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Using Polypyrrole Coating for Improving the Corrosion Resistance of Steel Buried in Corrosive Mediums

A.H. El-Shazly[*], *A.A. Wazzan*

Chemical and Materials Engineering Department, Faculty of Engineering, King Abdulaziz University, Jeddah, Saudi Arabia
[*]E-mail: elshazly_a@yahoo.com

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This work investigates the possibility of improving the corrosion resistance of buried steel by coating it with polypyrrole (PPy) layer. The potentiostatic technique was used in precipitating the PPy layer. Investigation for the characteristics of the formed layer using different techniques such as X-Ray Photoelectron Spectroscopy (XPS), scanning electronic microscope (SEM) and Ellipsometric analysis was carried out. The formed PPy layer was examined for its corrosion resistance while coupled with stainless steel cathode and buried in sand containing different known amounts of moisture, salt (NaCl) and sulphuric acid (H_2SO_4) using the potentiodynamic examination test. The results show that coating steel with PPy layer can improve its corrosion resistance against NaCl, H_2SO_4 and water by factors up to 1.7, 1.80 and 1.57 respectively.

Keywords: Polypyrrole, smart coats, electropolymerization, corrosion inhibition, buried steel

1. INTRODUCTION

Recently there has been a lot of interest in using conducting polymers such as polypyrrole and polyaniline coatings in corrosion prevention. These polymers act as anodic protection and significantly reduce the rate of corrosion [1-5]. Preliminary results indicate that the structure and properties of polypyrrole coatings formed on steel vary with the process conditions. Polypyrrole and polyaniline have been successfully electrodeposited on steel from aqueous media [6-18]. It was found that the longer the passivation period of polymerization reaction, the better the quality of the coatings. Electropolymerization of pyrrole on steel in oxalic acid solution is preceded by the coverage of the substrate by a crystalline passive film. Corrosion can be prevented by the isolation of the metal from the corrosive environment, by suppression of the anodic dissolution of the metal or by suppression of the corresponding cathodic reactions [1]. Isolation of metals from the corrosive environment is probably the most general mechanism of corrosion protection offered by polymer coatings. Proper isolation by a polymer coating requires that the polymeric material provides good barrier properties and remains adherent in the presence of water and corrosive products such as Fe_2O_3.

Buried steel lines have many important industrial applications such as petroleum oil transportation across countries, foundation of metallic structures, tanks, water pipelines etc. Protecting steel against corrosion using primers and paints, coating by organic or inorganic coats, metallic coating using either noble or less noble metals, using corrosion inhibitors, application of cathodic protection, etc. is a great deal in approximately all industrial applications. The above mentioned protection methods are all used and have their advantages and disadvantages such as cost and pollution problems. Replacement of all or part of these coat layers by less expensive, durable, environmentally stable and easy to be synthesized coat will be important for reducing the cost of protection process and increasing the lifetime of coated buried steel. From this point intrinsically conducting polymers were found to have a wide range of applications because of its specific properties in this research polypyrrole will be investigated for its corrosion performance when applied to buried steel in sand having different corrosive mediums such as NaCl, H_2SO_4, and moisture.

2. EXPERIMENTAL WORK

2.1. Electropolymerization of pyrrole

The electropolymerization of pyrrole (PPy) from aqueous solution was carried out in one-compartment cell. The working electrode was made from steel sheet of 2x3x0.1 cm. Both electrodes were polished and degreased with acetone for about 10 minutes prior to the electropolymerization process. An Ag/AgCl manufactured by Corning Company was used as the reference electrode. The potentiostatic technique (constant potential method) was used to electrochemically coat steel with the PPy layer from solution of pyrrole monomer with sodium tartrate electrolyte, using an EG&G Princeton Applied Research Potentiostat/Galvanostat Model 273A provided with powerCorr software. The main parameter parameters of electropolymerization process were as follows pyrrole concentration 0.5M, sodium tartrate concentration 0.2M, solution pH 9, applied potential 2 V and electropolymerization time was 20 minutes interval for all experiments. After each experiment, the PPy coated steel was rinsed with distilled water and methanol and left to dry.

