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Investigation for the Possibility of Improving the Reinforced Concrete Corrosion Resistance Using Polyaniline Coated Steel

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This work investigates the possibility of improving the corrosion resistance of reinforced concrete against corrosive mediums mainly represented by chloride and sulfate ions by using polyaniline (PANi) coating. The polyaniline layer was formed using the galvanostatic technique and investigated for its composition by using X-Ray Photoelectron Spectroscopy (XPS). The potentiodynamic technique was used for investigating the corrosion resistance of the PANi coated steel while coupled with stainless steel and used for reinforcing a layer of concrete, containing different concentrations of corrosive materials such as NaCl and H_2SO_4 the corrosion current was measured against Ag/AgCl reference electrode. The main variables investigated were the initial concentration of both Cl^- and $SO4^{-2}$ and the time interval from 0 to 28 days (initial hardening period). The results showed that using polyaniline coating has improved the corrosion resistance of reinforced concrete against Cl^- by a factor ranging from1.10 to 1.90 and by a factor ranging from 1.30 to 1.60% against $SO4^{-2}$ of its value compared to uncoated steel depending on initial concentration of Cl^- and $SO4^{-2}$ respectively. In addition the results showed that Cl^- is superior to SO_4^{-2} in causing corrosion of steel. The corrosion rate of steel subjected to Cl^- ions is higher than that of SO_4^{-2} by a factor of 1.688 and 1.815 for both bare and polyaniline coated steel respectively.

Keywords: Polyaniline, corrosion resistance, reinforced concrete, smart coating.

1. INTRODUCTION

Concrete installations deterioration is considered one of the main problems facing the construction industry worldwide. This phenomenon of deteriorating concrete cases principally to rust rebar due to chloride ion which permeates steel which is mainly arrived through concrete components, especially non-washed gravel. Finance reform deterioration of concrete resulting from rust in road installations in the world by about $ billions annually [1-3]. Several techniques and materials have been used to reduce the harmful effects of rust rebar. Some studies suggested that steel painted with epoxy could be of better performance when using the following materials: concrete with galvanized steel, or concrete exposed by water repelling agents [4]. The epoxy coated steel has been used in many countries in the world for more than two decades to increase the resistance ability of concrete installations for aggressive environments. Nevertheless, there were different views and conflicting about using these epoxy coated steel in concrete platforms, whether in USA or in Saudi Arabia [5, 6]. There are a number of general points that have not been agreed on this epoxy coated steel, including: lack of strength linking iron surface coated with smooth epoxy and the concrete [7,8] and the impact of the presence of small holes resulting from the process of developing the iron or damaged paint coatings arrange and stack rebar in building blocks. The first problem can be solved simply by compensating the smooth surface by increasing the length of steel used, the second problem, is still disputed point between researchers because no laboratory results and long-term farming on the performance of these gilded epoxy coated steel, especially with the existence of damage or holes in drawing up this steel in chloride salt-contaminated concrete. 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. Polyaniline (PANI) and its derivatives [9, 10] are among the most frequently studied ICPs used for corrosion protection. In addition, the use of PANI for corrosion protection of metals has been of wide interest since the works by DeBerry [11] and Beck et al. [12] reporting that electroactive coatings of the PANI could provide adequate protection against corrosion of stainless steels and iron sheets, respectively. Ever since, numerous studies have been published in which various ICPs in different configurations were evaluated for corrosion protection of different metals and alloys: mild steel [13-15], stainless steel [16-19], iron [20-23], copper [24], zinc [25, 26], aluminum [27], and other metals [28]. Preliminary results indicated that the structure and properties of polyaniline coatings formed on steel vary with the process conditions. The longer the passivation period, the better is the quality of the coatings.

The aim of the present work is to investigate the main parameters controlling the application of polyaniline coating on steel that will have application in concrete structures, in order to increase its life time and reduce the cost of protection. Electrochemical technique was used for the deposition of polypyrrole layer using galvanostatic mode of operation. The PANi coated steel in concrete will be investigated in different contaminant mediums such as chloride and sulphate ions.

2. EXPERIMENTAL WORK

2.1. Electropolymerization of aniline

Aqueous electropolymerization of aniline was performed in one-compartment cell. The working electrode was made of 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 current density ranging from 5 to 20 mA, other parameters were fixed at certain values as pH at 1.5, oxalic acid concentration 0.3 M, and aniline concentration of 0.5 M were 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 concrete reinforced with PANi coated steel against corrosion

Potentiodynamic examination was used for the examination of the corrosion resistance of PANi coated steel when coupled with stainless steel while buried in a layer of concrete. The concrete reinforced with the PANi coated steel was formed in a mold of 10*10*10 cm dimensions using a mixture of gravel, sand and cement in the proportion that gravel to cement in the ratio 1.6:1 while cement was about 350 kg/m^3 and water to cement in the ratio 0.45:1 in all concrete forms. Every concrete sample was contaminated with different materials as sodium chloride salt with different concentrations ranging from 0.5 to 2.5 wt% based on cement weight. Different H_2SO_4 concentrations with different concentrations ranging from 1 to 5 wt% based on cement weight. All samples were left for 14, 21 and 28 days for hardening before examination. Before each run the formed layer was investigated for its elemental composition chemical using the X-Ray Photoelectron Spectroscopy (XPS). 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.

