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Investigation Effect of 4-Aminophenol as a Corrosion Inhibitor for Mild Steel in Sulfuric Acid Medium

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Abstract

A high number of organic materials have been studied as inhibitors for corrosion in different conditions. In this paper, the effect of organic chemical (4-Aminophenol) as an inhibitor for mild steel metal corrosion was investigated in presence of sulfuric acid at different temperatures. The study was carried out using three known methods in testing corrosion process, methods of weight loss, thermometric, and polarization. The obtained results showed that when the inhibitor concentration increases, the corrosion rate decreases, and hence, the inhibition efficiency increases. Moreover, when the surface coverage at a temperature of 313 °C with organic inhibitor increases, the corrosion rate decreases as noticed in the weight loss method. For the thermometer method, the inhibitor was examined by temperature. The inhibition efficiency increases, as well as in the anodic and cathodic polarization method, where it is observed that the anodic and cathodic curves are present to measure the corrosion current and corrosion potential. As the higher the concentration of the inhibitor, the lower the current and the corrosion voltage. The reason for the effectiveness of this inhibitor is the presence of amine and phenol organic molecules in its composition, which can form a film on the metal surface and prevent corrosion from taking place.

Keywords: 4-Aminophenol, gravimetric, weight loss, polarization, mild steel, inhibition, reaction number, corrosion rate.

1. Introduction

Metal corrosion is a serious issue that many businesses encounter. As a result, scientists and engineers are spending substantial resources on corrosion research, focusing not only on metal corrosion behavior in diverse settings but also on strategies to shield metals against corrosion [1-7]. Because of its low cost, superior mechanical characteristics, high strength, environmental stability, weight ratio, and high thermal and electrical conductivities, mild steel is the most widely used metal alloy in industrial sectors for structural and scientific research purposes. Moreover, sulfuric acid is more effective and affordable, it is utilized for acid cleaning, acid descaling, petrochemical etching, and industrial cleaning. Preventing metal corrosion is a key industrial challenge; in addition, using inhibitors to prevent metals from corrosion in acidic conditions is a possible option [8-10]. Many organic and inorganic substances have been recorded to be used as corrosion inhibitors. These compounds have anti-corrosive action because they include hetero atoms in their long-chain structure [11-15]. One of the primary issues with using these inhibitors is that they are highly costly, and their poisonous nature frequently poses health and environmental risks. Several natural compounds help control corrosion attacks and have been described as having the capacity to prevent metal corrosion in various strong acids by several authors [12-16].

The organic chemical compound 4-aminophenol (also known as para-aminophenol or p-aminophenol) has the formula $H_2NC_6H_4OH$. This compound contains aromatic rings attached to amino and hydroxy groups. It was frequently used as a developer for black-and-white film, sold under the name Rodinal, and was often available as a white powder [14-20]. Metal corrosion is a serious problem found in different applications of life. Which has negative effects on that, so scientists and researchers tried to provide studies and research, focusing only on the behavior of metal corrosion in various environments with the lack of approaches to protect metals from corrosion and reduce the resulting erosion and distortion, so in this study, we focused on the use of some solutions such as inhibitors [16-18].

2. Experimental

Sulphuric acid was diluted with double-distilled water to make the test solution (1M H_2SO_4). Corrosion tests were conducted on polished mild steel samples, which were mechanically pressed into various coupons with dimensions of (3.5 × 2.5 × 0.2) cm a piece. Before being kept in a desiccator, the polished surface was cleaned with acetone and then washed with double distilled water. The white powder is moderately soluble in alcohols and may be recrystallized from hot water, indicating its somewhat hydrophilic nature. It rapidly oxidizes in the presence of a base. *N*-methylaminophenol and *N,N*-dimethylaminophenol are commercially valuable methylated derivatives. It is made by nitrating phenol and then reducing it with iron. Partial hydrogenation of nitrobenzene yields phenylhydroxylamine, which predominantly rearranges to 4-aminophenol. It is made by electrolytically converting nitrobenzene to phenylhydroxylamine, which then spontaneously rearranges to 4-aminophenol. In organic chemistry, 4-aminophenol is a building block. It is the most important intermediary in the industrial production of paracetamol. Paracetamol is made by reacting 4-aminophenol with acetic anhydride [10-15].

