

## Corrosion Protection of Carbon Steel in seawater by alumina nanoparticles with poly (acrylic acid) as charging agent.

Haider Abdulkareem Yousif Almashhdani<sup>a\*</sup>, Khulood Abid Al-Saadie<sup>b</sup>

<sup>a</sup>Al-Rasheed University College, Department of Dentistry, Baghdad, Iraq

<sup>b</sup>University of Baghdad, College of Science, Department of Chemistry, Baghdad, Iraq

### Abstract

Nanostructured  $\text{Al}_2\text{O}_3$  has been applied as a protective coating against corrosion of the carbon steel (C.S) in seawater environment (3.5% NaCl) at temperatures range (298-328)K. Alumina nanoparticles were deposited on carbon steel substrates by cathodic electrophoretic deposition (EPD) with ethanol as suspension medium and poly(acrylic acid) (PAA) as polymeric charging agent. Meanwhile, the surface morphology was examined using Atomic-force microscopy (AFM). The cross-section AFM showed that the particles sizes for the  $\text{Al}_2\text{O}_3$  NPs is around 60-80 nm. The anticorrosion behaviour of coated C.S was investigated in 3.5% NaCl at temperature range 298-328 K by potentiodynamic polarization measurements. Results show that using PAA in suspension coat increased PE% when compared with PE% in absence of PAA and gave resistance in above temperature range. Kinetic parameters (activation energy and pre-exponential factor) were calculated and discussed. Also, thermodynamic Values  $\Delta G$  and  $\Delta H$  were calculated and it shows that corrosion reaction was spontaneous and exothermic in nature

\* Corresponding author:

[H\\_R200690@yahoo.com](mailto:H_R200690@yahoo.com)

Received 06 Sept 2016,

Revised 19 Feb 2018,

Accepted 05 March 2018

**Keywords:** Alumina, carbon steel, AFM, nanoparticle.

## 1. Introduction

Corrosion is a natural phenomenon and is accompanied by the flow of electrical current involving the reversion from metallic to compound state. So it becomes clear that corrosion cannot be fully prevented instead it can be controlled to a greater extent. Many researchers have used various methods in corrosion prevention investigations. Such as coated metal surfaces by nanoparticles. The use of particles in nanoscale could also change the microstructure of the electrodeposits leading to a more compact structure and thus to improved corrosion resistance [1,2]. Nanoparticle coatings possess good thermal and electrical properties and they are resistant to oxidation, corrosion, erosion and wear in high temperature environments [3]. This property is a very important factor in the applications such as pipelines, castings and automotive industry. Electrophoretic deposition (EPD) is one of the liquid methods of coating [4–6], which elaborates stable suspensions of  $\text{Al}_2\text{O}_3$  particles in an appropriate liquid. Both sparse  $\text{Al}_2\text{O}_3$  particles and dense particle coating layers were invented on metal surface. Generally, EPD consists of two processes, i.e. the movement of charged particles in suspension in an electric field between two electrodes and the particle deposition on one of the electrodes to be protected. The mechanism of the formation of a deposit during EPD is reviewed and discussed in several theoretical papers and reviews [7,8,9]. The insufficiency of surface charge and excessive weight potentially can be overcome through the use of polymeric charging agents. Electrophoretic deposition (EPD) with ethanol as suspension medium and poly(acrylic acid) (PAA) as polymeric charging agent give good protection. Further, these polymeric charging agents play an important role as binders to improve adhesion between deposited particles and substrate [9,10]. The aim of the present work was to examine the efficiency of  $\text{Al}_2\text{O}_3$  nanoparticles (NPs) to protection of Carbon steel (C.S) using absolute ethanol as suspension medium and a PAA polymeric charging agent.

## 2. Materials and Methods

### 2.1. Materials

The steel used in this study is a carbon steel (C45) with a chemical composition (in wt%) of 0.42 % C, 0.40 % Si, 0.50 % Mn, 0.045 % S, 0.40 % Cr, 0.045 % P, 0.40 % Ni, 0.01 % Mo and the remainder is iron (Fe). The carbon steel samples were pre-treated prior to the experiments by grinding with emery paper SiC (120, 600 and 1200); rinse with distilled water, degreased in acetone, washed again with distilled water and then dried at room temperature before used synthesized seawater. The seawater solution was prepared by dissolving 35 g NaCl in 1L distilled water.  $\text{Al}_2\text{O}_3$  Nanoparticles were used in size range (20-30nm, Hongwu nanometer, purity 99.9%) and iodine was used in 99.8% purity (Aldrich).

### 2.2. Preparation of emulsion solution

Emulsion solution was prepared by adding 1% nanoparticles (NPs) ( $\text{Al}_2\text{O}_3$ ) powder to ethanol as solvent [16] (adding 1.5 g NPs to 150 ml ethanol). To study the effect of adding different PAA% (0.1, 0.25, 0.5 & 1)% in emulsion solution (0.1, 0.25, 0.5, 1)g of PAA was added to in 100 ml ethanol respectively. To homogenize the solution, an ultrasonic (50W) stirrer was used to mix the solution for 30 min. The solutions were applied for coating carbon steel (C45) pieces by using EPD technique method. Sometime few  $\text{I}_2$  were added to increase conductivity [11].