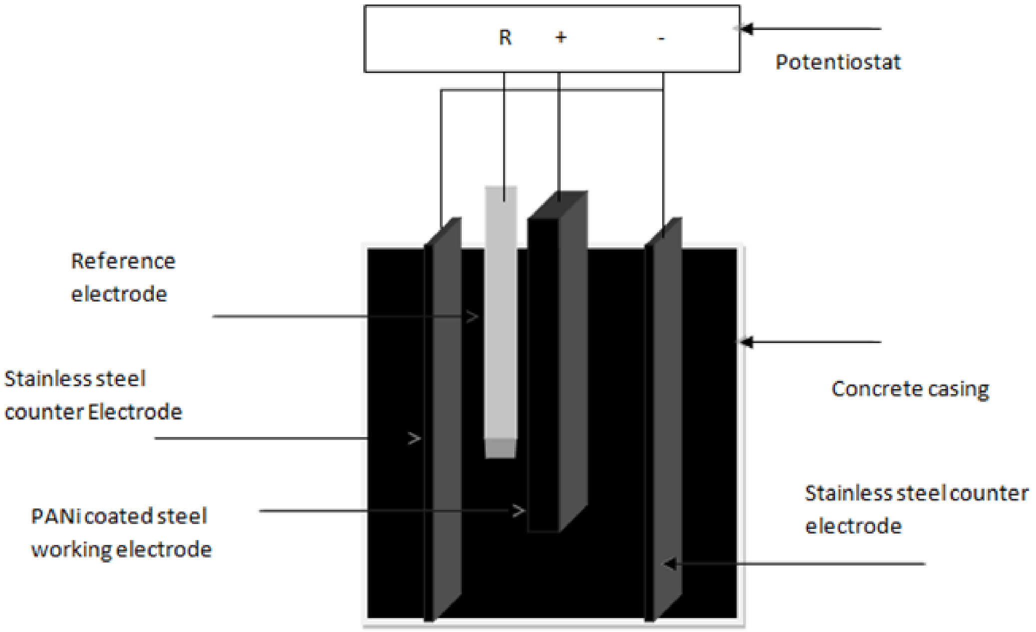
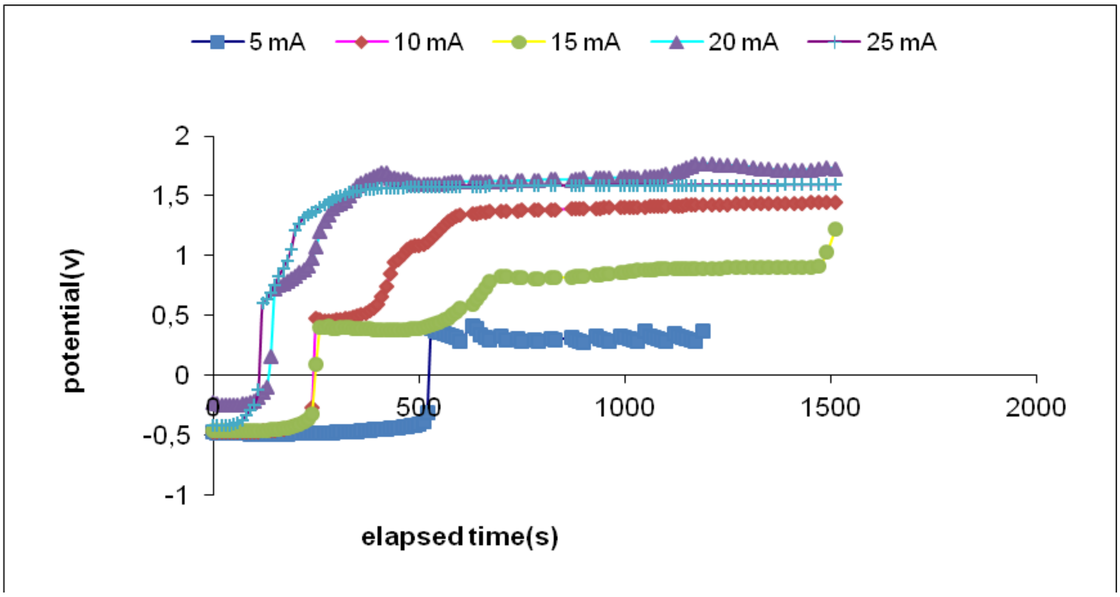


Figure 1. Experimental setup for potentiodynamic examination of the formed PANi layer

3. RESULTS AND DISCUSSIONS

3.1. Layer formation and characterization

3.1.1. Layer formation using the galvanostatic technique



Stainless steel cathode, 0.5 M aniline, 0.3 M oxalic acid, pH=1.5

Figure 2. Potential vs elapsed time for PANi layer formation under different current.

