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Developing of Polyaniline Coating on Rotating Steel Cylinder for Improving Its Corrosion Resistance

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This work investigates the possibility of using polyaniline (PANi) coating for improving the corrosion resistance of rotating cylinder subjected to saline solution. Galvanostatic technique was used for PANi layer formation under different conditions of current density, aniline monomer concentration, oxalic acid concentration and solution pH. The potentiodynamic technique was used for examination of PANi coated steel in corrosive medium composed of 3.5%NaCl under different rotating speed ranging from 200 to 1000 rpm. The results show that PANi layer formation at 0.5M aniline concentration, 0.3M oxalic acid concentration, current density of $20mA/cm^2$ and solution pH within the range from 1 to 2 has the better performance of the formed PANi layer against corrosion. The results show that coating steel with PANi layer can improve it corrosion resistance by a factor ranging from 1.2 to 1.8 compared to bare steel depending on the conditions at which the polymer layer was formed and the rotating speed.

Keywords: Polyaniline, corrosion resistance, rotating cylinders, smart coatings.

1. INTRODUCTION

In many industrial applications such as drugs and pharmaceuticals, food industry, and so sensitive applications, agitated vessels provided with rotating cylinders are considered as an important tool for not only mixing and homogenization of the reaction contents, but also as a tool for enhancing the rate of mass transfer and unit productivity. In such sensitive applications product poisonous by corrosion product from either vessels wall or from the rotating cylinders is a hazardous, which has to be considered in such vessels design and in its materials selection. Using the more noble precious metals such as stainless steel, silver or titanium coating is one of the methods used for construction for corrosion prevention and control. However, the possibility of poisonous by trace elements toxicity of these materials still present. In addition, these applications are considered of high fixed cost for the process plant economics.

In this direction a new smart coats of the so-called intrinsically conducting polymers (ICPs) such as polyaniline (PANi), polypyrrole (PPy), polythiophene, and others are now widely used [1-3]. In direction of improving the coat characteristics a double layer of more than one polymer or copolymerization of more than one monomer are now of great interest, such as double layer of polyaniline and polypyrrole and a copolymer of pyrrole and thiophene or copolymerization of pyrrole and furan are now of great interest [4-7]. Aqueous electrochemical polymerization has been found to be an attractive process for the production of primer coating on metal, which will replace hazardous method of traditional coating techniques and chromate pretreatment. The advantages of aqueous electropolymerization are: (1) the aqueous solutions used are environmentally favorable, (2) the technique combines the formation of polymer and deposition of coating in one process and this process can be easily automated, (3) the production cost is relatively low and (4) the properties of the coatings can be controlled by varying the electrochemical parameters. In recent years, polypyrrole and polyaniline coatings have been tried on steel, stainless steel, copper, aluminum, and others [8-17]. There are two methods to deposit an electroactive polymer on a metal surface, namely, electrochemically or chemically [18]. From the viewpoint of application convenience, electrochemical deposition is not recommended on large structures such as ships, bridges and pipelines [19]. In these cases, chemical deposition is the only feasible alternative. Most of previous studies were concerned with simple geometries such as sheets, rods and others, on the lab scale, but none of them was interested in coating rotating objects or measuring its corrosion stability against different conditions.

The aim of the present work is to investigate the application of the smart coats, such as Polyaniline(PANi), for coating rotating cylinders made of mild steel and measuring its stability against corrosion. Rotating cylinder is the main part of agitated vessels which can find many industrial applications such as pharmaceuticals, food and chemicals industry. Galvanostatic technique was used for PANi layer formation at different conditions while potentiodynamic one was used for examination of the performance of the formed PANi layer against corrosion under different rotating speed in 3.5% NaCl.

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 rod of 2mm diameter and 30 cm long. 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 1.0M, current density ranged from 10 to 50mA/cm^2, oxalic acid concentration that ranged from 0.1 to 1.0M and solution pH which ranged from 1 to 4. The electropolymerization time was fixed at 20 minutes interval for all experiments. After each experiment, the PANi coated steel was rinsed with distilled water and methanol and left to dry. Only 5cm of the rod length was coated with the PANi layer.

2.3. Examination of the performance of the PANi coated steel against corrosion

Potentiodynamic examination (Tafel test) was used for the examination of the corrosion resistance of PANi coated steel when rotating at 3.5% NaCl solution with different rotational speed ranged from 200 to 1000rpm. A variable speed D.C. motor of 0.33hp was used for changing the rotational speed of PANi coated steel. As shown in figure 1 the 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. The % improvement in corrosion resistance was evaluated with reference to bare steel subjected to the same conditions of rotational speed and NaCl concentration. The % improvement was calculated according to the following equation:

$$\%Improvement = \frac{C_{Rb} - C_{Rp}}{C_{Rb}} * 100$$

Where C_{Rb} and C_{Rp} are the corrosion rate of bare and PANi coated steel respectively.

