INTRODUCTION

The mechanism of anodic corrosion is usually explained by its effect occurs because of differential dissolution, as the current is applied and the oxidation film covering the lower peaks of the surface [1]. Elmore was studied the current-voltage relationship for the polishing of copper in orthophosphoric acid system. He attributed the polishing effect to a varying concentration gradient of the dissolved metal ions over the protrusions and valleys [2,3].

Mass-transport limitations for the anode are commonly believed to be responsible for anodic corrosion and this theory is supported by the observation in many experimental systems of polishing for anodic dissolution with a limiting-current plateau [4-8].

According to the wide range applications of carbon steel [9-13], several methods have been applied to reduce the corrosion and make up passive layer, which act as protective film on its surface. The use of inhibitors is one of the most practical methods for the protection against corrosion in acidic media.

To be effective, an inhibitor must also displace the water from the metal surface, interact with anodic or cathodic reaction sites to retard the oxidation and reduction corrosion reaction and prevent transportation of water and corrosion on active species to the surface [14].

The inhibiting action of these natural polymers is usually attributed to their interaction with carbon steel surface via their adsorption. Polar functional groups are regarded as the reaction center that stabilizes the adsorption process. In general, the adsorption of inhibitor on metal surface depends on the nature and the surface charge of the metal, the adsorption mode, its chemical structure and the type of electrolyte solution [8].

The aim of the present work is to study the effect of natural polymers namely starch, chitosan, cellulose acetate and carboxymethyl cellulose sodium salt on the rate of anodic corrosion of carbon steel and to make stabilization of a sacrificial protective film on its surface.

This work were supported with using scanning electron microscope (SEM) examination of surface morphology of carbon steel. The data obtained were ensured the experimental measurements. Dissolution rate and percentage inhibition were measured by weight loss method. Changes in temperature, concentration of inhibitors, type of cell and physical properties of solution such as density and viscosity are studied. Dimensionless analysis investigations used to correlated among all
these parameters. Adsorption isotherm and isokinetic temperatures were simulated.

**EXPERIMENTAL**

The electrolyte was prepared by using 8 M AnalR grade H₃PO₄ (98 % w/w), supplied by Sigma-Aldrich Chemicals Ltd. The solution used in cell consist of 8 M H₃PO₄ and different concentrations from the polymers in the range of concentration (100-800 ppm) were used.

As shown in Fig. 1, the electrodes were rectangular carbon steel sheets of 10 cm height and 5 cm width, Luggin tube filled with phosphoric acid was acted as a reference electrode. A porous PVC diaphragm was used in case of divided cell. The active surface of the anode was 3 cm height and another parts of it were insulated with polystyrene lacquers. The rate of anodic dissolution was measured as the limiting current that obtained from polarization curves [15]. A driven carbon steel metal cylinder shaft anode with 1 cm diameter and 3 cm length was used in case of forced convection mechanism.

**Weight loss method**: Analytical balance was used to weight a carbon steel coupon had a rectangular form with dimensions (length 5 cm), width (1 cm) and thickness (0.025 cm) before and after immersing in 100 mL of aerated 8 M H₃PO₄ solution containing the polymers at the desired concentration for 3 days at 25 °C. In each run the coupons were polished, washed with distilled water, degreased with ethanol and dried at room temperature [16].

**Density and viscosity measurements**: An Ubelhode type viscometer is used for measurement of the viscosity of the solutions used. The density was determined by using DA-300 Kyoto Electronics at 25, 30, 35 and 40 °C. Density and viscosity measurements were carried out in a circulating ultra thermostat mode (MWL type U 10) where the temperature is adjusted to an accuracy of ± 0.05 °C. The values of densities and viscosities of 8 M phosphoric acid and different polymers-water-phosphoric acid mixtures which were used in the process of dissolution were measured at different concentrations.

**Scanning electron microscope (SEM) examination**: The electron source was LAB6 Electron detection was carried out with a scintillation photodetector. The typical working pressure was 8 mbar and dimensional of (1 cm × 1 cm) carbon steel sheet anodes were used [17]. Before the SEM observation, each electrode was first rinsed with distilled water and with analytical grade acetone. The surface morphology of carbon steel samples immersed in acidic bath (H₃PO₄) with or without polymers additives has studied. All experiments were made when the limiting current obtained for all solutions at 25 °C, 8 M H₃PO₄.

**RESULTS AND DISCUSSION**

**Anodic dissolution of carbon steel**: Many mechanisms have been proposed successively for the process of anodic dissolution: Salt film (dissolution products) mechanism, acceptor mechanism, preferential adsorption of shielding molecules [18,19] and formation of solid oxide film for aluminum.

The rate of anodic dissolution was represented by the limiting current, which was observed from current-voltage polarization curves. Fig. 2 shown an elevation on rate of anodic dissolution with rising the experimental temperature.

**Concentration of corrosion inhibitors**: The stabilization of passive layer of polymers molecules as protective film on carbon steel surface was ensured by the result that shown in Table-1. The limiting current of anodic dissolution decreases with increasing concentration of the polymers which indicated the increase in inhibition efficiency according to the equation:

\[
\text{Inhibition (\%)} = \left( \frac{I-I^0}{I} \right) \times 100 \quad (1)
\]

where I is limiting current without inhibitor, I° is limiting current with inhibitor.

