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Investigation of Corrosion Protection for Steel by Eco-Friendly Coating

Abstract- The coupling effect of coating and inhibition has been investigated in the present work. polypyrrole coating with adding coumarin was applied on carbon steel to protect it against corrosion. Electropolymerization process by cyclic voltammeter was carried out in 0.2M oxalic acid electrolyte containing 0.1M pyrrole monomer without and with 0.01M coumarin as an eco-friendly inhibitor. SEM/EDS, AFM and FTIR techniques were used to identify the coating film. Corrosion test using Potentiostat was achieved for uncoated and coated specimens and the results indicated that the corrosion potentials became nobler compared with uncoated specimen, this means that the anodic sites were covered by undoped and doped PPy film as illustrated from the decreasing of anodic and cathodic Tafel slopes. Protection efficiencies were acceptable and good (71.46% for PPy film and 77.47% for coumarin/PPy film). The polarization resistance was increased from 0.114 $\Omega.cm^2$ for uncoated C.S. to 0.176 and 0.404 $\Omega.cm^2$ for PPy coated and coumarin/PPy coated C.S. While the porosity percentage was 0.44% and 4.50 for PPy coated and coumarin/PPy coated C.S. due to increasing the roughness of coumarin/PPy film.

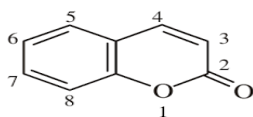
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1. Introduction

The coating and inhibition are the most common methods that use to protect carbon steel which used in many applications.

Carbon steel undergoes corrosion in many corrosive environments leading to occurring damages in its surface and creating galvanic cells by dissolving the iron. The coating act as a barrier to prevent or reduce the contact between the metallic surface and corrosive species, while the inhibitors may be adsorbed on metallic surface by formation complexes between the organic molecules that contain a functional group and metal ions or can be participated on cathodic and anodic sites. Coumarin and its derivatives are presented in many plants, coumarin (benzo- α -pyrones) is consists of fused pyrone and benzene rings, with the pyrone carbonyl group at position 2 as illustrated in the following formula:



Chemical structure of Coumarin.

Coumarin is widely distributed in the plant kingdom; large quantities of coumarin were used in the food industry, mostly associated with vanillin, for flavouring chocolates, baked goods, and in cream soda-flavored beverages. Coumarin has also found use in toothpastes, antiperspirant deodorants, bath products, hair sprays, body lotions, face creams, fragrance creams, shampoos, toilet soaps and shower gels. Therefore, coumarin is represented as eco-friendly material. There are many researches about physical properties of coumarin [1-4]. On the other hand, numerous researchers investigated coumarin as corrosion inhibitor [5-7], in addition to many papers about biological activity of coumarins.

In this research, coumarin was selected to be dopant with polypyrrole coating which applied on carbon steel surface to show its effect to reduce corrosion damage of steel in artificial seawater.

2. Experimental Work

1. Materials and Chemicals

Steel 37-2 was used in this work (chemical composition wt%: 0.121 C, 0.22 Si, 0.44 Mn,

0.014 P, 0.016 S, 0.041 Cr, 0.002 Mo, 0.022 Ni, 0.02 Al, 0.002 Co, 0.055 Cu and Fe remain) obtained by Spectro MAX, which analyzed in State Company for Inspection and Engineering Rehabilitation (SIER) Ministry of Industry & Minerals-Iraq. Cubic steel (10×10×3mm) with a square surface area (1cm²) was used in all experiments. The specimens were grinded with SiC emery papers in sequence of 200, 400 and 600 grit.

II. Preparation of PPy and Doped PPy Films

The PPy film (thickness≈5.5μm) was synthesized in solution containing 0.2 M H₂C₂O₄ and 0.1 M pyrrole (Fluka AG, Buchs SG) at room temperature using the three-electrode cell by cyclic voltammeter at potentials (-100 to +1500 mV) at scan rate 40 mV/sec. using potentiostat. Doping was achieved by adding 0.01 M of coumarin (Koh-light Laboratories Ltd, purity >99%).

III. Characterization of the Polypyrrole Films

The coated surfaces were characterized using some techniques. The morphology of the obtained thin films was characterized by SEM microscope with EDAX type (VEGA3 TESCAN). Atomic force microscopy (Veeco dinnova model) was used to observe the coated surfaces in tapping mode, using cantilever with linear tips. The scanning area in the images was 5×5 μm and the scan rate was 0.6 HZ/second. The FTIR spectra were recorded by FTIR-8400S Shimadzu Fourier Transform Infrared Spectrophotometer (Japan).