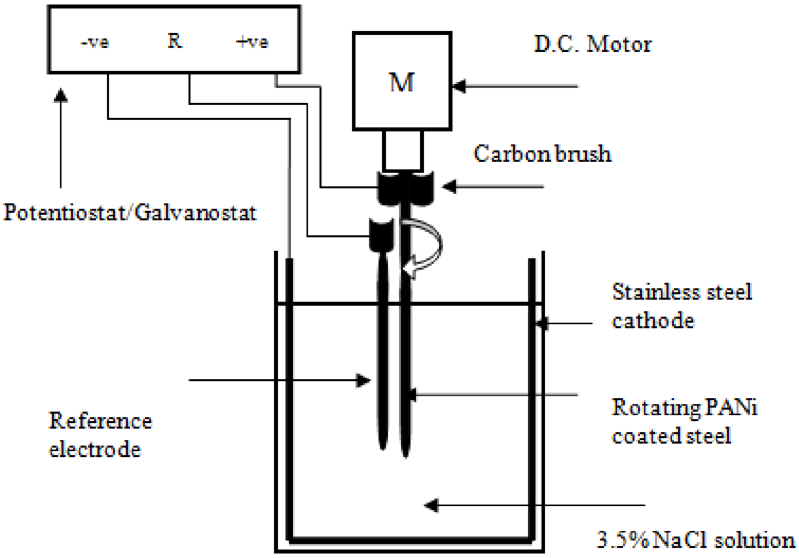


Figure 1. Experimental setup used for potentiodynamic examination of PANi coated steel in 3.5% NaCl at different rotational speed.

3. RESULTS AND DISCUSSIONS

3.1. Effect of aniline concentration

Polyaniline layer was formed under different aniline concentrations using the galvanostatic technique. As shown in figure 2 the results show that the incubation period has been increased by increased by increasing the aniline monomer concentration which may ascribed to the slow transfer of aniline ions and/or dissolved Fe^{+2} ions in case of higher aniline concentration in the solution, as presence of aniline can increase the solution viscosity and that decrease the diffusion of ions in the solution. In addition it is clear that the cell potential measured against Ag/AgCl reference electrode has been decreased by increasing the aniline concentration which confirm that the layer formed has low resistance i.e the coverage of iron surface is still incomplete for higher aniline concentration.

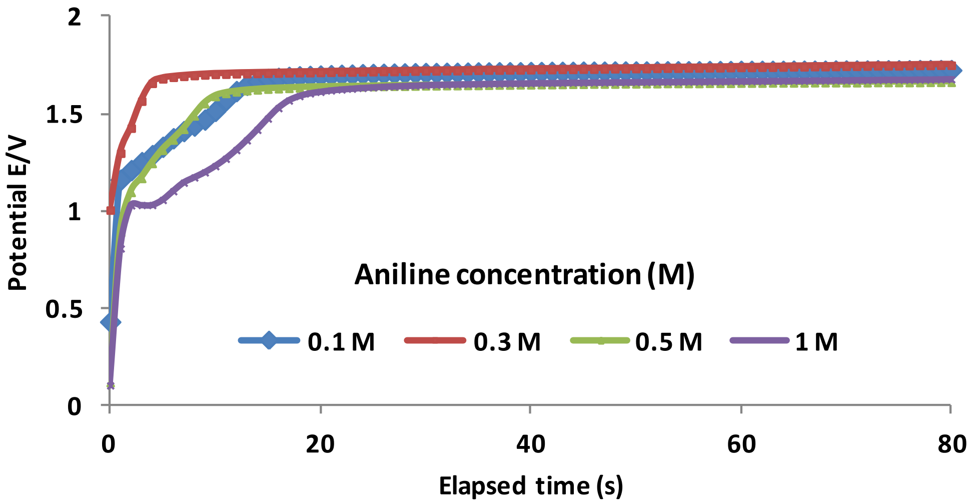
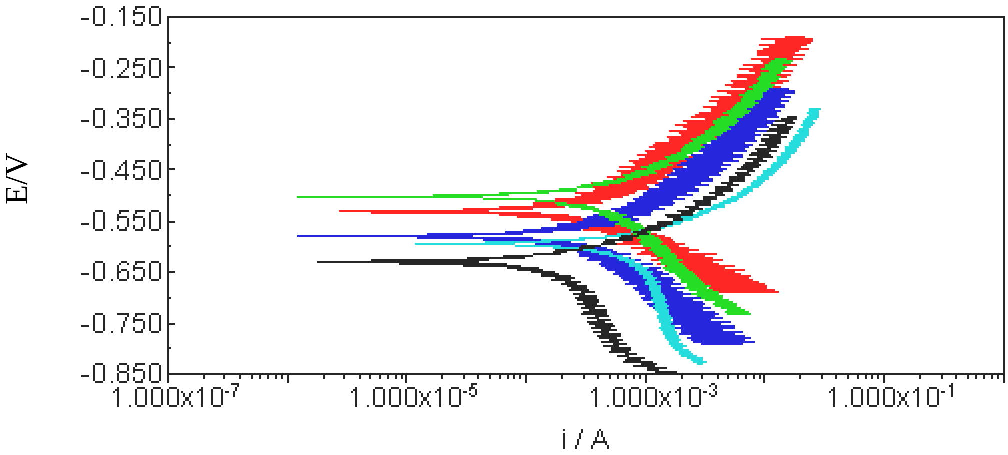


