

Comparative Experimental and Theoretical Studies of Three Different Expired Pharmaceutical Compounds as Green Corrosion Inhibitors of Mild Steel in Different Acidic Solutions

Ahmed H. Naggar^{1,*}, Mahmoud H. Mahross², Mohamed Tarek², Abd El-Aziz Y. El-Sayed², Tarek A. Seaf El-Nasr³, and Adel A. Abdelwahab¹

¹ Department of Chemistry, College of Science and Arts, Jouf University, Al Qurayyat, 75911, Saudi Arabia

² Chemistry Department, Faculty of Science, Al-Azhar University, Assiut Branch, 71524, Assiut, Egypt

³ Department of Chemistry, College of Science, Jouf University, Sakaka, Saudi Arabia

*E-mail: ahayoub@ju.edu.sa

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Mild steel (MS) corrosion is a crucial industrial problem and thus efficient inhibitors for MS corrosion are highly demanded. Here, the inhibition of MS corrosion in 1.0 M HCl or H₂SO₄ solutions utilizing three pharmaceutical compounds expired for human uses (as green inhibitors of MS corrosion) at different exposure times (2 h., 1 day, 2 days and 4 days). These pharmaceutical compounds named as metoclopramide hydrochloride (MCP), chlorpromazine hydrochloride (CPZ) and mebeverine hydrochloride (MEB) and it was studied using electrochemical technique (Potentiodynamic polarization). With raising expired drug concentrations up to 700 ppm, the inhibitory effectiveness of these drugs was improved. Potentiodynamic polarization suggests that at this concentration, CPZ is the most efficient antioxidant after 4 days' exposure time. Potentiodynamic polarization indicates a combined-type inhibition strategy, where the compounds inhibit both anodic and cathodic reactions. Langmuir adsorption isotherm governs the adsorption of investigated inhibitors on MS surface, and the adsorption equilibrium constant (K_{ads}) and free energy of adsorption (ΔG_{ads}°) were computed. Density functional theory (DFT) utilizing Becke's three parameter exchange functional (B3LYP) at 6-311G (d,p) level was utilized to compute quantum chemical descriptors of the investigated green corrosion inhibitors and their geometric and electronic structures. The theoretical results derived are in good accord with the obtained practical data. Additionally, scanning electron microscope (SEM) was also employed to explore MS surface before and after immersion in acidic media whether it contained the specified corrosion inhibitor or not.

Keywords: Expired pharmaceutical compounds; corrosion inhibitor, mild steel, acidic solution, DFT.

1. INTRODUCTION

The use of corrosion inhibitors is a well-known strategy to prevent metallic material degradation in acidic environments. Organic inhibitors (either natural or synthetic) were used to preserve metals against corrosion in severe acidic environments (e.g. in the acid pickling and cleaning processes of metals) [1-7]. The features of the corrosive environment, the metal surface characteristics, and the electrochemical potential at the metal-solution interface are all factors that influence metal corrosion inhibition. Additionally, the inhibitor molecular structure is an important factor since it impacts the molecular size, the number and charge density of active adsorption sites in the molecule, and the inhibitor capability to form metallic complexes [8,9]. In general, attractive interactions among both the adsorbate and the metal occur in either physisorption or chemisorption [10-12], and inhibitor adsorption on the associated active sites reduces either the anodic or cathodic reaction or both. [13].

Heterocyclic compounds which include P, N, O and S that have been demonstrated to be efficacious inhibitors [14-18]. Also, it was discovered that the inhibition effect of such heterocyclic compounds can be enhanced by addition of conjugated π -electron systems or other electron-rich functional groups such as -OR, -OH, -NR₂, -NH₂ and -SR. This is due to the existence of active adsorption sites with a high electron density, which aid in the inhibitor adsorption on the metal surface [19-20]. As corrosion inhibitors, a broad range of organic chemicals have been utilized, although many of them are costly and/or toxic [21]. Thus, organic corrosion inhibitors that are both low-cost and environmentally beneficial are so essential. Lately, pharmaceuticals compounds have gained popularity as green corrosion inhibitors for metals in acidic circumstances [22-28]. While using pharmaceuticals as green corrosion inhibitors help overcome utilizing hazardous chemicals, they are typically more expensive and researchers have thus focused their interest on utilizing expired pharmaceuticals as corrosion inhibitors [29-34].

The organic corrosion inhibitors efficacy was discovered to be tightly tied to some quantum chemical descriptors; E_{HOMO} (highest occupied molecular orbital energy), E_{LUMO} (lowest unoccupied molecular orbital energy), ΔE (energy gap), η (global hardness), σ (global softness) and ΔN (electrons number that have been moved to metal atom from inhibitor molecule). Theoretical models have evolved into an efficient tool for measuring the corrosion inhibition efficacy of organic compounds as a result of continual developments in hardware and software. To link the inhibitory efficacy of organic inhibitors to their molecular features, a number of quantum chemical modeling approaches have been developed [35-37]. Density functional theory (DFT), which is a potent tool for determining the relative corrosion inhibition activities of different molecules, is one of the most extensively used approaches in computational chemistry for calculating ground-state geometries [38-40]. DFT provides the capability of including some electron correlation effects at a substantially lower computing cost. It has also provided us with a foundation for creation of new standards for reasoning, anticipating, and ultimately comprehending several facets of chemical processes.

We have previously investigated a number of natural [41-45] and synthetic organic compounds [46,47] as mild steel (MS) corrosion inhibitors. Also, the current work is a continuation of our effort in the field of quantum theoretical studies and its applications in corrosion inhibition using green corrosion inhibitors [48,49]. Herein, the effectiveness of three different expired pharmaceuticals; metoclopramide

hydrochloride (MCP) (antiemetic), chlorpromazine hydrochloride (CPZ) (antipsychotic) and mebeverine hydrochloride (MEB) (antispasmodics) was investigated as green inhibitors for MS corrosion in 1.0 M HCl or H₂SO₄ using electrochemical techniques and the obtained results were proved and validated using microscopic (SEM) and theoretical (DFT) methods.

2. EXPERIMENTAL

2.1. Materials

MS samples were investigated at the Tabbin Institute for Metallurgical studies, Cairo, Egypt and the composition (wt. %) was found as: C 0.17 %, Si 0.022 %, Mn 0.71 %, P 0.010 %, Cr 0.045 %, Ni 0.072 %, Al 0.0017 %, Cu 0.182 %, Sn 0.011 %, F 0.022 %, Mo 0.011 % and Fe 98.74 %. To provide a smooth surface, MS samples were polished with 1200 to 1400 grade emery paper, rinsed with distilled H₂O, degreased utilized acetone for 5 minutes, laved again utilizing distilled H₂O, and finally dried.

2.2. Corrosive media and inhibitors

1.0 M aqueous HCl or H₂SO₄ are used as an acidic corrosive media. The corrosion-inhibitor pharmaceutical compounds; MCP, CPZ and MEB were obtained from medical company and were used without further purification. Each of these inhibitors was dissolved in a 500 mL of 1.0 M HCl or H₂SO₄ acidic media and applied at drug concentrations of 50, 200, 500 and 700 ppm.

2.3. Immersion Experiments

To ensure the accuracy for our suggested procedure, an immersion experiments were conducted for different MS samples in acidic corrosive media (1.0 M HCl or 1.0 M H₂SO₄) whether or not a different concentrations of expired pharmaceuticals which applied as corrosion inhibitor are present. For studied MS samples and considering the specified electrochemical experiment period, the immersion trials were executed in 1.0 M HCl or 1.0 M H₂SO₄ acidic corrosive media for different immersion times 2 h., 1 day, 2 days and 4 days at room temperature.

2.4. Corrosion cell

The corrosion cell used in potentiodynamic polarization involves three electrodes: MS as the working electrode, SCE as reference electrode, and platinum wire as auxiliary electrode. The working electrode has a solution-exposed area of 1 cm².

2.5. Experimental measurements

Open circuit (E (mV) vs. time (min.)) at no current and potentiodynamic polarization plots were measured with EG&G potentiostat/galvanostat model 273A. The polarization curves were measured

after steeping the MS working electrode in 1.0 M HCl or H₂SO₄ acidic solutions for (2 h., 1 day, 2 days and 4 days), and after the corrosion potential (E_{corr}) became stable. Potentiodynamic polarization were measured from ± 250 mV at a scan rate is 0.3 mV/sec.

2.6. Theoretical calculations:

The theoretical calculations of the various parameters were based on the density functional theory (DFT) [50] utilizing Becke's three parameter exchange functional (B3LYP) at the 6-311G (d,p) basis set [51] implemented in Gauss View 5.0 with Gaussian 09W program package [52].

2.6. Scanning electron microscope (SEM)

SEM is utilized to gain insight into the MS surface morphology after steeping in 1.0 M HCl or H₂SO₄ acidic media without and with the corrosion inhibitors. SEM analysis was proceeded in the electronic microscope office (JEOL, JSM5400LV) in Assiut University, Egypt.

