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Improving the Corrosion Resistance of Buried Steel by Using Polyaniline Coating

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This work investigates the possibility of improving the corrosion resistance of buried steel by coating it with polyaniline (PANi)layer. The galvanostatic technique was used in forming the PANi layer. Investigation for the characteristics of the formed layer using different techniques such as X-Ray Photoelectron Spectroscopy (XPS) and Ellipsometric analysis was carried out. The formed PANi 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 PANi layer can improve its corrosion resistance against NaCl, H_2SO_4 and water by factors up to 1.88, 1.89 and 1.54 respectively.

Keywords: Conducting polymers, polyaniline, buried steel, corrosion resistance, and electropolymerization

1. INTRODUCTION

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. One of the important and promising applications is corrosion protection. Of the conducting polymers, the polyaniline (PANi) families have been the most widely studied, due to their environment stability and ease of synthesis. In the field of corrosion protection, PANi can be used either as corrosion inhibitors or as protective coatings. PANi can function as inhibitors, because of the presence of the functional group C=N which can be adsorbed on the metal surface. It was found that soluble PANi absorbed on the metal restrain the anodic or cathodic reaction [1,2]. In much more cases, PANi was used as protective coatings. Since DeBerry [3] showed in 1984 that the electrochemically deposited PANi protected stainless steel by anodic protection, PANi was investigated for protection of stainless steel [3,4], iron [5,6], mild steel [7], copper [4], aluminum [8] and zinc [9]. It was also shown that PANi protects mild steel in chloride medium [7,10]. PANi can also be used as a blend with epoxy resin, or as an under layer with an epoxy top-layer [10–12]. Pereira da Silva et al. [13] studied PANi acrylic coatings for corrosion inhibition and found that counter-ions were a crucial factor for determining the protective performances of the coatings. El-Shazly and Wazan[14] found that the corrosion rate of the galvanic coupling of PANi coated steel and zinc has been decreased by a factor ranging from 1.4 up to 1.51 than the coupling without coat, depending on the operating conditions. .

The aim of the present work is to investigate the possibility of improving the corrosion resistance of buried steel by coating it with polyaniline (PANi) while subjected to different corrosive mediums as sand containing known amounts of water NaCl and/or H_2SO_4.

2. EXPERIMENTAL WORK

2.1. Electropolymerization of aniline

Aqueous electropolymerization of aniline was performed in one-compartment cell. The working electrode was made from steel sheet of 2x3x0.1 cm purchased from market. The working electrode was polished and degreased with acetone for about 10 minutes prior to the electropolymerization. An Ag/AgCl manufactured by Corning Company was used as the reference electrode. The galvanostatic technique (constant current method) was used to electrochemically coat steel with the PANi layer from solution of aniline monomer with oxalic acid electrolyte, using an EG&G Princeton Applied Research Potentiostat/Galvanostat Model 273A provided with powerCorr software. The main parameter investigated was the effect of aniline concentration ranged from 0.1 to 0.3 M, other parameters were fixed at certain values as pH at 1.5, oxalic acid concentration 0.3 M, and current density of 20 mA was used for 20 minutes interval for all experiments. After each experiment, the PANi coated steel was rinsed with distilled water and methanol and left to dry.

2.2. Surface elemental composition analysis

Elemental analysis of the polyaniline 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 PANi coated steel against corrosion

Potentiodynamic examination (Tafel test) was used for the examination of the corrosion resistance of PANi 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 PANi 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.

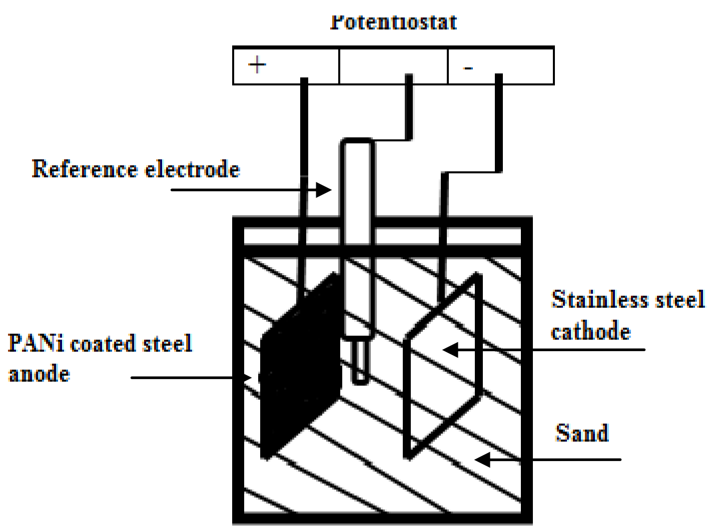

Figure 1. Experimental setup for potentiodynamic examination of the formed PANi layer