Figure 2. Potential vs elapsed time for different aniline concentration, oxalic acid concentration=0.3M, time=1200s, current density=20mA/cm^2, pH=1.5.

The formed PANi layers were examined for its corrosion resistance using the potentiodynamic technique under different rotational speed in 3.5% NaCl solution. Figure 3 shows the results of potentiodynamic test for different rotational speed.

The performance of the PANi layer was evaluated against the performance of bare steel in 3.5% NaCl solution. As shown in Figure 4 the results show that the percentage improvement in corrosion resistance has been increased by increasing the aniline concentration up to 0.5M. increasing the aniline concentration above this limit approximately has no effect on the layer performance. This result is consistent with the finding of El-Shazly et al [20,21] who found that increasing the monomer concentration slows down the electropolymerization process and less effective layer is formed.



Red is 200 rpm, Blue is 400 rpm, Green is 600 rpm, Oily is 800 rpm, Black 1000 rpm

Figure 3. Potentiodynamic examination of the formed PANi layer at different rotational speed at 0.3M aniline, 0.3m oxalic, 20mA/cm^2 and 20min.

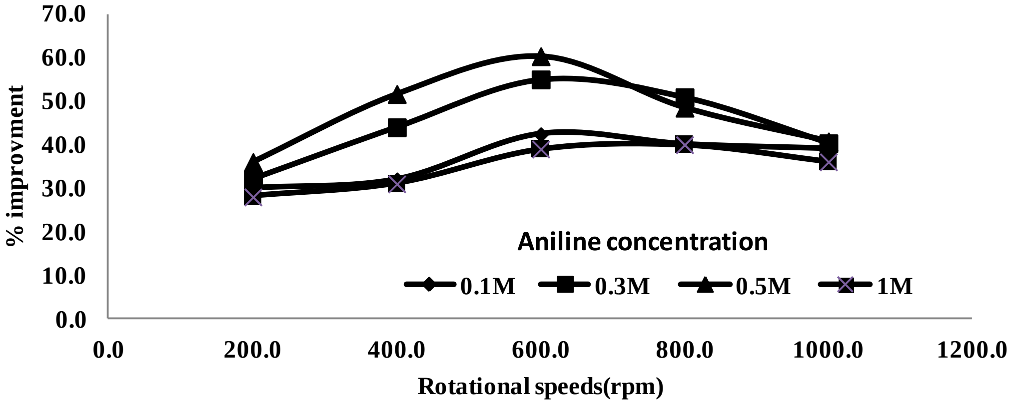


Figure 4. Percentage improvement vs rotational speed at different aniline concentrations in 3.5%NaCl.

For the effect of rotational speed figure 4 shows that the percentage improvement has been increased by increasing rotational speed up to 600 rpm. This results can be ascribed to the fact that increasing rotational speed can increase the corrosion rate of bare steel to higher extent according to the following reactions [22]:

At the anode : $Fe \rightarrow Fe^{+2} + 2e$ (1)

At the cathode: $H_2O + 1/2\ O_2 + 2\ e \rightarrow 2OH^-$ (2)

Covering steel with PANi layer can slowdown the anodic reaction and improves its corrosion resistance. It has to be clarified that increasing the rotational speed above 600rpm can affect performance of the PANi layer and decrease its efficiency in improving the corrosion resistance, which can be ascribed to the fact that increasing rotational speed will certainly increase the shear rate on the rotating PANi coated steel that can affect its adhesion to the steel shaft and decrease its efficiency. It has to be clarified that coating with PANi layer can improve its corrosion resistance by a factor ranging from 1.2 to 1.6 depending on rotational speed.

