Corrosion Protection and Biological Activity Studies for Electrochemical Polymerized Poly (N-benzothiozolyl tetrahydrophthalamic acid) on Stainless Steel Alloy

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Abstract

The present work reports the electrochemical synthesis of poly (N-benzothiozolyl tetrahydrophthalamic acid) on stainless steel 316 (S.S) which acts as working electrode by using electrochemical polymerization technique. The formed polymer film was characterized by Fourier Transform Infrared Spectroscopy (FT-IR) and Atomic Force Microscope (AFM). Corrosion protection tests for coated and uncoated S.S with polymer film were studied in 0.2 M of hydrochloric acid (HCl) solution by followed Tafel and potentiodynamic procedures. Kinetic and thermodynamic of activation parameters (Ea, A, ΔH*, ΔS* and ΔG*) were calculated. Also, investigations the effect of the synthesized polymer on some strain of bacteria a gram positive bacterium which is Staphylococcus aureus (*Staph.Aure*) and negative bacteria which is Escherichia coli (*E.Coli*). In addition the polymer film was modified with nanomaterials which are (ZnO_n (nano) and Graphene).

Keywords: *Electrochemical polymerization, Conducting polymer, Stainless steel, Anticorrosion, Antimicrobial activity*

Introduction

Electrochemical polymerization process involves oxidation of the monomer to produce radical, then these radical cations were reacted with each other, or with another monomer, to produce a radical dimer, which transferred to a trimer and longer chain length [1, 2]. Oxidation of monomer occurred on the working electrode (WE) which made from different materials such as stainless steel and indium tin oxide coated glass [3]. The electrochemical polymerization process involved specific interaction between the working electrode and the monomer that led to good coating adhesion [4].

Conductive polymers have a wide field in many applications, they commonly used in a chemical transistor, rechargeable batteries, production of indicators and ion selective electrodes, and biochemical analysis [5]. The corrosion protection is one of the applications of conducting polymer film [6]. Wessling indicated that the conducting polymer coating film possibly possessed self-healing properties in which passive oxide layer between the polymer and metal can spontaneously reformed by oxidation ability of conducting polymers [7]. Also, the polymer film has important role in antimicrobial activity, the antimicrobial polymers act as class of biocides that become important for existing biocides and sometimes in antibiotics, the polymeric materials have some advantageous which are: chemically stable, not volatile and not permeate into skin. Therefore, the polymers have the antimicrobial activity will be important step in the healthier living and though hundreds of thousands of polymeric compound were prepared, only few of them are of visible antimicrobial activities

Experimental

The electrochemical polymerization of monomer on stainless steel (S.S) surface (working electrode) carried out by using DC power supply (galvanostatic technique). The solution involved for electrochemical polymerization process 0.1 g of monomer in

100 ml H_2O with three drops of concentration (95% H_2SO_4).

For corrosion studies, S.S used as a working electrode (WE).It is grading by (2000 mesh) of carbide silicon and washed by distilled water and acetone, saturated calomel electrode (SCE) used as a reference electrode, platinum used as auxiliary electrode. All experiments studied in 0.2 M of HCl solution and at a temperature range (293-323) K. Also, nanomaterials (0.04g ZnO_n and 0.004g G) added into the solution of a monomer for improvement the coated-layer against bacteria and corrosion.

Results and Discussion

Mechanism of Polymerization

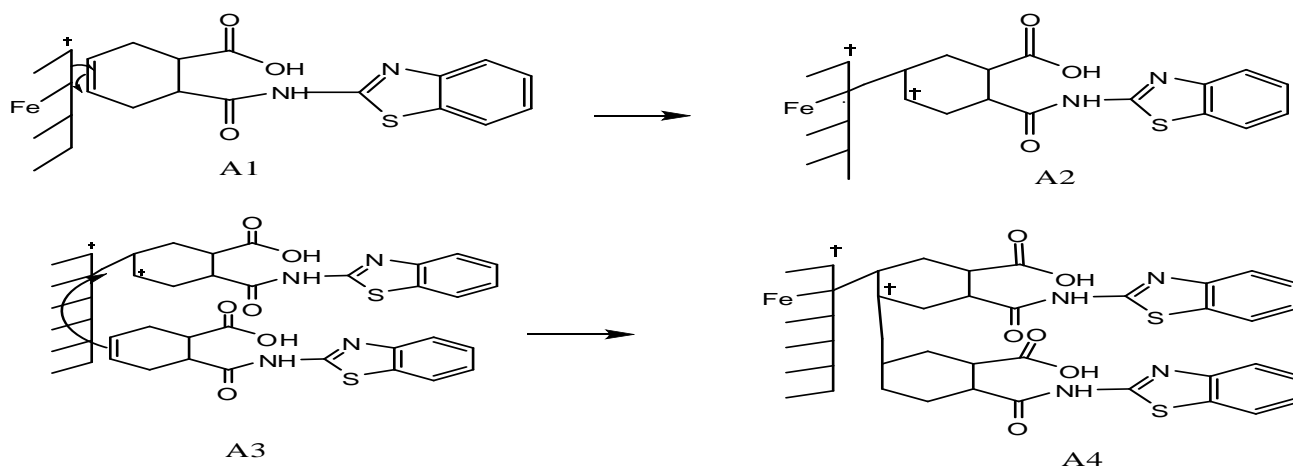Cationic Mechanism [8, 9] and radical mechanism [10, 13] explained electrochemical polymerization and growth of Polymer film. The mechanism is depicted in Scheme (1-A).