3. RESULTS AND DISCUSSION

3.1. Open circuit potential measurements (OCP)

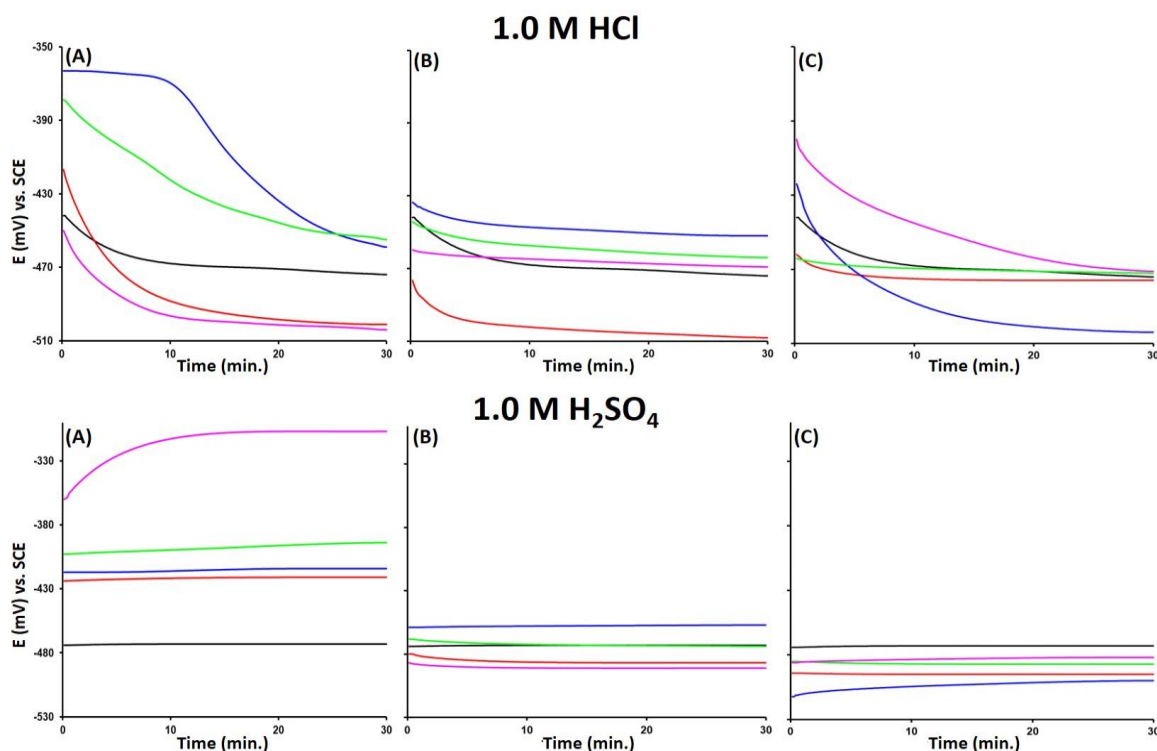


Figure 1. Potential-time curves for MS after 4 days' immersion time in blank 1.0 M HCl or H₂SO₄ acidic media (black line) and in existence of successive concentrations of: (A) MCP, (B) CPZ and (C) MEB; 50 ppm (red line), 200 ppm (blue line), 500 ppm (green line) and 700 ppm (magenta line).

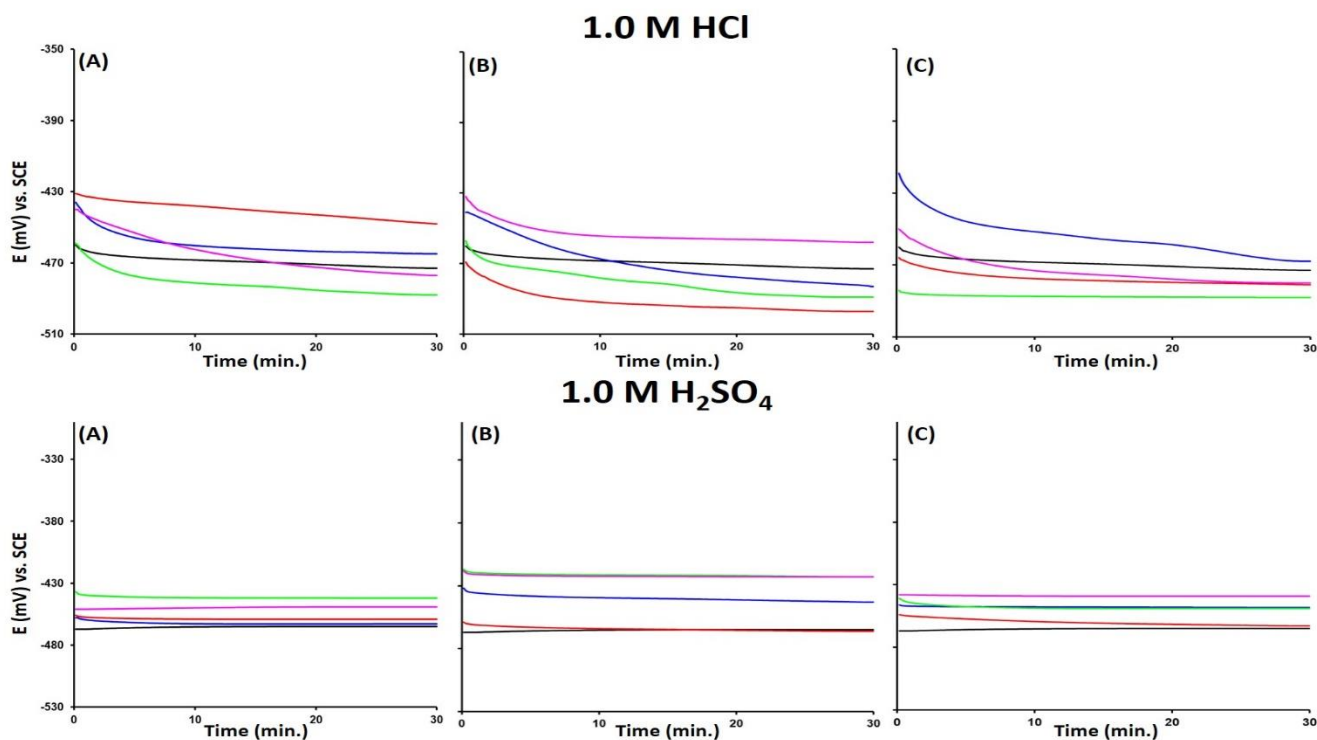


Figure 2. Potential-time curves for MS after 2 h. immersion time in blank 1.0 M HCl or H₂SO₄ acidic media (black line) and in existence of successive concentrations of: (A) MCP, (B) CPZ and (C) MEB; 50 ppm (red line), 200 ppm (blue line), 500 ppm (green line) and 700 ppm (magenta line).

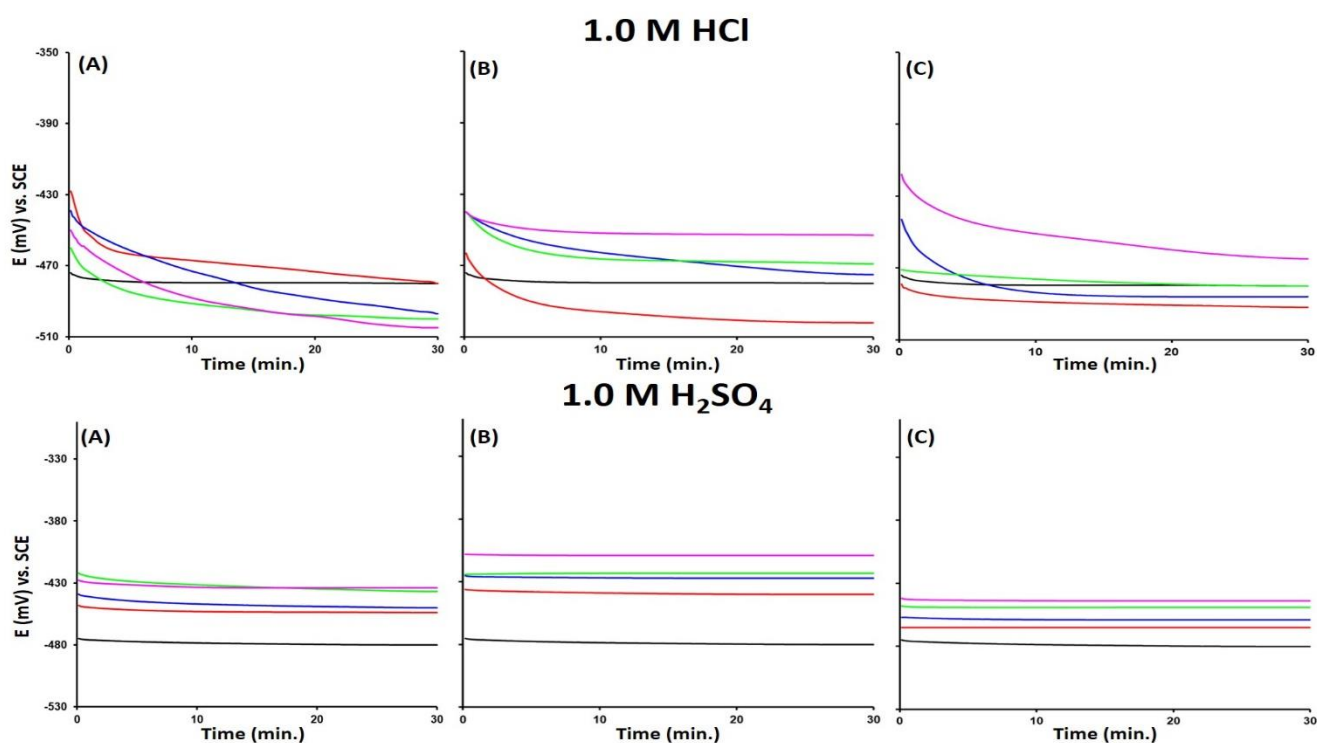


Figure 3. Potential-time curves for MS after 1-day immersion time in blank 1.0 M HCl or H₂SO₄ acidic media (black line) and in existence of successive concentrations of: (A) MCP, (B) CPZ and (C) MEB; 50 ppm (red line), 200 ppm (blue line), 500 ppm (green line) and 700 ppm (magenta line).