IV. Corrosion Protection Test

Corrosion measurements for uncoated and coated carbon steel specimens were tested using potentiostat (WENKING MLab 200/ Germany) which is connected to the computer device with software program. Working electrode holder was used to fix uncoated and coated specimens. Reference and counter electrode were Pt and saturated calomel electrode (SCE) respectively. The results of corrosion were calculated using Tafel extrapolation method. The base electrolyte of corrosion test was artificial seawater of 3.5% NaCl solution.

3. Results and Discussion

Cyclic voltammogram (CV) technique was used to apply polypyrrole (PPy) coating without and with 0.01 M of coumarin as eco-friendly material. Figure 1 shows the anodic and cathodic peaks that represent the reactions at anode and cathode respectively.

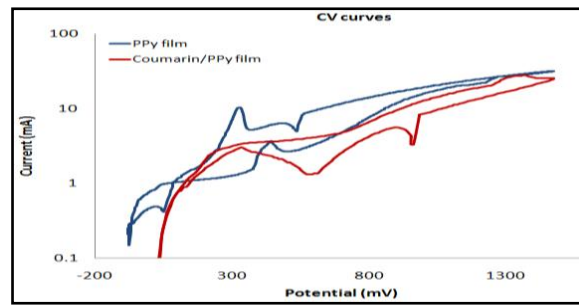
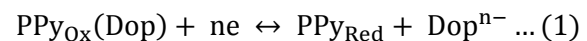


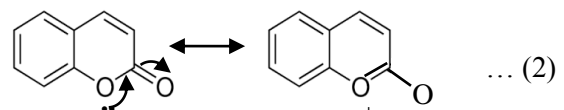
Figure 1: Cyclic voltammogram of polymerization for polypyrrole and doped polypyrrole with coumarin

The peaks appear at anodic region refer to the oxidation of monomer to form oligomers and then polymer at metallic surface carbon steel, the activation of pyrrole can occur in electropolymerization process through electron transfer from monomers to produce radical cations near the surface. This process is influenced by the presence of other materials as anions or inhibitors through the adsorption of these materials on metallic surface and their redox potentials in addition to their ionic size as illustrated in the following formula:



Where PPy_{Ox}, PPy_{Red} are the oxidized and reduced states of polypyrrole, respectively, and Dopⁿ⁻ is a dopant anion to give structure for polypyrrole and doped polypyrrole.

Coumarin can be found in ionic state as follows:



This ionic state may be attractive to metallic surface when electropolymerization occurs and this leads to incorporation between coumarin and polypyrrole coating. The presence of coumarin leads to increase the rate of electropolymerization through shifting CV curve to higher potentials, where some side reactions may occur at very high applied potential, these reactions include breaking of conjugated bonds and ring opening and this shifting is dependent on the charge of added anions.

The deposited film was characterized by SEM/EDS inspection, Figures 2 and 3 indicate the distribution of polypyrrole film, which electrochemically deposit on steel surface without and with doping by coumarin at four different magnifications. The polypyrrole film seems as cauliflower like structure with regular distribution. The presence of coumarin with polypyrrole increases the growth of polymer and

achieves more coverage for carbon steel surface. EDS analysis for undoped and doped PPy film is shown in Figures 4 and 5, these figures indicate the increasing in carbon wt% from 59.26 to 62.02 % after adding coumarin which confirm the incorporation of coumarin within polypyrrole film, also the oxygen wt% increased from 0.07 to

20.35 % after adding coumarin. On the other hand the iron wt% was decreased from 13.89 to 6.84 % confirming the formation of iron–coumarin complexes to reduce iron dissolution and forming adsorbed film.

Table 1: Corrosion parameters for polarization of uncoated and coated carbon steel in seawater

Medium	E_{corr} mV	i_{corr} $\mu A.cm^{-2}$	$-b_c$ mV.dec ⁻¹	$+b_a$ mV.dec ⁻¹
Uncoated C.S.	-757	175.2	169.9	62.8
PPy coated C.S.	-610	50.00	30.5	59.9
Coumarin/PPy coated C.S.	-696	39.47	93.9	60.2

Table 2: Calculated data of corrosion for uncoated and coated carbon steel.