2.2. Surface elemental composition analysis

Elemental analysis of the polypyrrole coated steel was carried out by X-ray Photoelectron Spectroscopy (XPS). The XPS technique used was part of a multi-technique surface analysis system (MAX200, Leybold). From each sample a specimen of 20x20 mm size was cut and mounted on the sample holder with four screws. All the samples were examined with Mg-k (1253.6 eV) at 100 watt X-ray power (10 kV x 10 mA). The pressure in the analysis chamber during sample analysis was less than 10^{-8} mbar. As a precaution not to damage the carbon signal incorporated with the polyaniline, carbon element was scanned first, followed by a general survey of the sample, and the rest of the elements. In addition to the carbon, N, O, and Fe elements were scanned and the area under each element peak was calculated. The scan area was 7 mm × 4 mm and the resulted data are the average of 50 scans of each element analysed. The surface composition in atomic percentage was calculated using the element relative cross sectional area as supplied by the XPS manufacturer.

2.3. Examination of the performance of the buried PPy coated steel against corrosion

Potentiodynamic examination (Tafel test) was used for the examination of the corrosion resistance of PPy coated steel when coupled with stainless steel while buried in a layer of 250 g sand. The sand was washed with deionised water for three times and then mixed with known amounts of different corrosive materials such as NaCl, H_2SO_4, and moisture.

As shown in figure 1 the buried PPy coated steel and stainless steel were used as anode and cathode respectively, the corrosion current and potential were measured against Ag/AgCl reference electrode using the EG&G Princeton Applied Research Potentiostat/Galvanostat Model 273A provided with powerCorr software.

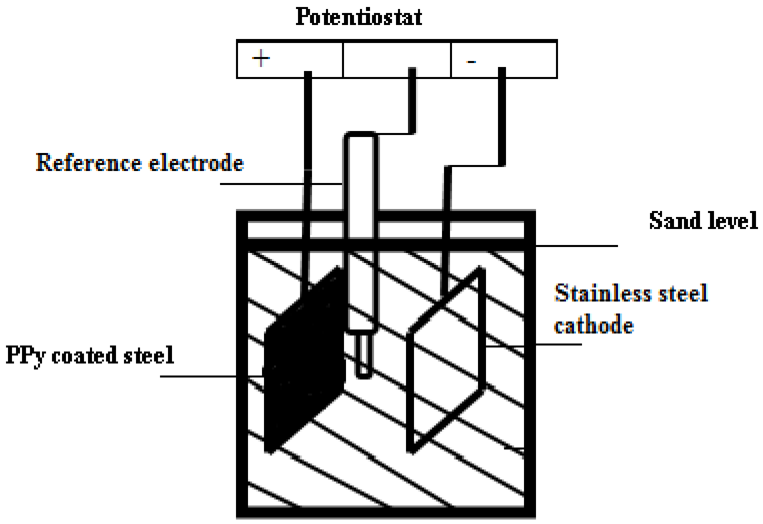

Figure 1. Experimental setup for potentiodynamic examination of the formed PPy layer

3. RESULTS AND DISCUSSIONS

3.1. Layer formation and characterization

3.1.1. Layer formation using the potentiostatic technique

The potentiostatic technique was used for PPy layer formation, as shown in figure 2 the results show that polymerization process takes place through incubation period of approximately 250s.

through this period passivation of iron surface takes place and layer of iron tartrate will be formed as a buffer layer between the iron surface and the PPy polymer layer. In addition a well defined plateau is formed at approximately 0.125 A, which indicates layer formation at constant current and potential conditions.