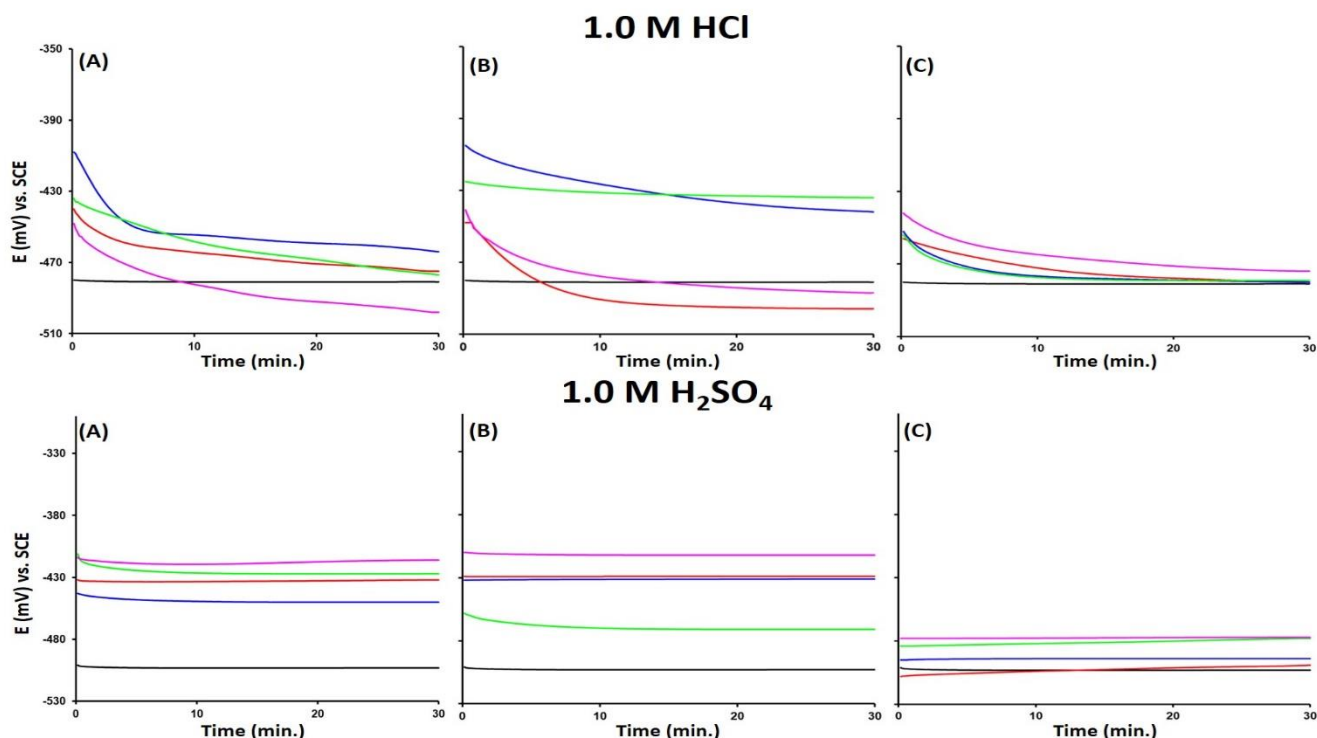


Figure 4. Potential-time curves for MS after 2 days' immersion time in blank 1.0 M HCl or H₂SO₄ acidic media (black line) and in existence of successive concentrations of: (A) MCP, (B) CPZ and (C) MEB; 50 ppm (red line), 200 ppm (blue line), 500 ppm (green line) and 700 ppm (magenta line).

Figure 1 presents OCP measurements for MS in the blank 1.0 M HCl or H₂SO₄ acidic media and in existence of specified concentrations of MCP, CPZ and MEB after 4 days' exposure time. Corresponding results for 2 h., 1 day and 2 days' exposure times are shown in Figures 2, 3 and 4, respectively.

The slightly negative of steady state potential ($E_{s,s}$) compared to the immersion potential (E_{im}) for almost blank solution indicates destruction of the pre-immersion oxide stratum on MS electrodes surface.

Compared to the blank solution, addition of the inhibitors results in slightly negative or positive $E_{s,s}$ compared to $E_{s,s}$ of blank, showing the creation of an inhibitor stratum on the MS surface that blocks the cathodic and anodic sites, respectively. The obtained $E_{s,s}$ values of the studied solutions were recorded in Table 1.

Table 1. Values of $E_{s,s}$ (mV) for MS in 1.0 M HCl or H₂SO₄ acidic media in absent and existence of numerous concentrations of MCP, CPZ and MEB at different immersion times.

Test Solution	Conc. (ppm)	1.0 M HCl								1.0 M H ₂ SO ₄							
		2 h		1 day		2 days		4 days		2 h		1 day		2 days		4 days	
		- E_{im}	- $E_{s,s}$	- E_{im}	- $E_{s,s}$	- E_{im}	- $E_{s,s}$	- E_{im}	- $E_{s,s}$	- E_{im}	- $E_{s,s}$	- E_{im}	- $E_{s,s}$	- E_{im}	- $E_{s,s}$	- E_{im}	- $E_{s,s}$
Without drug	-----	460	473	474	480	480	481	442	474	467	465	475	480	501	503	474	473
MCP	50	431	448	428	480	440	475	417	501	456	459	448	454	432	432	424	421
	200	436	465	439	497	408	464	363	459	458	463	439	450	443	450	417	414
	500	459	488	460	500	434	477	379	455	437	442	422	437	411	427	403	394
	700	440	477	450	505	448	498	450	504	451	449	428	434	414	416	360	307
CPZ	50	469	497	463	502	448	496	477	508	459	466	436	440	429	429	480	487

MEB	200	441	483	440	475	405	442	434	452	432	443	425	427	432	431	459	457
	500	457	489	440	469	425	434	444	464	417	423	424	423	458	471	468	474
	700	432	458	440	453	441	487	460	469	418	423	408	409	410	412	487	491
	50	466	481	479	492	456	480	462	476	454	463	465	465	508	499	494	495
	200	419	468	443	486	452	480	424	504	446	448	457	459	495	494	512	500
	500	484	488	471	480	454	479	464	472	441	449	448	449	484	478	485	487
	700	450	480	418	465	442	474	400	471	438	439	442	444	478	477	486	482

3.2. Potentiodynamic measurements

Potentiodynamic polarization was executed to get a full information about the corrosion current density (I_{corr}), polarization resistance (R_p), corrosion rate ($C.R.$) and inhibition efficiency ($I.E.$ %).

Figure 5 represents Potentiodynamic polarization plots (anodic and cathodic polarization curves) for the MS electrodes in 1.0 M HCl or H₂SO₄ acidic media at 4 days' exposure time in absent and existence of numerous concentrations of selected pharmaceutical compounds which used as green organic inhibitors. Corresponding results for 2 h, 1 day and 2 days' exposure times are shown in Figures 6, 7 and 8, respectively. These figures showed that the presence of selected pharmaceutical compounds resulting in shift E_{corr} values for the MS electrode to slightly positive or negative potentials against blank indication to blocking of inhibitor molecules on the anodic and cathodic reactions, respectively.

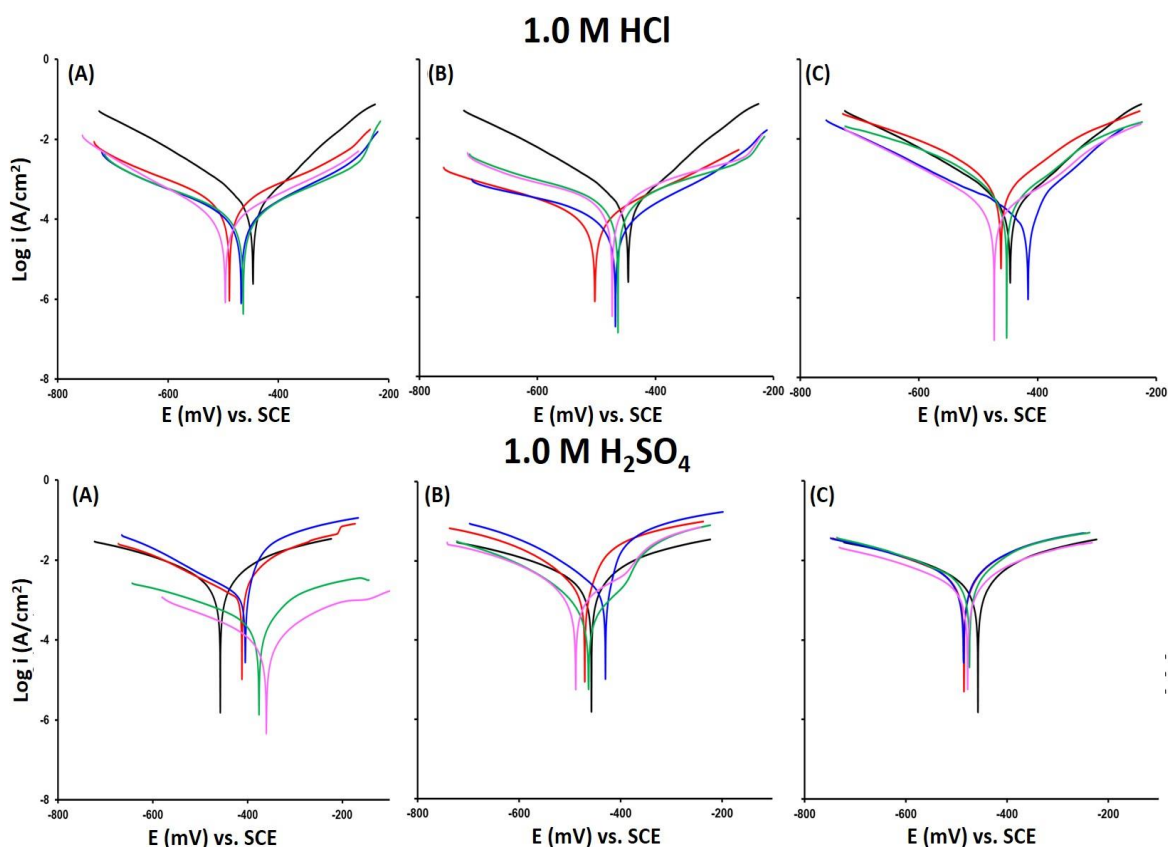


Figure 5. Potentiodynamic polarization curves for MS after 4 days' immersion time in blank 1.0 M HCl or H₂SO₄ acidic media (black line) and in existence of successive concentrations of: (A) MCP, (B) CPZ and (C) MEB; 50 ppm (red line), 200 ppm (blue line), 500 ppm (green line) and 700 ppm (magenta line).