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 decreased by increasing applied current which may be ascribed to the fact that increasing current will increase the amount of iron dissolved according to faradays low [29], which will accelerate the formation of iron oxalate which is considered the binding layer between iron surface and the PANi layer. Also it has to be mentioned that the layer formation potential increased by increasing the current used which can be attributed to higher thickness of layer formed which increase polarization and consequently the potential of the cell.

3.1.2. XPS analysis of the PANi coated steel

The XPS analysis of the formed PANi layer at different applied current as shown in figure 3 shows that there are two main peaks representing the occurrence of C1s atoms which appear clearly at 288ev and 285ev.

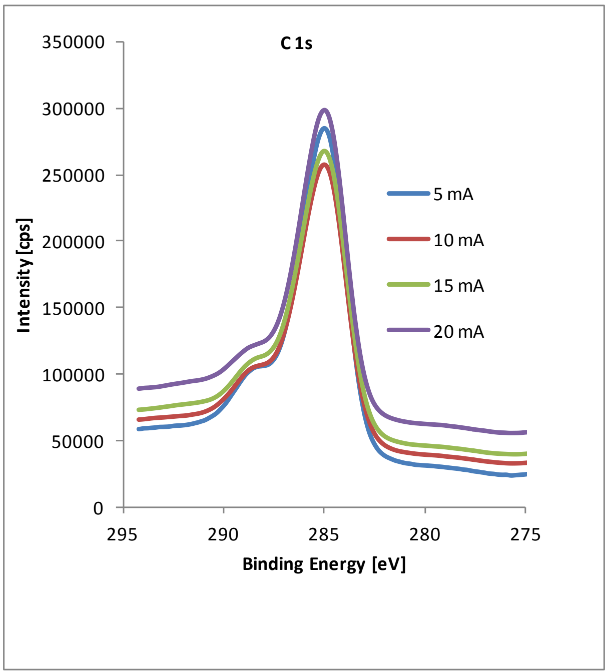


Figure 3. XPS Spectra of Carbon (C1s)PANi coated steel at different applied current.

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 oxalate which precipitates on the anode surface and forming a binding layer between the iron surface and the polyaniline layer. The first peak (at 288ev) indicates the formation of oxalate layer while the second (at 285ev) is due to the outer polyaniline layer.

Table 1 and figure 4 show the atomic percentages of different elements forming the deposited PANi layer. The results show that the percentages of both C1s and N1s for PANi layer formed at 20 mA are the highest which indicates denser PANi layer at higher current density (the main source of N1s is aniline).

Table 1. Atomic percentages of different elements forming the deposited PANi layer for different applied current**.**

Name	% Atomic concentration			
	5 mA	10 mA	15 mA	20 m A
C 1s	66.49125	68.65977	69.53843	71.79041
N 1s	4.312517	5.112014	5.500299	5.774126
O 1s	27.21826	25.34685	24.07083	21.51011
Na 1s	0.389334	0.169097	0.187355	0.15676
Fe 2p3/2	1.588637	0.712263	0.70308	0.702594

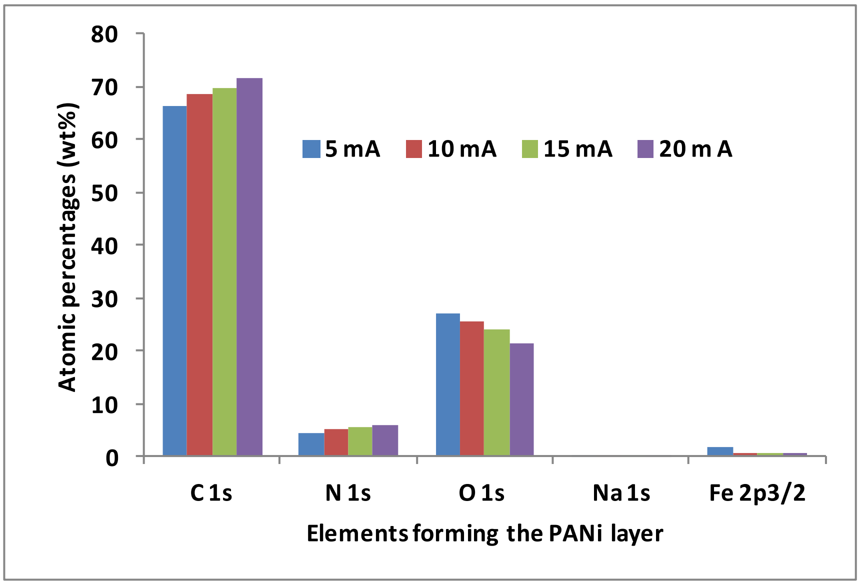


Figure 4. Atomic percentages for main elements forming the PANi layer at different current.