### 2.3. Electrophoresis Deposition of Emulsion Solution (Coating Samples)

To deposit emulsion solution on a piece of carbon steel surfaces, deposition cell device was used. The electrodes were connected to a D.C power supply; it can be used in anodic or cathodic deposition by reversing electrodes of the power supply [12]. The deposition cell device composed of the following components:

- Beaker 250 ml capacity and cover contain two slit with distance between them equal to 1cm.

- Power supply used to supply constant direct current D.C voltage (0 – 20) V.
- An electrical circuit was connected by ammeter, respectively, to measure the current generated between the poles.
- Stainless steel rode used as inert electrode in deposition process cell [13].
- A piece of carbon steel catch by tong made of stainless steel fixed with 1cm distance between it and inert electrode.
- The deposition on C.S specimens were carried for (3,4,5 and 6) minutes, then all specimens thermally dried at 150 °C for 2 min.

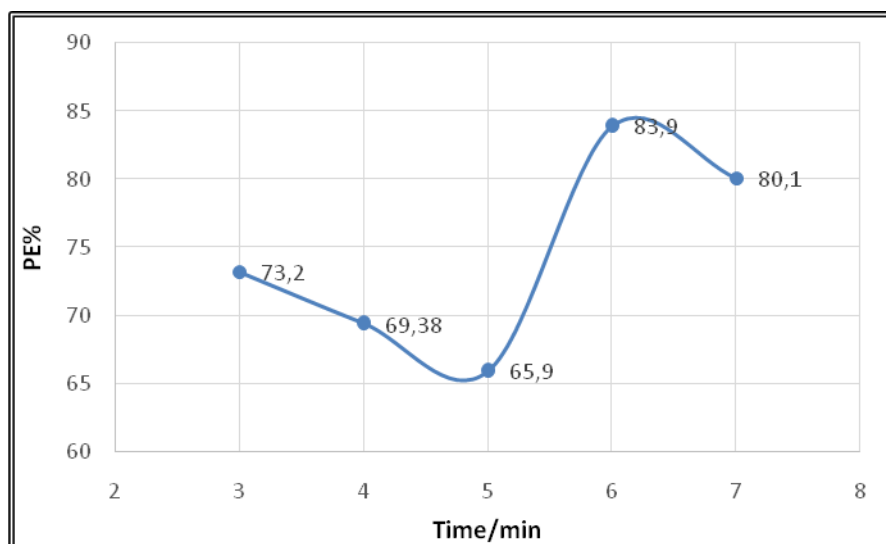
## 2.4. Electrochemical measurements

The electrochemical measurements were carried out using Mlab (Germany, 2000) potentiostate and controlled by computer and MLabSci software which were used for data acquisition and analysis under static condition. The corrosion cell used had three electrodes, the reference electrode was a silver- silver chloride, platinum electrode was used as auxiliary electrode with 1 cm<sup>2</sup> surface area of and the working electrode was carbon steel. All potentials given in this study were referred to this reference electrode. The working electrode was immersed in test solution for 15 minutes to a establish steady state open circuit potential ( $E_{ocp}$ ), then electrochemical measurements were performed in potential range ( $\pm 200$ ) mV. All electrochemical tests have been performed in aerated solutions at (208-328) K.

## 3. Result and discussion:

### 3.1. Effect of time:

The deposition on C.S specimens were carried for (3,4,5 and 6) minutes, to study the effect of time on the deposition on C.S specimens and chose the optimization time for deposition to get high protection efficiency, where the perfect time for coated C.S by Al<sub>2</sub>O<sub>3</sub> NPs using EPD technique was 6 minute, which gave PE% (83.9%) at 298K as shown in figure (1).