3.2. Effect of current density

As shown in figure 5 the results show that the incubation period for polymer formation has been decreased by increasing applied current density, which may be ascribed to the fact that increasing current density will increase the amount of Fe^{+2} dissolved per unit time according to Faraday'a law [22],

$$m = \frac{eIt}{96500}$$

where m is the amount of dissolved iron (g), e is the equivalent weight of iron(g/mol), I is the applied current (A) and t is the time in (s). increasing the amount of available Fe^{+2} present at the solution will speed up the rate of iron oxalate formation which is considered as the binding layer between the iron surface and the polymer and that will decrease the incubation period . Also it has to be mentioned that the layer formation potential increased by increasing the applied current which confirm the layer formation that reduces the conductivity of iron surface and increase the resistance to ion transfer which increase the overall cell potential (measured against Ag/AgCl reference electrode).

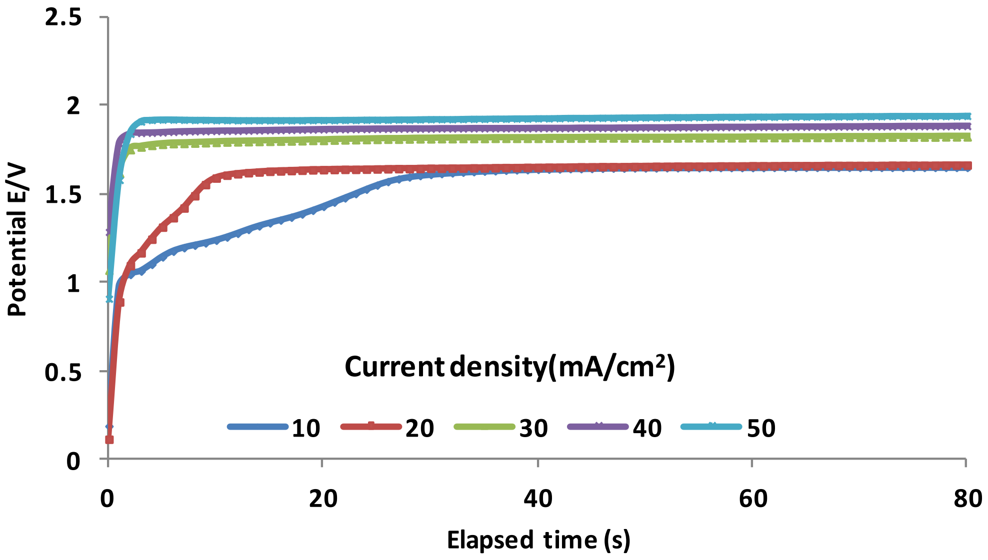
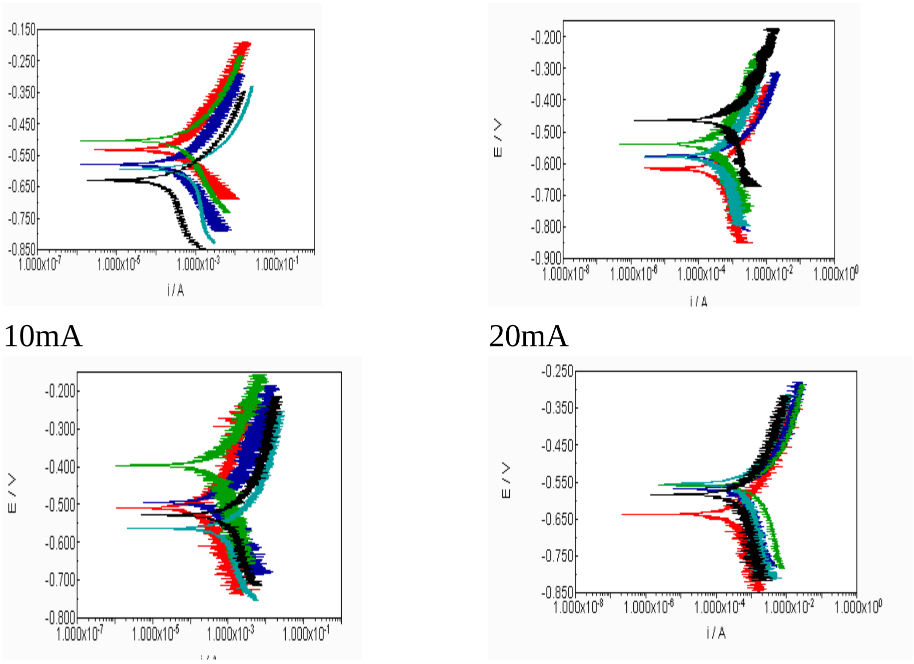


Figure 5. Potential vs elapsed time for different applied current density oxalic acid concentration=0.3M, time=1200s, aniline concentration=0.5M, pH=1.5.