Medium	$R_p \times 10^3 \Omega.cm^2$	PE%	PP%
Uncoated C.S.	0.114	--	--
PPy coated C.S.	0.176	71.461	0.44
Coumarin/PPy coated C.S.	0.404	77.471	4.50

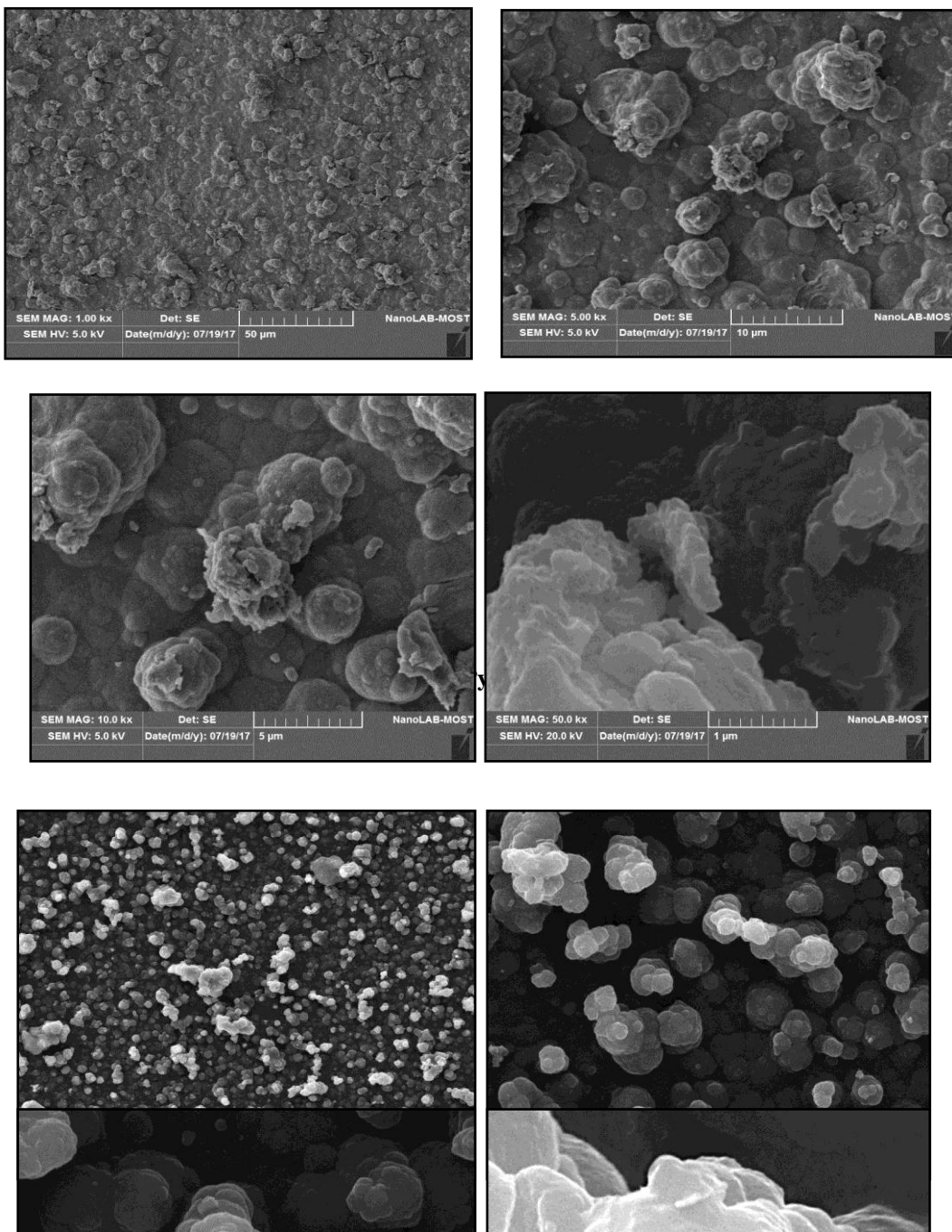


Figure 3: SEM images of Coumarin/PPy film growth on carbon steel.