3.2. Study for the performance of PANi coated steel in reinforced concrete against corrosion

All the subsequent 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 , 20 minute polymerization time and applied current of 20 mA. The formed layer composition is %C1s =71.79, % N1s = 5.77, O1s = 21.5

3.2.1. Effect of NaCl Concentration

Figure (5) shows the results of potentiodynamic examination test in different concentration of NaCl% in concrete after 14 days. The results show that the corrosion rate has been increased by increasing the NaCl concentration within the range from 0.5 to 2.5 wt%. Same figures were obtained for different time intervals of 0, 14, 21 and 28 days for both uncoated steel (bare steel) and PANi coated steel. The results are shown in figure (6) for bare steel and in figure (7) for PANi coated steel. The results show that for both bare steel and PANi coated steel, the corrosion rate has been increased by increasing the NaCl concentration and by increasing the time interval. The above results can be attributed to the fact that the passivity provided by the alkaline conditions in concrete can be destroyed by the presence of chloride ions, even though a high level of alkalinity remains in the concrete. The chloride ion can locally depassivate the metal and promote active metal dissolution [30, 31]. Chlorides react with the calcium aluminate (C_3A) and calcium aluminoferrite in the concrete to form insoluble calcium chloroaluminates and calcium chloroferrites in which the chloride is bound in non-active form; however, the reaction is never complete and some active soluble chloride always remains in equilibrium in the aqueous phase in the concrete. It is this chloride in solution that is free to promote corrosion of the steel. At low levels of chloride in the aqueous phase, the rate of corrosion is very small, but higher concentration increases the risks of corrosion. This detrimental effect of Cl^- species which become incorporated into the passive film, leading to its local dissolution or to the development of conductive paths. Once initiated, corrosion propagates autocatalytically according to the generalized reaction:

$$M^{+n} + nH_2O + nCl^- \rightarrow M(OH)_n + nHCl \qquad (1)$$

resulting in acidification of the active region and corrosion at an accelerated rate (M^{+n} and M are the ionic and metallic forms of the corroding metal)[30-33].

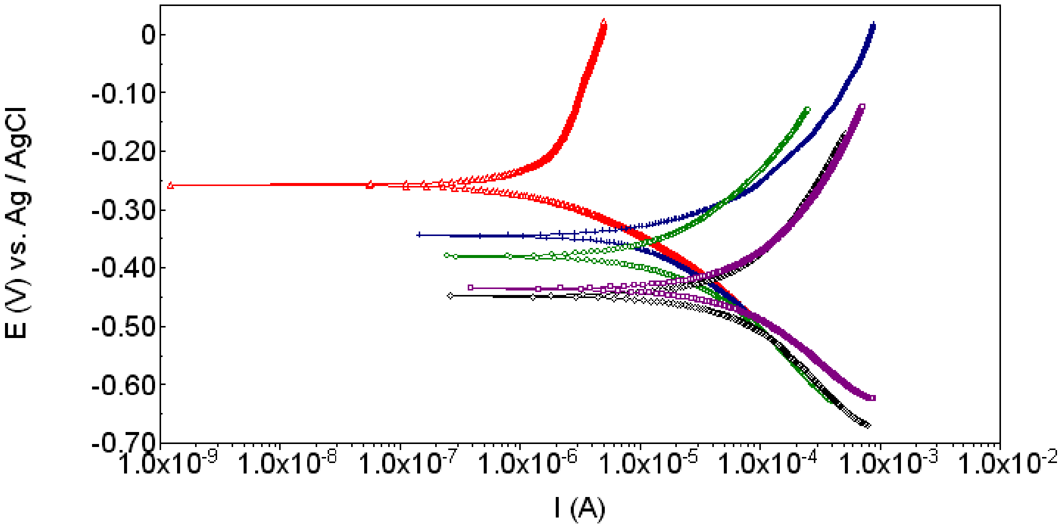


Figure 5. Tafel test results for PANi coated steel reinforced concrete with different NaCl concentrations after 14 day. 0.5% NaCl red line, 1.0 % NaCl blue line, 1.5 % NaCl Green line, 2.0 % NaCl black line, 2.5% NaCl magenta line

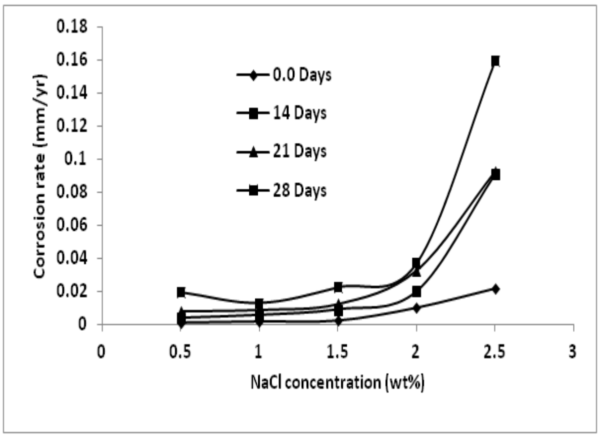


Figure 6. Corrosion rate of bare steel reinforced concrete vs NaCl concentration at different time intervals