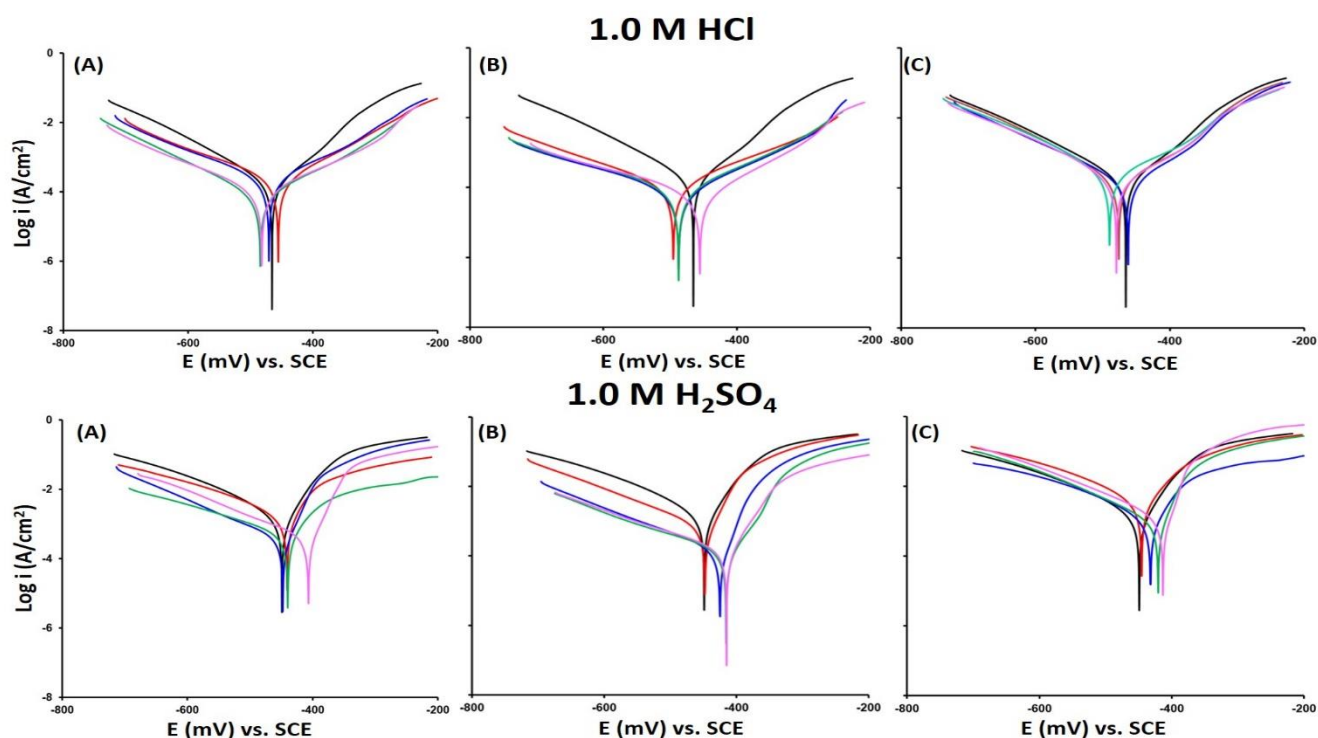


Figure 6. Potentiodynamic polarization curves for MS after 2 h. immersion time in blank 1.0 M HCl or H₂SO₄ acidic media (black line) and in existence of successive concentrations of: (A) MCP, (B) CPZ and (C) MEB; 50 ppm (red line), 200 ppm (blue line), 500 ppm (green line) and 700 ppm (magenta line).

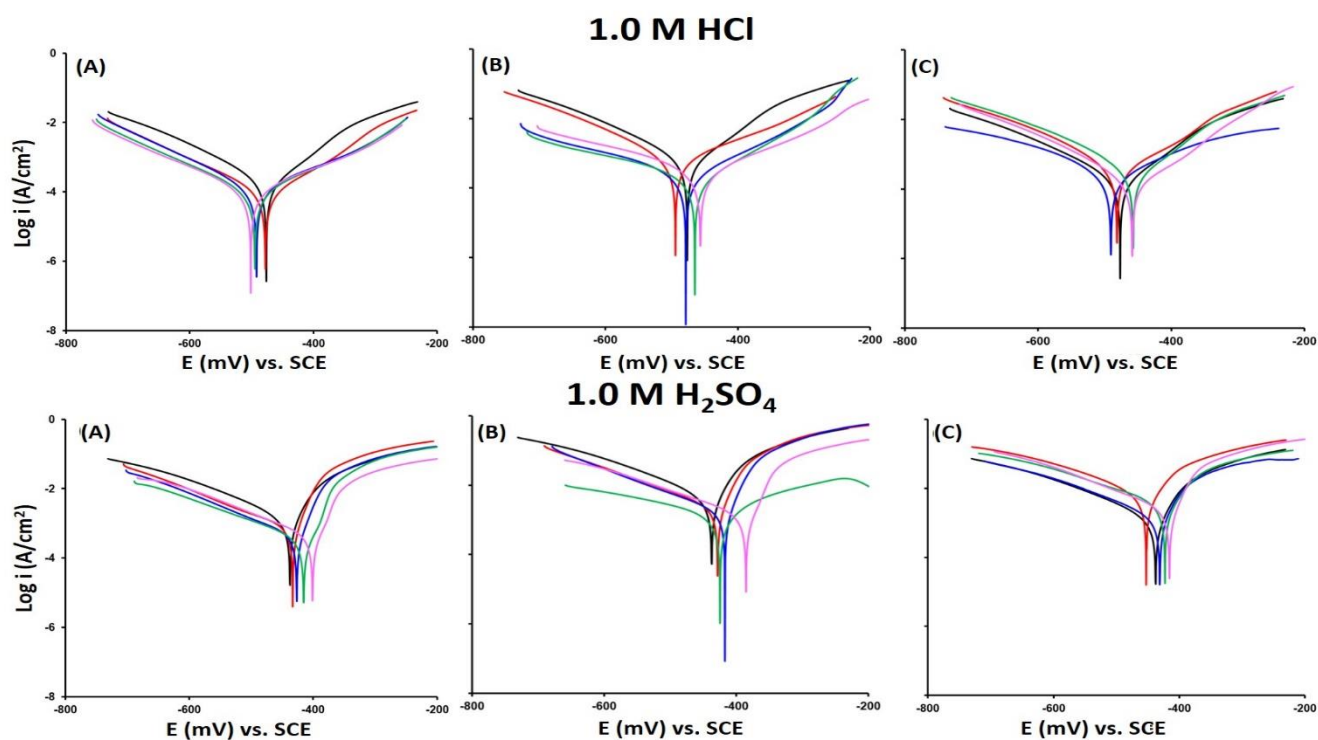


Figure 7. Potentiodynamic polarization curves for MS after 1-day immersion time in blank 1.0 M HCl or H₂SO₄ acidic media (black line) and in existence of successive concentrations of: (A) MCP, (B) CPZ and (C) MEB; 50 ppm (red line), 200 ppm (blue line), 500 ppm (green line) and 700 ppm (magenta line).