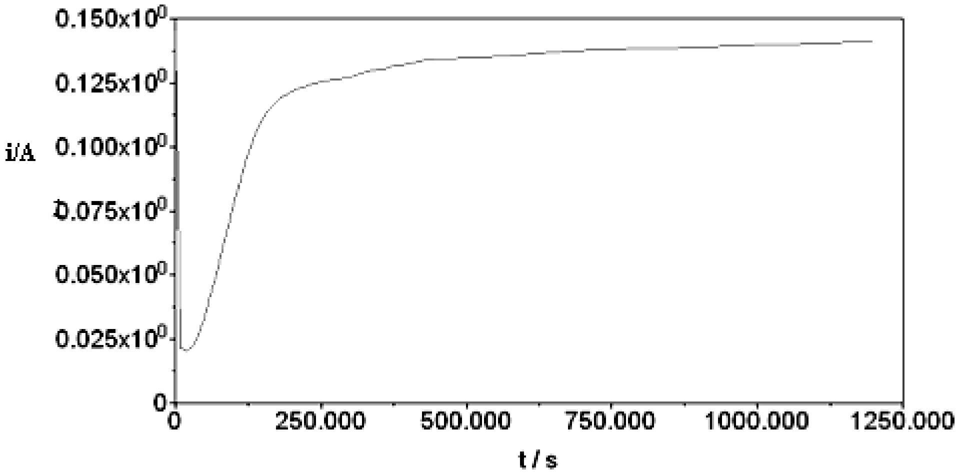

Figure 2. Current vs elapsed time for polypyrrole layer formation using potentiostatic technique. Coating steel anode and stainless steel cathode vs Ag/AgCl reference electrode, potential=2 V, 0.5M pyrrole, 0.2M sodium tartrate, pH= 9

3.1.2. XPS analysis of the PPy coated steel

Table 1. Atomic percentages of different elements forming the deposited PPy layer for different pyrrole concentrations.

Element	%Atomic concentration of the ppy layer at different pyrrole concentration	
	0.1M pyrrole	0.5 M pyrrole
C 1s	60.957	65.468
O 1s	28.847	23.398
N 1s	9.194	10.036
Fe 2p3/2	1.001	1.098

As shown in figures 3a the XPS analysis of the formed PPy layer shows that there are two main peaks representing the occurrence of C1s atoms which appear clearly within the range from 285 to 290 ev.

The above results confirm the mechanism considered for the process that electropolymerization starts with iron anode dissolution and formation of Fe^{+2} which dissolve in the solution.

Parts of these ions react to form iron tartrate which precipitates on the anode surface and forming a binding layer between the iron surface and the polypyrrole layer. The first peak (at 287ev) indicates the formation of tartrate layer while the second is due to the outer polypyrrole layer. Figure

3b shows that the a uniform peak of N1s is fomed within the range from 400 to 397 ev, this element indicates the formation of PPy layer.

Table 1 shows the atomic percentages of different elements forming the deposited PPy layer, the results show that the percentage C1s and N1s for PPy layer formed at 0.5M initial pyrrole concentration is the highest which indicates denser PPy layer.