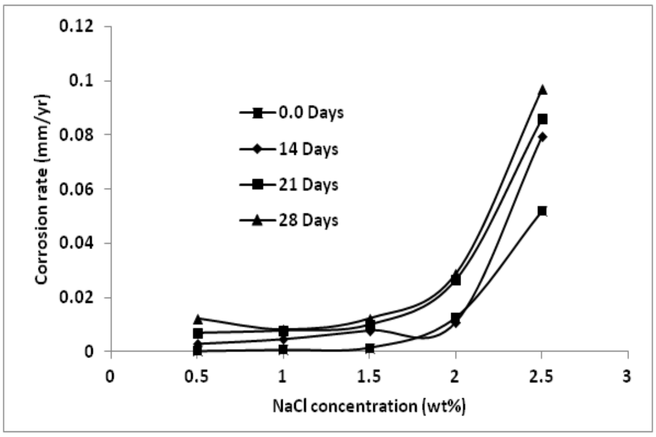


Figure 7. Corrosion rate of PANi coated steel reinforced concrete vs NaCl concentration at different time intervals.

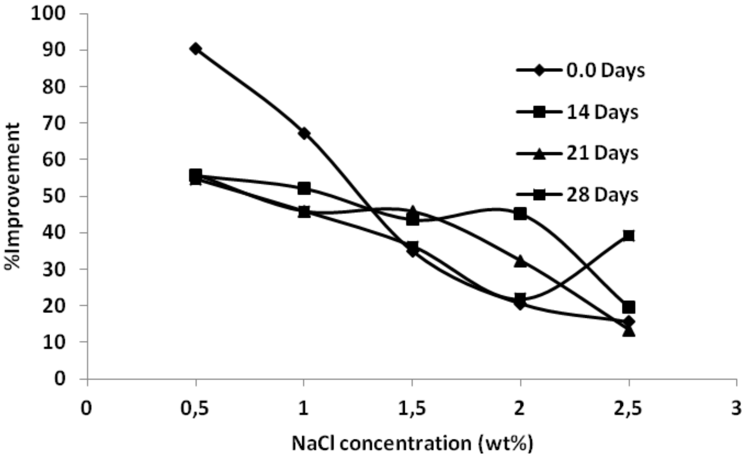


Figure 8. %Improvement vs NaCl concentration at different time intervals

Figure (8) shows that coating steel used in reinforced concrete with PANi layer has improved the corrosion resistance by a factor ranging from 10 to 90% of its value compared to uncoated steel. The protection effect of PANi can be ascribed to the fact that presence of PANi layer decreases the diffusion of O_2 to the metal surface and that decrease the rate of the cathodic reaction that [34]:

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

Decreasing the rate of cathodic reaction (2) will certainly decrease the rate of corrosion.

We have to clarify that the % improvement has been decreased by increasing the NaCl concentration which attributed to that at higher chloride ion concentration its penetration rate through the PANi layer increases and causes higher corrosion rate as explained above.

3.2.2 Effect of SO_4^{--} concentration

As shown in figure (9) the results of potentiodynamic examination for PANi coated steel reinforced concrete for different H_2SO_4concentrations after 14 days, show that the corrosion rate has been increased by increasing the H_2SO_4 concentration within the range from 1 to 5 wt%. Same figures were obtained for different time intervals of 0, 14, 21 and 28 days for both uncoated steel (bare steel) and PANi coated steel. The results are shown in figure (10) for bare steel and in figure (11) for PANi coated steel. The results show that for both bare steel and PANi coated steel, the corrosion rate has been increased by increasing the H_2SO_4 concentration and by increasing the time interval.