3. RESULTS AND DISCUSSIONS

3.1. Layer formation and characterization

3.1.1. layer formation using the galvanostatic technique

The galvanostatic technique was used for PANi layer formation, as shown in figure 2 the results show that the incubation period for polymer formation has been increased by increasing aniline concentration which may be ascribed to the slow transfer of electrolyte ions in the solution in case of higher aniline concentrations. Also it has to be mentioned that the layer formation potential decreased by increasing the aniline concentration that is indicates higher dissolution of iron ions which increase the conductivity of the solution and reduce the electrode potential.

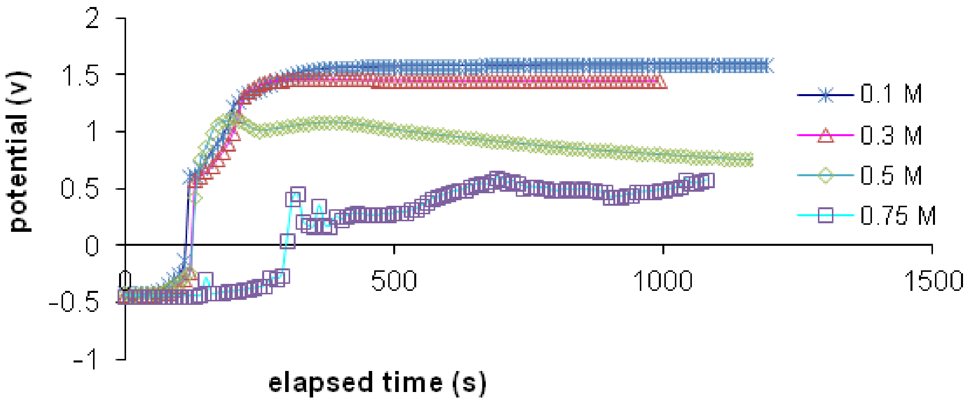

Figure 2. Potential vs elapsed time for polyaniline layer formation using different aniline concentrations

3.1.2. XPS analysis of the PANi coated steel

The XPS analysis of the formed layer as shown in figure 3 shows that there are two main peaks representing the occurrence of C1s atoms which appear clearly at 287ev and 283ev.

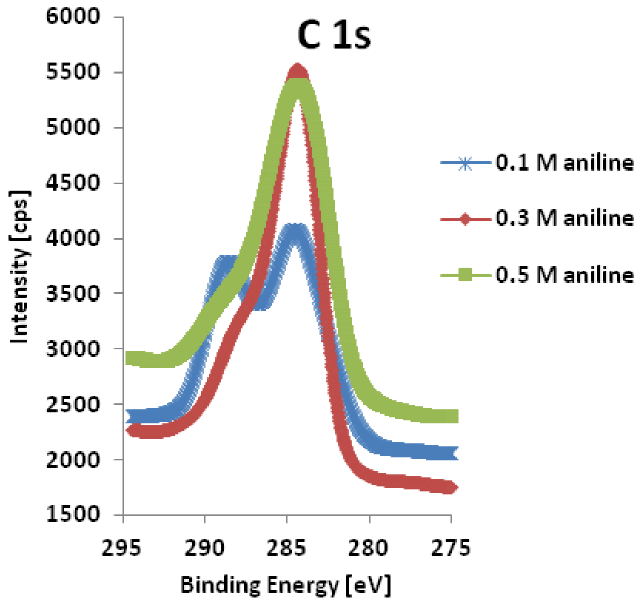

Figure 3. XPS Spectra of Carbon (C1s)PANi coated steel at different aniline concentrations.

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

Table 1 shows the atomic percentages of different elements forming the deposited PANi layer the results show that the percentage Fe 2P3/2 has been decreased by increasing the aniline concentration and that the % N1s for PANi layer formed at initial aniline concentration is the highest which indicates denser PANi layer (the main source of N 1s is from aniline).