Figure 6 shows the results of examination of the formed PANi layers at different current densities for its corrosion resistance in 3.5%NaCl solution for different rotational speed ranging from 200 to 1000rpm.



10mA

20mA

30 mA

40 mA

Red is 200 rpm, Blue is 400rpm, Green is 600rpm, Oily is 800rpm, Black 1000 rpm

Figure 6. potentiodynamic results for the % improvement for PANi layer formed at different current density at 3.5%NaCl.

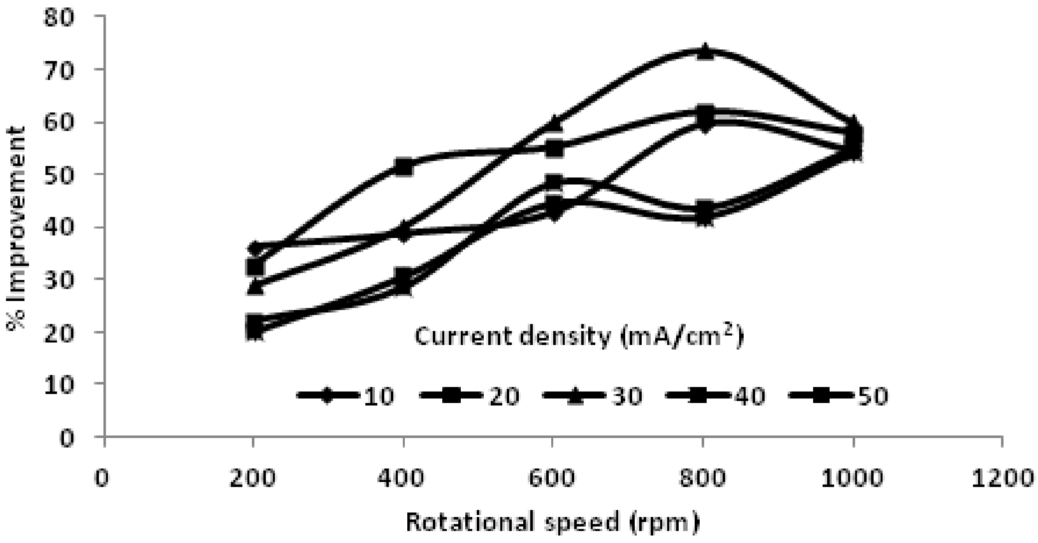


Figure 7. Percentage improvement vs rotational speed for different current densities

As shown in figure 7 the results show that the percentage improvement has been increased by increasing the current density within the range from 20 to 40 0mA. Increasing the current density up this range causes reduction in the percentage improvement. The above results can be ascribed to the fact that increasing the current density will oxidize the formed layer and reduce its stability on the steel surface to certain level which reduces its efficiency in corrosion prevention and hence reduces the percentage improvement. On the other hand it is clear from figure 7 that the percentage improvement has been increased by increasing the speed of rotation up to 800 rpm for PANi layer formed at different current densities. We have to clarify that coating steel with PANi layer has improved its corrosion resistance within the range from 1.2 to 1.7 depending on both current density and rotational speed.

3.3. Effect of oxalic acid concentration

As shown in figure 8 the results show that oxalic acid concentration of 0.3M has the lower induction period required for the electropolymerization reaction to take place these results are consistent with previous investigations [20, 21]. The above results can be ascribed to that increasing the oxalic acid concentration above certain limit will reduce the diffusivity of Fe^{+2} ions and increase anodic polarization which increase the time required for polymerization to take place. Also reducing oxalic acid concentration below certain level will reduce the amount of available oxalate ions which reduce the driving force for the reaction of iron oxalate formation. Iron oxalate is the binding layer between the iron surface and the PANi layer.

