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Poly (N, N-dimethyl aniline) Coating for Stainless Steel, Synthesis, Characterization and Corrosion Protection in Sea Water 3.5% NaCl Solution

Naema A. Alshanwi*and Sahar A. Alsammaraie
Department of Chemistry, College of Science, Baghdad University, Baghdad, Iraq.

Abstract

This research involves the synthesis of conductive polymer includes: poly (N, N-dimethyl aniline) on metal surface which is stainless steel 316 by using electrochemical polymerization technique. Parameters of this research are voltage rang, scan rate, number of cycles. The tests for corrosion protection of the polymer coated and uncoated stainless steel substrate was investigated in artificial sea water of 3.5% NaCl solution by tafel and potentiodynamic procedures. Fourier Transform Infrared Spectroscopy (FTIR), UV-Visible absorption spectroscopy, Scanning Electron Microscope (SEM) and Atomic Force Microscope (AFM) were used to diagnose and describe the structure and morphology of the coating. Parameters of corrosion are: corrosion current I_{corr}, corrosion potential E_{corr}, protection efficiency (PE %), polarization resistance (R_p) and the effect of different temperatures range (293 to 323) K in the inhibition efficiency of coated and uncoated stainless steel surface. Change in the free, enthalpy and entropy have been determined. Apparent energies of activation have been calculated for the corrosion process from the corrosion rates and Arrhenius plots. This results of corrosion test showed that Poly (N, N-dimethyl aniline) ensure chemically stable, environmentally viable and have good corrosion protection of stainless steel in artificial sea water of 3.5% NaCl solution**.**

Keywords: Corrosion protection, Coating, Synthesis, Stainless steel, Poly (N, N-dimethyl aniline)

تركيب وتوصيف بولي (N,N-ثنائي مثيل انيلين) في طلاء وحماية الفولاذ المقاوم للصدأ من التآكل في ماء البحر(3.5% محلول كلوريد الصوديوم)

نعيمة احمد الشنوي* وسهر احمد السامرائي
قسم الكيمياء، كلية العلوم, جامعة بغداد، بغداد، العراق.

الخلاصة

يتضمن البحث تخليق بوليمر موصل يشمل بولي (N,N- ثنائي مثيل انيلين) على سطح الفولاذ المقاوم للصدأ باستخدام تقنية البلمرة الكهروكيميائية. من معالم البحث: مدى الجهد ومعدل المسح وعدد الدورات. اختبارات الحماية من التآكل للفولاذ المقاوم للصدأ غير المطلي والمطلي بالبوليمر في ماء البحر (3.5% محلول كلوريد الصوديوم) باستخدام طرق تافل والجهد الحركي . تم تشخيص ووصف شكل وهيئة الطلاء باستخدام الاشعة تحت الحمراء،الامتصاص الطيفي للاشعة فوق البنفسجية المرئية ، المسح الالكتروني المجهري والقوى الذرية المجهرية . معالم التآكل هي : تيار التآكل ، جهد التآكل ، كفاءة الحماية ، مقاومة

*Email: naema.hikmat@hotmail

الاستقطاب وتأثير درجات الحرارة المتراوحة بين (293-323) كلفن في كفاءة تثبيط ألفولاذ المقاوم للصدأ المطلي وغير المطلي. وتم تعيين القيم الثرموداينمكية وحسابها من سرع التآكل ومنحنيات ارينيوس . نتائج التآكل اثبتت انه بولي (N,N-ثنائي مثيل انيلين) ثابت كيميائيا وله حماية جيدة من التآكل للفولاذ المقاوم للصدأ في ماء البحر (3.5% محلول كلوريد الصوديوم).

1. Introduction

Corrosion of metal has been a persisting problem in society and hence it is an important area of research. Corrosion can be defined as a chemical or electrochemical reaction between a material, usually a metal, and its environment that produces a deterioration of the material and its properties [1]. The study of corrosion processes and their inhibition by organic inhibitors is a very active field of research [2]. The two models have joined into the modern electrochemical theory of corrosion, which describes metallic corrosion as a coupled electrochemical reaction consisting of anodic metal oxidation and cathodic oxidant reduction. The electro chemical theory is applicable not only to wet corrosion of metals at normal temperature but also to dry oxidation of metals at high temperature [3].Usually; the corrosion process consists of a set of reduction/oxidation (redox) reactions which are electrochemical in nature. Thus, the metal is oxidized to corrosion products at anodic sites and some species are reduced at cathodic sites Corrosion of metallic materials can be divided in two main groups:

a. **Wet corrosion**: where the corrosive environment is a liquid such as water with dissolved species. The liquid is an electrolyte and the process is typically electrochemical; also corrosion may occur in other fluids such as fused salts and molten metal's.