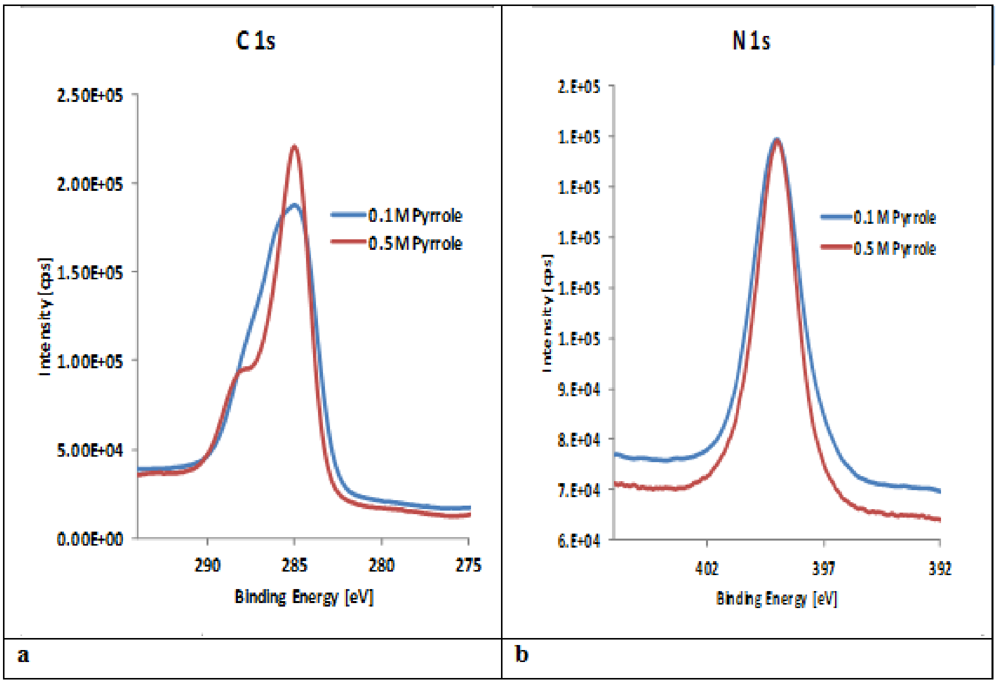

Figure 3. XPS Spectra of (a) Carbon (C1s) (b) (N1s) PPy coated steel at different pyrrole concentrations

3.1.3. Scanning electronic microscope analysis (SEM) of formed PPy layer

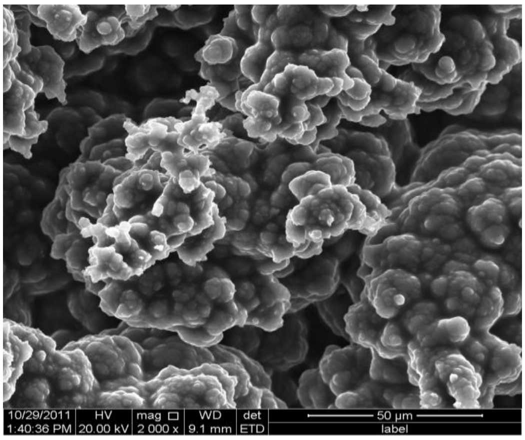

Figure 4. SEM analysis of the formed PPy layer

As shown in figure 4 the results show that a uniform shape of cauliflower microstructure distributed uniformly over the iron surface was found. This figure indicates a possible uniform layer to be formed on the iron surface.

3.1.4. Determination of PANi layer thickness using Ellipsometry

Ellipsometric analysis was carried out for the PPy layer formed from a solution containing 0.5 M pyrrole, 0.2 M sodium tartrate at solution pH of 9. As shown in figure 5 the results show that there are two main layers existing on the iron surface which are mainly iron tartrate and PPy layers, and that the thickness of tartrate layer is 27.076 (±12.594) nm and that of PPy layer it is 364.318(± 45.742) nm. In addition the results show that the value of index n is 1.136 and that of k is 4.143 for the deposited layer which indicates that the formed layer is much opaque and of higher light absorption capacity.

Parameters

1) L1 Thickness [nm] = 364.318 ± 45.742
2) L2 Thickness [nm] = 27.076 ± 12.594
3) n = 1.136
4) k = 4.143

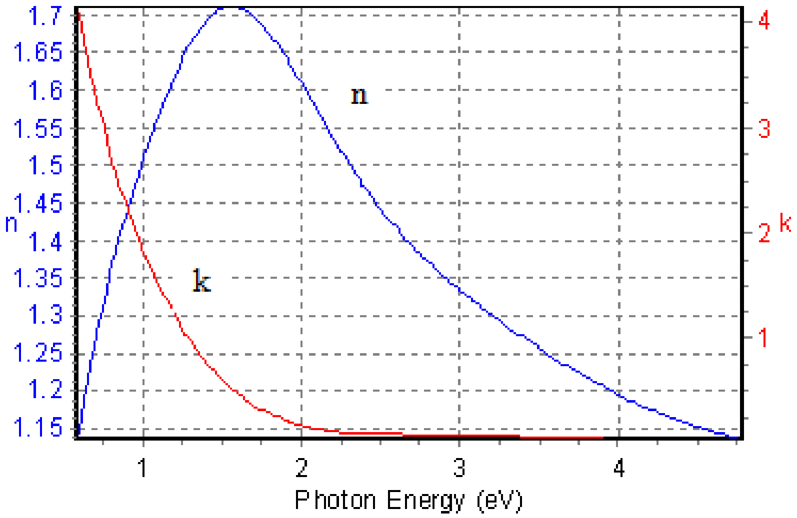

Figure 5. Ellipsometric analysis of the deposited PPy layer.