A1- anodic potential applied to monomer solution to transfer one electron from monomer to the working electrode (WE).

A2- the transfers of an electron in (A1) refer to formation radical cation adsorbed on the surface of the electrode.

A3- the radical cation desorbed and reacted in solution to increase the molecular weight of species.

A4- monomer added by a cationic mechanism at the charged end of desorbed oxidized monomer.

Scheme 1: Cationic mechanism for growth polymer film

The radical mechanism (Scheme1-B): The radical mechanism proceed by hemolytic scission of double bond hemolytic rupture double bond highly improbable considered initial polarization of bond which improved under field produced by electric double [14].
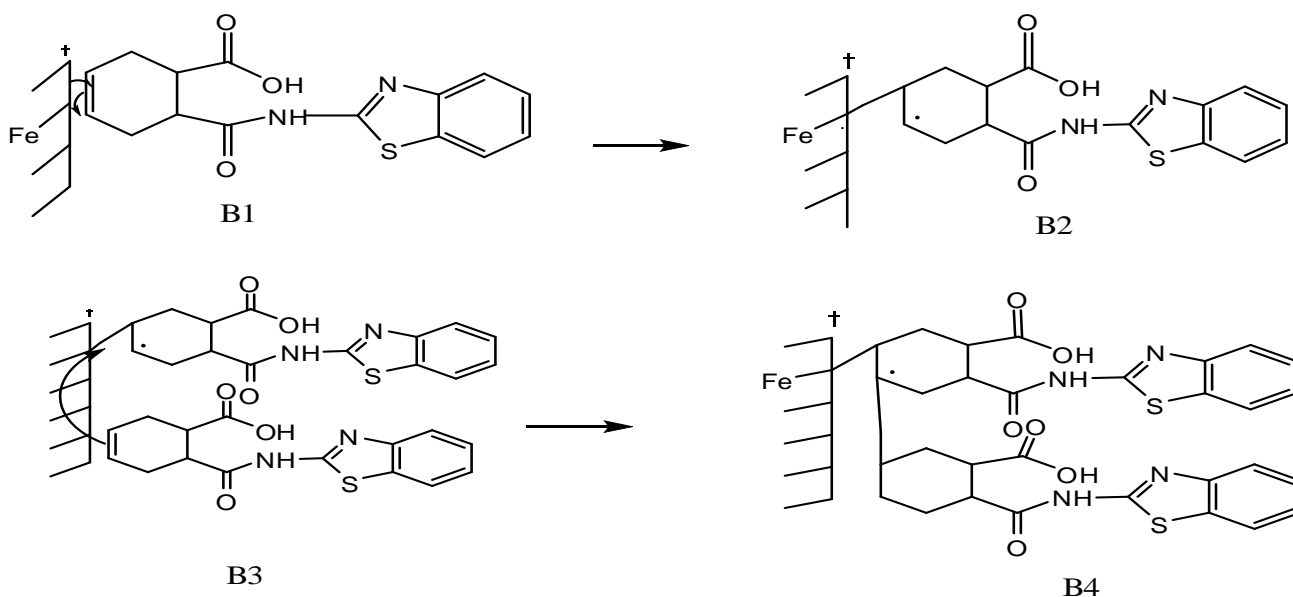
Scheme 2: Free radical (B) mechanism for growth polymer film