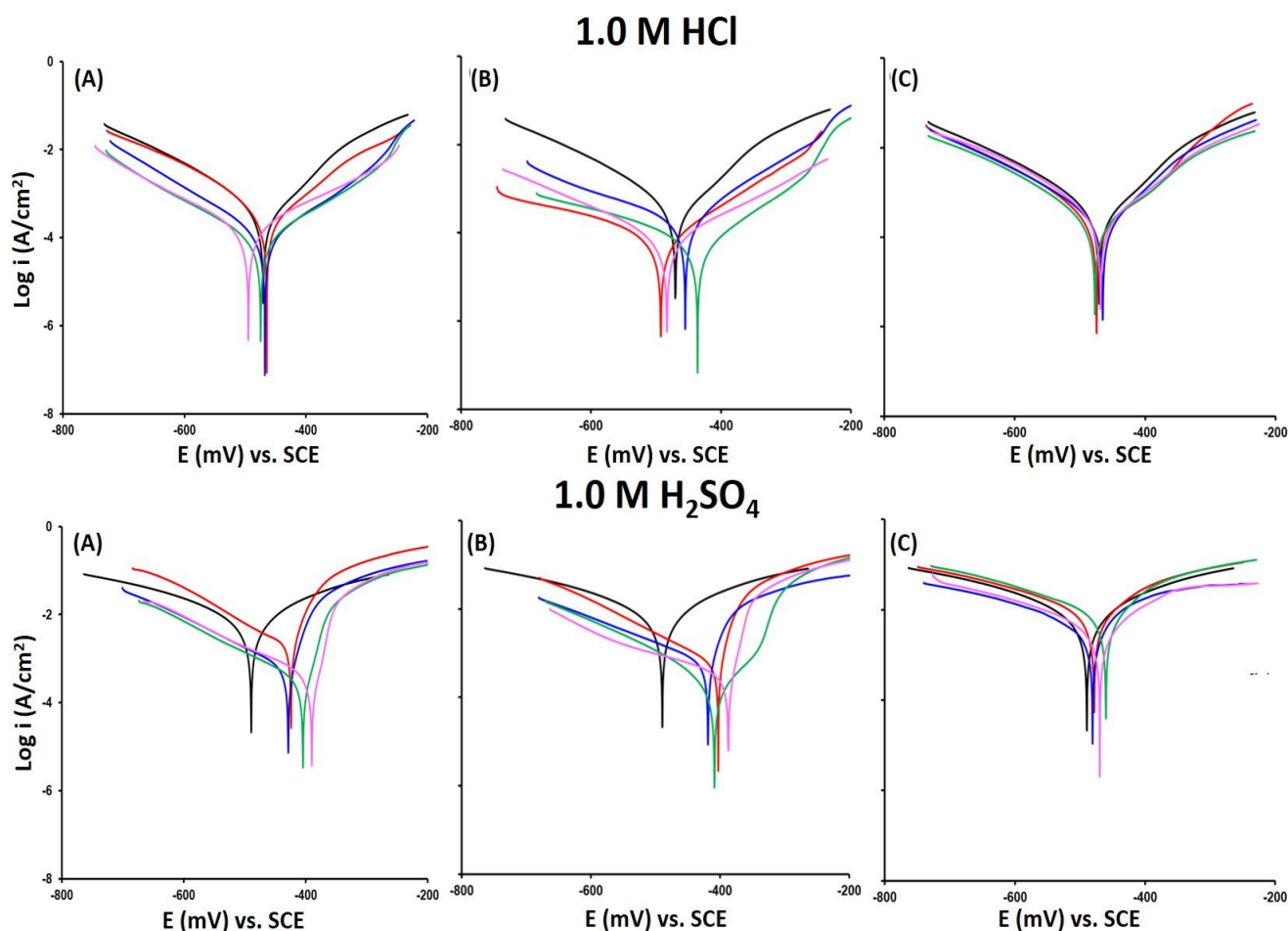


Figure 8. Potentiodynamic polarization curves for MS after 2 days' immersion time in blank 1.0 M HCl or H₂SO₄ acidic media (black line) and in existence of successive concentrations of: (A) MCP, (B) CPZ and (C) MEB; 50 ppm (red line), 200 ppm (blue line), 500 ppm (green line) and 700 ppm (magenta line).

MS electrochemical characteristics in the existence and absent of varied amounts of expired medicinal drugs in 1.0 M HCl or H₂SO₄ acidic medium after 4 days' immersion time are given in Table 2 while the same parameters after 2 h, 1 day and 2 days' exposure time are shown in Tables 3, 4 and 5, respectively.

From data presented in Table 2, it is apparent that blank H₂SO₄ is more corrosive than HCl as a result of SO₄²⁻ is more aggressive than Cl⁻. Also, the calculated values in Table 2, indicates high performance of selected expired pharmaceuticals as corrosion inhibitors. It could be seen that, both of resistance polarization (R_p) and inhibition efficiency ($I.E.\%$) raises as expired MCP, CPZ and MEB concentrations raised (50, 200, 500 and 700 ppm) as the immersion time in studied acidic media (1.0 M HCl or H₂SO₄) raises; 2 h, 1 day, 2 days' and 4 days. Moreover, and at the same conditions, Table 2 illustrate a notable decrease in corrosion rate ($C.R.$). So, it can be seen that the best result was achieved using 700 ppm of CPZ in each acidic media to reach 85.10 % and 97.13 % in 1.0 M HCl or H₂SO₄, respectively.

Table 2. Polarization parameters of MS in 1.0 M HCl or H₂SO₄ acidic media in absent and existence of various MCP, CPZ and MEB concentrations after 4 days' immersion times

1.0 M HCl													
Polarization Parameter	Without Inhibitor	With Inhibitor											
		MCP Conc. (ppm)				CPZ Conc. (ppm)				MEB Conc. (ppm)			
		50	200	500	700	50	200	500	700	50	200	500	700
R _p (Ω)	20	66	221	250	280	374	391	433	461	65	101	168	192
E _{corr} (mV)	-447	-489	-467	-463	-496	-502	-468	-463	-473	-461	-419	-452	-473
I _{corr} (μA/Cm ²)	565.2	302.1	150.0	110.0	95.04	301.1	142.0	106.0	84.00	303.3	156.3	125.0	101.0
C.R (mpy)	516.8	275.9	137	100.5	86.79	275.0	129.6	96.77	76.67	277.0	142.7	114.1	92.19
I.E (%)	---	46.55	73.46	80.53	83.20	46.72	74.90	81.20	85.10	46.34	72.35	77.90	82.10
Surface coverage (θ)	---	0.465	0.735	0.805	0.832	0.467	0.749	0.812	0.851	0.463	0.724	0.779	0.821

1.0 M H ₂ SO ₄													
Polarization Parameter	Without Inhibitor	With Inhibitor											
		MCP Conc. (ppm)				CPZ Conc. (ppm)				MEB Conc. (ppm)			
		50	200	500	700	50	200	500	700	50	200	500	700
R _p (Ω)	4	25	40	89	121	34	76	118	156	11	25	37	56
E _{corr} (mV)	-457	-411	-405	-376	-343	-470	-430	-488	-463	-485	-486	-475	-478
I _{corr} (μA/Cm ²)	7118.0	1317.0	1154.0	516.2	255.0	1523.0	1164.0	590.0	204.0	2890.0	2015.0	1210.0	450.0
C.R (mpy)	6500.0	1252.0	1053.0	471.4	232.9	1391.0	1063.0	538.7	186.3	2663.8	1857.3	1115.3	414.8
I.E (%)	---	80.74	83.8	92.75	96.42	78.6	83.65	91.71	97.13	59.02	71.43	82.84	93.62
Surface coverage (θ)	---	0.807	0.838	0.928	0.964	0.786	0.836	0.917	0.970	0.590	0.714	0.828	0.936

Table 3. Polarization parameters of MS in 1.0 M HCl or H₂SO₄ acidic media in absent and existence of various MCP, CPZ and MEB concentrations after 2 h immersion times.

1.0 M HCl													
Polarization Parameter	Without Inhibitor	With Inhibitor											
		MCP Conc. (ppm)				CPZ Conc. (ppm)				MEB Conc. (ppm)			
		50	200	500	700	50	200	500	700	50	200	500	700
R _p (Ω)	79	100	140	253	260	251	325	340	360	96	118	127	153
E _{corr} (mV)	-465	-455	-470	-484	-482	-495	-487	-487	-455	-476	-462	-490	-479
I _{corr} (μA/Cm ²)	209.0	177.0	144.1	119.0	100.0	178.0	117.0	100.0	88.05	181.0	161.0	131.0	110.1
C.R (mpy)	190.9	161.7	131.6	108.7	91.30	162.6	106.9	91.92	80.41	165.3	147.0	119.7	100.5
I.E (%)	---	15.30	31.06	43.10	52.20	14.82	44.00	52.20	57.90	13.41	23.00	37.30	47.35
Surface coverage (θ)	---	0.153	0.311	0.431	0.522	0.148	0.440	0.522	0.579	0.134	0.230	0.373	0.474
1.0 M H ₂ SO ₄													
Polarization Parameter	Without Inhibitor	With Inhibitor											
		MCP Conc. (ppm)				CPZ Conc. (ppm)				MEB Conc. (ppm)			
		50	200	500	700	50	200	500	700	50	200	500	700
R _p (Ω)	10	12	17	26	32	21	29	36	62	5	14	15	24
E _{corr} (mV)	-449	-440	-448	-427	-406	-448	-425	-416	-415	-445	-432	-420	-413
I _{corr} (μA/Cm ²)	1620	1294	407.7	376.0	316.0	691.0	301.0	248.0	214.0	1290	909.0	670.0	525.0
C.R (mpy)	1480	1182	372.3	343.5	288.6	631.0	275.0	226.5	195.51	1178	830.1	611.9	479.4
I.E (%)	---	20.14	74.84	76.79	80.50	57.36	81.40	84.70	87.79	20.41	43.91	58.66	67.61
Surface coverage (θ)	---	0.201	0.748	0.768	0.805	0.574	0.814	0.847	0.878	0.204	0.439	0.587	0.676

Table 4. Polarization parameters of MS in 1.0 M HCl or H₂SO₄ acidic media in absent and existence of various MCP, CPZ and MEB concentrations after 1-day immersion times.

1.0 M HCl													
Polarization Parameter	Without Inhibitor	With Inhibitor											
		MCP Conc. (ppm)				CPZ Conc. (ppm)				MEB Conc. (ppm)			
		50	200	500	700	50	200	500	700	50	200	500	700
R _P (Ω)	41	226	247	250	270	134	293	360	390	53	77	100	173
E _{corr} (mV)	-476	-477	-492	-494	-501	-294	-478	-465	-456	-481	-490	-457	-458
I _{corr} (μA/Cm ²)	257.0	205.0	180.0	138.0	106.0	223.1	138.8	110.0	90.0	227.7	187.0	151.0	126.0

C.R (mpy)	234.7	187.2	164.9	126.0	96.82	203.7	126.8	100.5	82.19	207.9	170.8	137.9	115.1
I.E (%)	---	20.24	30.00	46.30	58.80	13.21	45.97	57.20	65.00	11.42	27.23	41.20	51.00
Surface coverage (θ)	---	0.202	0.300	0.463	0.588	0.132	0.460	0.572	0.650	0.114	0.272	0.412	0.510
1.0 M H₂SO₄													
Polarization Parameter	Without Inhibitor	With Inhibitor											
		MCP Conc. (ppm)				CPZ Conc. (ppm)				MEB Conc. (ppm)			
		50	200	500	700	50	200	500	700	50	200	500	700
R _p (Ω)	6	11	30	56	80	26	31	62	91	6	14	26	38
E _{corr} (mV)	-438	-433	-426	-416	-401	-428	-417	-407	-385	-447	-432	-422	-415
I _{corr} (μ A/Cm ²)	2279.0	710.0	422.0	354.0	300.2	694.0	473.0	365.0	212.0	1749	1425	920.0	505.9
C.R (mpy)	2082.0	648.3	385.4	323.3	274.3	633.8	432.0	333.3	193.7	1597	1301	847.9	466.3
I.E (%)	---	68.86	81.49	84.47	86.83	69.56	79.25	83.99	90.70	23.30	37.51	59.27	77.60
Surface coverage (θ)	---	0.689	0.815	0.845	0.868	0.696	0.793	0.840	0.907	0.233	0.375	0.593	0.776

Table 5. Polarization parameters of MS in 1.0 M HCl or H₂SO₄ acidic media in absent and existence of various MCP, CPZ and MEB concentrations after 2 days' immersion times.