3.2. Study for the performance of buried PPy coated steel against corrosion

All the consequent analysis will be carried out using a PPy layer formed from a solution having the composition of 0.5 M pyrrole, 0.2 M sodium tartrate at solution pH of 9 , applied potential of 2V and 20 minute polymerization time.

The formed layer characteristics can be summarized as follows:
%C=65.5, % N= 10, PPy layer thickness= 364.318 (± 45.742)nm, index n = 1.136
And that of k = 4.143.

3.2.1 Effect of NaCl concentration

As shown in figure 6 the potentiodynamic polarization test shows that the corrosion current of all test samples of PPy coated steel is less than that of uncoated steel. Figure 7 shows that the corrosion rate has been decreased by increasing the salt concentration for both coated and uncoated steel. This results can be ascribed to the fact that in the pH range from 4 to 10, the corrosion rate is independent of pH, and depends only on how rapidly O_2 diffuses to the metal surface [19] which affect the cathodic reaction that:

$$H_2O + 1/2\ O_2 + 2\ e \rightarrow 2OH^- \qquad (1)$$

the presence of NaCl with higher concentration will decrease the concentration of dissolved O_2 in the surrounding soil to steel.

The decrease in O_2 concentration will lower the rate of the cathodic reaction and consequently decrease the corrosion rate to certain level. In addition at higher chloride concentration the possibility of $FeCl_2$ and $FeCl_3$ will increase, these salts will precipitate on the anode surface and increase anodic polarization which hider the anodic reaction and decrease the corrosion rate as well. Also from figure 7 the results show that coating steel with PPy layer can improve the corrosion resistance of steel by a factor ranging from 1.2 to 1.7 depending on the salt concentration.

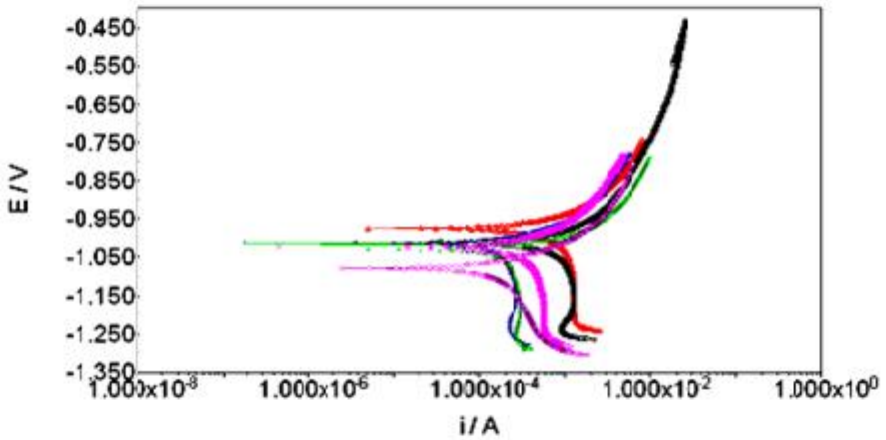

Figure 6. Potentiodynamic examination of buried PPy coated steel coupled with stainless steel vs Ag/AgCl reference at different H_2SO_4 concentrations. Bare steel at 1% NaCl red; buried PANi coated steel at (1%NaCl black; 2% NaCl blue; 3%NaCl green; 5% NaCl light magneta; 10% NaCl magneta color)