2.1 Gravimetric Measurement

The Weight Loss technique was used to establish the fundamental corrosion rate measurement. The mild steel coupons were submerged in 100 mL of the acidic environment test solution (1M H_2SO_4) in presence and absence of the inhibitor at varied temperatures in triplicate. After 6 hours, at temperatures of (313, 323, and 333) K. The metal specimens were removed from the test solutions. After being removed, the specimens were washed with double distilled water, degreased with acetone, and dried. To determine the difference in weight of the specimens before and after immersion, a Citizen CY 220 digital balance with a sensitivity of 0.001g was used [15-19].

$$C.\ R = (87.6 \times W) / DAT \quad \text{……....... (1)}$$

Where C. R stands for corrosion rate (millimeters per year, mm py), W stands for weight loss (mg), D stands for sample density (gm/cm^3), and a stand for sample area (cm^2), and T stands for time (hour).

The inhibitory efficiency (percent IE) and degree of surface coverage (θ) were calculated using equations (2) and (3).

$$IE\ \% = (W1-W2) \times 100 \quad \text{………... (2)}$$

$$\theta = (W1-W2) / W1 \quad \text{....……... (3)}$$

The corrosion rates in the absence and presence of the inhibitor are denoted by W1 and W2, respectively [9-14].

2.2 Thermometric Method

Thermometric techniques were also utilized to evaluate the effectiveness of the inhibition. The reaction vessel used in thermometry investigations was substantially the same as that used by Mylius. Based on the temperature rise per minute, equations 4 and 5 were used to calculate the reaction number (RN) and inhibition efficiency (IE %) [11-20].

$R.N = (Tm - Ti) / t$ ……. (4)

Where Tm is denoted the maximum temperature, Ti is denoted the initial temperature and t denotes the time. Using the equation below, the inhibition efficiency (% IE) of the employed inhibitor will be calculated.

$\% IE = (RNaq - RNwi) / RNaq \times 100$ …. (5)

In the absence of inhibitors, RNaq is the aqueous acid reaction number, while in the presence of inhibitors, RNwi is the aqueous acid reaction number [14-18].

2.3 Weight loss measurement

Weight loss measurements at (313, 323, and 333) K after six hours of immersion were used to evaluate the effect of various concentrations of (4-Aminophenol) on mild steel corrosion in 1M H_2SO_4 solution. Tables 1 to 3 show the inhibitory efficiency (% IE) and corrosion rate (C.R) achieved using the weight loss technique. The results indicated that the corrosion rate is proportional to the inhibitor concentration and that the plant extract inhibits corrosion more effectively at low concentrations [16-20].

Table 1: Corrosion properties of mild steel in 1M H_2SO_4 solution at 313 K in the absence and presence of various concentrations of (4-aminophenol).

Inhibitor conc (ppm)	Weight loss (mg)	Corrosion rate (mmpy)	Inhibition efficiency (%E)	Surface coverage (θ)
blank	1065	249.44	-----	------
100	672	157.39	36.9	0.369
200	589	138.43	44.5	0.445
300	513	117.99	52.7	0.527
400	431	99.13	60.2	0.602
500	288	67.45	72.9	0.729
600	211	49.42	80.1	0.801

Table 2: Corrosion properties of mild steel in 1M H_2SO_4 solution at 323 K in the absence and presence of various concentrations of (4-aminophenol).