b. **Dry corrosion**: where the corrosive environment is a dry gas. Dry corrosion is also frequently called chemical corrosion and the best-known example is a high temperature corrosion. The metal corrosion involves the transfer of electrical charge in aqueous solution at the metal electrolyte interface. Corrosion protection is often afforded by isolating metals from the corrosive environment using chemical compound as a corrosion inhibitor, inhibitor is one of the most practical methods for protection against corrosion usually organic compounds are widely used for preventing corrosion environment. In most recent times Practical applications of conductive polymers have received considerable interest as corrosion protective coating on oxidizable metals [4]. This because these polymers are chemically stable, environmentally viable, and have good corrosion resistance.Since then, several research groups[5] have systematically investigated the electrochemical synthesis of various conducting polymer on oxidizable metals for corrosion protection purposes .In our present work, we investigated the corrosion protection of Stainless steel coating with poly (N, N-dimethylaniline) in sea water. The term "conductive polymer" was first used in 1977, after the synthesis of polyacetylene and the discovery that its conductivity is of metallic structure [6].Conducting polymer coatings have been controversially discussed as being useful for corrosion protection of oxidizable metals during last decade years. The electrochemical polymerization is a simple, relatively in expensive and most convenient route for synthesizing novel conducting polymers on metallic surfaces [7]. Mengoly et al. [8] was the first to examine the protective behavior of polyaniline on stainless steel and then in 1985, DeBerry [9] showed that the electrochemically synthesized polyaniline act as corrosion protective layer on stainless steel in 1.0M H_2SO_4

2. Experimental

2.1 Material and Sample Preparations:

Electrochemical polymerization studies (such as investigation of electrochemical behaviour, stability tests, and corrosion tests) were carried out in a conventional three electrode system using stainless steel as working electrode, platinum wire as counter electrode and Ag/AgCl (3 mol/dm KCl) as reference electrode. The working electrode was embedded in a Teflon holder. Prior to each electrochemical polymerization, this stainless steel specimen with 2.5 cm in diameter and thickness of 1mm was subjected to surface cleaning and coating with Poly (N, N-dimethyl aniline) nanopartical by electrochemical polymerization. The stainless steel was polished by silicon carbide grit (SiC) abrasive paper from 400,600,800,1200 and 2000 and degreased with acetone and washed with distilled water and finally with ethanol. Therefore, the stainless steel was put inside desiccator for protecting and preventing them from oxidation.

2.2 Poly (N, N-dimethyl aniline) coated Stainless steel electrode

The Poly (N, N-dimethyl aniline) film was synthesized by electrochemical polymerization of N,N- dimethyl aniline on stainless steel substrate from (0.3M monomer in 0.3M oxalic acid) .The potential range was varied between (-200 to 1800 mV) and scan rate 40 mV/S with eight repetition at room temperature. Some conditions affecting electrochemical polymerization such as applied potential, electrolyte composition, polarization time, and N, N-dimethyl aniline were to exhibit influence on the properties of the polymer coating.

2.3 The Electrolyte Media:

Artificial sea water of 3.5 wt% NaCl solution was prepared by dissolving 35g of NaCl in 1000 ml of distilled water.

2.4 Characterization of Poly (N, N-dimethyl aniline) film

The confirmation of Poly (N, N-dimethyl aniline) was examined by Fourier Transform infrared (FT-IR) spectroscopy. The various electrons transitions present in the Poly (N, N-dimethyl aniline) was determined by UV-Vis spectroscopy. Scanning Electron Microscope (SEM) and Atomic Force Microscope (AFM) were used to diagnose and describe the morphology of the coating.

2.5 Corrosion measurements

Corrosion studies of uncoated and stainless steel coated with Poly (N, N-dimethyl aniline) were carried out in 3.5 wt% NaCl solution by potentiostatic polarization curves. The anodic and cathodic polarization curves were recorded by changing the electrode potential between −200 mV and +200 mV from open circuit potential with a constant sweep rate of 3 mV s^{-1}.