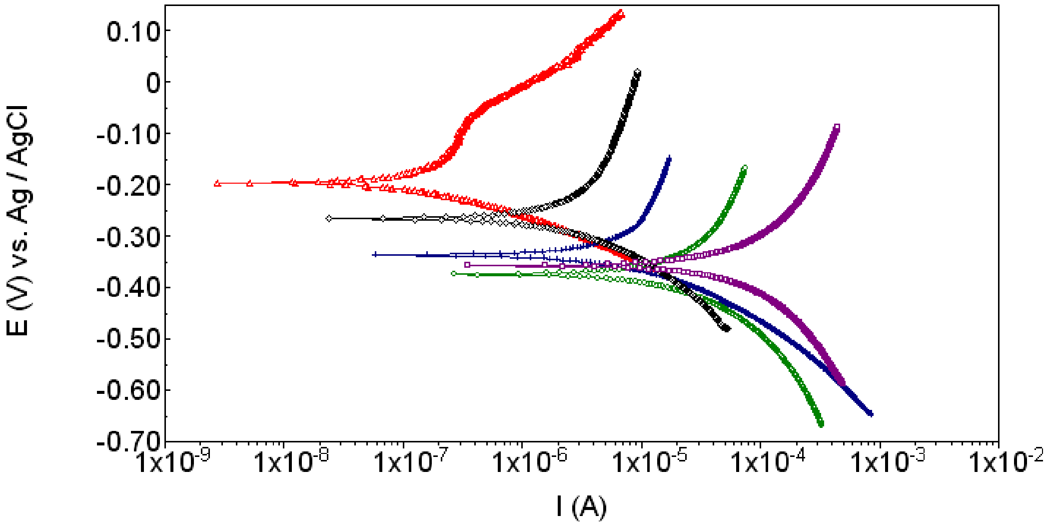


Figure 9. Potentiodynamic examination results for PANi coated steel reinforced concrete with different H_2SO_4 concentrations after 14 day. 1% H_2SO_4 red line, 2% H_2SO_4 black line, 3% Green line, 4% H_2SO_4 blue line, 5 % H_2SO_4 magenta line.

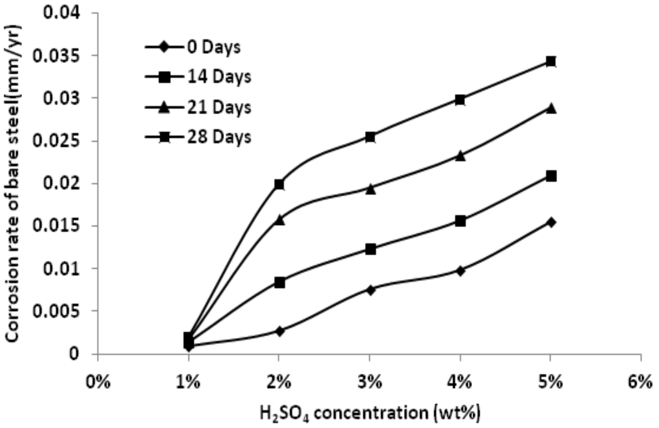


Figure 10. Corrosion rate of bare steel vs H_2SO_4 concentration at different time intervals

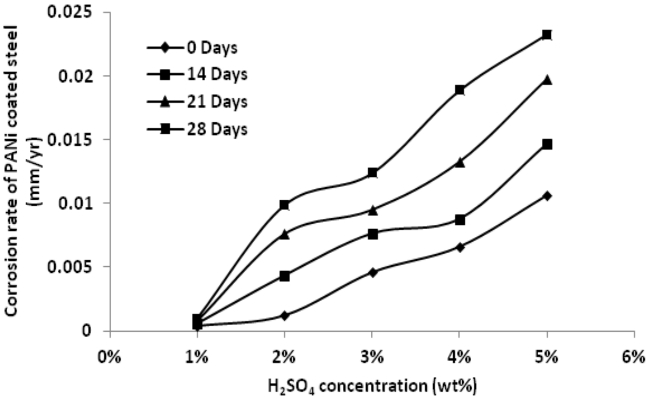


Figure 11. Corrosion rate of PANi coated steel vs H_2SO_4 concentration at different time intervals.

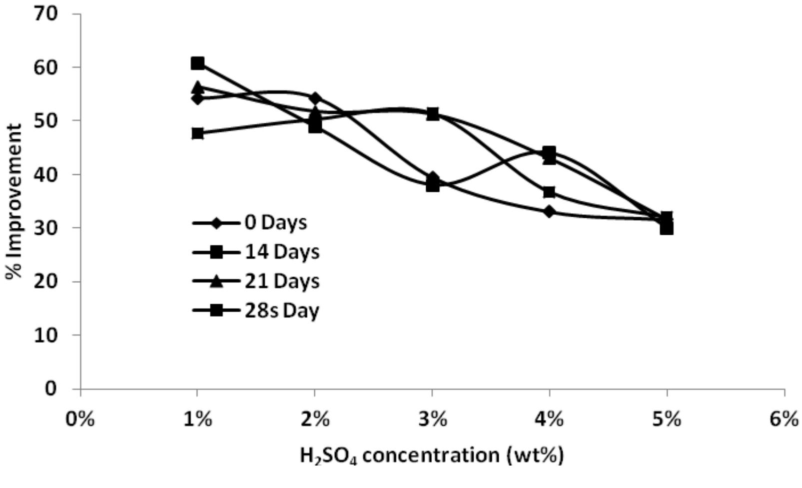


Figure 12. % Improvement in corrosion resistance vs H_2SO_4 concentration at different time intervals.