FT-IR of Polymer

FTIR spectrum of polymer coating film from monomer show in Figure 1-a. In this spectrum the characteristic bands of polymer is obtained in Figure.1-b. Aliphatic double bond (=CH) at 3026.10 cm-1 disappeared and confirm the polymer formation.
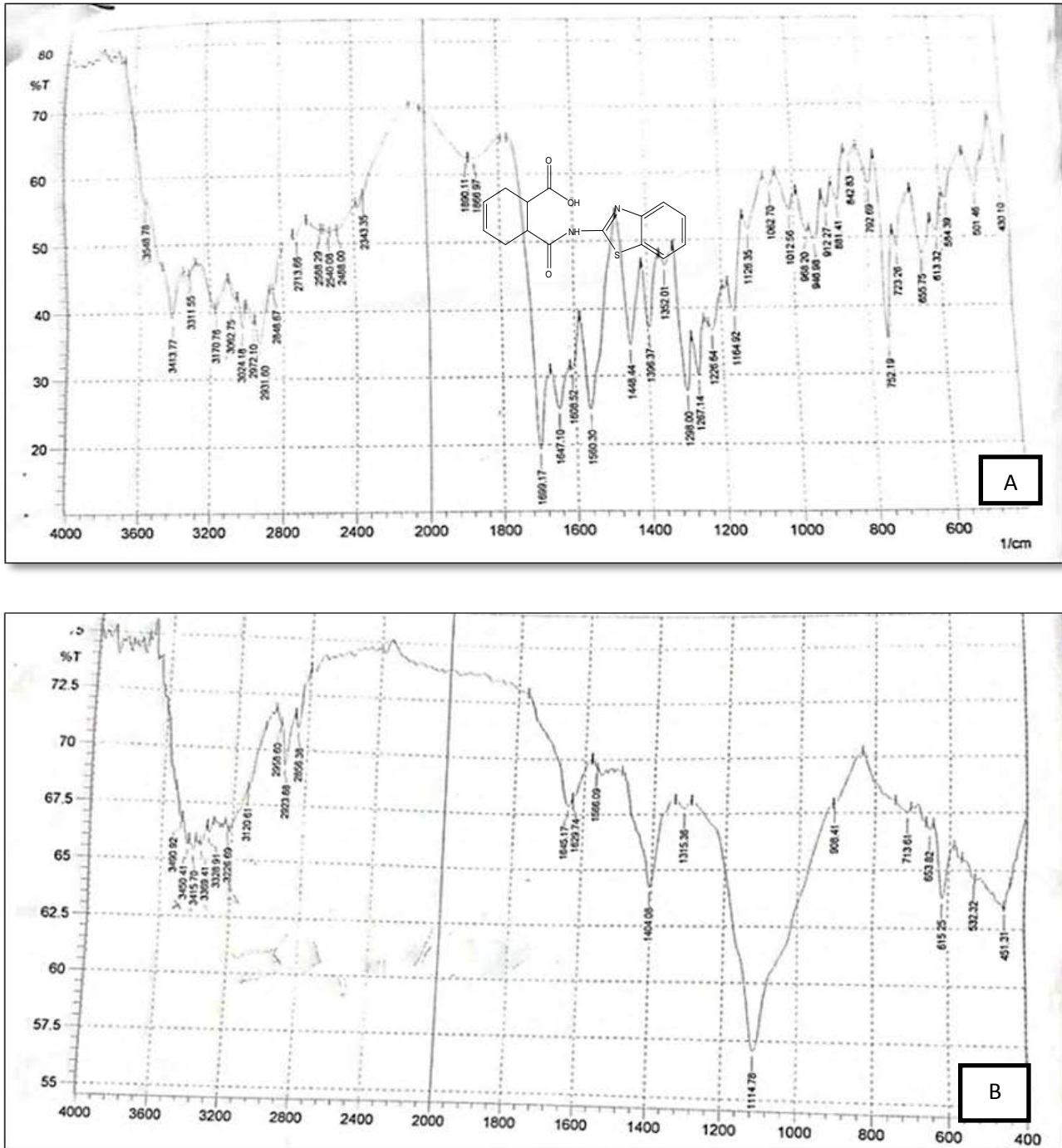

Figure 1: FT-IR spectrum for a) monomer b) polymer

According to Figure 1-a, the band appeared at 1699.17 cm^{-1} for C=O of carboxylic acid, the band appeared at 1647.10 cm^{-1} according to C=O of amide group, the band of OH of carboxylic acid appeared at 2530.43cm^{-1}, the band of NH of amide appeared at 3413.77 cm^{-1}, the band of aromatic C=C appeared at 1560.30 cm^{-1}, the band of C=N appeared at 1560 cm^{-1} the band of C-N appeared at 1396.37 cm^{-1}[15, 17].