**Figure 1** - Relationship between PE% and coating time for coated C.S by Al<sub>2</sub>O<sub>3</sub> NPs at 298K.

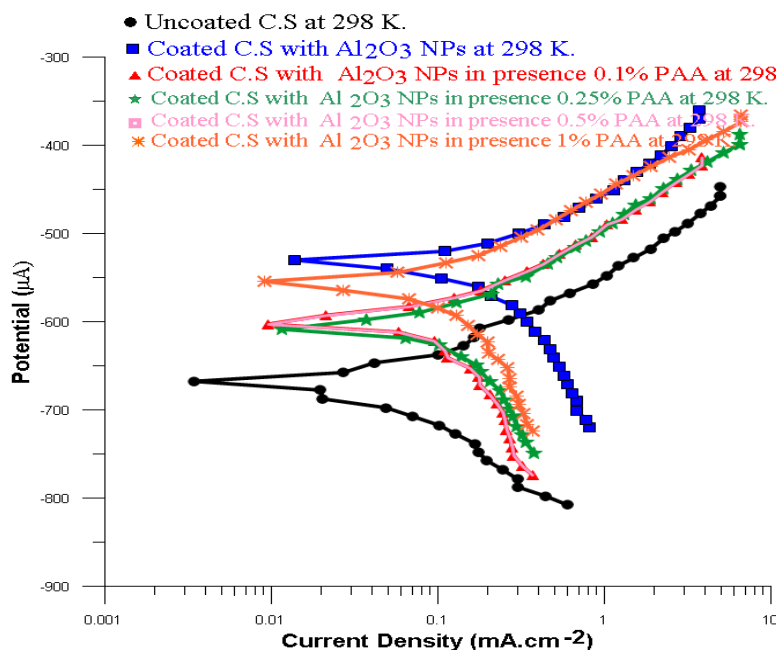
### 3.2. Polarization Curve:

Figure (2) shows the polarization curves of carbon steel coated with Al<sub>2</sub>O<sub>3</sub>NPs in absence and presence of various PAA%. It could be observed that both the cathodic and anodic reactions were suppressed with the addition of different PAA%, which suggests that coated by Al<sub>2</sub>O<sub>3</sub>in absence PAA the polarization curve shifted to more positive value (less

active) reach to (-730.0) mV at 328 K but when add PAA in different concentration the value of corrosion potential shifted to more active value but don't reach to the corrosion potentials of uncoated C.S. Protection efficiencies (PE%) of all types of coating estimated by comparison with the measurements of the uncoated surface of carbon steel alloy using equations (1):

$$PE\% = \frac{(i_{corr})_{uncoated} - (i_{corr})_{coated}}{(i_{corr})_{uncoated}} \times 100 \quad (1)$$

Where PE% ; protection efficiency percentage ,  $i_{corr}$  (uncoated) and  $i_{corr}$  (coated); are corrosion current densities for uncoated and coated specimen respectively.



**Figure 2.** Polarization curves for C.S in 3.5% NaCl for uncoated and coated C.S with Al<sub>2</sub>O<sub>3</sub> NPs in absence and percent of different PAA%.

### 3.3. Effect of PAA%

The thickness of coat layer on C.S surface measured, the basic following equation can be used:

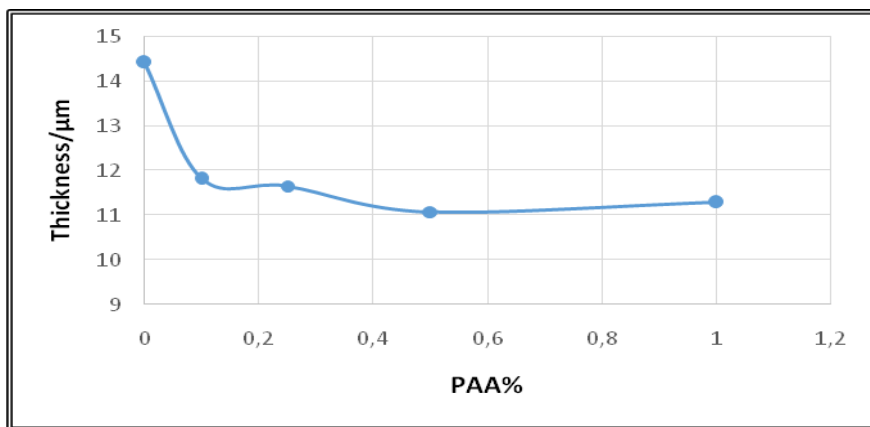
$$\rho = \frac{wt}{V} \quad (2)$$

Where:  $\rho$ = density of NPs, Wt.= weight of coated and V= volume of coated.

$$V = r^2 * 3.14 * d \quad (3)$$

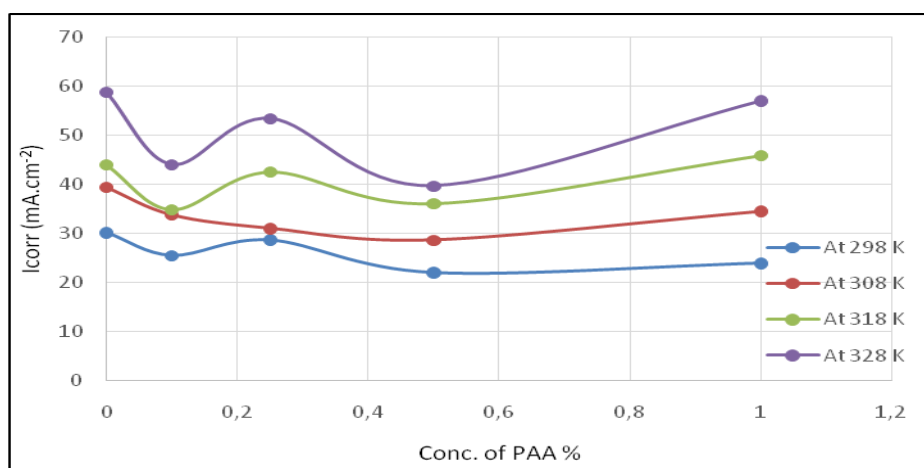
Where:  $r$  = radius of C.S piece and  $d$  = thickness of coated.