The increase in reinforcement corrosion can be attributed to the modification of the protective ferric oxide film to a sulfate film, which may be less protective than the former. Dehwah et al. [35] reveal that the increase in reinforcement corrosion due to the presence of sulfate ions was attributed to a decrease in the chloride binding and the electrical resistivity of concrete. Treadaway et al. [36] indicated that presence of SO_4^{-2} decreases the electrical resistivity of concrete which is helpful in sustaining the electrochemical reactions.

As shown in figure (12) the results show that coating steel with PANi layer for concrete reinforcement has improved the corrosion resistance by a factor ranging from 30 to 60% of its value compared to uncoated steel. The protection effect of PANi can be ascribed to the fact that presence of PANi layer decreases the diffusion of SO_4^{-2} and O_2 to the metal surface and that decrease the rate of the anodic AND cathodic reactions respectively which will certainly decrease the rate of corrosion.

3.2.3. Effect of time interval

For clarifying the effect of time we have to identify that concrete can be modeled in terms of three component steps: (1) time for corrosion initiation, Ti; (2) time, subsequent to corrosion initiation, for appearance of a crack on the external concrete surface (crack propagation), Tp; and (3) time for surface cracks to progress into further damage and develop into spalls, Td, to the point where the functional service life, Tf, is reached. The main considered in this research is the initial hardening period ranging from 0 to 28 days. Figures 13 and 14 show the effect of NaCl and H_2SO_4concentrations at different time intervals on the corrosion rate of reinforced steel with both bare steel and PANi coated steel respectively.

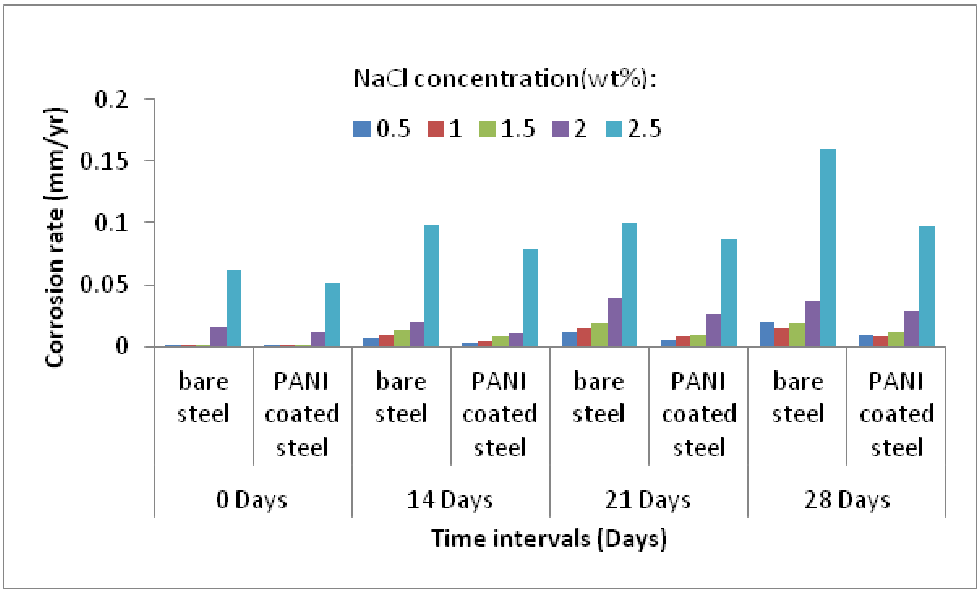


Figure 13. Corrosion rate vs time intervals for different NaCl concentrations for both bare and PANi coated steel