3. Results and discussion

3.1 Potentiostatic polymerization measurements

3.1.1 Corrosion parameters

The corrosion current density (i_{corr}) and the corrosion potential (E_{corr}) have been obtained by extrapolation of cathodic and anodic Tafel curves of uncoated and stainless steel coated with Poly(N,N-dimethyl aniline) in 3.5% NaCl aqueous solution. The anodic (b_a) and cathodic (b_c) Tafel slopes were calculated from figures -1 and 2.

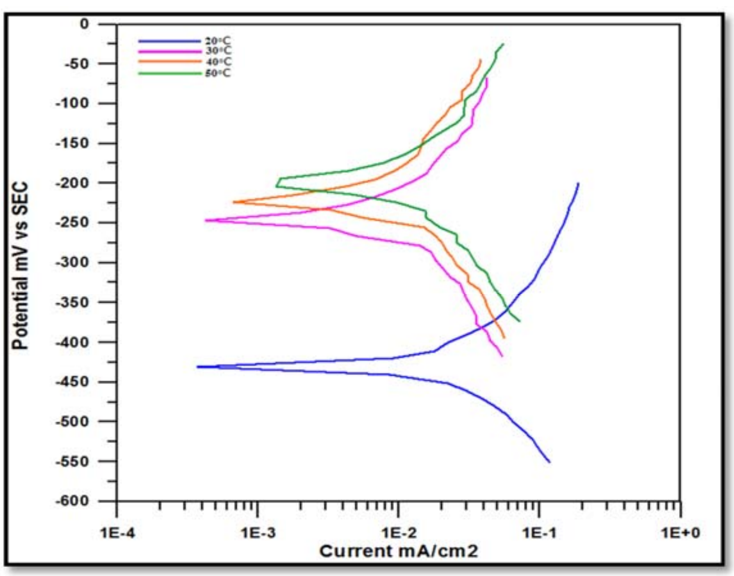


Figure 1- Polarization plots of uncoated S.S316 in sea water at different temperatures.

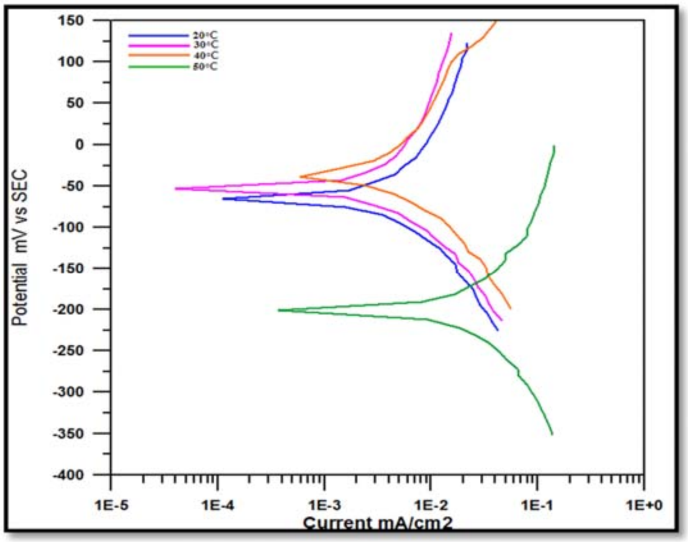


Figure 2- Polarization plots of coated S.S316 with Poly (N, N-dimethyl aniline) in sea water at different temperatures.

Table -1 show the resulting data of the corrosion potential E_{corr} (mV) ,corrosion current density i_{corr} ((mA/cm^2)), cathodic and anodic Tafel slopes b_c and b_a(mV/ Dec) ,corrosion rate CR (gm/m^{2}d) ,protection (inhibition) efficiency(PE%), polymerization resistance R_p(Ωcm^2) and corrosion penetration CP (mm/y). The data of the table show that the corrosion current density (i_{corr}) and corrosion potential (E_{corr}) generally increased with increasing temperature. The relation determining the inhibition efficiency (PE %) as shown in the following [10] :

$$PE\% = \frac{(i^0_{corr})_{uncoated} - (i_{corr})_{coated}}{(i^0_{corr})_{uncoated}} \times 100 \quad \ldots\ldots\ldots\ldots (1)$$

Where i^0_{corr} and i_{corr} are the corrosion current density without and with coared polymer obtained from Tafel polarization method.