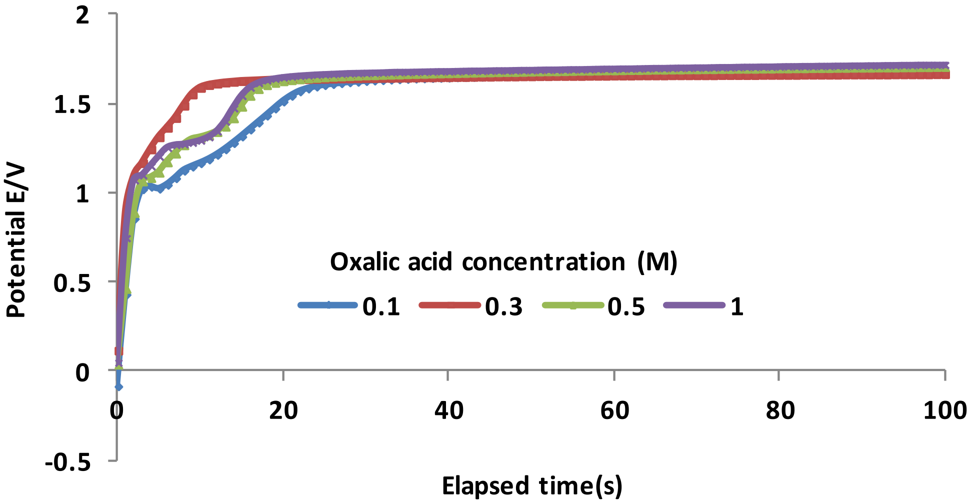
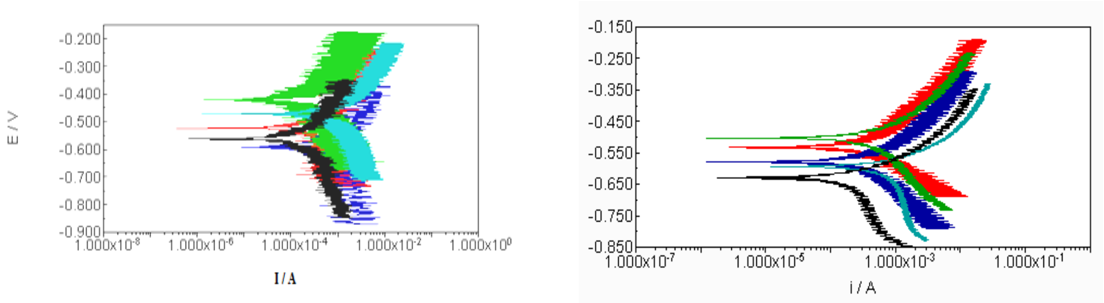
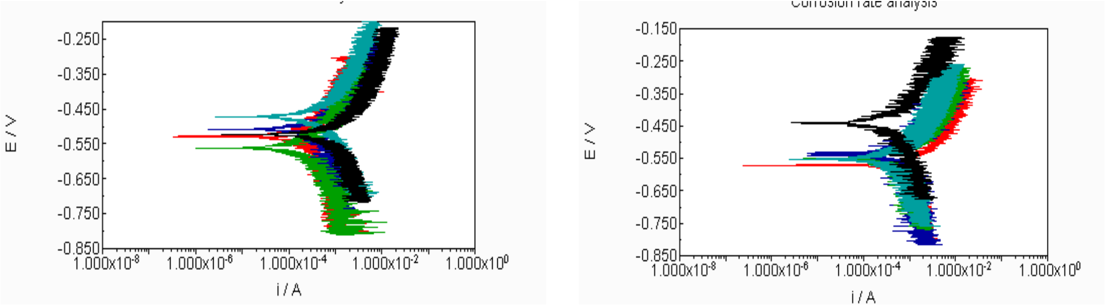


Figure 8. Potential vs elapsed time for different oxalic acid concentrations, current density= 20mA/cm^2, time=1200s, aniline concentration=0.5M, pH=1.5.

The potentiodynamic examinations for the PANi layer formed at different oxalic acid concentrations are shown in figure 9. The range of oxalic acid used was from 0.1 to 1.0M.



(a) 0.1 M oxalic acid (b) 0.3 M oxalic acid



(c) 0.5 M oxalic acid (d) 1 M oxalic acid

Red is 200 rpm, Blue is 400rpm, Green is 600rpm, Oily is 800rpm, Black 1000 rpm

Figure 9. Potentiodynamic results for the % improvement for PANi layer formed at different oxalic acid concentration in 3.5%NaCl.

Figure 10 shows that the percentage improvement has been increased with oxalic acid concentration up to 0.3M. increasing the acid concentration above this limit approximately has no effect on the performance of the PANi layer formed. The above results can be attributed to the fact that at a given current density the amount of dissolved Fe^{+2} is limited by Faraday's law, this amount will react with the certain amount of oxalic acid, increasing the oxalic acid above this definite amount will not affect the process. On the other hand figure 10 show that the formed PANi layer can improve the corrosion of steel by a factor ranging from 1.3 up to 1.6 depending on oxalic acid concentration and rotational speed.