1.0 M HCl													
Polarization Parameter	Without Inhibitor	With Inhibitor											
		MCP Conc. (ppm)				CPZ Conc. (ppm)				MEB Conc. (ppm)			
		50	200	500	700	50	200	500	700	50	200	500	700
R _p (Ω)	31	83	180	230	275	330	345	425	443	60	96	134	182
E _{corr} (mV)	-470	-464	-467	-474	-495	-492	-455	-436	-483	-474	-465	-477	-468
I _{corr} (μ A/Cm ²)	337.0	271.0	215.1	133.0	105.0	245.1	201.0	112.0	88.05	287.0	233.0	162.0	118.0
C.R (mpy)	307.7	247.4	196.5	121.4	95.87	223.8	183.6	102.3	80.41	262.1	212.7	147.9	107.7
I.E (%)	---	19.60	36.20	60.50	68.80	27.27	40.40	66.80	73.90	14.82	30.87	51.90	65.00
Surface coverage (θ)	---	0.196	0.362	0.605	0.688	0.273	0.404	0.668	0.739	0.148	0.309	0.519	0.650
1.0 M H₂SO₄													
Polarization Parameter	Without Inhibitor	With Inhibitor											
		MCP Conc. (ppm)				CPZ Conc. (ppm)				MEB Conc. (ppm)			
		50	200	500	700	50	200	500	700	50	200	500	700
R _p (Ω)	5	20	35	77	98	24	67	96	118	7	22	32	49
E _{corr} (mV)	-489	-424	-428	-404	-390	-403	-419	-416	-387	-478	-480	-460	-466
I _{corr} (μ A/Cm ²)	5060.0	1700.0	579.0	309.0	279.0	774.6	598.0	497.0	208.0	3010.0	1434.0	901.0	473.0
C.R (mpy)	4620	1552	528.7	282.2	254.8	707.4	546.1	453.0	189.9	2774.4	1321.8	830.48	435.98
I.E (%)	---	66.41	88.56	93.89	94.48	84.69	88.18	90.18	95.88	39.95	71.39	82.02	90.56
Surface coverage (θ)	---	0.664	0.886	0.939	0.945	0.847	0.882	0.902	0.957	0.400	0.714	0.820	0.906

Our finding is consistent with the notion that organic inhibitors comprising nitrogen and sulfur (such as CPZ in this work) exhibit stronger inhibition than those having only one of these elements (MCP and MEB) [53-55].

The adsorption of organic corrosion inhibitors in aggressive acidic media is generally assumed to be the 1st stage in their own action mechanism, which is impacted by the metal's properties and surface change, inhibitor chemical formula, change in molecule arrangement, aggressive electrolyte type, and manner of contact among both inhibitor molecules and metallic surface [56]. It was concluded from the additives' molecules intervene with metallic surface, that corroded metal surface was changed and the mechanism of the electrochemical process at the metal solution boundary is influenced. From obtained data shown in Tables 2-5, for different exposure times, that studied expired pharmaceutical compounds; MCP, CPZ and MEB, can be used as good inhibitors for MS corrosion in 1.0 M HCl or H₂SO₄ acidic medium. Adhesion, inhibitor molecule adsorption on metal surfaces, and the creation of a stable extract complex on metal surfaces are all aspects that impact the inhibitor's mechanism.

3.3. Adsorption isotherm

The practical results were examined utilizing numerous adsorption isotherms, including Langmuir, Frumkin, Freundlich, and Temkin isotherms, in order to obtain further data regarding adsorption mechanism of studied expired pharmaceuticals on MS surface. However, the best compatibility was provided utilizing Langmuir isotherm. The relationship among both surface coverage (θ) defined by ($I.E. \% / 100$) and inhibitor concentration (C) can be elucidated by the Langmuir adsorption isotherm which is expressed by Eq. 1 [57]:

$$\frac{C}{\theta} = \frac{1}{K_{ads}} + C \quad (1)$$

Where K is the adsorption constant, C is the inhibitor concentration and θ is the surface coverage values which acquired from the potentiodynamic data of numerous inhibitor concentrations. To establish the isotherm that best suited the practical data, the correlation coefficient (R^2) was utilized. The highest R^2 values ($R^2 > 0.999$) indicates that inhibitor adsorption on MS surface pursued this isotherm. The Langmuir adsorption isotherm was followed by (MCP, CPZ, and MEB) adsorption on MS surfaces. Adsorbed molecules fill only one site and interact with no further adsorbed species, according to this isotherm. The adsorption equilibrium constant is correlated to the free energy of adsorption (ΔG_{ads}) and is expressed using following Eq. 2 [58]:

$$K_{ads} = \frac{1}{55.5} \exp\left(-\frac{\Delta G_{ads}}{RT}\right) \quad (2)$$

Where 55.5 is molar concentration of water in the solution expressed in M (mol L^{-1}), T is absolute temperature (K) and R is gas constant ($8.314 \text{ J K}^{-1} \text{ mol}^{-1}$). Eq. 2 is modified into Eq. 3 for calculating ΔG_{ads} as follow:

$$\Delta G_{ads} = -2.303 RT \log (55.5 K) \quad (3)$$

ΔG_{ads} of MCP, CPZ and MEB for MS in 1.0 M HCl or H_2SO_4 acidic media at different exposure times (2 h, 1 day, 2 days and 4 days) were computed using the slope and the ordinate axis intercept of the straight lines. The calculated values were outlined in Table 6. Negative ΔG_{ads} values imply that the adsorption process occurs spontaneously and with great efficiency.

Table 6. Calculated values of Langmuir adsorption parameters of MS exposed to expired pharmaceuticals as green inhibitors in 1.0 M HCl or H_2SO_4 acidic media.

Immersion Time	Langmuir Adsorption Parameters	1.0 M HCl			1.0 M H_2SO_4		
		Inhibitor			Inhibitor		
		MCP	CPZ	MEB	MCP	CPZ	MEB
2 h	Slope	1.580	1.405	1.656	1.020	1.102	1.230
	Log K_{ads}	0.530	0.640	0.360	0.860	1.510	0.700
	R^2	0.981	0.990	0.934	0.966	1.000	0.994
	$-\Delta G_{ads} (\text{kJ mol}^{-1})$	12.97	13.58	12.13	14.83	18.56	13.92
1 Day	Slope	1.420	1.147	1.455	1.132	1.086	1.194
	Log K_{ads}	0.550	0.560	0.390	1.730	1.540	0.620
	R^2	0.934	0.978	0.979	1.000	0.997	0.906
	$-\Delta G_{ads} (\text{kJ mol}^{-1})$	13.09	13.14	12.15	19.84	18.73	13.50
2 Days	Slope	1.118	1.109	1.112	1.024	1.040	0.900
	Log K_{ads}	0.590	0.720	0.450	1.650	1.810	0.430
	R^2	0.972	0.966	0.951	1.000	0.998	0.950
	$-\Delta G_{ads} (\text{kJ mol}^{-1})$	13.31	14.04	12.53	19.36	20.28	12.40

4 Days	Slope	1.135	1.111	1.157	1.016	1.011	1.235
	Log K _{ads}	1.310	1.300	1.300	1.640	1.590	1.100
	R ²	0.999	0.999	0.999	0.998	0.998	0.982
	-ΔG _{ads} (kJmol ⁻¹)	17.43	17.38	17.38	19.29	19.02	16.22

In general, ΔG_{ads} values of -20 kJmol^{-1} or less suggest electrostatic contact among both charged organic molecules and the charged metal, whereas values of -40 kJmol^{-1} suggest charge distribution or relocation from inhibitor molecules to metal surface via a co-ordination bond (chemisorption) [59]. The computed ΔG_{ads} values showed in Table 6 were ranged from -12.13 to $-20.28 \text{ kJmol}^{-1}$. In other words, these values indicating that studied pharmaceutical compounds; MCP, CPZ and MEB are physically adsorbed on MS surface.

3.4. Quantum chemical calculations

Actually, DFT has emerged as special theoretical calculation for to illustrate the process that takes place at the metal-inhibitor particle interaction [60].