Inhibitor conc. (ppm)	Weight loss (mg)	Corrosion rate, (mmpy)	Inhibition efficiency (%E)	Surface coverage (θ)
blank	1338	307.74	-----	----
100	933	214.59	30.3	0.303
200	789	181.47	41.0	0.410
300	682	156.86	49.1	0.491
400	553	127.19	58.6	0.586
500	433	99.59	67.7	0.677
600	398	91.54	70.3	0.703

Table 3: Corrosion properties of mild steel in 1M H_2SO_4 solution at 333 K in the absence and presence of various concentrations of (4-aminophenol).

Inhibitor conc (ppm)	Weight loss (mg)	Corrosion rate (mmpy)	Inhibition efficiency (%E)	Surface coverage (θ)
blank	1663	382.49	-----	----
100	1225	281.75	26.4	0.264
200	1088	250.24	34.5	0.345
300	903	207.69	45.8	0.458
400	815	187.45	51.0	0.510
500	635	146.05	61.4	0.614
600	552	126.96	67.0	0.670

As the inhibitor concentration grows, the inhibitor molecules are adsorbed on the mild steel surface, creating a greater surface area and a barrier to mass and charge transfer. The inhibitory efficiency (% IE) of the inhibitor rises with increasing concentration starting at 600 ppm and reaching a maximum of 80.1 % at 313 K, 70 % at 323 K, and 66 % at 333 K. The higher the surface area covered (θ) by the number of molecules adsorbed on the metal surface, the better reaction site protection. Figures 1 and 2 show the influence of inhibitor concentration on the variation of corrosion rate and inhibition efficiency versus inhibitor concentration at 313, 323, and 333 K respectively [12-19].

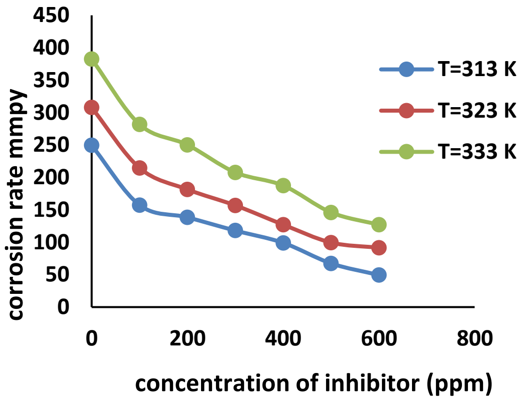

Figure 1: Relation between the concentration of inhibitor and corrosion rate of mild steel in several concentrations of (4-aminophenol) at various temperatures in 1M H_2SO_4 solution.

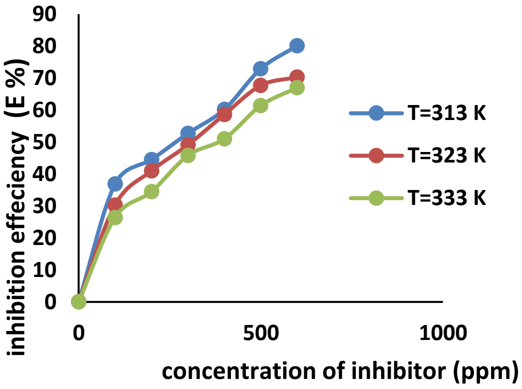

Figure 2: Relationship between inhibitor concentration and mild steel inhibition effectiveness in 1M H_2SO_4 solution at various temperatures and concentrations of (4-aminophenol).

2.4 Effect of temperature

The dissolving behavior of mild steel in 1M H_2SO_4 solution containing varying concentrations of (4-aminophenol) was examined for six hours at various temperatures; including 313, 323, and 333 K. The findings are presented in figure 2. At all temperatures examined, inhibitor molecules adsorb on the metal surface, and inhibition efficacy diminishes as temperature rises in a 1M H_2SO_4 solution, according to table 4. A rise in the temperature of metal corrosion in acidic environments is frequently followed by the generation of H_2 gas, which usually speeds up the corrosion processes, resulting in a faster rate of metal dissolution. Inhibition efficiency reduces as the temperature of the test solution rises [13-17].