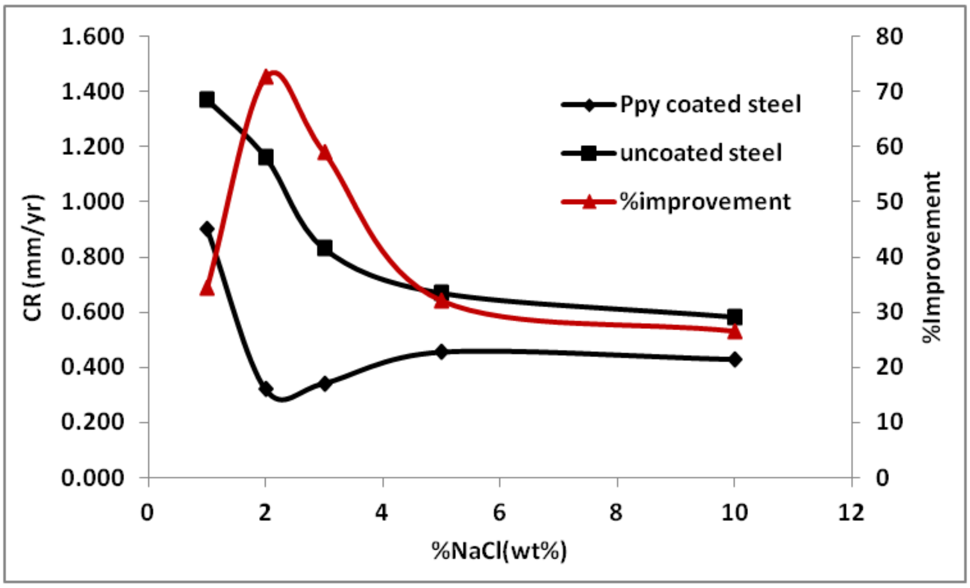

Figure 7. Corrosion rate of bare steel, PPy coated steel and the % Improvement in corrosion resistance when buried in sand containing different NaCl concentrations.

3.2.2. Effect of H_2SO_4 concentration

As shown in figure 8 the potentiodynamic polarization results show that the corrosion current of all test samples of PPy coated steel buried in sand containing different concentrations of H_2SO_4 is less than that of uncoated steel (both are coupled with stainless steel and the corrosion current was measured vs Ag/AgCl reference electrode) As shown in figure 9 the results show that coating steel with PPy layer has improved the corrosion resistance by decreasing the corrosion rate within the range from 1.6 to 1.8 depending on the acid concentration.

To clarify the above results the following has to be considered, for bare steel in acidic medium two main reactions take place:

$$\text{Anodic: } Fe \rightarrow Fe^{+2} + 2e \qquad (2)$$

$$\text{Cathodic: } H^{+} \rightarrow H_2 + 2e \qquad (3)$$

The dissolution of iron (anodic reaction) is rapid in all mediums, and the rate of iron corrosion is usually controlled by the cathodic reaction which is usually much slower. In acidic mediums the cathodic reaction proceeds rapidly [19], which explain the results obtained in figure 8 that the corrosion rate of bare steel has been increased by increasing the acid concentration. While In case of coating steel with PPy layer, it is clear that the controlling step is no longer the cathodic reaction, it is now the anodic one which was decreased by coating the steel surface with PPy layer and consequently improved the corrosion resistance of steel.

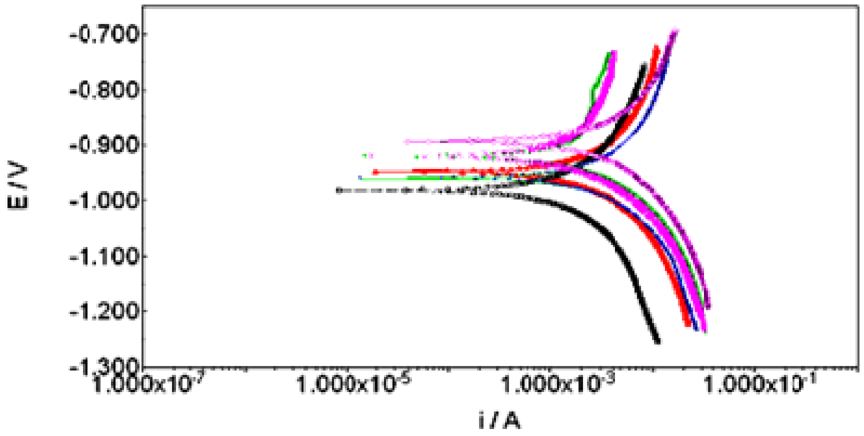

Figure 8. Potentiodynamic examination of buried PPy coated steel coupled with stainless steel vs Ag/AgCl reference at different H_2SO_4 concentrations. Buried bare steel at 1% H_2SO_4 red; buried PANi coated steel at (1% H_2SO_4 black; 2% H_2SO_4 blue; 3% H_2SO_4 green; 4% H_2SO_4 light magneta; 5% H_2SO_4 magneta color)