Table 1. Atomic percentages of different elements forming the deposited PANi layer for different aniline concentration**.**

Element	% Atomic concentration of the layer at different aniline concentration		
	Aniline concentration		
	0.1 M	0.3M	0.5 M
C 1s	41.013	50.395	54.757
N 1s	1.439	2.987	2.18
O 1s	50.645	41.445	38.883
Fe 2p3/2	6.652	4.793	3.742

3.1.3. Determination of PANi layer thickness using Ellipsometry

Ellipsometric analysis was carried out for the PANi layer formed from a solution containing 0.5 M aniline, 0.3 M oxalic acid at solution pH of 1.5. As shown in figure 4 the results show that there are two main layers existing on the iron surface which are mainly iron oxalate and PANi layers, and that the thickness of oxalate layer is 26.143 (±1.972) nm and that of pani layer it is 419.26(± 7.082) nm. In addition the results show that the value of index n is 0.941and that of k is 1.829 for the deposited layer which indicates that the formed layer is much opaque and of higher light absorption capacity.

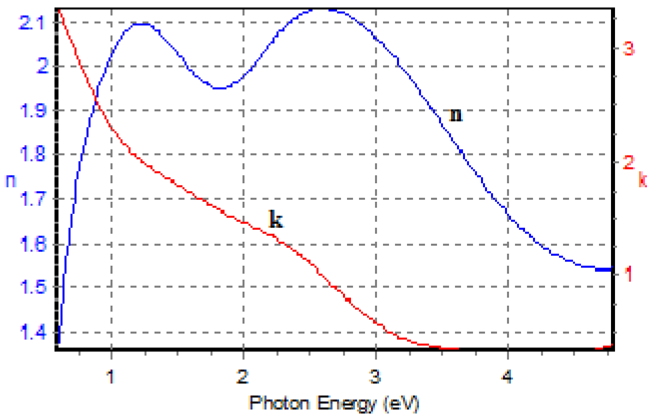

Figure 4. Ellipsometric analysis of the deposited PANi layer.

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

All the consequent analysis will be carried out using a PANi layer formed from a solution having the composition of 0.5 M aniline, 0.3 M oxalic acid at solution pH of 1.5 and 20 minute polymerization time. The formed layer characteristics can be summarized as follows:

%C=54.757, % N= 2.18, layer thickness= 419.26(± 7.082) nm PANi, index n=0.941and that of k is 1.829.

3.2.1. Effect of NaCl concentration

The potentiodynamic polarization test was carried out for finding out the corrosion current of the coupling of PANi coated steel with stainless steel while buried in sand containing different concentrations of NaCl. Figure 5 shows that the corrosion current of all test samples of PANi coated steel is less than that of uncoated steel. Figure 6 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 [15]

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 Tugoose [16] and Weizhen [17] suggested that in presence of chloride species the surface of the buried iron is gradually covered with insoluble corrosion products and then becomes further passivated. orAlso from figure 6 the results show that coating steel with PANi layer can improve the corrosion resistance of steel by a factor ranging from 1.68 to 1.88 depending on the salt concentration.

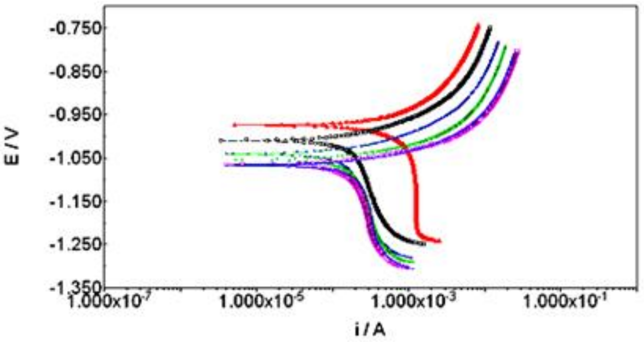

Figure 5. Potentiodynamic examination of buried PANi coated steel coupled with stainless steel vs Ag/AgCl in different NaCl concentrations.