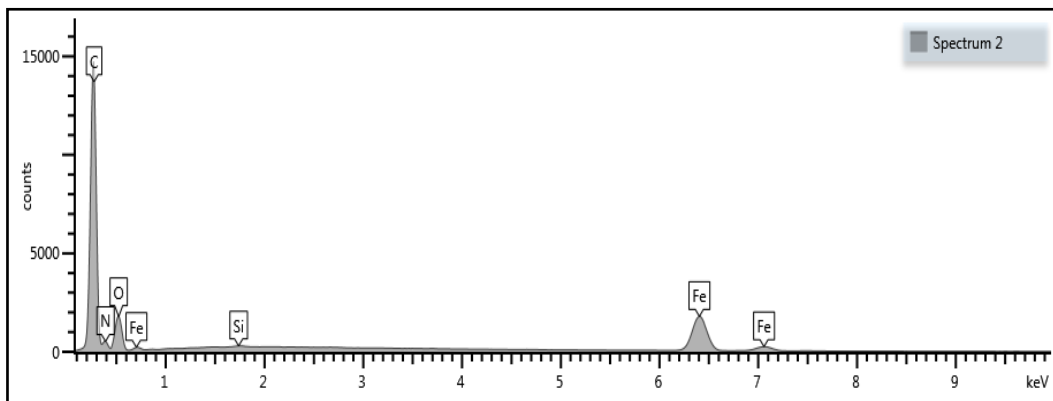


Figure 4: EDS analysis of PPy film growth on carbon steel.

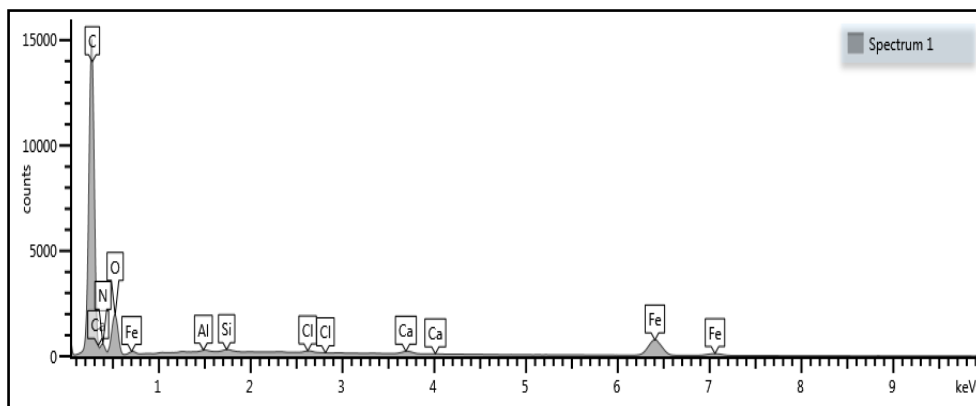
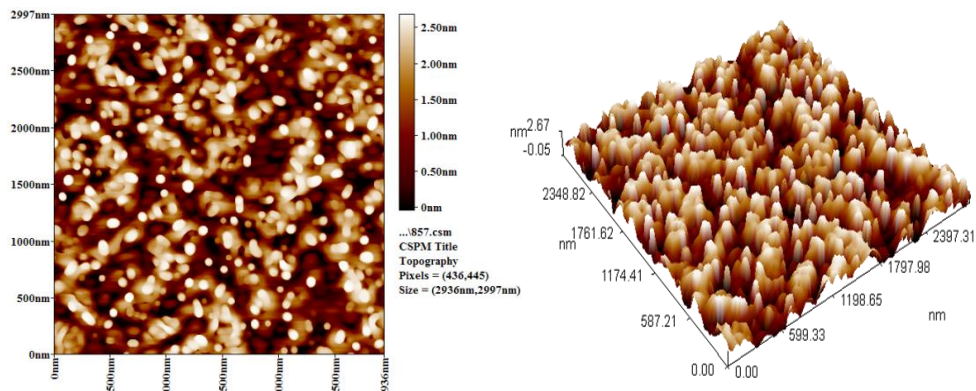


Figure 5: EDS analysis of Coumarin/PPy film growth on carbon steel.



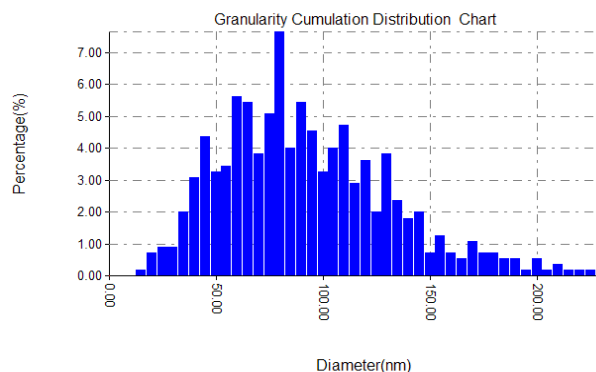


Figure 6: AFM analysis of coated C.S. by PPy.