AFM of Polymer Film Surface

AFM was employed to determine more information due to it was considered one of the surface investigation instruments for nanoscale structure. Figure 2 was showed the two and three dimensions for prepared polymers in absence and presence nanomaterials. In AFM analysis, average roughness (Ra) and Root Mean Square

Roughness (RMS) are the most widely used parameters to characterize the surface roughness for prepared polymer films, the obtained RMS and Ra values are listed in Table1 and the results were indicated there was a decrease in the surface roughness after modification of the polymers with nanomaterials due to the decrease in the grain size, also indicated the modified of surface of polymer film with nanomaterials became more smooth than non-modified surface with nanomaterials [18].
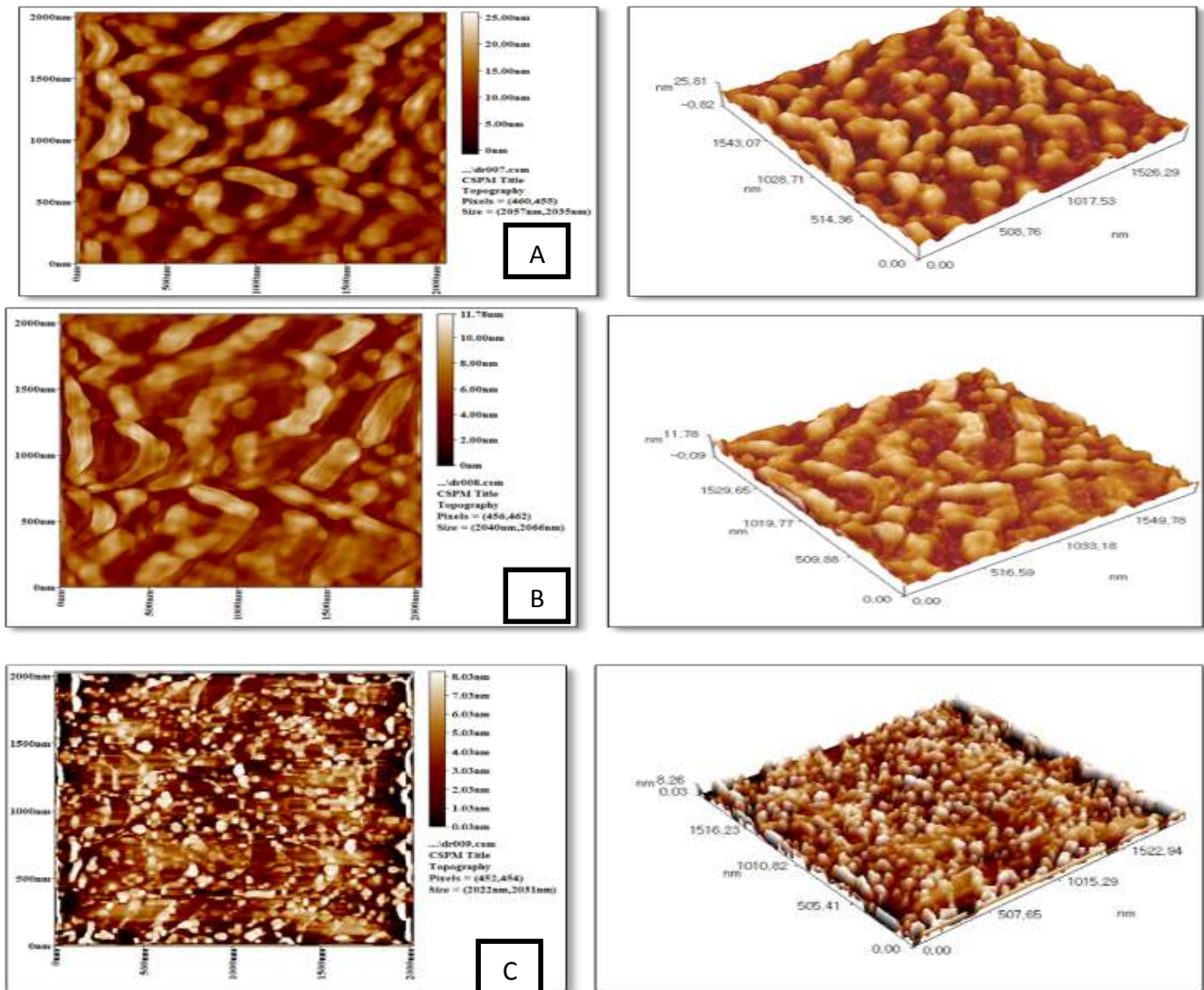

Figure 2: AFM images 2D image (left) and 3D image (right) for a) S.S coated with polymer film only, b) S.S coated with polymer film modified with ZnOn, c) S.S coated with polymer film modified with graphene

Table 1: Average roughness (Ra), root mean square roughness (RMS) and mean grain size for coated S.S by polymer film modified with ZnOn and graphene.

Coating	Ra (nm)	RMA (nm)	Mean grain size (nm)
a	4.170	4.890	74.12
b	1.470	1.730	61.51
c	2.060	2.380	59.43

Potentiostate Polarization Measurement

The effect of polymeric layer on cathodic and anodic polarization curve of S.S in 0.2M of HCl solution and temperature range (293-303)K in absence and presence nanomaterials that shown in Figure 3. The corrosion current density determined by extrapolation Tafel lines.