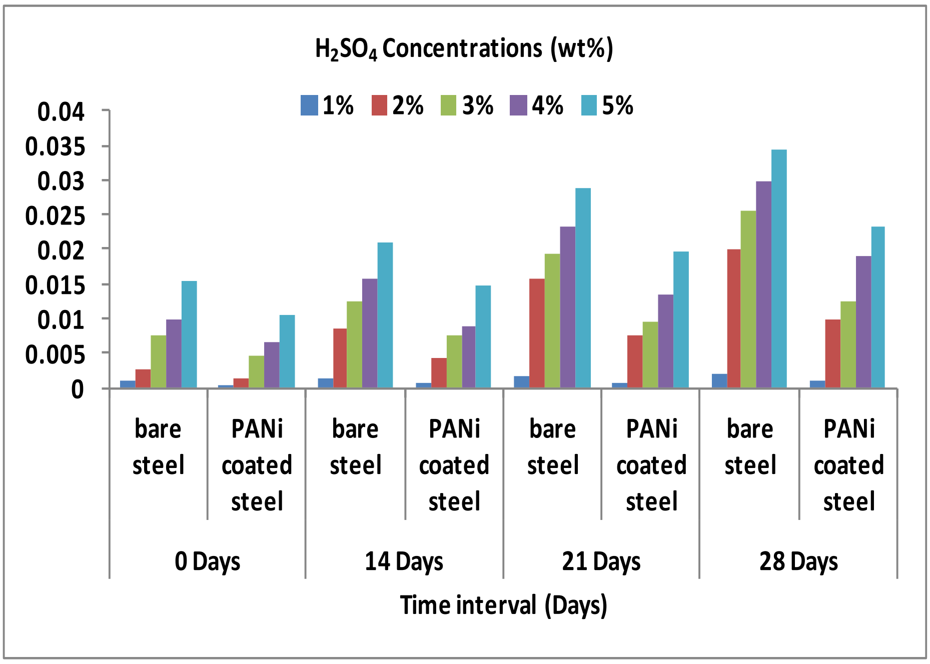


Figure 14. Corrosion rate vs time intervals for different H_2SO_4 concentrations for both bare and PANi coated steel

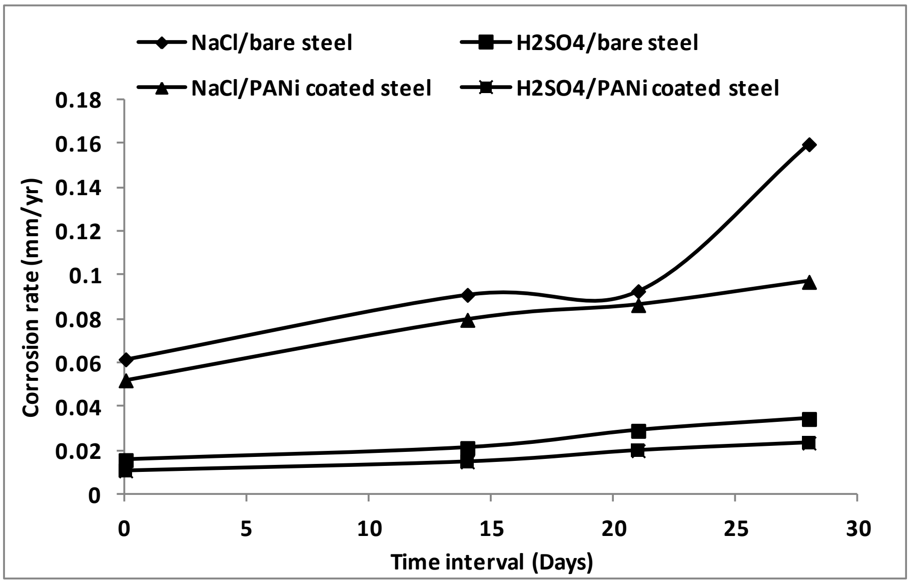


Figure15. Comparison between corrosion behavior of both bare and PANi coated steel in concrete against NaCl and H_2SO_4 with time

The results show that corrosion rate have been increased by increasing the time interval which can be ascribed to fact that for longer time the amount of both Cl^- , SO_4^{-2} and O_2 penetrated to iron surface will increase and there effects as discussed above will be tangible and increase the corrosion rate. As shown in figure (15) it has to be clarified that Cl^- is superior to SO_4^{-2} in causing corrosion rate of steel. The corrosion rate of steel subjected to Cl^- ions is higher than that of SO_4^{-2} by a factor of

1.688 and 1.815 for both bare and PANi coated steel respectively. The above results can be ascribed to the fact that the diffusivity of Cl^- in hardened steel is higher than that of SO_4^{-2} [37-40]. Oberholster [37] reported that the diffusion of chloride ions is generally 10 to 100 times faster than that of sulfates.

4. CONCLUSIONS

This work investigates the possibility of improving the corrosion resistance of reinforced concrete against corrosive mediums mainly represented by chloride and sulfate ions by using polyaniline (PANi) coating. The polyaniline layer was formed using the galvanostatic technique and investigated for its composition by using X-Ray Photoelectron Spectroscopy (XPS). The potentiodynamic technique was used for investigating the corrosion resistance of the PANi coated steel while coupled with stainless steel and used for reinforcing a layer of concrete, containing different concentrations NaCl and H_2SO_4. The corrosion current was measured against Ag/AgCl reference electrode. The main variables investigated were the initial concentration of both Cl^- and $SO4^{-2}$ and the time interval from 0 to 28 days (initial hardening period). The results show that the corrosion rate of both bare and PANi coated steel have been increased by increasing the the initial concentrations of both NaCl and H_2SO_4. Using polyaniline coating has improved the corrosion resistance of reinforced concrete against Cl^- by a factor ranging from1.10 to 1.90 and by a factor ranging from 1.30 to 1.60% against $SO4^{-2}$ of its value compared to uncoated steel depending on initial concentration of Cl^- and $SO4^{-2}$ respectively. In addition the results showed that Cl^- is superior to SO_4^{-2} in causing corrosion of steel. The corrosion rate of steel subjected to Cl^- ions is higher than that of SO_4^{-2} by a factor of 1.688 and 1.815 for both bare and polyaniline coated steel respectively.

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