AFM analysis was used to identify the deposited films of PPy and doped PPy, Figure 6 shows the 2D and 3D views of AFM for PPy film in addition to view the granularity of accumulation of particle sizes. These images indicate some hills and valleys of short chains of PPy film with average roughness of 0.682 nm and average diameter of particle equal to 90.02 nm. While Figure 7 shows images of doped PPy by coumarin with higher roughness and average diameter equal to 1.49 and 132.78 nm respectively. The increasing in roughness and diameter of particles comes from the higher size of six – membered ring in coumarin compared with five – membered ring of pyrrole.

FTIR spectra are important to characterize the formed films. Figure 8 shows the FTIR spectrum of deposited PPy film, the spectrum of PPy film indicates the peaks at 1512.19 cm^{-1} and 1458.18 cm^{-1} corresponded to the C=C stretching, whereas peaks at 1653.0 cm^{-1} and 1305.81 cm^{-1} are attributed to C=N and C–N bonds respectively [9].

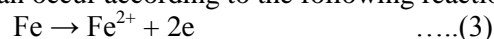
The occurrence of small peaks at 3616.53 cm^{-1} is assigned to presence of N–H stretching vibrations. The observed peaks are agreement with the ones observed in the literature [8, 9] confirming the formation of Polypyrrole (PPy). In addition to appear the peaks at 1188.15 cm^{-1} for C-H in-plane deformation and 1035.77 cm^{-1} for N-H in-plane deformation.

Generally, FTIR spectrum of coumarin must be contained the stretching of CH–aromatic around 3000 cm^{-1} , stretching of C=O group appears at $\approx 1700\text{cm}^{-1}$ which shifted to 1637.56 cm^{-1} in Figure 9. Weak band of C–C stretch occurs at 1544.98 cm^{-1} in addition to stretching of C–O at $\approx 1100 \text{cm}^{-1}$. Many peaks appear in the range of 600 to 1000 cm^{-1} due to vinyl group (=CH) and aromatic (=CH) bending out of plane [10,11].

The spectrum of doped PPy with coumarin is shown in Figure 9 and the most significant peaks

in this figure are appeared at 3354.21 and 1637.56 cm^{-1} that attributed to stretching of C–H and C=O respectively. These peaks confirm the incorporation of coumarin within PPy chains.

Corrosion behavior of PPy coated C.S. with and without coumarin was investigated by Potentiostat at 5 $\text{mV}\cdot\text{sec}^{-1}$ as scan rate. Figure 10 shows the Tafel plots of uncoated and coated carbon steel. These plots show the cathodic region, where the reduction of oxygen can occur, and the anodic region where dissolution of iron can occur according to the following reaction:



The coating with polypyrrole behaves as a barrier to prevent the connection between steel and its environment. Therefore, the dissolution of iron will decrease after coating and the flow of current decreases. The current density was decreased from 175.2 $\mu\text{A}\cdot\text{cm}^{-2}$ for uncoated C.S. to 50.00 $\mu\text{A}\cdot\text{cm}^{-2}$ for PPy coated C.S. Nevertheless, when the coumarin was added to coating electrolyte, the decreasing in current density was reached to 39.47 $\mu\text{A}\cdot\text{cm}^{-2}$ because of the coupling effect of coating with inhibition by coumarin, which can occur. Generally, the inhibitive effect of coumarin is due to the formation of complex adsorbed on the metal surface with iron ions. The corrosion potential in Table 1 was shifted to noble direction; this means that the coatings achieve an anodic protection for carbon steel.

Tafel slopes also decreased, which refer to reduction in cathodic and anodic polarization at cathodic and anodic sites respectively. But the reduction in cathodic Tafel slope more than that of anodic one; this means that the PPy and coumarin are covered the cathodic region more than the anodic one. The polarization resistance (R_p) was also determined according to Stern-Geary equation [12, 13]:

$$R_p = \frac{b_a \times b_c}{2.303 (b_a + b_c) i_{corr}} \quad \dots(4)$$

Where b_a and b_c are anodic and cathodic Tafel slopes respectively. The results indicated that the highest resistance was for undoped and doped PPy coating as listed in Table (2).