Table 1- Corrosion data of S.S316 in sea water at absence and presence of Poly (N, N-dimethyl aniline) at different temperatures.

System	T k	E_{corr}/mV	I_{corr} (mA/cm^2)	b_a mV/Dec	$\lvert b_C \rvert$ mV/Dec	R_p Ωcm^2	CRgm /m^{2}d	CP mm/y	PE%
Uncoated S.S316	293	-426.7	12.13	94.8	88.4	1637.496552	3.04	0.135	-----
	303	-243.1	12.9	320.2	283.5	5061.38725	3.23	0.144	
	313	-219.8	13.85	398.9	275.8	5112.153393	3.47	0.154	
	323	-205	15.38	328.7	260.4	4102.054138	3.86	0.172	
S.S316coated with poly (N,N-DMA)	293	-65.7	1.93	92.2	71.5	9060.184392	0.485	0.0216	84.1
	303	-51.4	2.53	152.1	98.6	10266.85281	0.635	0.0283	80.38
	313	-37.7	3.55	182.8	100.7	7942.007772	0.89	0.0396	74.36
	323	-200.3	6.1	50.8	51.4	1818.662712	1.53	0.068	60.34

In table1.corrosion data of S.S316 in sea water at presence of Poly (N, N-dimethyl aniline) at 323 K were unstable. The corrosion potential E_{corr} for the coated electrode is less negative than that observed in the uncoated. The most values of E_{corr} indicate that the stainless steel coated with Poly (N, N-dimethyl aniline) should have higher corrosion potential because Poly (N, N-dimethyl aniline) act as anodic type inhibitor. The polarization resistance, R_p was evaluated from Tafel plots according to the Stearn-Geary equation [11]:

$R_p = b_a\, b_c /2.303(b_a + b_c)\, I_{corr}$ .... (2)

Where, I_{corr} is the corrosion current determined intersection of the linear portion of the anodic and cathodic curves, and b_a and b_c are anodic and cathodic Tafel slopes respectively .The value of R_p

increased due to the Poly (N, N-dimethyl aniline) coating which suggest a complete coverage of the metal surface because the polymers is less conductive than the bare metal.

3.1.2 Kinetic of corrosion and Thermodynamic activation parameters

The effect of temperature on the inhibition efficiency for sample under investigation in seawater solution in the absence and presence of Poly (N, N-dimethyl aniline) coating at temperature ranging from (293to 323) K was obtained and expressed as E_a, ΔS_a, ΔH_a, and ΔG_a. The results are given in Table -2. The data show that the thermodynamic activation functions (E_a and ΔH_a) of the corrosion of Poly (N, N-dimethyl aniline) coated sample are higher than those of the uncoated ones indicating higher activation energy E_a and higher value of ΔH_a. The entropy of activation ΔS_a for the uncoated and coated sample is negative value. This indicates that the activated complex in the rate determining step represents an association rather than a dissociation step, meaning that, a decrease in disordering takes place on going from reactants to the activated complex. The measured ΔG_a values listed in Table -2. Takes positive values and showed almost small change with increasing temperature.

Table 2-Values of the thermodynamic quantities for S.S316 in sea water at absence and presence of Poly (N, N-dimethyl aniline) at different temperatures.

system	T k	E_a kJ/mol	ΔH_a kJ/mol	ΔS_a kJ/mol	ΔG_a kJ/mol
Uncoated S.S316	293	6.17	3.6	-223.32	65.43
	303				67.67
	313				69.90
	323				72.14
S.S316 coated with poly(N,N-DMA)	293	29.6	27.07	-159.01	46.62
	303				48.21
	313				49.8
	323				51.39

In order to calculate activation parameters for the corrosion process, Arrhenius Eq. (3 and 4) and transition state Eq. (5 and 6) were used [12]:

$CR = A \exp^{(-Ea/RT)}$ ……………………………..……….. (3)

$\text{Log } CR = \log A - Ea/2.303RT$………………………….. (4)

$CR = RT/Nh \exp^{(\Delta Sa/R)} \exp^{(-\Delta Ha/RT}$…………………………………….... (5)

$\text{Log } (CR/T) = \log R/Nh + \Delta Sa/2.303R - \Delta Ha/2.303RT$ … (6)

Where, CR is the corrosion rate, R the gas constant, T the absolute temperature, A the pre exponential factor, h the Plank's constant and N is Avogadro's number, E_a the activation energy for corrosion process, ΔH_a the enthalpy of activation and ΔS_a the entropy of activation. The apparent activation energy (E_a) was determined by linear regression between log CR and 1/T as shown in figure -3.and the enthalpy of activation (ΔH_a) and the entropy of activation (ΔS_a) was determined by linear regression between log CR/T and 1/T as shown in figure -4.