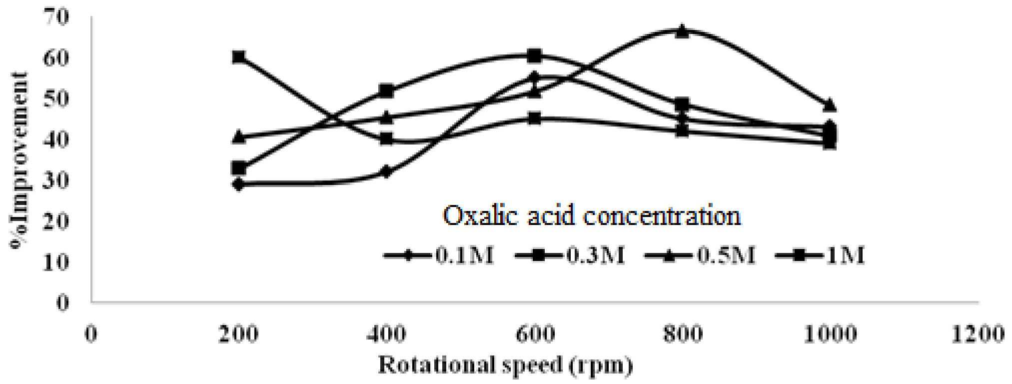


Figure 10. Percentage improvement vs rotational speed for different oxalic acid concentration.

3.4. Effect of solution pH

Figure 11 shows that forming PANi layer at solution pH of 3 has the lower induction period and higher formation potential.

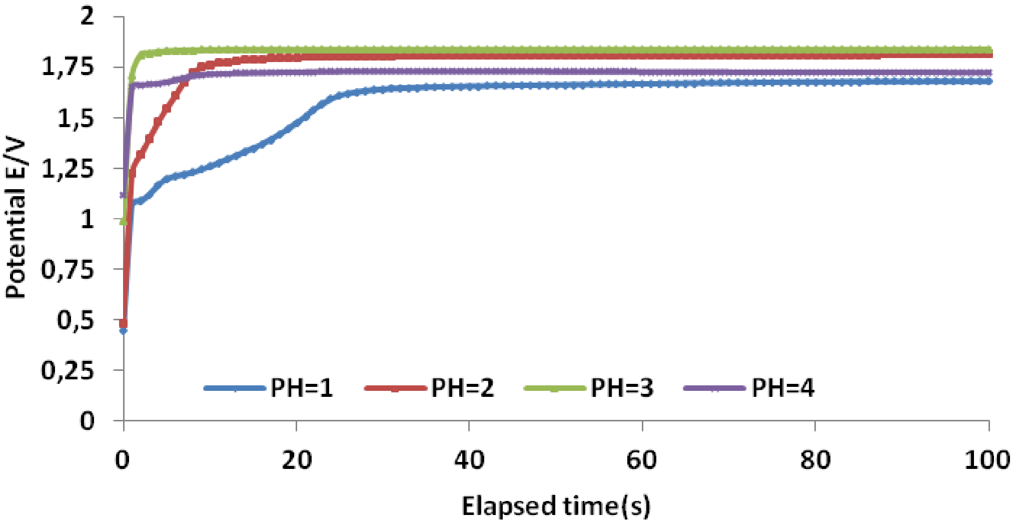
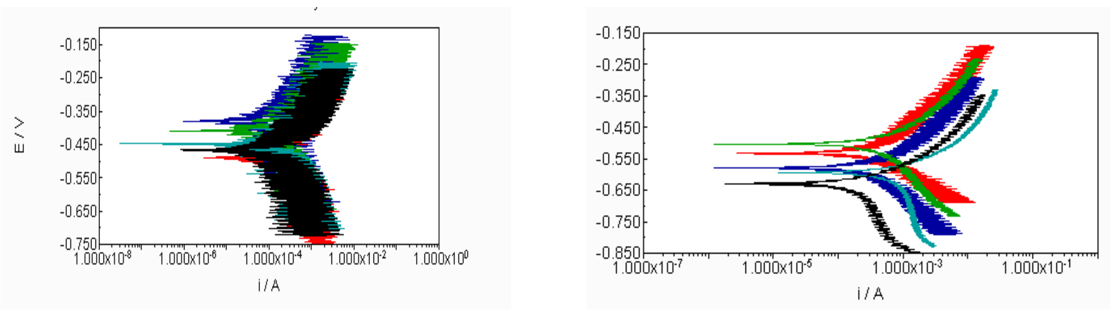
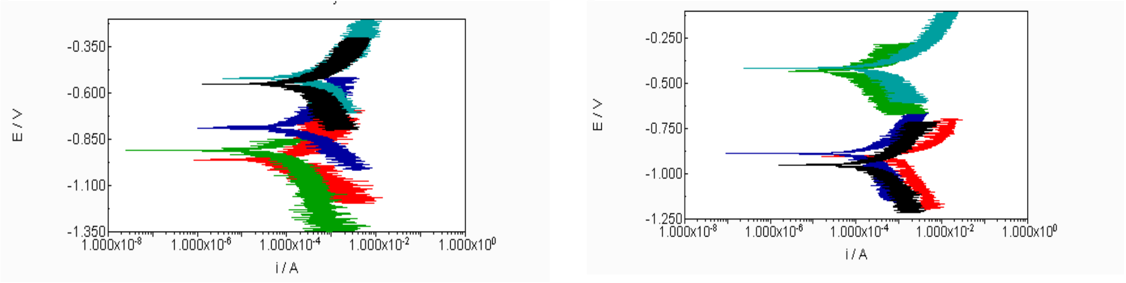