2.5 Adsorption Isotherm

The development of the adsorption isotherm helps explain the process of corrosion inhibition on metal surfaces. The method of adsorption and adsorption isotherm was used to investigate the interaction of inhibitor compounds on metal surfaces. The Langmuir adsorption isotherm is a basic isotherm that defines the adsorption process for inhibitors at 313, 323, and 333 K, and it fits the experimental data. Equation six can be used to investigate the Langmuir adsorption isotherm [9-14].

$$C / \theta = (1/ K) + C \qquad \text{...........} (6)$$

C is denoted to a concentration of inhibitor, Kads is denoted to a coefficient of adsorption, and θ is denoted to surface coverage. The plots of C/ θ and C show a straight line with a slope close to unity, indicating Langmuir adsorption in figure 3. The mild steel surface is covered by H2O molecules in an acidic solution, which is replaced by each inhibitor molecule, indicating that each adsorption site contains one adsorbate (molecule). Because the linear regression coefficient (R2) values are almost unity at all temperatures, the adsorption behavior is considered to have obeyed Langmuir adsorption isotherms. Using the following equation, the free energies of adsorption, ΔGads, were derived from the equilibrium constant of adsorption:

$$\Delta G_{ads} = -2.303RT\text{Log}\,[55.5K_{ads}] \qquad \ldots (7)$$

Where R denotes the universal gas constant, T is denoted absolute temperature. Physisorption, which is an electrostatic connection between charged inhibitor molecules and charged metal, is generally indicated by Gads values up to -20 kJ/ mol, whereas ΔGads values around -40 kJ/ mol suggest a coordinate sort of binding between metal and inhibitor molecules. The value of

Gads reflects the poor adsorption capacity. As shown by the negative values of ΔGads, inhibitor molecules adsorb spontaneously on the metal surface [13-17]. The reciprocal of the intercept of the Langmuir plotline (table 4) averages 0.0048 l/g, and the slope of this line is close to unity, suggesting that each inhibitor molecule occupies one active site on the metal surface. Table 4 reveals that the values of ΔGads were -3.136 kJ/ mole at 313 K, -3.609 kJ/ mole at 323 K, and -3.841 kJ/ mole at 333 K indicating that the molecules adsorb on the metal surface via physisorption, whereas the negative value of ΔGads indicates that adsorption occurs spontaneously.

Table 4: the relationship between temperature, coefficient of adsorption and free energy of adsorption.

Temp. K	K_{ads}	Slope	$-\Delta G_{ads}$ (kJ /mol)
313	0.0054	0.956	3.136
323	0.0047	1.046	3.609
333	0.0045	1.034	3.841
average	0.0048	1.012	3.528

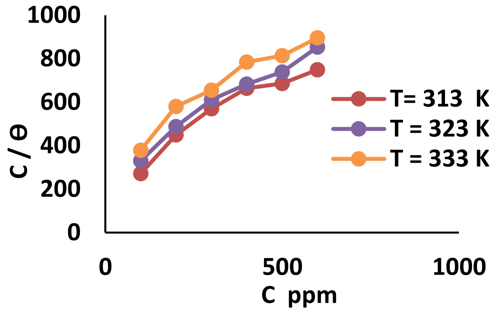

Figure 3: Plot relation Langmuir adsorption isotherm adsorption of different concentrations of (4-aminophenol) on mild steel in 1M H_2SO_4 solution for six hours at several temperatures.

2.6 Thermometric Measurement

This technique demonstrated that the corrosion process on metal behaves differently in inhibited and uncontrolled media. Table 6 shows the corrosion rates and reaction numbers for mild steel corrosion in the presence and absence of different amounts of (4-Aminophenol) at 300 °C. Table 6 shows that the reaction number reduces as the inhibitor concentration increases, and it was deduced that inhibition efficiency increases as inhibitor concentration increases. Figure 4 depicts the relationship between reaction number (R.N.) and inhibitor concentration, indicating that the (R.N) drops as concentration rises. Figure 5 shows a thermometric plot of temperature vs. time for mild steel corrosion in 1M H_2SO_4

solution in the absence and presence of various inhibitor concentrations where the relationship is inverse, as time increases, the temperature decreases. The thermometric technique yielded the best inhibitory effectiveness (92.64 % at 313 K) where the relationship is direct, the higher the concentration of the inhibitor, the higher the inhibition efficiency as shown in figure 6, which agreement with references [10-19].