The effect of polymeric layer in absence and presence nanomaterials which shown in Table2. The corrosion parameters involved corrosion potential (Ecorr), corrosion current density (icorr), cathodic Tafel slope (bc), anodic Tafel slope (ba), were found. Protection efficiency (%PE) was calculated by the following equation [19]:

$$\%PE = \frac{(icorr)_o - (icorr)}{(icorr)_o} * 100 \qquad (1)$$

Where $(i_{corr})_o$ the corrosion current density for uncoated S.S, (i_{corr}) the corrosion current density for coated S.S. The corrosion potential (E_{corr}) shifted into more positive values (noble direction) and i_{corr} decreased after addition nanomaterials [20]. The polarization resistance (Rp) was determined by Stern-Gery equation [21]:

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

The polarization resistance (Rp) measurements have similar requirements to the measurements of full polarization curves and it is useful as a method to identify corrosion upsets and initiate remedial action [22]. The values of Rp are listed in Table2.
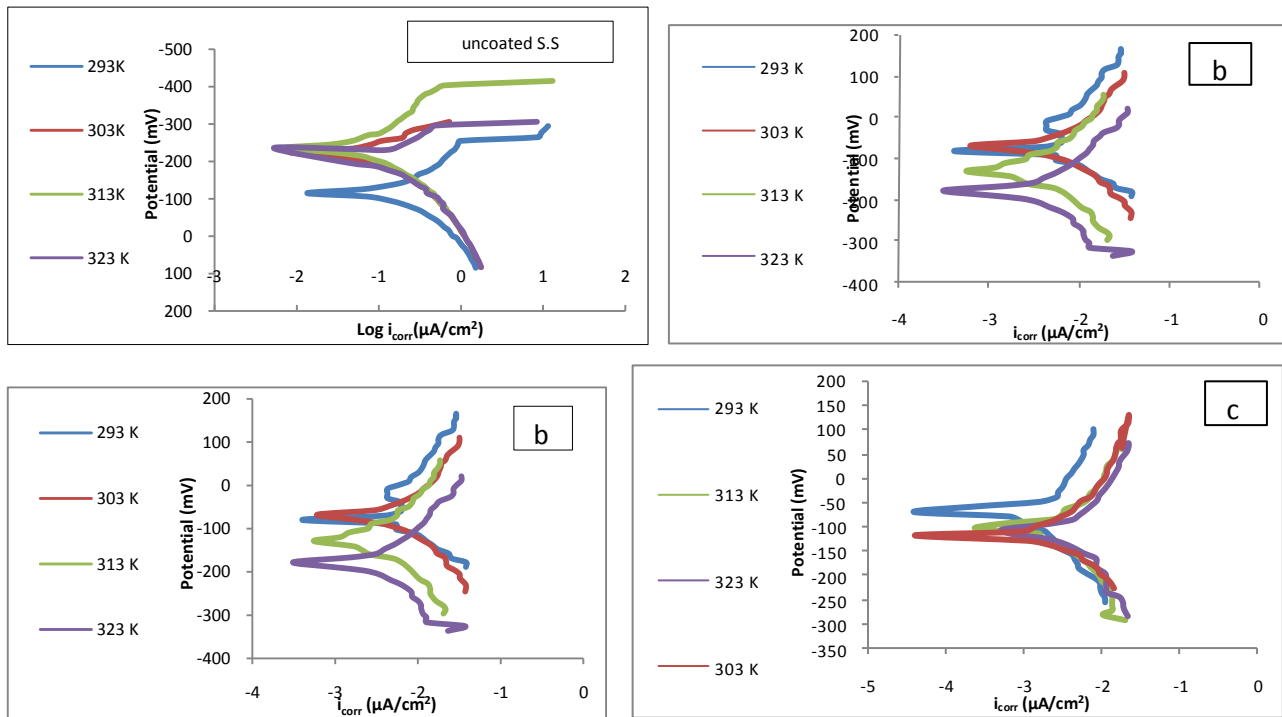

Figure 3: Tafel plot for uncoated S.S, a) coated S.S with polymer film, b) coated S.S with polymer film modified with ZnOn, c) coated S.S with polymer film modified with graphene

Table 2: Corrosion parameters for coated and uncoated S.S in 0.2M HCl solution.