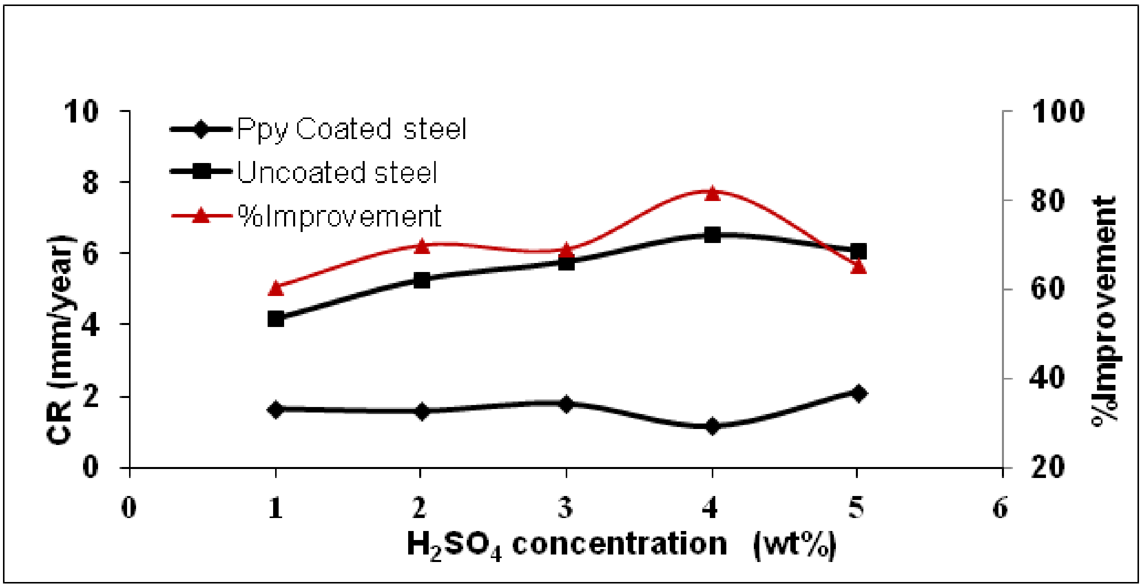

Figure 9. Corrosion rate of bare steel and PANi coated steel and the % Improvement in corrosion resistance when buried in sand containing different H_2SO_4 concentrations.

3.2.3. Effect of moisture content

As shown in figure 10 the Tafel polarization results show that the corrosion current of all test samples of PPy coated steel buried in sand containing different amounts of moisture content is less than that of uncoated steel (both are coupled with stainless steel and the corrosion current is measured vs Ag/AgCl reference electrode)

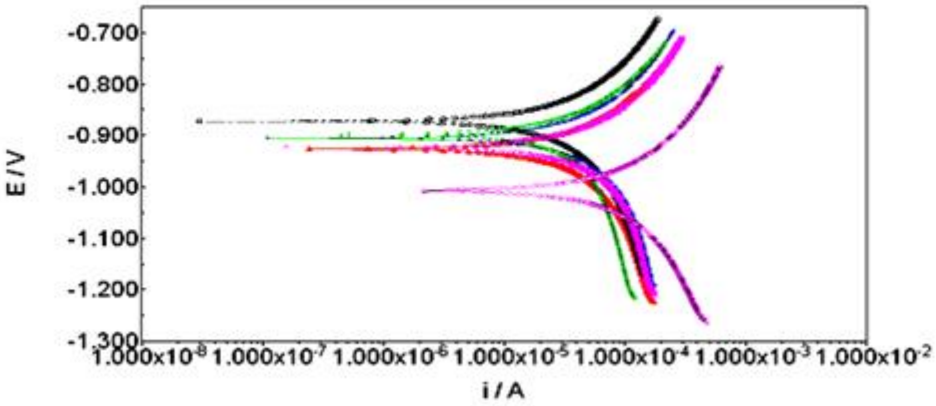

Figure 10. Potentiodynamic results of buried PANi coated steel coupled with stainless steel vs Ag/AgCl reference at different percentages of moisture. Buried bare steel at 10%H_2O red, buried PANi coated steel at (10% H_2Oblack; 20% H_2O blue; 30% H_2O green; 40% H_2O light magneta; 50% H_2O magneta color).