Table 5: Reaction number and inhibition efficiencies of several concentrations for mild steel in 1M H_2SO_4 solution.

The concentration of Inhibitor ppm	Initial temp. Ti C	Final temp. Tm C	Time min.	Reaction No. R. N	%IE
blank	40	57	25	0.68	----
100	40	52	30	0.40	46.66
200	40	51	35	0.31	54.41
300	40	49	40	0.22	67.64
400	40	47	45	0.15	77.94
500	40	45	50	0.10	85.29
600	40	43	55	0.05	92.64

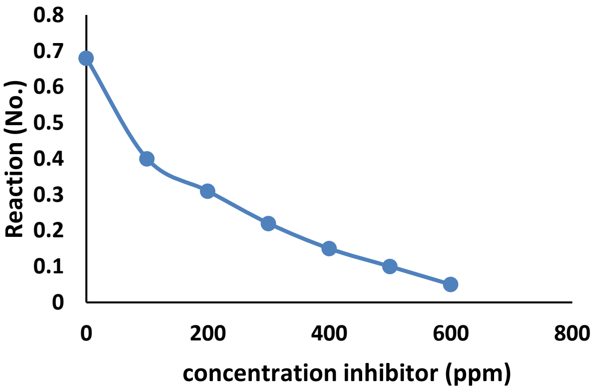

Figure 4: relation between Reaction number and inhibitor concentration for mild steel of H_2SO_4 solution.

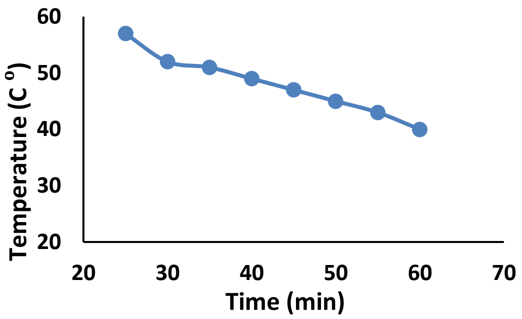

Figure 5: Temperature-time curve for mild steel in various inhibitors concentrations of H_2SO_4 solution at 40 °C.

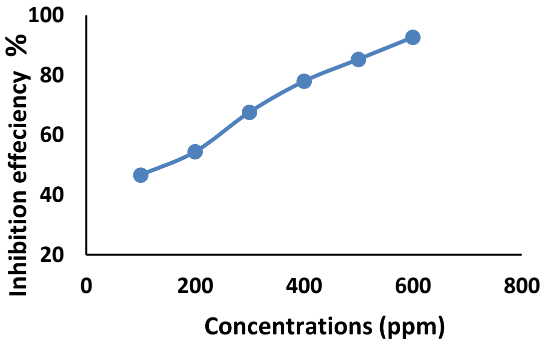

Figure 6: Inhibition efficiency- Inhibitor concentration curve for mild steel in H_2SO_4 solution at 40 °C.

2.7 Measurement of polarization

A mild steel sample was cleaned in a 1 M H_2SO_4 acid and varied inhibitor dosages were used in a 30-minute dynamic polarization method (100-600 ppm). The electrode fitting is made of mild steel, standard calomel electrode (SCE), and platinum electrode. Polarization curvatures were discovered through polarization research. Current corrosion density (I corr) and potential corrosion density (I corr) can be determined using cathodic and anodic curves (E corr). The corrosion rate was calculated using the equation below [11-18].

$$\eta\ \% = \left((I_{corr})_w - (I_{corr})_i \right) / \left((I_{corr})_w \right) \quad *100 \quad ....(8)$$

Without and with inhibitor, the corrosion current densities are denoted by (Icorr) w and (Icorr) i, respectively. The variations in anodic and cathodic polarization are seen in figure 7. The polarization curve changes as the inhibitor concentration increases, the corrosion current, and potential decrease, and efficiency increases due to forming a film layer on metal and protecting it from external conditions, as shown in table 7 [13-20].