The Protection efficiencies (PE%) of applied coatings can be estimated by corrosion current densities for uncoated and coated specimens as follow [14, 15]:

$$PE\% = \left[1 - \frac{i_{corr, coated\ specimen}}{i_{corr, uncoated\ specimen}} \right] \times 100 \quad \dots (5)$$

The protection efficiencies were got good values especially for doped PPy coating which was 77.471%. The porosity percentage (PP%) also calculated using the following equation[16, 17]:

$$PP\% = \frac{R_{p, uncoated}}{R_{p, coated}} 10^{-\frac{-\Delta E_{corr}}{b_a}} \times 100 \quad \dots (6)$$

Where $R_{p, uncoated}$ and $R_{p, coated}$ are the polarization resistances of the uncoated and coated carbon steel respectively, ΔE_{corr} is the corrosion potential difference between them, and b_a is the anodic Tafel slop of the uncoated specimen. The lower porosity percentage was for PPy coating which was equal to 0.44%, while the doped PPy with coumarin gave porosity equal to 4.5% because of

the difference in particle size of deposited molecules and the difference in roughness.

I. Technical and economic feasibility

The coating with polypyrrole needs very small amount of pyrrole monomer; also, the coating can be achieved in short time according to the thickness from 10 min. to 30 min. at room temperature. Coumarin is available material and also presented in many kinds of plants that may be added to coating as extract.

4. Conclusions

Producing eco-friendly coating was done by applying polypyrrole coating doped by coumarin on carbon steel. Some techniques were confirmed the obtaining compact and adhesive film include SEM/EDS, AFM and FTIR. Addition of coumarin to PPy coating gave more roughness and average diameter due to the difference in size of coumarin molecules and polymer chains. This roughness led to increase the porosity of deposited film on carbon steel. Good corrosion properties were obtained after adding coumarin to polypyrrole coating such as polarization resistance and protection efficiency.

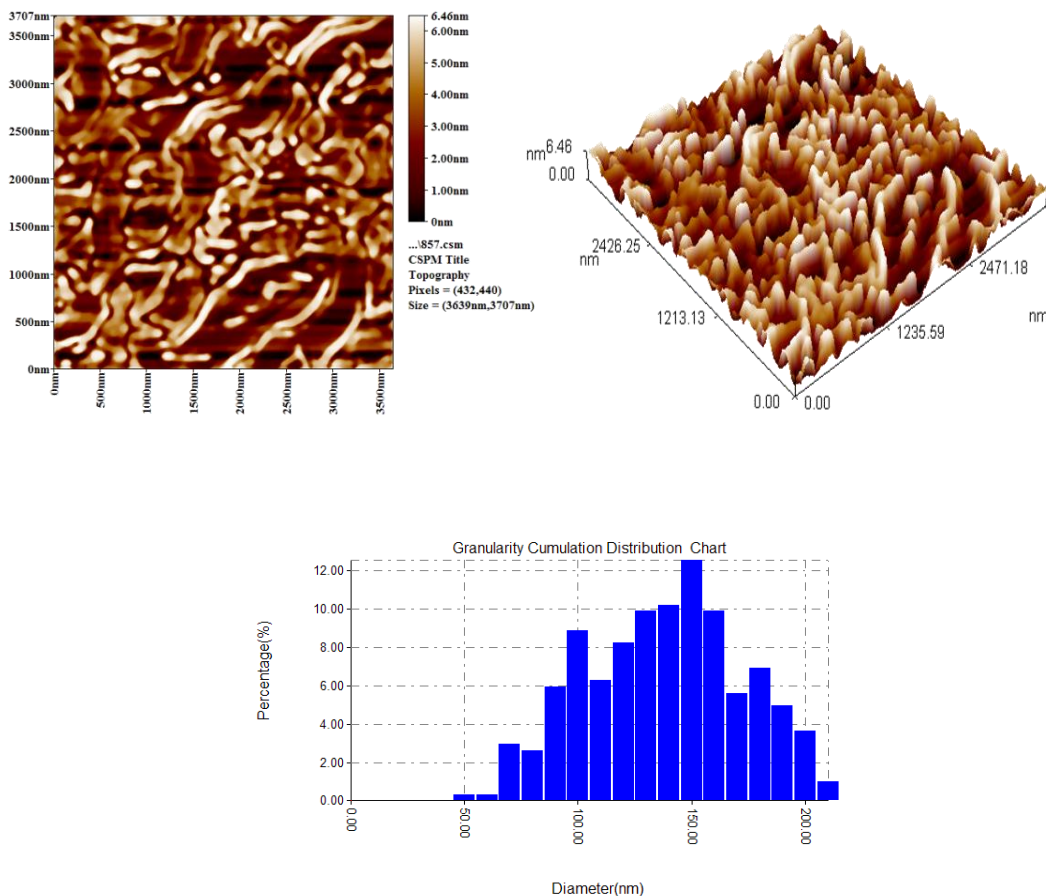


Figure7: AFM analysis of coated C.S. by doped PPy.