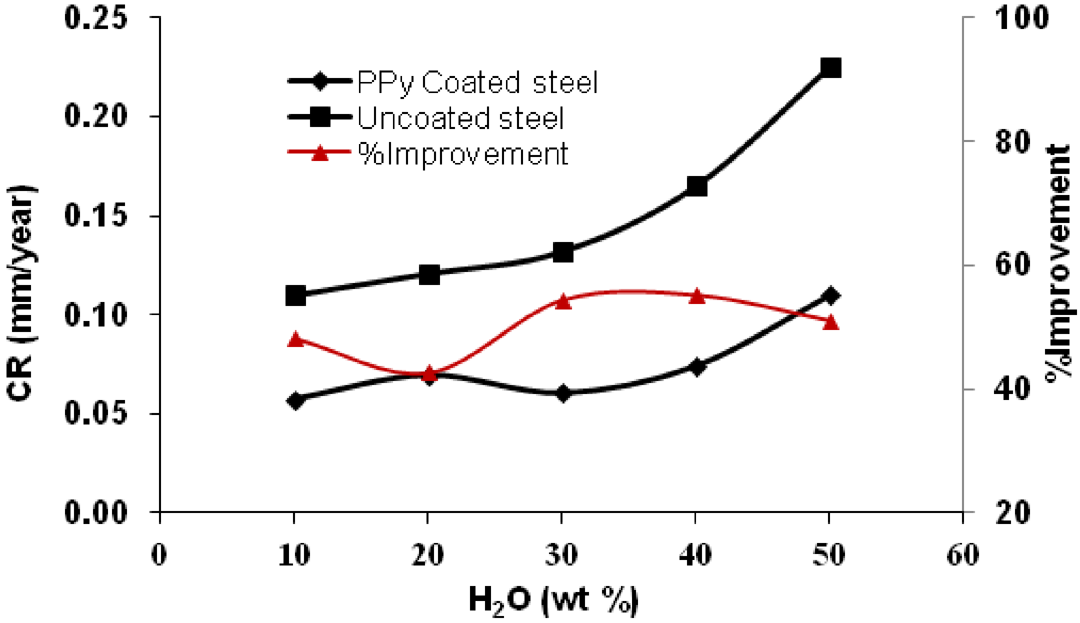

Figure 11. Corrosion rate of bare steel, PANi coated steel and the % Improvement in corrosion resistance for PANi coated steel when buried in sand containing different moisture content.

As shown in figure 11 the results show that the corrosion rate have been increased by increasing the % moisture content which can be ascribed to the increased conductivity of the soil due to presence of water. In addition presence of water will accelerate the cathodic reaction equation 1 it is clear that presence of PPy layer slowed down the anodic reaction to the extent that it controls the process. Presence of the PPy has improved the corrosion resistance by a factor ranging from 1.40 to 1.57 depending on the moisture content in the soil. It has to be mentioned that figure 10 shows that the

% improvement decreased by increasing the moisture content above 40 which can be ascribed to the higher corrosion rate at higher moisture content.

4. CONCLUSIONS

This work investigated the possibility of improving the corrosion resistance of buried steel by coating steel with a layer of polyaniline (PPy). The potentiostatic technique was used for forming the PPy layer, using PG&G Potentiostat galvanostat A 273 Model. The layer formed was investigated for its composition using the X-Ray Photoelectron Spectroscopy (XPS), and scanning electronic microscope (SEM) and for its thickness by using Ellipsometric analysis. The potentiodynamic technique (Tafel test) was used for investigating the corrosion resistance of the PPy coated steel while coupled with stainless steel and buried in sand containing different concentrations of different contaminant such as NaCl, H_2SO_4 and water, the corrosion current was measured against Ag/AgCl reference electrode. The results show that coating buried steel with PPy layer can improve its corrosion resistance against NaCl, H_2SO_4 and water by a factor up to 1.7, 1.80 and 1.57 respectively. The above results show that coating steel with a layer of polypyrrole can improve the life time when buried in sand containing different contaminant such as NaCl, H_2SO_4 and water.

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