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)

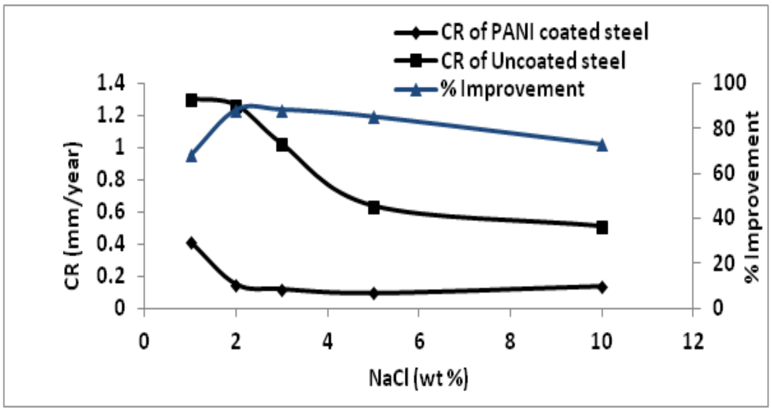

Figure 6. Corrosion rate of bare steel, PANi coated steel and the % Improvement in corrosion resistance when buried in sand containing different NaCl concentrations.

3.2.2. Effect of H_2SO_4 concentration

As shown in figure 7 the potentiodynamic polarization results show that the corrosion current of all test samples of PANi 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)

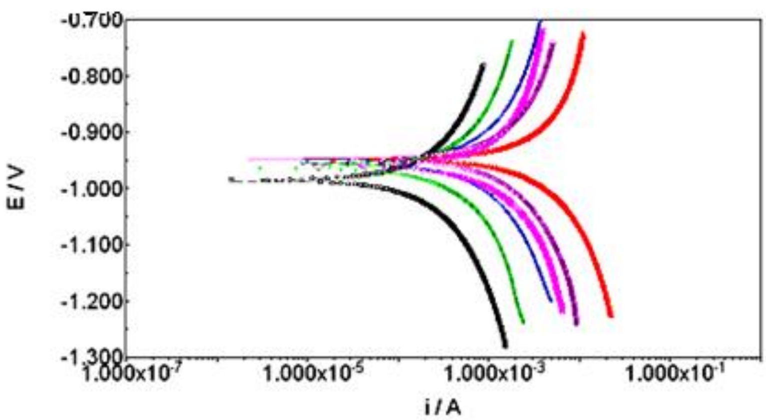

Figure 7. Potentiodynamic examination of buried PANi coated steel coupled with stainless steel vs Ag/AgCl reference at different H_2SO_4 concentrations. Buried bare steel at 1% H_2SO_4 red; buried PANi coated steel at (1% H_2SO_4 black; 2% H_2SO_4 blue; 3% H_2SO_4 green; 4% H_2SO_4 light magneta; 5% H_2SO_4 magneta color)

As shown in figure 8 the results show that coating steel with PANi layer has improved the corrosion resistance by decreasing the corrosion rate within the range from 1.58 to 1.9 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 [15], 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 PANi 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 PANi layer and consequently improved the corrosion resistance of steel. We have to clarify that the reduction in corrosion rate at higher pH can be explained by that at higher pH values the corrosion products can form passive layer which prevent diffusion of O2 to the iron surface and reduce the corrosion current this results are consistent with the results of Liang et al.[18]

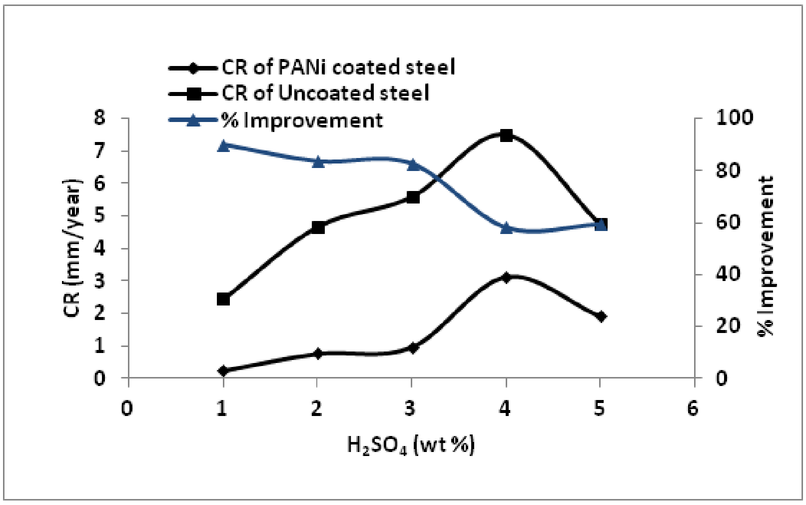

Figure 8. Corrosion rate of bare steel and PANi coated steel and the % Improvement in corrosion resistance when buried in sand containing different H_2SO_4 concentrations.