Effect of different PAA concentration in the Al<sub>2</sub>O<sub>3</sub> NPs suspension solution , were investigated, PAA lead to decrease the thickness of Al<sub>2</sub>O<sub>3</sub> layers from (14.424 $\mu$ m) in absence PAA to thickness ranged between (11.1 – 11.8  $\mu$ m) in presence of different PAA%,as shown in figure (3).



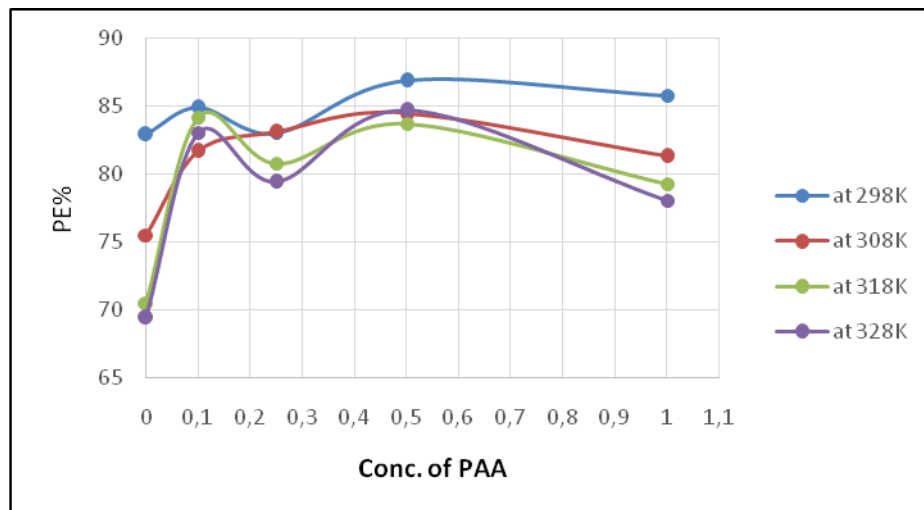
**Figure 3** - Relation between thickness and PPA% after (6) minutes coating time with  $\text{Al}_2\text{O}_3$ .

Adding 0.5% of PAA for the suspension of  $\text{Al}_2\text{O}_3$  coating lead to the lowest  $i_{\text{corr}}$  value in temperature range (298-328)K, as shown in figure (4).



**Figure 4.** Effect of adding different PAA% to SiC NPs coating suspension on  $i_{\text{corr}}$ .

The best PE% was obtained in presence of (0.5%) PAA at 298K. So (0.5%) PAA was perfect concentration added to suspension solution of coating which give PE% range between (87 – 85 %) at temperatures range 298- 328 K, as shown in figure 5.