Coating	T (K)	- E_{corr} (mV)	icorr ($\mu A/cm_2$)	-bc (mV/Dec)	ba (mV/Dec)	Rp (Ω/cm^2)	%PE
Uncoated S.S	293	113.5	43.27	48.5	47.1	239.786	
	303	226	53.20	79.4	110.2	376.668	
	313	235.4	56.77	149.0	120.7	510.035	
	323	235.9	56.90	78.6	78.9	300.286	
a	293	62.2	4.00	179.8	260.4	11545.87	90.756
	303	79.2	5.32	217.5	159.1	7499.694	90.000
	313	94.3	6.13	308.2	210.6	8862.099	89.200
	323	110.3	6.41	198.6	148.7	5760.146	88.735
b	293	74.1	2.87	88.8	96.4	7002.277	93.367
	303	75.0	3.60	196.0	223.9	12622.17	93.233
	313	152.2	4.04	288.9	209.4	13065.44	92.883
	323	174.1	4.87	292.2	239.9	11761.44	91.441
c	293	79.0	1.20	146.4	134.1	25325.72	97.227
	303	110.9	1.77	104.6	119.9	13704.63	96.673
	313	114.5	2.25	131.8	167.5	14234.66	96.037
	323	114.5	3.27	146.6	164.1	10281.57	94.253

Kinetic and Thermodynamic Activation Parameters

Thermodynamic activation parameters involved activation energy Ea, enthalpy of activation ΔH* and entropy of activation ΔS*calculated by using Arrenhius equation and its alternative formulation called transition state, activation energy determined from the plot that represent the relationship between Log C.R and reciprocal of absolute temperature (1/T) [23] as shown in Figure 4.

$$\text{Log C. R} = \text{Log A} - \frac{Ea}{2.303RT} \qquad (3)$$

Where C.R: corrosion rate, A: pre-exponential factor, Ea: Activation energy, R: Gas constant (8.315 $JK^{-1}mol^{-1}$), T: Absolute temperature (K). While transition state expressed in the following equation [24]:

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

Where N: Avagadrous number (6.022×10^{23}mol), h: Blanks constant (6.62×10^{-34} JS). The entropy of activation $\Delta S*$ and enthalpy of activation $\Delta H*$ were determined from the plot that represent the relationship between log (C.R/T) and reciprocal of absolute temperature (1/T) as shown in Figure 5. Where slope represent (- $\Delta H*$/2.303RT) and the intercept represent (Log (R/Nh) + $\Delta S*$/2.303R). The free energy of activation determined from the following equation:

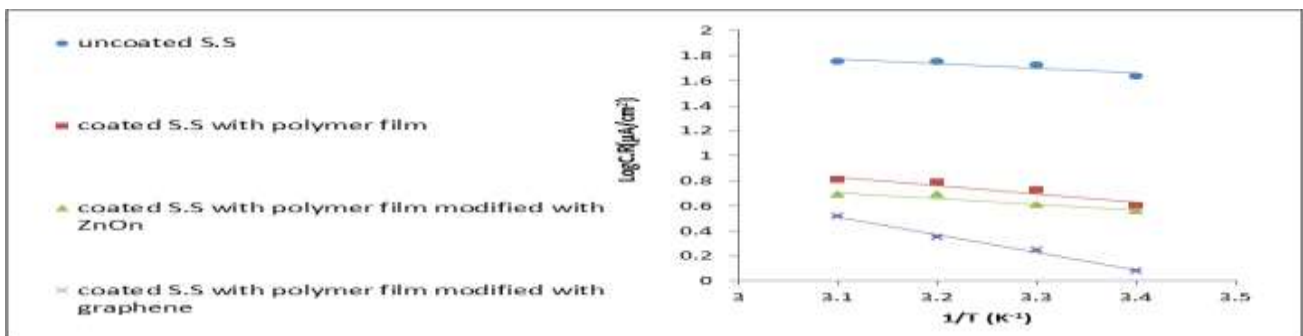$$\Delta G* = \Delta H* -T\Delta S* \qquad (5)$$

Figure 4: Plot of log C.R vs. 1/T for uncoated and coated S.S with polymer film absence and presence nanomaterials in 0.2M HCl
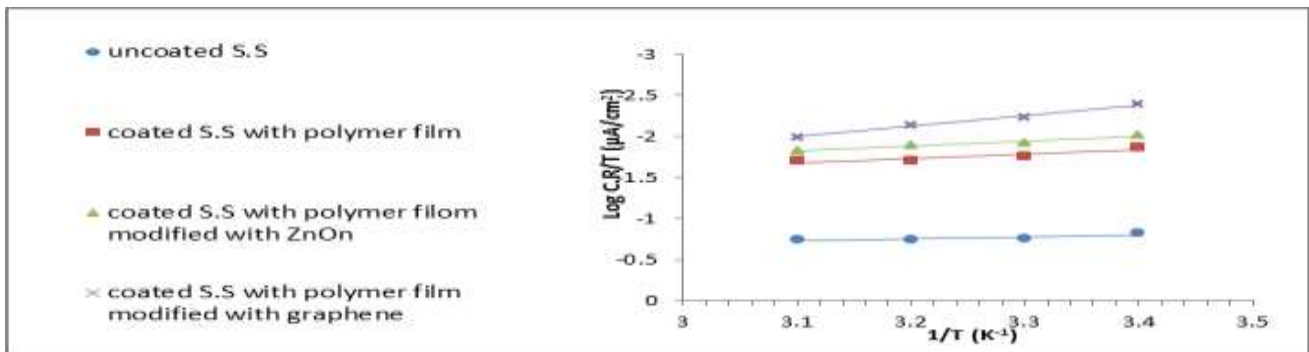