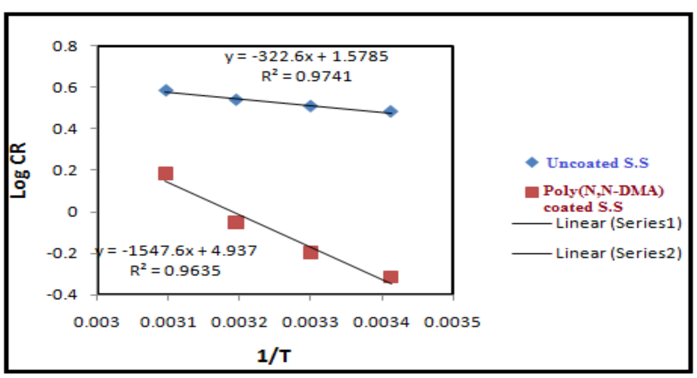


Figure 3-Arrhenius Plot of log CR versus 1/T for the corrosion of uncoated and S.S316 coated with Poly (N, N-dimethyl aniline) in sea water at different temperatures.

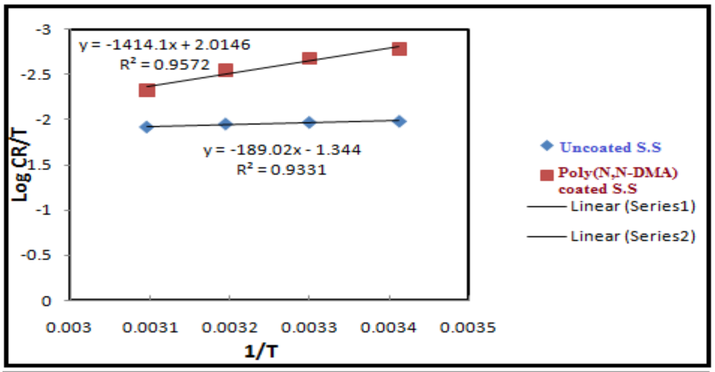


Figure 4- Arrhenius Plot of log CR/T versus 1/T for the corrosion of uncoated and S.S316 coated with Poly (N, N-dimethyl aniline) in sea water at different temperatures.

3.2 Surface Analysis

3.2.1 FT-IR results

As expected FT-IR gave good information about the complex behavior with metal ion FT-IR spectra of Poly (N, N-dimethyl aniline) sample doped with oxalic acid is shown in Figure -5. In a spectrum the band observed at 3444.63 cm^{-1} is due to characteristic N-H stretching vibration suggests the presence of NH groups in N, N dimethyl aniline units ,The polymer shows the absorption band at 1612.38 and 1506.30 cm^{-1} is an indicative of stretching vibration in quinoid rings and benzoid rings. Absorption band at 1357.79 cm^{-1} evidenced to the C-H stretching of CH3 group. The polymer shows absorption band at 1197.71 cm^{-1} which confirms the C-N stretching of tertiary aromatic amine. The absorption band appeared at 808.12, 707.83 cm^{-1} corresponds to the C-H (in-plane and out-plane).