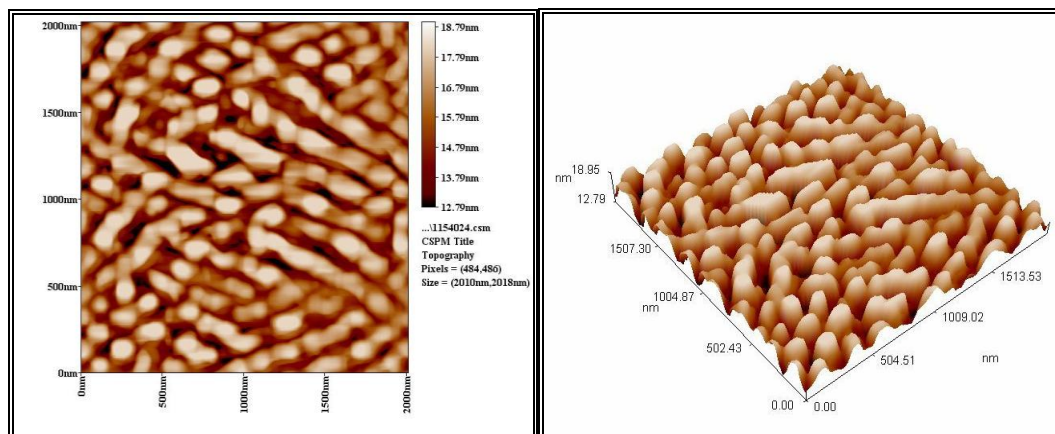


**Figure 5.** Effect of adding different PAA% to SiC NPs coating suspension on PE%.

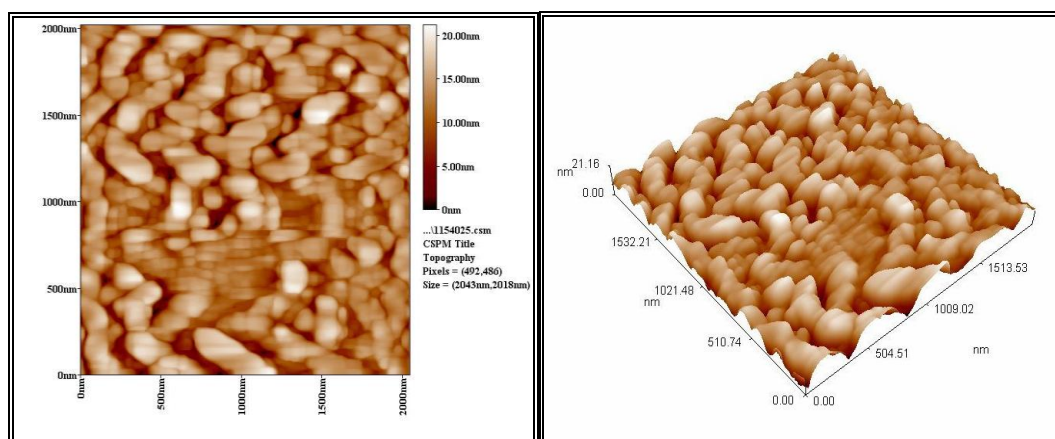
### 3.4. The Surface Morphology

The morphologic analysis by AFM for layers of  $\text{Al}_2\text{O}_3$  NPs without PAA and  $\text{Al}_2\text{O}_3$  NPs with 0.5% PAA.

Since we started with alumina particles of 20-30 nm in size, AFM images shows little largest average particles sizes for the  $\text{Al}_2\text{O}_3$  NPs without PAA and  $\text{Al}_2\text{O}_3$  NPs with 0.5% PAA, figures (6) to (7), around 66nm and 82nm respectively.



**Figure 6** - 2D and 3D views of AFM image of  $\text{Al}_2\text{O}_3$  without PAA applied on carbon steel.



**Figure 7**- 2D and 3D views of AFM image of  $\text{Al}_2\text{O}_3$  with PAA applied on carbon steel.

### 3.5. FTIR spectroscopy

**Table 1.** Wave number of FT-IR adsorption for pure P.h.e. and P.h.e. as corrosion inhibitor

| Pure PAA                         | $\text{Al}_2\text{O}_3$ NPs deposition<br>in presence PAA |             |
|----------------------------------|---|-------------|
| Wave number ( $\text{cm}^{-1}$ ) | Wave number ( $\text{cm}^{-1}$ )                          | Assignment  |
| -                                | 3401,13   | OH stretch  |
| 3143                             | 3350  | NH stretch  |
| 1436                             | 1458  | C-O stretch |
| 1176                             | 1172  | C=N stretch |
| 1735                             | 1739  | C=O stretch |

Fourier Transformation Infrared Spectra for Al<sub>2</sub>O<sub>3</sub> NPs deposition on C.S in presence PAA and the pure PAA are represented as shown in (Figure 8 and Figure 9) respectively, The spectrum shows a multi peak band at 3304-3350 cm<sup>-1</sup> which indicates the presence of the OH group or N-H, but not show in the spectrum of pure PAA, also it shows a peak at 1735-1793 cm<sup>-1</sup> due to the presence of the carbonyl group for ketone. In this spectrum, there are bands at 1176 and 1172 cm<sup>-1</sup> indicating the presence of C=H groups.

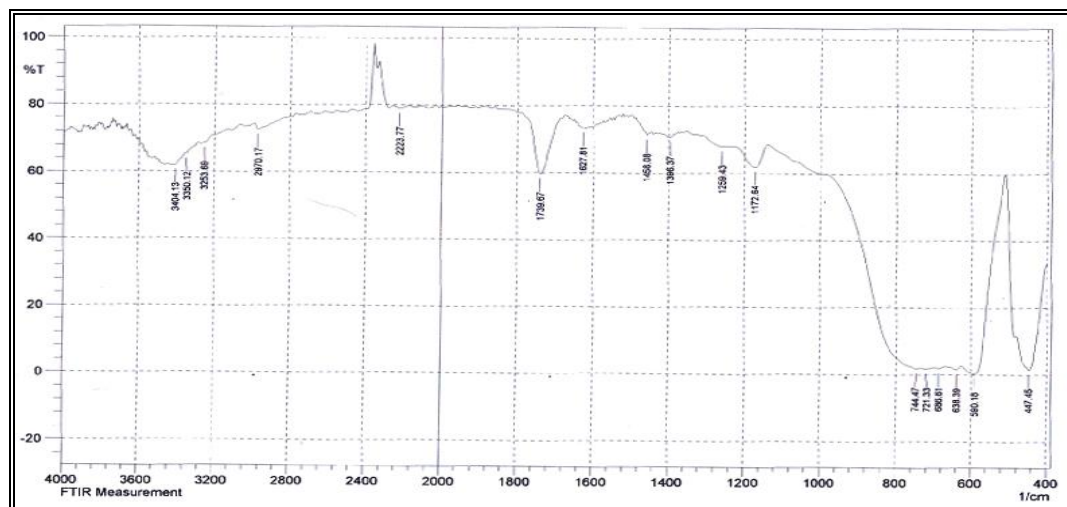


Figure 8 - FT-IR spectra of Al<sub>2</sub>O<sub>3</sub> NPs deposition on C.S in presence PAA .