Table 7: Corrosion current density, potential, and inhibition efficiency for polarization characteristics.

Inhibitor conc (ppm)	Potential Ecorr, (mV)	Corrosion current density ($\mu A/cm^2$)	%Inhibition efficiency
Blank	-441	142	--
100	-413	90	36.61
200	-380	65	54.22
300	-365	53	62.67
400	-360	42	70.42
500	-323	33	76.76
600	-298	24	83.09

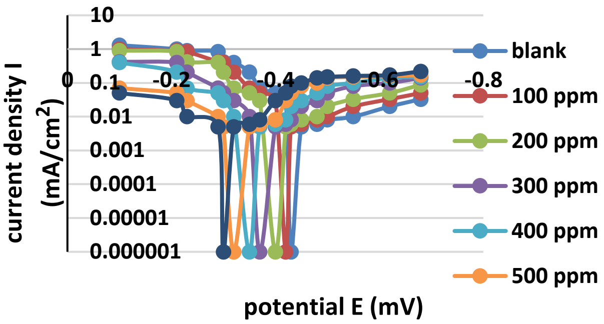

Figure 7: polarization curves, the relation between potential and current density at various concentrations of inhibitor.

3 Conclusion

Using three well-known methodologies in corrosion process tests, including weight loss, thermometric, and polarization, the organic chemical inhibitor (4-aminophenol) was tested on mild steel metal in sulfuric acid at various temperatures. Corrosion rate reduces as inhibitor concentration increases. With organic inhibitors, the surface covering at 313 °C rises, as in the weight loss procedure. When it comes to the thermometer technique, the inhibitor was evaluated at a certain temperature range. The inhibition efficiency rises, as well as in the anodic and cathodic polarization methods, where the anodic and cathodic curves are present to assess the corrosion current and corrosion potential, as the greater the inhibitor concentration, the lower the current and corrosion voltage. This inhibitor's efficacy is due to the presence of amine and phenol molecules in its structure, which can create a film on the metal's surface and protect it against corrosion.

4 References

1. Al-Amiery A. A, Mohamad, A. B., Kadhum, A. A., Shaker, L. M., Roslam, W. N., Isahak, W., and Mohd S. Takriff, M.S. (2022). Experimental and theoretical study on the corrosion inhibition of mild steel by nonanedioic acid derivative in hydrochloric acid solution, Scientific Reports, 12, 4705:4726.
2. Prabakaran M., Seung-Hyun Kim S. H., Hemapriya V., Gopiraman M., Ick Soo Kim I. S. and Chung I. M., (2016). Correction: Rhus verniciflua as a green corrosion inhibitor for mild steel in 1 M H2SO4. Royal Society of Chemistry Advances. 6, 57144-57153
3. Al-Uqaily R. A., Al-Bayaty S. A., and Hameed S. (2019). 2-Amino-6-Chlorobenzothiaozole as Effective Corrosion Inhibitor for Copper in Acidic Media, Journal of International Pharmaceutical Research. 46, 4, 342:345.
4. Ojha L. K., Kaur K., Kaur R., and Bhawsar J. (2017). Corrosion inhibition efficiency of fenugreek leaves extract on mild steel surface in acidic medium, Journal of Chemical and Pharmaceutical Research. 9, 6, 57-67.
5. Ebenso E., Eddy N., and Odiongenyi A., (2008). Corrosion inhibitive properties and adsorption behavior of ethanol extract of Piper guinensis as a green corrosion inhibitor for mild steel in H_2SO_4, African Journal of Pure and Applied Chemistry. 2, 11, 107-115.
6. Al-Uqaily R. A. H. (2015), Inhibition by 1-methyl isoquinoline for mild steel corrosion in 1 M HCl media, American Scientific Research Journal for Engineering, Technology, and Sciences. 14, 1, 55-63.
7. Li W.H., Qiao He Q., Zhang, S. T., Pei C. L., and Bao-rong Hou, B. R., (2008). Some new triazole derivatives as inhibitors for mild steel corrosion in acidic medium, Journal of Applied Electrochemistry. 38, 289-295.
8. Bentiss F., Lebrini M., and M. Lagrenée M., (2005). Thermodynamic characterization of metal dissolution and inhibitor adsorption processes in mild steel /2, 5-bis (n-thienyl)-1, 3, 4-thiadiazoles/hydrochloric acid system, Corrosion Science. 47, 12, 2915-2931.
9. Singh A. K., Shukla S. K., Singh M., and Quraishi, M. A., (2011). Inhibitive effect of ceftazidime on corrosion of mild steel