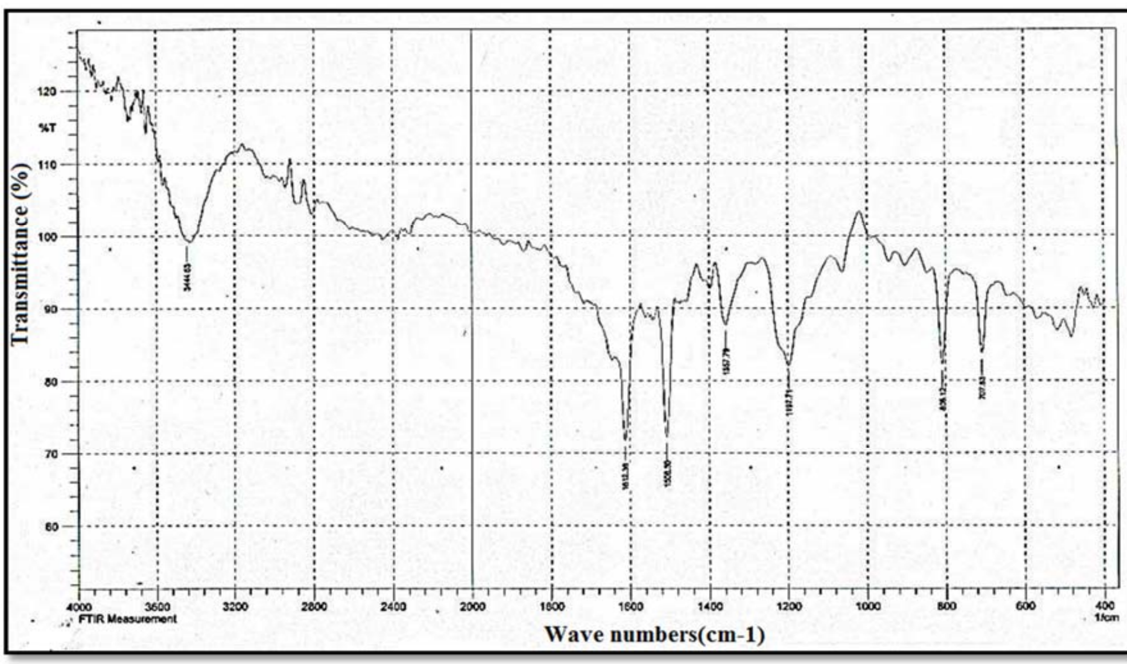


Figure 5- FTIR spectrum of Poly (N, N-dimethyl aniline) coated S.S316.

3.2.2 UV-Visible Spectra of Poly (N, N-dimethyl aniline) Coated ITO Electrode

Electrochemical polymerization of Poly (N, N-dimethyl aniline) has been studied with UV–visible spectra electrochemical technique at a transparent ITO glass electrode and the potential dependence of the absorbance at two selected wavelengths, respectively. The absorption around λ = 412 nm is caused by the $\pi \rightarrow \pi^*$ transition of benzoid ring, the electrode potential shifted to higher values at λ = 821 nm. As a result, film of Poly (N, N-dimethyl aniline) has been obtained at ITO glass electrode is shown in Figure -6.

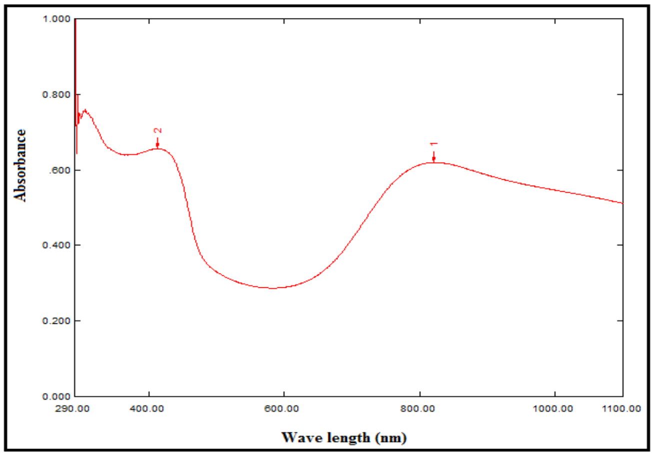
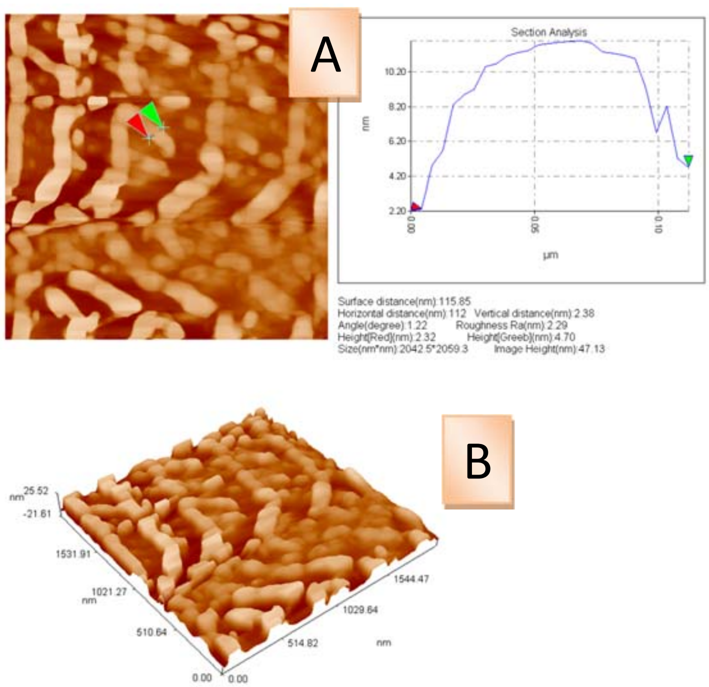


