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Study the Efficiency of Poly Nicotine Amide as Anticorrosion Coating on Stainless Steel and Study Its Biological Activity

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Abctract

Using an electrochemical polymerization technique at room temperature, poly nicotine amide (PNA) was produced from the monomer nicotine amide (NA) in aqueous solution. The structure of polymer layer generated on the stainless steel surface (316 L) (working electrode) is investigated by Fourier Transmission Infrared Region (FT-IR). The anti-corrosion activity of polymer coating on the stainless steel (SS 316 L) is investigated by electrochemical polarization in 0.20M solution of HCl at 293-323K. The graphene -modified polymer film-coated SS had greater protection efficiency (PE percent) when compared to Nano ZnO -modified polymer film-coated SS. For the corrosion process of SS 316 L, kinetic and thermo-dynamic parameters of activation are estimated. The antibacterial activity of coated film has been tested on both gram positive as well as gram negative bacteria by well diffusion approach, which include Staphylococcus aureus (Staph.Aure) and Ecoli. Through adding nanoparticles to a monomer solution to raise the effecincy of the polymer against the corrosion and bacterial, As a result, after modifying poly nicotine amide with nanomaterial, the inhibition zone values increased (Nano ZnO and Graphene).

Keywords: corrosion, electrochemical polymerization, stainless steel, poly Nicotinamide, biological activity, nanomaterials, protection efficiency

1. Introduction

The process of the electro-chemical polymerization involves oxidizing monomer for the purpose of producing radical, after that, those radical cations have been reacted with one another, or with some other monomer, the purpose of producing radical dimer that transferred to longer and trimer chain [1, 2]. Monomer Oxidation had happened on working electrode (WE) that is made of

a variety of the materials, like the indium tin oxide coated glass and stainless steel [3,4]. The conductive polymers have wide field in numerous applications, they are typically utilized in the rechargeable batteries, chemical transistors, producing indicators and ion selective electrodes, corrosion inhibitors and bio-chemical analyses [5-7]. Using the coating that has anti-microbial activities is one of the effective methods for the decrease of the microbial numbers on the health-care surfaces. The anti-microbial agents can be defined as materials having a capability to kill the pathogenic micro-organism [8]. Sufficient anti-microbial polymers have to be biocidal to a wide variety of the pathogenic micro-organism, may be re-generated in the case of activity loss, insolubility in the water for different applications, and inability of being de-composed into toxic substances [9]. In the present study, an electro-chemical polarization approach has been implemented for the purpose of studying protection efficiency of conductive polymer film upon SS corrosion in 0.20M of the HCl solution at temperature that ranges between 293 and 323 K. The effects of the addition of the Nano-materials (ZnO (Nano) and Graphene) upon anti-corrosion actions of polymer films on the SS surfaces are studied.

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2. Experimental part

2.1. Preparation of samples

The sample used in this work is SS 316, which diameter disk 2.2 cm prepared according to the following steps:-

Step one:- the samples were polished by different grade of silicone carbide include (800,1200 and 2000 mesh grit), and after that, washed with the distilled water and acetone and kept it in desiccator.

Step two:- the sample was immersed in monomer solution (nicotine amide) which is (0.1 g) of nicotine amide in (100ml) of H_2O with adding 3 drop

ps of (98% conc.H_2SO_4) to increase conductivity of the solution at room temperature for electrochemical polymerization process by DC power supply [10].

Step three:- addition of nanomaterial, the nanomaterial used in this work are (0.04 g of Nano ZnO) and (0.004 g of Graphene) to improve the efficiency of the polymer film against corrosion and bacterial.

2.2. Corrosion measurement

The tests of corrosion have been carried out with an advanced potentio-stat (Winking MLab200, Bank Electronic–Intelligent controls GmbH, Germany) complete with all of the accessories, including a cell, electrodes (working electrode, reference electrode, and auxiliary electrode), and a working electrode holder. Corrosive media was a 0.2 M HCl solution, and curves of polarization have been scanned from (-200mv) to (+200mv) from open circuit potential, corrosion currents, and corrosion potentials. Ecorr have been calculated with extrapolating anodic and cathodic Tafel lines from the curves of polarization at 4 temperature degrees: 293, 303, 313, and 323K.