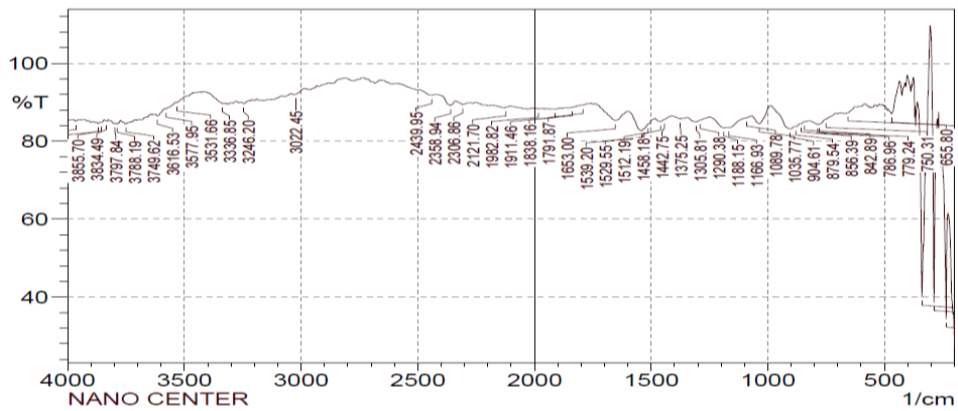


Figure 8: FTIR spectrum of PPy film formed on C.S.

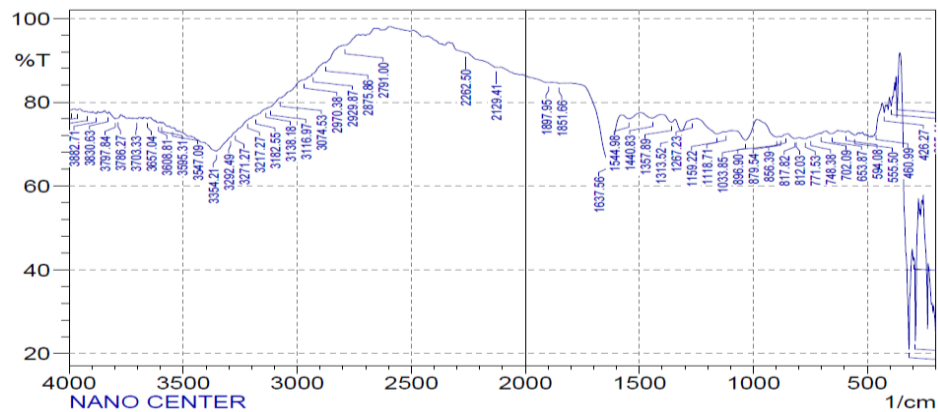


Figure 9: FTIR spectrum of doped PPy film formed on C.S.

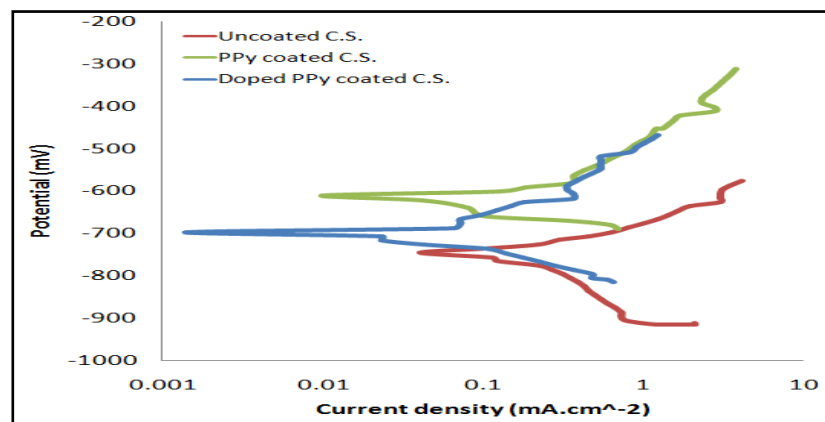


Figure 10: Tafel plots of uncoated and coated C.S.