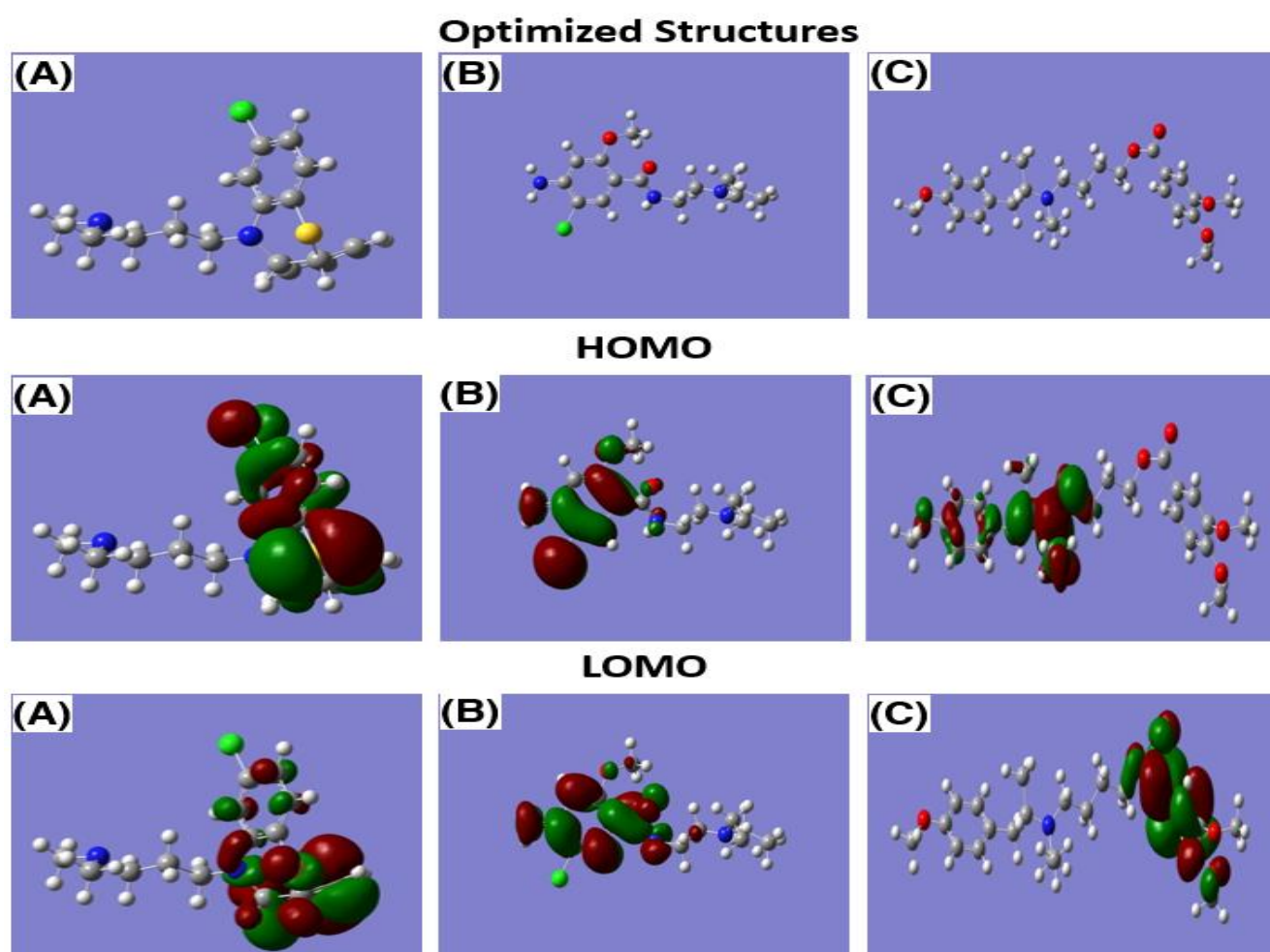


Figure 9. Optimization structures, HOMO and LUMO representation utilizing DFT method, B3LYP, 6-311 (d,p) base set: (A) CPZ, (B) MCP and (C) MEB

Structures with optimal geometry of HOMO and LUMO of the presented drugs (CPZ, MCP and MEB) are showed in Figure 9. Understanding the reactive sites of pharmaceutical compounds requires a thorough examination of the LUMO and HOMO. Also, energy gap ($\Delta E = E_{LUMO} - E_{HOMO}$), ionization potential (I), global hardness (η), global softness (σ), and ΔN (number of transported electrons) may all be utilized to investigate the reactivity of the molecules given.

According to Koopmans' theorem [61], The quantum chemical parameters were computed utilizing the E_{LUMO} and E_{HOMO} energies utilizing Eqs. (4-8):

$$I = -E_{HOMO} \quad (4)$$

$$\Delta E = E_{LUMO} - E_{HOMO} \quad (5)$$

$$\eta = (I - A)/2 \quad (6)$$

$$\sigma = 1/\eta \quad (7)$$

$$\Delta N = \mu/\eta \quad (8)$$

Where, μ and η are chemical potential and global hardness, respectively.

The efficiency of preventing MS corrosion using H_2SO_4 and HCl acidic media containing CPZ molecule was determined to be 97.19 % and 85.10 %, respectively, predicated on computed DFT variables. E_{HOMO} is correlated to the CPZ molecule capability to provide the available pair of electrons whereas E_{LUMO} is refers to its propensity to gain electrons from MS [62]. The reality that E_{HOMO} has a negative sign indicates that the corrosion inhibition might follows the physical adsorption isotherm [63]. ΔE is essential DFT-based calculations to discuss the interrelations occurring for both the MS surface and CPZ molecules. A lower ΔE value is correlated with high chemical activity and inhibition capability through the short distances among both HOMO and LUMO orbitals. The qualities of global hardness (η) and softness (σ) are essential variables in determining molecular activity & selectivity. E_{LUMO} , E_{HOMO} , η and σ values are determined and summarized in Table 7 for expired pharmaceuticals utilized in current work. The preferential adsorption performance of CPZ as ideal corrosion inhibitor molecules on MS surface may be demonstrated using the computed low values of η or high values of σ (which promotes higher adsorption) [64]. As corrosion inhibitor, CPZ has a quite high values of global softness (σ) (33.58 eV), indicating that soft molecules are more responsive than hard ones due to they can quickly transfer electrons to acceptors [65].

Table 7. Quantum calculation descriptors for the data of tested compounds by DFT, B3LYP, 6-311 (d,p) base set

Drug	- E_{HOMO}	- E_{LUMO}	ΔE	$I = -E_{HOMO}$	$\eta = (E_{LUMO} - E_{HOMO})/2$	$\sigma = 1/\eta$	$\Delta N = -\mu/\eta$
CPZ	0.27181	0.21225	0.060	0.272	0.030	33.580	8.127
MCP	0.29171	0.18227	0.109	0.292	0.055	18.275	4.331
MEB	0.32105	0.19198	0.129	0.321	0.065	15.495	3.975

Because of its low ΔE value, high softness, low hardness and strong chemical activity, the inhibitor molecule has a high inhibitory effectiveness [66, 67]. As a corrosion inhibitor must have low values of ΔE and η as well as a high value of σ . The number of transported electrons, denoted by ΔN , is thought to signify excellent inhibitory efficiency. The presence of electron transport from CPZ to MS

surface is shown by the favorably high values of ΔN for CPZ as corrosion inhibitor (8.127 eV) [68]. Another calculation takes place to emphasize the electronegativity of the tested compounds of drugs which belong to studying the surface by molecular electrostatic potential (MEP) and contour plots which show in Figure 10 indicated the electronegativity for the tested compounds (CPZ, MCP and MEB) which appearance in CPZ compound than MCP and MEB. Figure 11 show Mulliken diagram that show the red charge which represent the electronegativity of tested compounds and blue color for the positivity charge presented in the same compounds, CPZ represented more negative charge than MCP and MEB that emphasized the calculated value of $\Delta E = 0.060$ eV approve the experimental data for the same tested compound CPZ (97.13 % and 85.10 %) for tested media of H_2SO_4 and HCl, respectively.

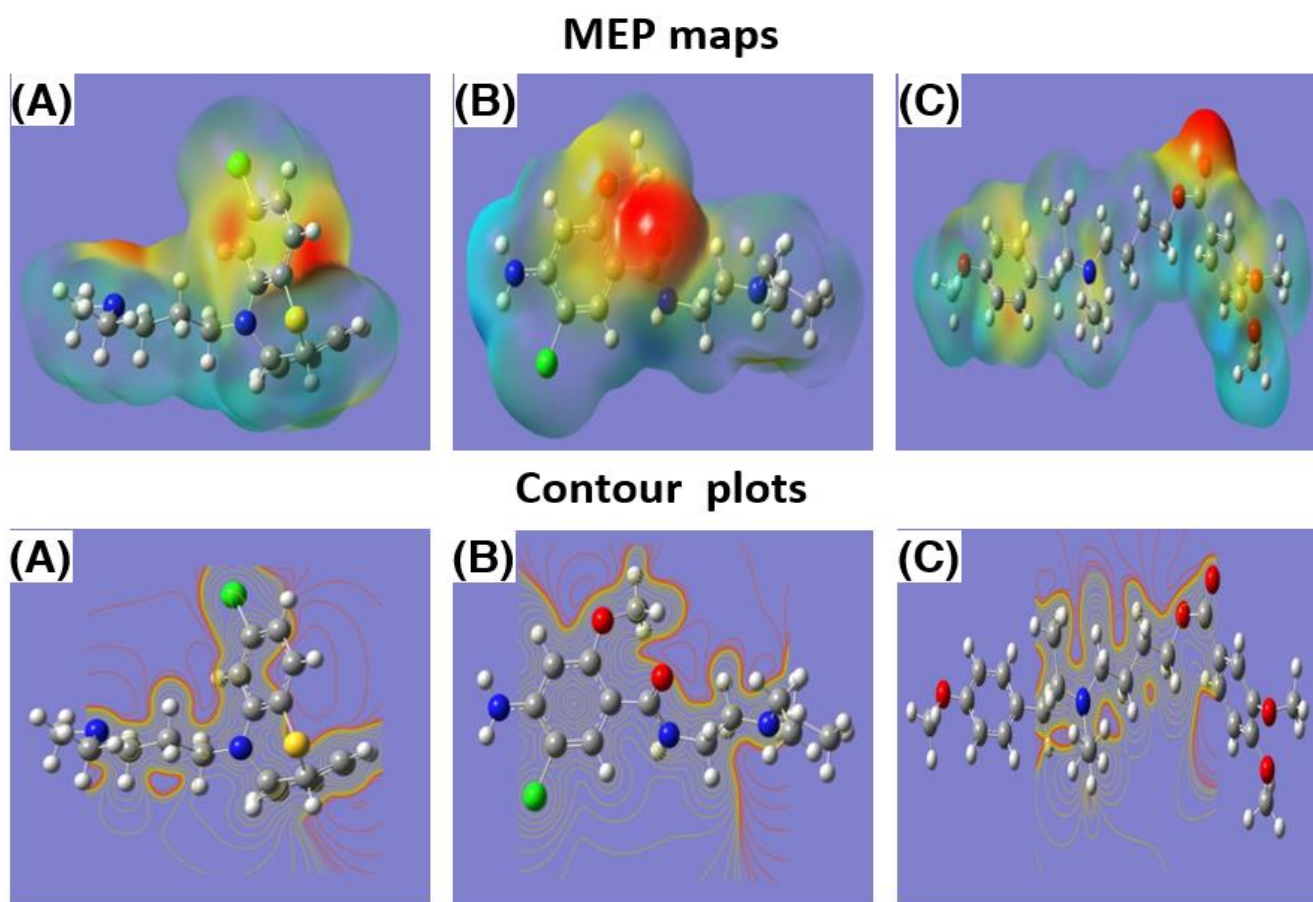


Figure 10. Represented MEP map and contour plots of studied drugs using DFT, B3LYP, 6-311 (d,p) base set: (A) CPZ, (B) MCP and (C) MEB