2.3. Biological activity

In this work, the prepared polymer (poly nicotine amide) (800 µg/ml) evaluated for biological activities towards gram-positive bacteria (*S.aureus*) as well as the gram negative bacteria (Ecoli). Well diffusion approach that has been utilized for the determination of inhibition potential of the prepared poly nicotine amide against bacterium and the used solvent is Dimethyl Sulfoxide (DMSO).

3. Results and Discussions

3.1. Fourier Transform Infrared Region (FTIR) for monomer and polymer

The asymmetric and symmetric stretching vibrations of NA (monomer) resulted in two absorption bands at (3335.13 and 3238.40) cm-1 (-NH2). Other absorption bands at (1525.5 and 1618.23) cm-1 are a result of (C=N) imine, (C=C) aromatic, and other absorption bands at (1525.5 and 1618.23) cm-1 are a result of the (C=N) imine, (C=C) aromatic, respectively.

PNA (polymer) exhibited bands of absorption at (3448, 3425) cm-1 as a result of (O-H) carboxyl and (N-H) amide, as well as absorption bands at (1718.48 and 1668) cm-1 due to (C=O) carboxyl and (C=O) amide [11,12].

Table1: FT-IR spectral data (cm-1) for monomer (NA)

	Absorption band intensity (cm-1)	Functional group
Monomer (NA)	3335.13& 3238.40	ν N-H
	3065.53	Aromatic C-H
	1690.8	C=O (amide)
	1618.23	Aromatic C=C
	1525.5	C=N
Polymer (PNA)	3453.13	ν O-H
	3425	ν N-H
	2914.24 & 2898.81	Aliphatic C-H
	1718.48	C=O (carboxyl)
	1668	C=O (amide)

3.2 Corrosion measurements

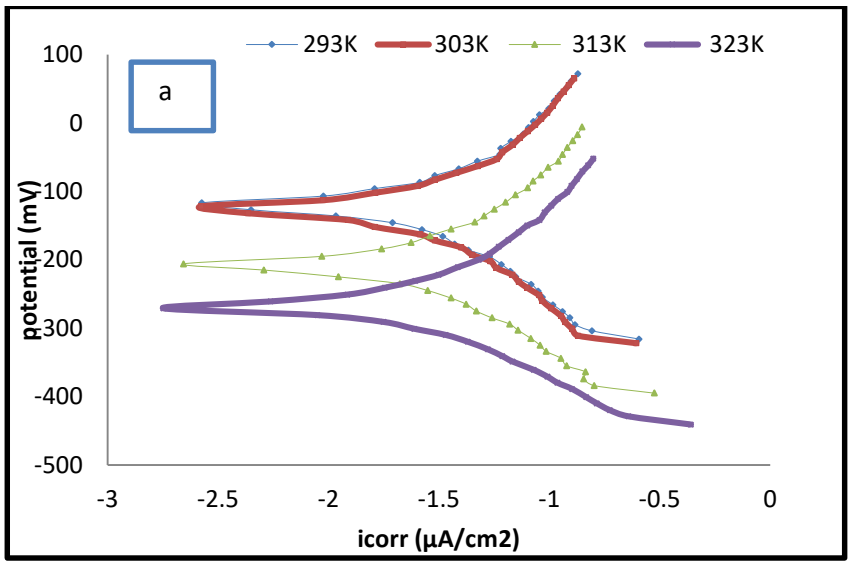
Figure 1 shows the impact of a polymeric layer upon cathodic and anodic curves of polarization of SS in 0.2M solution of HCl at temperatures ranging from 293K to 303K in the absence and presence of nanomaterial. Extrapolation Tafel lines were used to determine the corrosion current density. Table 2 shows effects of a polymeric layer in the presence and absence of the nanoparticles. Corrosion potential (Ecorr), cathodic Tafel slope (c), corrosion current density (icorr), and anodic Tafel slope (a) were discovered to be corrosion characteristics. The following equation [13] is used to calculate protection efficiency:

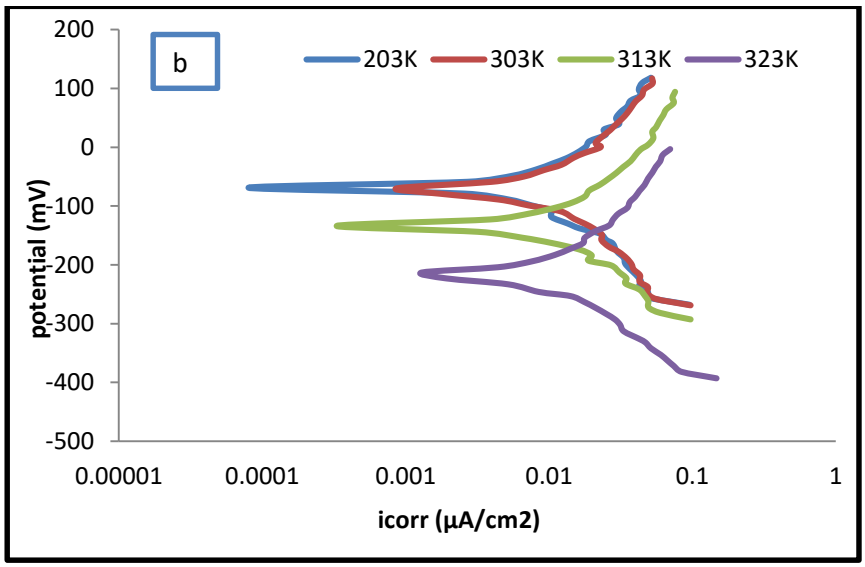
$$\%\mathrm{PE} = \frac{(\mathrm{icorr})\mathrm{o} - (\mathrm{icorr})}{(\mathrm{icorr})\mathrm{o}} * 100 \quad (1)$$

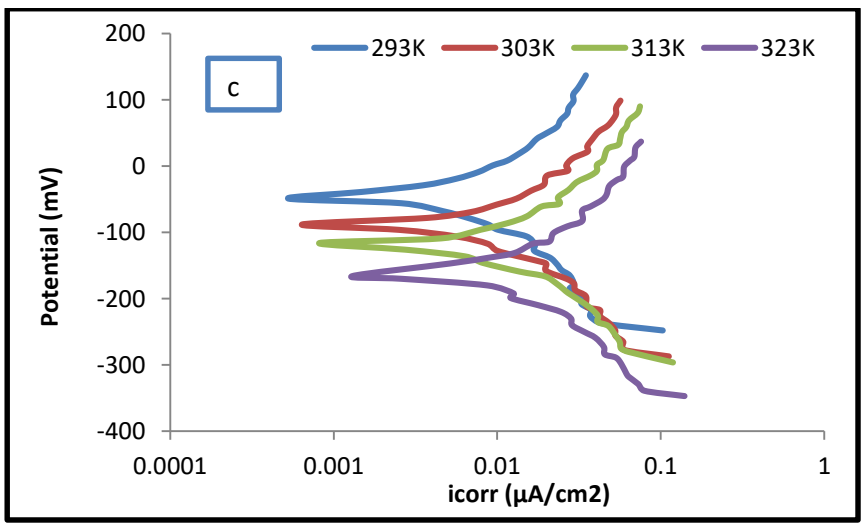
Where the (icorr)o represents current density of the corrosion for the uncoated SS, (icorr) the density of the corrosion current for the coated SS. Corrosion potential (Ecorr) has been shifted to more positive values (i.e. towards the noble direction) and icorr has been reduced after adding the Nano-materials. The resistance of polarization (Rp) has been determined by the Stern-Gerry eq. [14]:

$$\mathrm{Rp} = \frac{\mathrm{ba}+\mathrm{bc}}{2.303\ (\mathrm{ba}+\mathrm{bc})\mathrm{icorr}} \quad (2)$$

The measurements of the polarization resistance (Rp) have similar requirements to full polarization curve measurements and it has been considered beneficial as one of the methods for the identification of the corrosion upsets and initiate the remedial actions [15]. Rp values have been presented in **Table 1**.