Figure 6- UV-Visible spectrum of Poly (N, N-dimethyl aniline) coated S.S316.

3.2.3 The Surface Morphology Analysis by AFM &SEM

3.2.3.1 AFM

The morphology and the roughness of the coating were determined by using AFM at a scan size of 20 µm. The approximate thickness of the coating can also be obtained from AFM as shown in figure-7



Diameter(nm)<	Volume(%)	Cumulation(%)	Diameter(nm)<	Volume(%)	Cumulation(%)	Diameter(nm)<	Volume(%)	Cumulation(%)
70.00	10.96	10.96	120.00	10.27	70.55	170.00	3.42	97.26
80.00	17.81	28.77	130.00	10.27	80.82	180.00	2.05	99.32
90.00	10.27	39.04	140.00	5.48	86.30	200.00	0.68	100.00
100.00	13.01	52.05	150.00	4.11	90.41			
110.00	8.22	60.27	160.00	3.42	93.84			

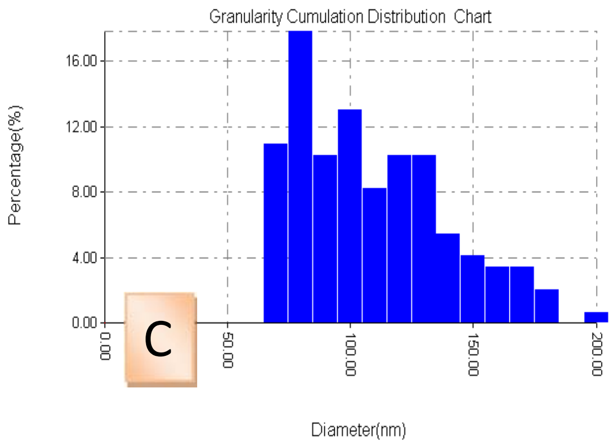


Figure 7- The AFM images of Poly (N, N-Dimethyl aniline) films electrodeposited on S.S 316, A-2D view section line analysis, B-3D view and C-particle size distribution.

3.2.3.2 SEM

Scanning electrone microscopy photograph was taken to show the corrosion inhibition is due to the formation of adsorption film reflect a nanofiber of Poly(N, N-dimethyl aniline) on the S.S surface figure 8 observed that the Poly(N, N-dimethyl aniline) coating is uniform , strongly adherent on S.S surface and the quality of coating is so excellent.

Figure 8- The SEM image of Poly (N, N-dimethyl aniline) film electrodeposited on S.S316.

4. Conclusions

The following conclusions can be drawn from the present study:

1. Poly (N, N-dimethylaniline) coated metal under investigation undergoes enhancing of the corrosion protection properties in sea water at different temperatures.
2. The polarization resistance R_p for coated stainless steel higher than uncoated sample with Poly (N, N-dimethylaniline) and R_p increase with increase temperatures.
3. The polymer coating hindered the attack of the corrosive ions on Stainless steel surface.
4. The Poly (N, N-dimethyl aniline) coating synthesized using a current density of 1.93Acm^{-2} is more compact and provide 84.1% corrosion protection.
5. The corrosion rate is found to be ~ 10 times lower than that observed from uncoated.
6. The thermodynamic and kinetic parameters ΔS, ΔH_a, ΔG_a, ΔE_a were determined to indicate the activated parameters for the corrosion process.
7. The new complex nanostructured composite obtained from this process is promising and might lead to industrial application in the protection of the S.S substrate against corrosion in sea water 3.5% NaCl solution.

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