Figure 5: Plot of log C.R/T vs. 1/T for uncoated and coated S.S with polymer film absence and presence nanomaterials in 0.2M HCl

Table 3: Transition state thermodynamic parameter at different temperatures for the corrosion of uncoated and coated S.S with polymer film in absence and presence nanomaterials in 0.2M HCl solution.

Coating	T(K)	ΔG* (kJ/mol)	ΔH* (kJ/mol)	-ΔS* (J/mol.K)	Ea (kJ/mol)	A (Molecule. Cm⁻² .S⁻¹)
uncoated S.S	293	68.252	4.711	216.864	7.373	$5.605*10^{26}$
	303	70.421				
	313	72.589				
	323	74.758				
a	293	72.092	10.283	217.102	12.351	$3.968*10^{26}$
	303	74.027				
	313	75.962				
	323	77.897				
b	293	73.036	11.700	215.273	14.171	$5.776*10^{26}$
	303	74.839				
	313	76.642				
	323	78.445	24.301	179.723	27.039	$4.646*10^{28}$
c	293	73.664				
	303	75.501				
	313	77.338				
	323	79.175				

Commonly the results shown the thermodynamic activation parameters (Ea and ΔH*) for S.S coated by polymer film are higher than S.S uncoated by polymer film, this indicated to increase the energy barrier.

The values of the entropy of activation for S.S coated by polymer film and S.S uncoated by polymer film are negative , this refers to that the activated complex in the rate determining step was association rather than dissociation step, and refers to decrease the disordering which occurs on going from reactants to activated complex [25].The free energy activation is had a positive values as

shown in Table 3, and in addition showed almost small change with increasing temperature, this indicating that the activated complex not stable and the probability of its formation decreased with increasing of temperature.

Antimicrobial Activity

The inhibition zones examined for prepared polymers in absence and presence nanomaterials (ZnO_n and Graphene) on two types of bacteria (*S. aureus and E. coli*) at concentration (800μg/ml) and the solvent used is Di - Methyl Sulfoxide (DMSO). The results listed in Table 4.

Table 4: The inhibition zones in (mm) for polymers films

System	Inhibition zone (mm)	
	Gram positive (*S. aureus*)	Gram negative (*E. coli*)
Polymer	13	9
Polymer + ZnO_n	16	17
Polymer + graphene	22	23

The results showed good inhibitory ability for polymer against both *S. aureus and E. coli.* The ability of polymers to kill the bacteria is the function of stable interaction complex which formed between cleaved DNA and drug-bound topoisomerases.

The inhibition of topoisomerase function by polymers and the formed stable complexes with DNA have negative substantial consequence for cell according to its ability to deal with drug-DNA damage [26]. Nanomaterials have increasingly important in the pharmaceutical and biomedical applications as antimicrobial strategy because of the appearance of antibiotic resistant strains and reemergence infection diseases [27], and nanomaterials considered as biocidal effectiveness suggested to be

owing to combination of their high surface to volume ratio and small size that enable to intimate the interactions with microbial membranes [28].

Conclusions

Electrochemical measurements data show that the polymer film was acted as good anticorrosion coating in 0.2M of HCl solution for corrosion of S.S. The protection efficiency (%PE) decreased with increasing the temperature. Also, %PE increased with adding nanomaterials into monomer solution especially with graphene. Beside the resistance to corrosion, polymer film gives antimicrobial activity against *S. aureus and E. coli* bacteria and shows that modified polymer film with nanomaterials has strong activity against *S. aureus* and *E. coli.*

References

1. Guimard NK, Gomez N, Schmidt CE (2007) Conducting polymers in biomedical engineering. Progress in Polymer Science, 32(8): 876-921.

2. Pringle JM, Ngamna O, Chen J, Wallace GG, Forsyth M, MacFarlane (2006) DR Conducting polymer nanoparticles synthesized in an ionic liquid by chemical polymerisation. Synthetic metals, 156(14): 979-983.