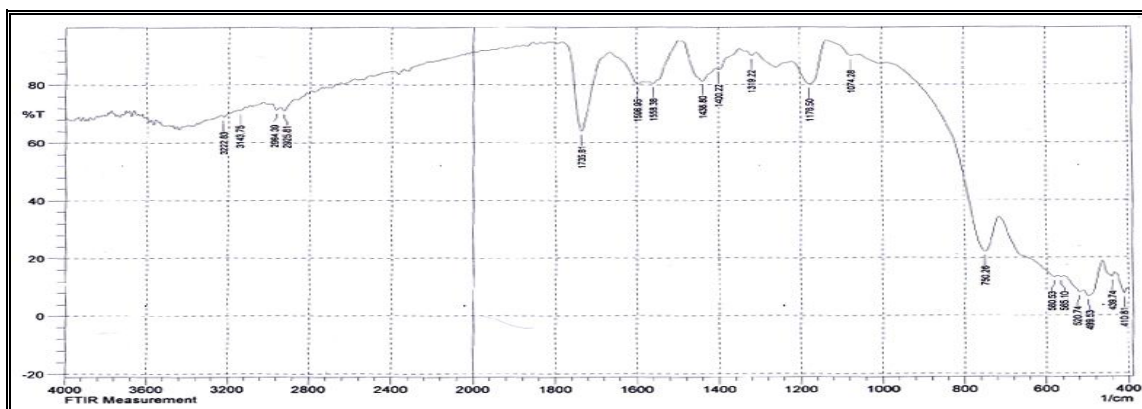


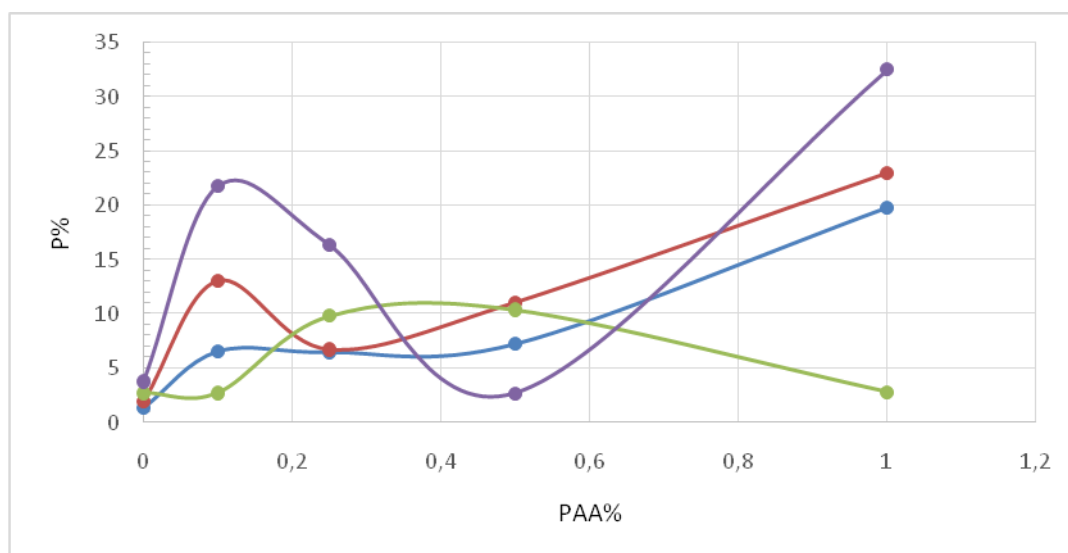
Figure 9 - FT-IR spectra of PAA.

### 3.6. Surface porosity

Surface porosity percentage fraction was estimated by potentiostatic polarization. In this case, the porosity percentage (P%) can be calculated using the following equation:

$$P\% = \frac{R_{p,uncoated}}{R_{p,coated}} 10^{-\left(\frac{\Delta E_{corr}}{\beta_a}\right)} \times 100 \quad (4)$$

where  $R_{p,uncoated}$  and  $R_{p,coated}$  are the polarization resistances of the uncoated C.S and the coating C.S by NPs, respectively,  $\Delta E_{corr}$  is the corrosion potential difference between them, and  $\beta_a$  is the anodic Tafel coefficient of the uncoated C.S. In generally adding PAA increase surface porosity percentage (P%) for coated C.S by Al<sub>2</sub>O<sub>3</sub> NPs at all concentration of PAA, 1% PAA lead to higher P% which reach to 32.5% at 328K, as shown in figure (10).