5. References

[1] K. Jannette, N. Jamal and A. Rana, “ β -coefficients and apparent molal volume of coumarin in (H₂O, C₂H₅OH) mixtures at different temperature,” Iraqi Journal of Chemistry: Vol. 28, No.1, 169-175, 2002.

[2] K. Jannette, N. Jamal and A. Rana, “Study of thermodynamic function for hydrolysis of lactone ring in coumarin and its derivatives in 70% ethanol – water at five temperature,” Engineering & Technology Journal Vol.22, No.5, 2003.

[3] K. Jannette, N. Jamal and A. Rana, “Study of chemical kinetics for hydrolysis of coumarin and its derivatives at five temperature”, Engineering & Technology Journal Vol.26, No.9, 386-400, 2008.

[4] K. Mostafa and A. Rana, “Study of some electrical properties of coumarin in (ethanol-water) mixtures with three weight percentage at five temperature” Engineering & Technology Journal Vol.26, No.3, 115-130, 2008.

[5] A. A. Rana, A. Mohammed and Hiba Anwer, “Coumarin as inhibitor for Steel in Petroleum medium, ID: CS12204512, Chemical Science Review and Letters, Vol.3, issue 12, 1358-1364, 2014.

[6] M. Abdallah, O.A. Hazazi, B.A. ALJahdaly, A. S. Fouda and W. El-Nagar, “Corrosion Inhibition of Zinc in Sodium Hydroxide Solutions using Coumarin Derivatives”, International Journal of Innovative Research in Science, Engineering and Technology Vol. 3, Issue 6, 13802-13819, 2014.

- [7] A.S. Fouda, S.M. Rashwan, M.M. Kamel and M.M. Khalifa, "4-Hydroxycoumarin Derivatives as Corrosion Inhibitors for Copper in Nitric Acid Solutions," *J. Mater. Environ. Sci.*, Vol. 7, No.8, 2658-2678, 2016.
- [8] B. Tian and G. Zerbi, "Lattice-Dynamics and Vibrational Spectra of Polypyrrole," *Journal of Chemical Physics*, Vol. 92, No. 6, 3886-3891, 2009.
- [9] K. Arora, A. Chaubey, R. Singhal, R.P. Singh, M. K. Pandey, S.B. Samanta., B.D. Malhotra and S. Chand, "Application of Electrochemically Prepared Polypyrrole Polyvinyl Sulphonate Films to DNA Biosensor," *Biosensors and Bioelectronics*, Vol. 21, No. 9, 1777-1783, 2006.
- [10] D. Barton and W. David Ollis, "Comprehensive Organic Chemistry," *The Synthesis & Reaction of Organic Compounds*, Vol. 14, P. 629, Ch. 18, 1975.
- [11] Silverstein, Bassler and Morrill, "Spectrometric Identification of Organic Compounds," 4th ed. P. 319, 1981.
- [12] A.A. Rana, "Corrosion inhibition of Al-Si-Cu alloy in the basic media by using six inhibitors at four temperatures: Um – Salama Science Journal: Vol.5, No.3, 427-439, 2008.
- [13] A.A. Rana, "Behavior of Ti/HA in Saliva at Different Temperatures as Restorative Materials", *Journal of Bio- and Tribocorrosion*, Vol.2, No.5, 2016.
- [14] A.A. Rana, "Improvement the Corrosion Resistance of pure Al, Al-Si and Al-Zn alloys by Nanoalumina Coating," *International Journal Innovative Science, Engineering and Technology*, Vol.1, Issue 4, P.494-505, June 2014.
- [15] A.A. Rana, "Corrosion Inhibition of Monel in 0.2N HCl Solution by Tris (hydroxymethyl) aminomethane," *International Journal of Scientific and Engineering Research (IJSER)* –Vol. 6, Issue 4, P.683-686, April 2015.
- [16] A.A. Rana and A. Marwah, "Effect of Nanoparticles Coating on Properties of Al-12Si alloy", *International Journal of Scientific Research in Science, Engineering and Technology*, Vol. 1• Issue 2, 363-367, 2015.
- [17] A.A. Rana, "Properties of Functionally Graded Coating of Al₂O₃/ZrO₂/HAP on SS 316L," *International Journal of Scientific and Engineering Research (IJSER)* –Vol. 6, Issue 5, P.953-957, 2015.