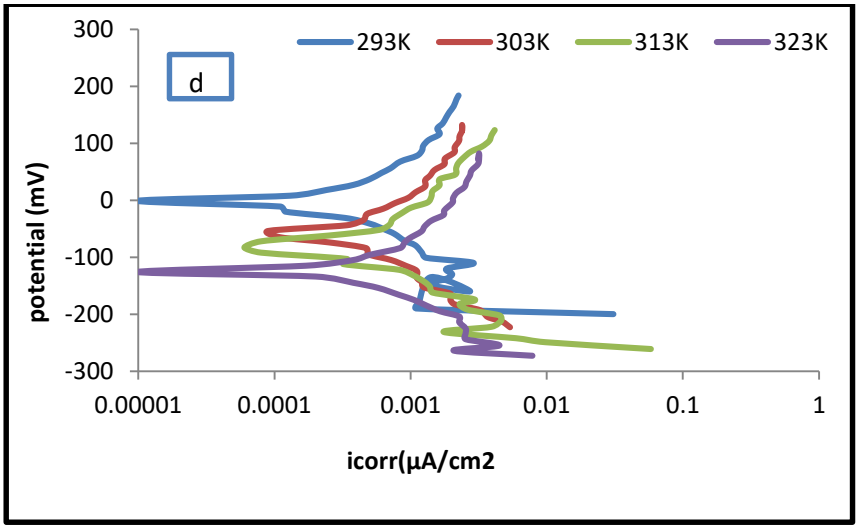


Figure1. Tafel plot for: a) uncoated SS, b) coated SS with polymer film, c) coated SS with the polymer film that has been modified by Nano ZnO, d) coated SS with polymer film that has been modified with the graphene.

Table2. Parameters of corrosion for the coated as well as the uncoated SS in 0.20M solution of the HCl

Coating	T/K	-Ecorr [mV]	Icorr [µA/cm²]	- βc mV/Dec	βa [mV/Dec]	PE%	WL [g/m²d]	PL [mm/y]	Rp [Ω.cm2]
Uncoated SS	293	116.7	18.42	188.7	159.8	-	1.48	0.20	2039..681
	303	126.0	21.37	199.1	185.8	-	1.72	0.23	1952.858
	313	206.6	24.35	207.7	220.5	-	1.96	0.27	1906.821
	323	271.8	25.89	171.6	258.5	-	2.08	0.28	1729.746
Coated SS with PNA	293	68.7	4.09	112.6	100.0	77.796	0.033	0.004	5622.868
	303	72.3	6.47	134.8	144.4	69.724	0.052	0.007	4678.897
	313	132.4	7.44	137.1	141.4	69.446	0.059	0.008	4062.513
	323	210.6	8.21	153.6	166.1	68.250	0.066	0.009	4220.667
Coated SS with PNA modified with nano ZnO	293	48.9	3.29	93.3	108.0	82.139	0.265	0.036	6606.505
	303	89.4	4.48	97.7	94.1	79.036	0.361	0.049	4645.833
	313	117.7	6.60	125.4	120.3	72.895	0.531	0.072	4039.43
	323	163.5	7.39	129.5	136.4	71.456	0.595	0.080	3903.259
Coated SS with PNA modified with Graphene	293	10.5	0.472	185.4	255.5	97.438	0.038	0.005	98838.15
	303	58.6	0.529	335.5	254.2	97.525	0.043	0.006	118710
	313	87.1	0.606	148.8	256.5	97.511	0.049	0.007	67475.66
	323	125.3	0.813	215.8	319.0	96.859	0.066	0.009	68748.98

3.3. Kinetic and Thermo-dynamic Parameters of Activation

The thermo-dynamic parameters of activation include energy of activation Ea, activation entropy S* and activation enthalpy H* that have been computed with the use of Arrenhius eq. and its alternative formulation that has been referred to as the state of transition, and the energy of activation has been determined from plot which represents correlation between the Log icorr and reciprocal of the absolute degree of the temperature (1/T) [16].