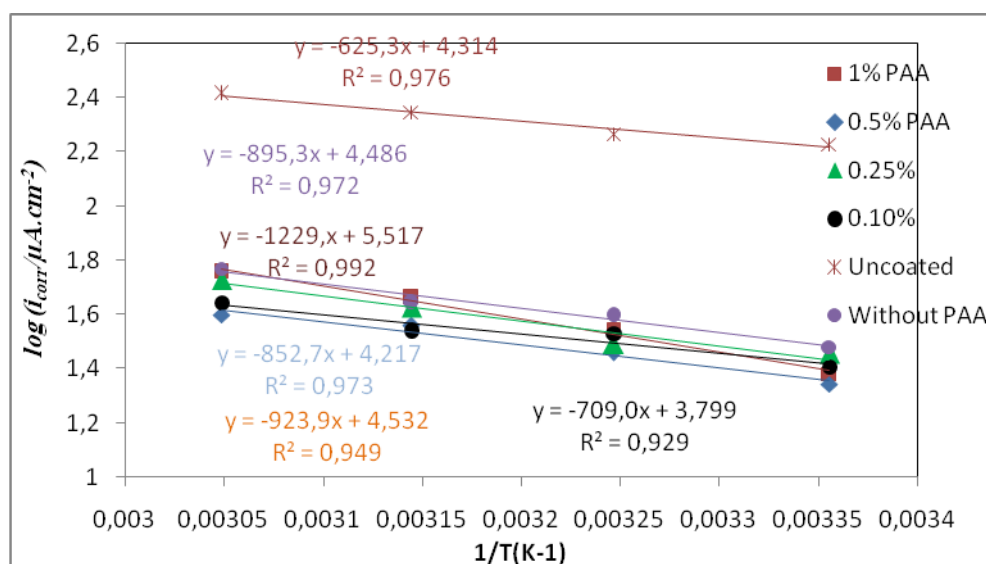
**Figure 10.** Variation of porosity percentage P% with PAA% at different temperatures for C.S coated by Al<sub>2</sub>O<sub>3</sub> NPs in absence and presence of different PAA%.

### 3.7. The kinetic studies:

The corrosion reaction can be regarded as an Arrhenius modified Arrhenius equation [28]:

$$\log i_{\text{corr}} = \log A - E_a / 2.303 RT \quad (5)$$

Where  $i_{\text{corr}}$  is the corrosion current density, is the apparent activation energy of the corrosion reaction, R is the gas constant, T is the absolute temperature and A is the Arrhenius pre-exponential factor. Fig.(11) presents the Arrhenius plots of the natural logarithm of the current density vs 1/T, for C.S samples uncoated and coated C.S by Al<sub>2</sub>O<sub>3</sub> in presence and absence of different concentrations of PAA, in artificial seawater.



**Figure 11.**  $\log i_{\text{corr}}$  Vs 1/T for coated C.S with Al<sub>2</sub>O<sub>3</sub> NPs in absence and presence of different PAA% in 3.5% NaCl.

Values  $E_a$  of and A for the corrosion reaction in the absence and presence of different concentrations of the PAA are calculated by a linear regression method and given in Table (2). It is found that the activation energy is increaseafter coated C.S by Al<sub>2</sub>O<sub>3</sub> in absence and presence PAA, and the higher value was when coated C.S with Al<sub>2</sub>O<sub>3</sub> in presence 1% PAA reach to (23.54)) kJ.mol<sup>-1</sup>. But Value of A increase slightly when coated C.S.

**Table 2.** Kinetic parameter for C.S coated with Al<sub>2</sub>O<sub>3</sub> in absence and presence of different PAA% in 3.5% NaCl .

|  | Conc.       | Ea/kJ.mol <sup>-1</sup> | A/Molecules.cm <sup>-2</sup> .S <sup>-1</sup> |
|--|-------------|-------------------------|---|
|  | Uncoated    | 12.330                  | 1.32*10 <sup>28</sup>                         |
| Coated by Al <sub>2</sub> O <sub>3</sub> | Without PAA | 20.105                  | 3.271*10 <sup>28</sup>                        |
|  | (0.1%) PAA  | 12.33                   | 3.79*10 <sup>28</sup>                         |
|  | (0.25%) PAA | 17.69                   | 2.02*10 <sup>28</sup>                         |
|  | (0.5%) PAA  | 16.30                   | 9.9*10 <sup>27</sup>                          |
|  | (1%) PAA    | 23.54                   | 1.9*10 <sup>29</sup>                          |

Ea increases with coated C.S Al<sub>2</sub>O<sub>3</sub> in absence and presence PAA, it is obvious that thin layer of coat is playing a role in increasing the activation energy value, thereby indicating a more efficient inhibiting effect. According to Eq. (5) low values of A and high values of lead to lower corrosion rates. For the present study, is lower in the presence PAA. Therefore, the decrease in the carbon steel corrosion rate is decided by the pre-exponential factor A.

### 3.8. Thermodynamic Studies:

The values of thermodynamic parameters are represented in Table (3). Where the value of  $\Delta G$  calculated from equation [6] dependence on corrosion potential.