3. Malinauskas A (2001) Chemical deposition of conducting polymers. Polymer, 42(9): 3957-3972.

4. Schuhmann W, Kranz C, Wohlschläger H, Strohmeier J (1997) Pulse technique for the

electrochemical deposition of polymer films on electrode surfaces. Biosensors and Bioelectronics, 12(12): 1157-1167

5. Naoki T, Susumu H (1995) Direct synthesis of conducting polymers from simple monomers. Prog. Polym. Sci., 20: 155-183.

6. DeBerry DW (1985) Modification of the electrochemical and corrosion behavior of stainless steels with an electroactive coating, Journal of the Electrochemical Society, 132(5): 1022-1026.

7. Wessling B (1994) Passivation of metals by coating with polyaniline:corrosion potential

shift and morphological changes, Advanced Material, 6(3): 226-228.

8. Younang E, Léonard-Stibbe E, Viel P, Defranceschi M, Lécayon G, Delhalle J (1992) Prospective theoretical and experimental study towards electrochemically grafted poly (N-vinyl-2-pyrrolidone) films on metallic surface, Molec. Engin., 1(4): 317-332.

9. Léonard-Stibbe E, Lécayon G, Deniau G, Viel P, Defranceschi M, Legeay G, Delhalle J (1994) The cationic polymerization of N-vinyl-2-pyrrolidone initiated electrochemically by anodic polarization on a Pt surfac, J. Polym. Sci.: Part A, Polym. Chem., 32(8): 1551-1555.

10. Jerome R, Mertens M (1995) The Electrochemical Polymerization of Acrylonitrile and N-Vinylpyrrolidone- New Insight into the Mechanism, L. Adv. Mater., 7(9): 807-809.

11. Beamson G, Briggs D (1992) High Resolution XPS of Organic Polymers, John Wiley & Sons: Chichester, 192.

12. Ivanov DV (1996) Chemical-Sensitivity of the Thickness-Shear-Mode Quartz-Resonator Nanobalance, A. J. Electrochem. Soc., 143(9): 2835-2841.

13. Czerwinski WK (1991) Solvent effects on free-radical polymerization, 2. IR and NMR spectroscopic analysis of monomer mixtures of methyl methacrylate and N-vinyl-2-pyrrolidone in bulk and in model solvents, Chem., 192(6): 1297-1305.

14. Raynaud M, Reynaud C, Ellinger Y, Hennico G, Delhalle J (1990) High Electric-Field Effects on the Acrylonitrile Molecule - an Abinitio Study, J. Chem. Phys., 142(2): 191-201.

15. Silverstein RM, Webster FX, Kiemle DJ (1963) Spectrometric Identification of Organic Compounds, 7th ed., John Wiley & Sons, Westford, US.

16. Shirner R, Fuson R, Cartin D, Mrril T (1980) The systematic identification of organic compound, 8th ed., John Wiley & Sons, Ne.

17. Koj N (1962) Infrared absorption spectroscopy, 1st ed., Nankodo Cmpany Limited, Tokyo.

18. Khanam R, Taparia D, Mondal B, Mohanta D (2016) Black titania: effect of hydrogenation on structural and thermal stability of nanotitania. Applied Physics A, 122(2): 92.

19. Tretherwey KR, Chamberlain J (1996) Corrosion for Science and Engineering, 2nd, ed., Addision Wesley Longman Ltd.

20. Heitz E, Schwenk W (1976) 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., 11(2): 74-77.

21. Jalal M, Yousif K (1989) Bulletin of the Chemical Society of Japan, 62: 1237.

22. Jsseling F (1974) The application of the polarization resistance method to the study of the corrosion behaviour of CuNi 10Fe in sea-water, Corrosion Science, 14(2): 97-100.

23. Enders D, Shilvock JP (2000) Some recent applications of α- amino nitrile chemistry, Chemical Society Reviews, 29(5): 359-373.

24. Fontana M, Greene N (1986) Corrosion engineering: New York: McGraw- Hill.

25. Gomma M, Wahdan M (1995) Corrosion behavior of Zn in alchol- water solvents. Mater. Chem. Phys., 39(3): 209-213.

26. Kohanski MA, Dwyer DJ, Collins JJ (2010) How Antibiotics Kill Bacteria: from Targets to Networks, *Nature Reviews: Microbiology*, 8: 423-435.

27. Abd El-Rehim SS, Hassan HH, Amin MA (2001) Corrosion inhibition of aluminium by 1,1(lauryl amido) propyl ammonium chloride in HCl solution, Mater. Chem. Phys., 70(1): 64-72.

28. Osama MM, Omar AM (1997) Corrosion inhibition of benzyl triethanol chloride and its ethoxylate on steel in sulphuric acid solution, Mater. Chem. Phys., 50(3): 271-274.

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