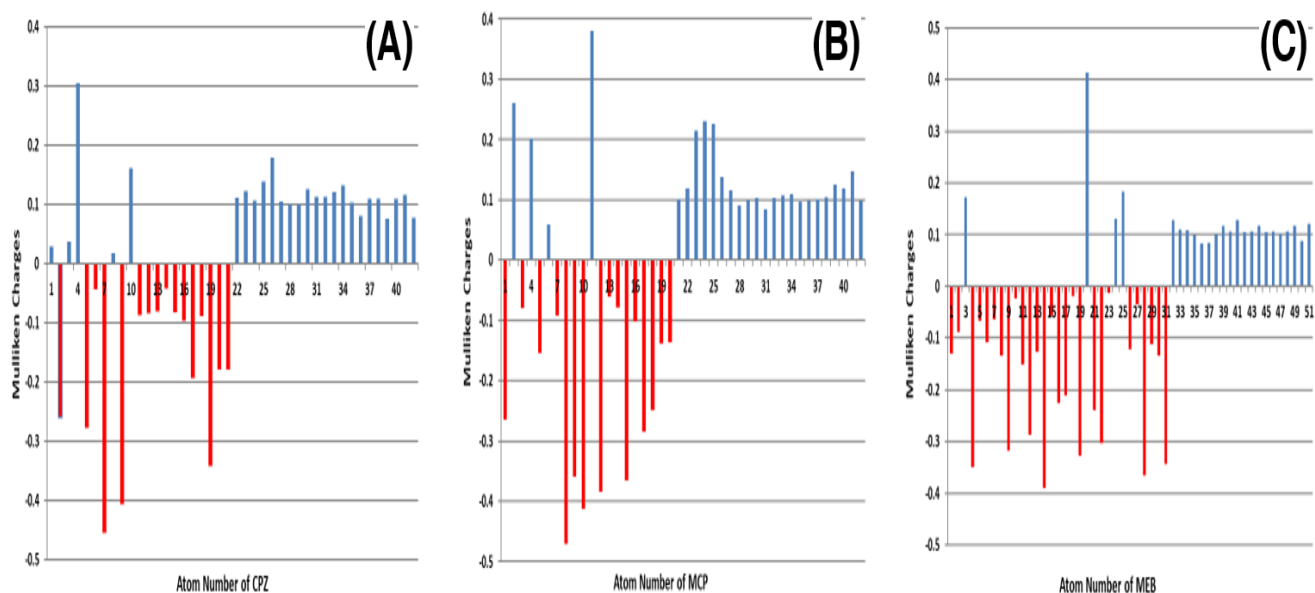


Figure 11. Represented Mulliken charges diagram of studied drugs using DFT, B3LYP, 6-311 (d,p) base set: (A) CPZ, (B) MCP and (C) MEB

3.5. Scanning electron microscope (SEM)

Figure 12 (A) reveals the polished MS electrode's smoothed surface before it is immersed in corrosive fluids. Images shown in Figure 12 (B and D) shows polished specimen which was immersed in blank solutions (1.0 M HCl or H₂SO₄), respectively, for 24 h which is associated with polishing scratches. From these figures the surface of MS electrode was damaged and destroyed. The corroded areas are appeared on MS surfaces as black grooves with white & gray regions, probably belongs to FeO flakes. It suggested that the exposed surface of a metal electrode had been corroded multiple times, and when desiccated without surface protection, the highly oxidized phase may have developed under atmospheric air. Figure 12 (C and E) illustrates the removal of such black grooves in the specimen surfaces after 24 h. of immersion in 1.0 M HCl or H₂SO₄ acidic media containing 700 ppm CPZ as an organic corrosion inhibitor, compared to being exposed to simply blank acidic solution. It is well known that the calculated I.E. % values is dependent on the applied inhibitor concentration [69]. This might be used to explain why an organic corrosion inhibitor is adsorbed on the MS surface, considerably slowing the rate of metal corrosion.

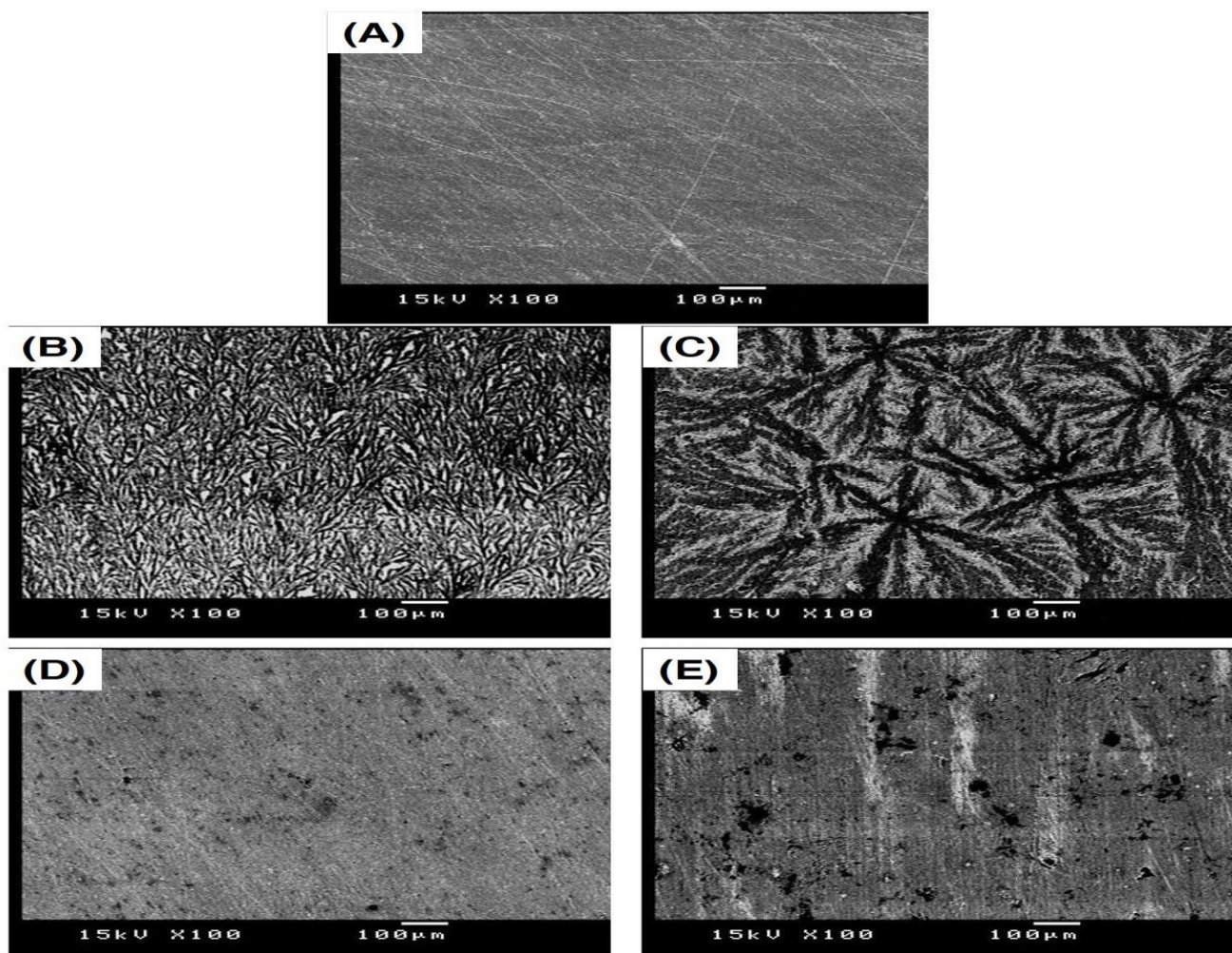


Figure 12. Scanning electron micrographs of: (A) polished MS surface, (B) polished MS + 1.0 M HCl after 24 h immersion time at room temperature, (C) polished MS + 1.0 M HCl + 700 ppm CPZ, (D) polished MS + 1.0 M H₂SO₄ after 24 h immersion time at room temperature, (E) polished MS + 1.0 M H₂SO₄ + 700 ppm of CPZ compound.

4. CONCLUSIONS

Potentiodynamic polarization observations shows that on addition of expired pharmaceuticals as examples for organic inhibitors leads to increases both anodic and cathodic overvoltage, and an inhibition effectiveness increases as raising inhibitor concentrations. Between the studied expired pharmaceuticals in current study; metoclopramide hydrochloride (MCP), chlorpromazine hydrochloride (CPZ) and mebeverine hydrochloride (MEB), CPZ shows a good inhibition behavior for MS in 1.0 M acidic media (whether HCl or H₂SO₄). The inhibition effectiveness increased with raising CPZ concentration to 700 ppm and achieve its maximum values after 4 days' contact time (85.10 % and 97.13 % for HCl and H₂SO₄, respectively). The adsorption of some environmental substances on metal surface is physical adsorption comply with Langmuir adsorption isotherm. The calculated quantum chemical descriptors utilizing DFT, B3LYP, 6-311 (d,p) base set shows a great accordance with recorded experimental data. SEM images reveal a visual idea about the creation of an insulating layer on MS surface, and so retards the corrosion rate.

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