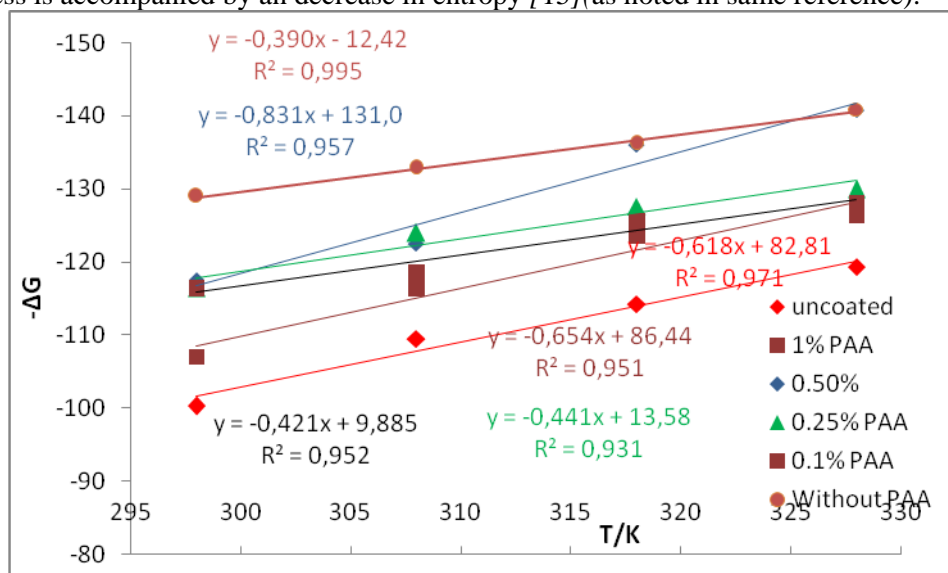
$$\Delta G = -nFE_{\text{corr}} \quad (6)$$

The entropy ( $\Delta S$ ) and enthalpy ( $\Delta H$ ) are obtained from the plot of  $\Delta G$  vs T.  $\Delta S$  and  $\Delta H$  were obtained from the slope and intercept, respectively (figure 11). The value of  $\Delta G$  indicates that the coated function by chemically process on the surface of the metal. Generally, the values of  $\Delta G$  up to -20 kJ/mol are consistent with electrostatic interaction between charged molecules and a charged metal (physical process), while those more negative than -40 kJ/mol involve charge sharing or transfer from the inhibitor molecules to the metal surface, to form a co-ordinate type of bond (chemical process) [14].

**Table 3.** Thermodynamic parameter for coated C.S with Al<sub>2</sub>O<sub>3</sub> in absence and presence of different PAA% in 3.5% NaCl

|               | Conc.       | $-\Delta G_{\text{avg}}/ \text{kJ.mol}^{-1}$ | $-\Delta H_{\text{avg}}/ \text{kJ.mol}^{-1}$ | $-\Delta S/\text{J.K}^{-1} .\text{mol}^{-1}$ |
|---------------|-------------|--|--|--|
|               | Uncoated    | 110.86                                       | 304.55                                       | 618.6  |
| Coated by SiC | Without PAA | 136.66                                       | 257.06                                       | 390.8  |
|               | (0.1%) PAA  | 122.17                                       | 254.22                                       | 421.9  |
|               | (0.25%) PAA | 124.52                                       | 262.61                                       | 441.2  |
|               | (0.5%) PAA  | 129.24                                       | 389.53                                       | 831.6  |
|               | (1%) PAA    | 118.40                                       | 323.26                                       | 654.5  |

The negative sign of the  $\Delta G$  obtained indicates that the process is spontaneous, while the negative sign of  $\Delta S$  indicates that a process is accompanied by an decrease in entropy [15]/(as noted in same reference).



**Figure 12.** Plot of  $-\Delta G$  Vs  $T$  for coated C.S with SiC NPs in absence and presence of different PAA% in 3.5% NaCl .

#### 4. Conclusion

- The coat C.S by alumina nanoparticles act as a good protection thin layer to prevent metal from corrosion, which were give PE% reach to 82%.
- The rate of corrosion increased with increasing temperatures ranged from 298 to 328 K.
- 3. Add PAA in suspension solution of coat act as stabilizer agent, which were adsorbed onto the surfaces of ceramic particles, could generate steric and electrostatic stabilization and prevent particles agglomeration.
- These additives of PAA increase the PE% reach to 87% at 0.5% of PAA.
- The surface porosity percentage P%, generally increase with temperature increase, and adding different PAA% increase the P% because P% depended on  $R_p$  and  $E_{corr}$ .
- 6.The activation energy of C.S alloys corrosion increase after coated.
- The corrosion reaction was spontaneous reaction (values of  $\Delta G$  was negative) with exothermic reaction (values of  $\Delta H$  was negative).
- The AFM images detection The Particles size increase after coated by different NPs in all cases.

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