in hydrochloric acid solution. Materials Chemistry and Physics. 129, 1-2, 68-76.

10. Singh A. K., and M. Quraishi, M. (2010). Inhibiting effects of 5-substituted isatin-based Mannich bases on the corrosion of mild steel in hydrochloric acid solution, Journal of Applied Electrochemistry. 40, 1293-1306.
11. Obot I. and Obi-Egbedi, N., (2010). Adsorption properties and inhibition of mild steel corrosion in sulphuric acid solution by ketoconazole:experimental and theoretical investigation. Corrosion Science. 52, 1, 198-204.
12. Emregül K. C., and Atakol O., (2004). Corrosion inhibition of iron in 1 M HCl solution with Schiff base compounds and derivatives. Materials Chemistry and Physics. 83, 2-3, 373-379.
13. Bhawsar J., and Jain P., (2018). Investigation of Mentha spicata extract as Green Corrosion Inhibitor for Mild Steel in 2 M Sulphuric Acid Medium. Research Journal of Pharmacy and Technology. 11, 10, 4627-4634.
14. Bentiss F., Traisnel M., and Lagrenee M., (2000). The substituted 1, 3, 4-oxadiazoles: a new class of corrosion inhibitors of mild steel in acidic media. Corrosion Science. 42, 1, 127-146.
15. Wang S., Zhang J., Gharbi O., Vivier V., Gao M., Mark E., and Orazem M. E. (2021). Electrochemical impedance spectroscopy. Nature Reviews Methods Primers. 1, 1, 1-21.
16. Bredar A. R., Chown A. L., Burton A. R., and Farnum B. H. (2020). Electrochemical impedance spectroscopy of metal oxide electrodes for energy applications. American Chemical Society, Applied Energy Materials. 3, 1, 66-98.
17. Vadhva P., Hu J., Johnson M. J., Stocker R., Braglia M., Brett D. J. L., and Rettie A. J. E. (2021). Electrochemical Impedance Spectroscopy for All-Solid-State Batteries: Theory, Methods, and Future Outlook. ChemElectroChem. 8, 11, 1930-1947.
18. Polat K., Aksu M., and Pekel A. (2002). Electroreduction of nitrobenzene to p-aminophenol using voltammetric and semipilot scale preparative electrolysis techniques, Journal of Applied Electrochemistry. 32, 2, 217-223.
19. Ahamad I, Prasad R, Quraishi MA. (2010). Thermodynamic, electrochemical and quantum chemical investigation of some Schiff bases as corrosion inhibitors for mild steel in hydrochloric acid

solutions. Corrosion Science, 52, 3, 933-942.

20. Feliu S., (2020). Electrochemical impedance spectroscopy for the measurement of the corrosion rate of magnesium alloys: Brief review and challenges. Metals. 10, 6, 775-775.