$$\textbf{Log icorr} = \textbf{Log A} - \frac{\textbf{Ea}}{\textbf{2.303RT}} \quad (3)$$

icorr: represents the current density of corrosion, A: represents pre-exponential factor, Ea: represents energy of activation, R: represents gas constant (8.315JK-1mol-1), T: denotes absolute temperature (K). whereas the state of transition is represented by the equation below[17]:

$$\text{Log}\frac{\text{icorr}}{\text{T}} = \text{Log}\left[\frac{\text{R}}{\text{Nh}} + \frac{\Delta\text{S}*}{2.303\text{R}}\right] - \frac{\Delta\text{H}*}{2.303\text{RT}} \quad (4)$$

N denotes the Avogadro's number (6.0220 1023mol) and h is the Blanks constant (6.620 10-34JS). The activation entropy S* and enthalpy H* have been calculated using plot in Figure 3 that depicts correlation between log (icorr/T) and reciprocal of absolute temperature (1/T). Where the intercept is (Log (R/Nh) + S*/2.303 R) and slope is (- H*/2.303RT). The activation free energy is computed with the use of the equation below:

$$\Delta G^* = \Delta H^* - T\Delta S^* \quad (5)$$

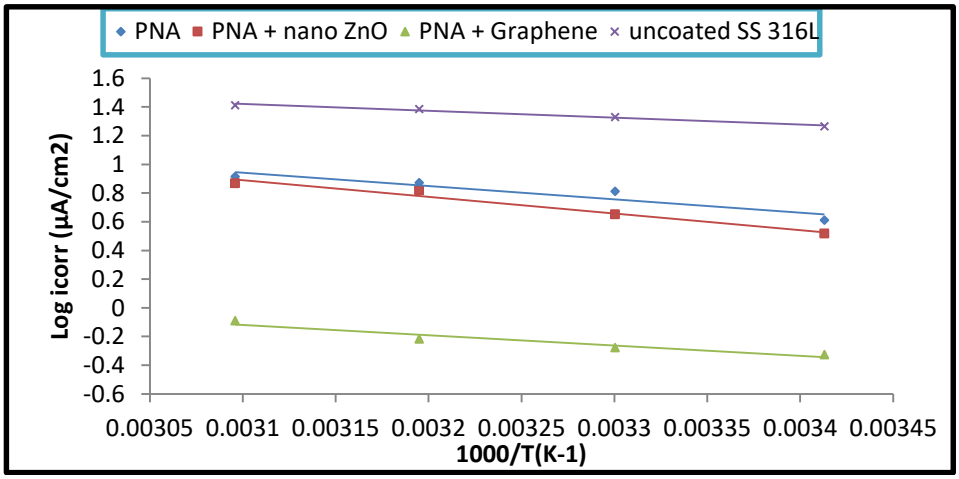


Figure 2.Plot of log icorr versus 1/T for uncoated and coated SS with polymer film absence and presence of nano-materials in 0.20M HCl

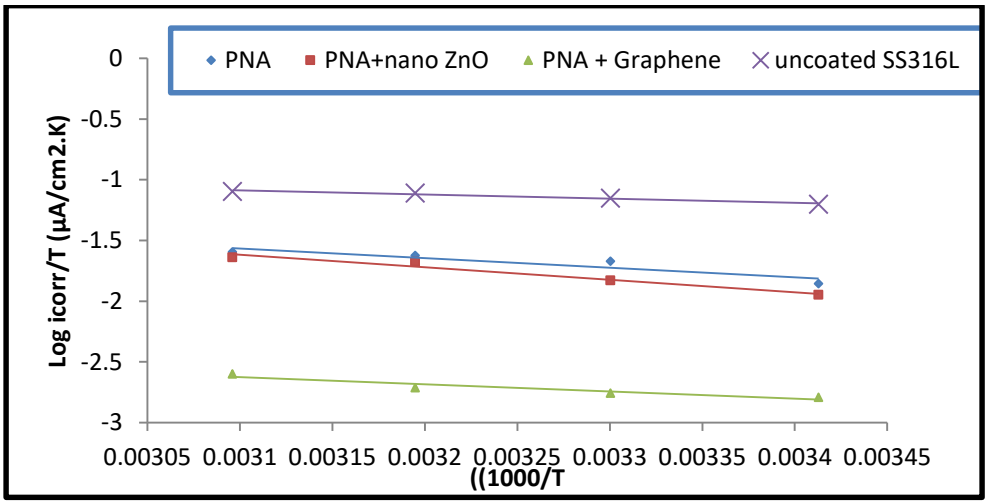


Figure 3. Plot of log icorr/T versus 1/T for coated SS with polymer film with presence and absence nano-material in 0.20M HCl