Figure 11. Potential vs elapsed time for different solution Ph, oxalic acid concentration=0.3M, current density= 20mA/cm^2, time=1200s, aniline concentration=0.5M.



pH =1.0 pH =1.5



pH =3 pH =4

Red is 200 rpm, Blue is 400rpm, Green is 600rpm, Oily is 800rpm, Black 1000 rpm

Figure 12. potentiodynamic results for the % improvement for PANi layer formed at different solution pH.

The potentiodynamic examination for the PANi layer formed at different solution pH is shown in figure 12. The pH range studied was within the range from 1.0 to 4.0. The percentage improvement data are shown in figures 13. The results show that the percentage improvement has been increased with pH range from 1 to 3. Increasing the solution pH above this limit decreases the performance of the formed PANi layer against corrosion. The above results can be attributed to the fact that the solubility of aniline decreases with increasing the solution pH which reduce the amount of aniline available in the solution for the electropolymerization reaction[23].

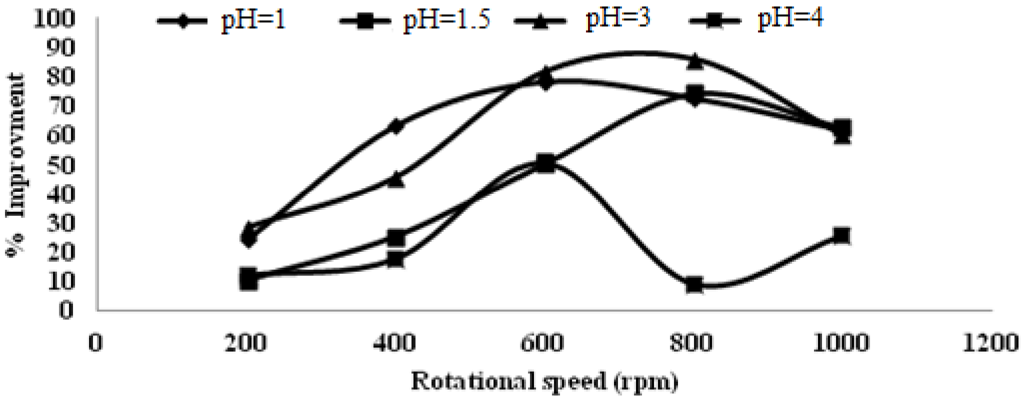


Figure 13. Percentage improvement vs rotational speed for different solution pH.

Figure 13 show that coating rotating steel with polyaniline layer can improve its corrosion resistance compared to bare steel by a factor ranging from 1.1 to 1.85 depending on the solution pH and the rotational speed.

4. CONCLUSIONS

Investigation for the possibility of using polyaniline smart coating for improving the corrosion resistance of rotating steel shafts in corrosive medium such as NaCl was carried out. Polyaniline layer was formed under different conditions . The results show that PANi layer formation at 0.5M aniline concentration, 0.3M oxalic acid concentration, current density of 20mA/cm^2 and solution pH within the range from 1 to 2 has the better performance of the formed PANi layer against corrosion. For examination under rotation conditions, the results show that coating steel with PANi layer can improve it corrosion resistance by a factor ranging from 1.2 to 1.8 compared to bare steel depending on the conditions at which the polymer layer was formed and the rotation speed**.**

This work can find applications in agitated vessels that are used in corrosive NaCl mediums in food and pharmaceutical and other different industries.

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