3.2.3. Effect of moisture content

As shown in figure 9 the Tafel polarization results show that the corrosion current of all test samples of PANi 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)

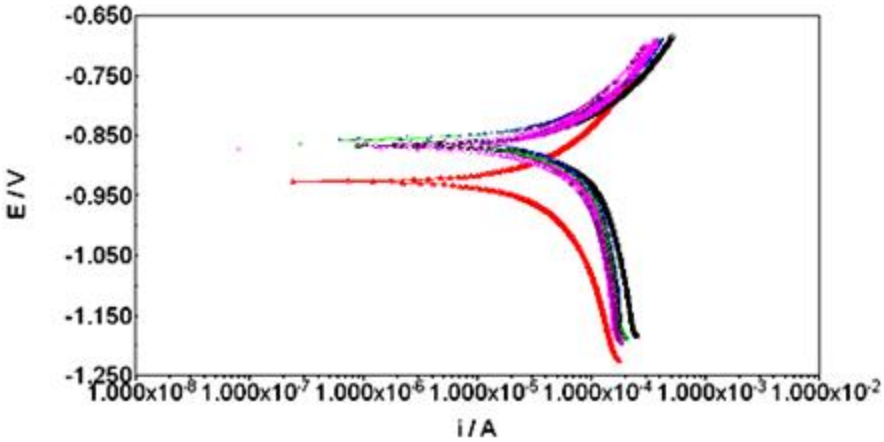

Figure 9. Potentiodynamic results of buried PANi coated steel coupled with stainless steel vs Ag/AgCl reference at different percentages of moisture. Buried bare steel at 1%H_2O red, buried PANi coated steel at (10% H_2Oblack; 20% H_2O blue; 30% H_2O green; 40% H_2O light magneta; 50% H_2O magneta color).

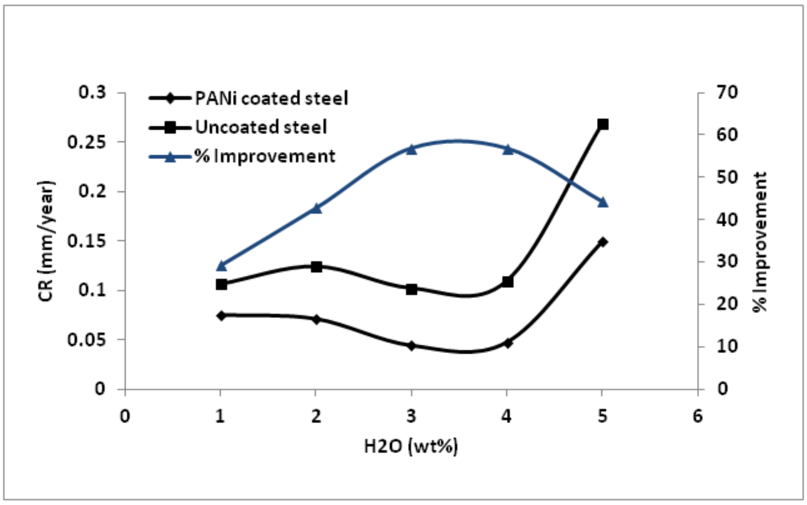

Figure 10. Corrosion rate of bare steel, PANi coated steel and the % Improvement in corrosion resistance for PANi coated steel when buried in sand containing different moisture content.

As shown in figure 10 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 PANi layer slowed down the anodic reaction to the extent that it controls the process. Presence of the PANi has improved the corrosion resistance by a factor ranging from 1.35 to 1.54 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 4 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 (PANi). The galvanostatic technique was used for forming the PANi layer for its simplicity and ease of industrial application using PG&G Potentiostat galvanostat A 273 Model. The layer formed was investigated for its composition using the X-Ray Photoelectron Spectroscopy (XPS), and for its thickness by using Ellipsometric analysis. The potentiodynamic technique (Tafel test) was used for investigating the corrosion resistance of the PANi 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 PANi layer can improve its corrosion resistance against NaCl, H_2SO_4 and water by a factor up to 1.88, 1.89 and 1.54 respectively. The above results show that coating steel with a layer of polyaniline can improve the life time when buried in sand containing different contaminant such as NaCl, H_2SO_4 and water.

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