Table3. Transition state thermo-dynamic parameter at a variety of the temperature degrees for corrosion of coated as well as uncoated SS with polymer film in presence and absence of nano-materials in 0.20M HCl solution

Coating	R2	Ea kJ.mol^{-1}	A/Molecule. Cm^{-2}S^{-1}	R2	ΔH* KJ. K^{-1}mol^{-1}	-ΔS* J.K^{-1}mol^{-1}	ΔG KJ. K^{-1}mol^{-1}
Uncoated SS316L	0.9789	9.103	4.721*1026	0.958	6.546	198.112	64.593
							66.574
							68.555
							70.536
Coated SS with PNA	0.981	17.726	3.901*1023	0.855	15.169	199.737	73.692
							75.689
							77.687
							79.684
Coated SS with PNA+ nano ZnO	0.969	22.242	1.861*1028	0.961	19.685	186.745	74.401
							76.269
							78.136
							80.004
Coated SS with PNA+Graphene	0.932	13.808	7.878*1025	0.903	11.252	201.342	70.245
							72.259
							74.272
							76.285

Thermodynamic activation values (Ea & H*) for polymer layer on SS surface were higher than for SS uncoated by polymer film, indicating that the energy barrier was increased. The activation entropy values for SS coated with polymer film and SS uncoated with polymer film are negative, indicating that activated complex in rate-determining step has been an association instead of a dissociation step, and that disordering which happens in the case of going from the reactants to the activated complex has been decreased [18]. **Table 3** shows that the free energy activation has positive values and that the change with rising temperature is essentially negligible, which indicates that activated complex isn't stable and that a chance of its creation decreases with increasing the degree of the temperature.

3.4 Biological Activity

Results have demonstrated that PNA inhibited Staph.Aures and E.coli effectively at concentrations of 800 g/ ml, as shown in Table 4. The role of stable complex that has been generated between cleaved DNA and drug-bound topoisomerases is thought to be responsible for the polymer's capacity to kill bacteria. However, because of its capacity to disrupt the drug–DNA combination, topoisomerase inhibition may have serious ramifications for the cell. As a result of their high ratio of surface area to volume (S/V) and compact sizes, nanomaterials are regarded biocidal effective materials [19,20]. As a result, after modifying poly nicotine amide with nanomaterial, the inhibition zone values increased (Nano ZnO and Graphene).

Table 4. Anti-microbial activity of polymer in the presence and absence of the nano-materials.

Compounds	Stap.Aure (gram positive)(mm)	E.coli (gram negative) (mm)
PNA	15	14
PNA modified with Graphene	18	18
PNA modified with nano ZnO	18	17
Amoxicillin	30	30

4. Conclusions

With rising temperature, corrosion current density (icorr) and corrosion potential (Ecorr) increased. In absence and presence of a nanomaterial, corrosion current density (icorr) has been reduced after covering SS with a layer of polymer. In presence and absence of nano-material, corrosion potential (Ecorr) of SS that has been coated with polymer film shifts to higher position than that of uncoated SS, which implies that polymer film works as anodic protection. In presence and absence of nanomaterial, protection efficiency (PE percent) of the uncoated and coated SS reduced with rising temperature. The graphene-modified polymer film-coated SS had greater protection efficiency (PE percent) when compared to Nano ZnO-modified polymer film-coated SS.

