild steel surface.

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