References

1. Guimard, N; K Gomez ; N , Schmidt , C. E . Conducting polymers in biomedical engineering. *Progress in Polymer Science*, **2007,** *32(8),* 876-921.
2. Pringle, J; M., Ngamna, O., Chen, J., Wallace, G. G., Forsyth, M., MacFarlane, D. R; Conducting polymer nanoparticles synthesized in an ionic liquid by chemical polymerisation. *Synthetic metals*, **2006**, *156(14),* 979-983.
3. Hammond, P. T. Form ; function in multilayer assembly: new applications at the nanoscale. *Advanced Materials*, **2004**,*16(15):* 1271-1293.
4. Amaal, S. Sadiq ;Entesar, O. Al-Tamimi; Synthesis and Characterization of New Polymers Bearing Tetrazole and Triazole Moieties with Studying their Corrosion Protection of Stainless Steel Surface in Hydrochloric Acid.*Iraqi Journal of Science*, **2020**,*61, (10),*2467-2478.
5. Holder, E., Tessler, N.; Rogach, A. L . Hybrid nanocomposite materials with organic and inorganic components for opto-electronic devices**,** , *Journal of Materials Chemistry*, **2008,***18(10),* 1064-1078.
6. Joanny, J. Polyelectrolyte adsorption ; charge inversion. *The European Physical Journal B-Condensed Matter and Complex Systems*, **1999,** *9(1),* 117-122.
7. Kenawy E.R. Biologically active polymers. IV. Synthesis ; antimicrobial activity of polymers containing 8-hydroxyquinoline moiety, , *J. Appl. Polym. Sci.*, **2001**, *82(6),* 1364-1374.
8. Kenawy E.R, Worley S.D ;Broughton, R. The Chemistry and applications of antimicrobial polymers: A State-of-the-Art Review, polymers of high molecular weight have been used**,** *Biomacromolecules, ,* **2007,** *8(5),* 1359-1384**.**
9. -Khulood, A.S. Khalil, S.K ;Muna, I.K. Preparation of poly (N-imidazolylmaleamic acid) /nanomaterial coating films on stainless steel by electrochemicalpolymerization to study

the anticorrosion and antibacterial action.,*Journal of Pharmacy and Biological Sciences*, **2018**,*13*,30-36.

10. Silverstein R.M., Webster, F.X; Kiemle, D.J. Spectrometric Identification of Organic Compounds, **1963**, 7th ed., *John Wiley & Sons, Westford, US.*
11. Shirner, R., Fuson, R., Cartin, D; Mrril, T. The systematic identification of organic compound, **1980,** 8th ed**.,** *John Wiley & Sons*, Ne.
12. Tretherwey, K.R; Chamberlain, J. Corrosion for Science and Engineering, **1996**,2nd, ed., **,** *Addision Wesley Longman Ltd*.
13. Heitz, E; Schwenk, W. Theoretical basis for the determination of corrosion rates from polarization resistance: prepared for the european federation of corrosion working partyon Physiocochemical testing method of corrosion fundamentals and application, *British Corrosion J*., **1976**, *11(2),*74-77.
14. Jalal M. ; Yousif K. Bulletin of the Chemical Society of Japan **,1989,***62*, 1237.
15. Jsseling, F. The application of the polarization resistance method to the study of the corrosion behaviour of CuNi 10Fe in sea- water, *Corrosion Science*, **1974,***14(2),* 97-100.
16. Enders, D. ; Shilvock, J. P. Some recent applications of α- amino nitrile chemistry, *Chemical Society Reviews*, **2000**,*29(5),*359-373
17. Fontana, M ; Greene, N. Corrosion engineering: New York: McGraw- Hill. **1986.**
18. Gomma, M; Wahdan, M. Corrosion behavior of Zn in alchol- water solvents. *Mater. Chem. Phys*, **1995**,*39(3),*209-213.
19. Roselli, M., Finamore, A., Garaguso, I., Britti, M.S; Mengheri, E. Zinc oxide protects cultured enterocytes from the damage induced by E.coli, *J.Nutr*. **2003**,,*133(12),*4077-4082.
20. Khulood, A. Saleh; Mayasa, I. Ali**.** Electro polymerization for (N-Terminal tetrahydrophthalamic acid) for Anti-corrosion and Biological Activity Applications, *Iraqi Journal of Science,* **2020**, *61(1).*