It is indicated that when raising the temperature the limiting current increases, due to the catalytic effect of anodic dissolution process.

**Cell with diaphragm versus cell without diaphragm**: A porous PVC diaphragm was used to make the division of the cell. Table-1 showed the comparison between the limiting current measured using divided and undivided cell at the same temperatures.

As shown in Fig. 3, divided cell (using a diaphragm) had been reduced the anodic limiting current. A diaphragm had been prevented the uprising hydrogen bubbles that induce a radial momentum transfer. So that the rate of anodic dissolution on carbon steel surface was decreased in case of divided cell which make support to the stabilization of passive layer of polymers as a corrosion inhibitors on carbon steel surface [20].
Fig. 3. Limiting current with and without diaphragm for blank solution at 298 K

Effect of solution on viscosities: The motions of the molecules and the movement of one layer of molecules with respect to another layer are responsible for viscous solution [21]. These motions had been illustrated as transitional and rotational motions. The effect of raising the temperature on the viscosity can be tested by the Arrhenius relationship [22].

\[ \eta = A e^{E/R T} \]  

where, E is the activation energy of the flow of the polymer molecules to surpass the energy barrier, T is the temperature and R is the molar gas constant.

It was found that as the viscosity increase, the mobility of the polymer molecules in the examined solution have been decreased. Decreasing the mobility retard the rate of anodic dissolution. As shown in Table-2, the viscosity increase by the increasing the concentration of solution containing polymers and decreased by increasing temperature.

Kinematic viscosity (v) that used to get the diffusion coefficient (D), of Fe\(^{2+}\) ions in solutions containing polymers molecules can be calculated from the following equation [20]:

\[ v = \eta/\rho \]

where \( \eta \) is the viscosity in g cm\(^{-1}\) s\(^{-1}\) and \( \rho \) is the density in g cm\(^{-3}\). It is noted that (1 poise = 1 g cm\(^{-1}\) s\(^{-1}\)) so (1 centipoise = 0.01 g cm\(^{-3}\) s\(^{-1}\)).

**Flory-Huggins adsorption isotherm:** Reactions in electrochemistry have been suggested by using the application of adsorption isotherm. Flory-Huggins, Langmuir, Bockris-
Swinkels, Temkin, and Frumkin relations are generally used to calculate the isotherms [23].

The adsortion mechanism of formation and stabilize of a protective layer on the carbon steel were estimated form of these isotherms which have the general form:

\[ f(x, \theta) e^{-\Delta H/K} = KC \]  

where \( f(\theta, x) \) is the configuration factor which depends essentially on the physical and assumptions underlying the derivation of the isotherm [24].

The degree of surface coverage \( \theta \) at constant temperature was determined from this equation:

\[ \theta = 1 - \frac{I^O}{I} \]  

where \( I \) is limiting current without inhibitor, \( I^O \) is limiting current with inhibitor.

Flory-Huggins adsorption isotherm for carbon steel anode in \( \text{H}_3\text{PO}_4 \) solution, plotted as \( \log \theta/C \) against \( \log (1-\theta) \) at 25 °C. The experimental data fit the Flory-Huggins adsorption isotherm, which is represented by [25]:

\[ \log \theta/C = \log xK + x \log (1-\theta) \]  

where \( x \) is the number of water molecules replaced by one molecule of the inhibitor. The calculated values of \( x \) and \( K \) are given in Table-3.

<table>
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| Cellulose acetate         |            |       |       |       |       |
| 0.00                      | 1.395      | 1.75  | 1.350  | 1.62  | 1.304  | 1.50 |
| 100                       | 1.309      | 2.75  | 1.268  | 2.60  | 1.241  | 2.47 |
| 200                       | 1.308      | 2.80  | 1.288  | 2.68  | 1.238  | 2.50 |
| 300                       | 1.298      | 2.83  | 1.286  | 2.70  | 1.244  | 2.55 |
| 400                       | 1.309      | 2.88  | 1.282  | 2.73  | 1.240  | 2.58 |
| 500                       | 1.295      | 2.90  | 1.273  | 2.75  | 1.238  | 2.60 |
| 600                       | 1.296      | 2.93  | 1.274  | 2.79  | 1.224  | 2.62 |
| 700                       | 1.307      | 2.98  | 1.279  | 2.84  | 1.212  | 2.63 |
| 800                       | 1.326      | 3.05  | 1.271  | 2.86  | 1.205  | 2.65 |

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<table>
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<th>Values of free energy of adsorption (kcal mol⁻¹) and the values of K and X of phosphoric acid in presence of different polyblmers using Flory-Huggins adsorption isotherm</th>
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<td>Polymers additives</td>
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<td>Cell without diaphragm</td>
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</tr>
<tr>
<td>Cell with diaphragm</td>
<td></td>
</tr>
<tr>
<td>X</td>
<td>K</td>
</tr>
<tr>
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<td>-------</td>
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<td>Starch</td>
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<td>Chitosan</td>
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</table>
The adsorption of inhibitors at metal-solution interface may be due to the formation of electrostatic or covalent bonding between the adsorbents and the metal surface [26].

Adsorption free energy ($\Delta G_{ads}$) at different concentrations was calculated from the following equation [25,27]:

$$\Delta G_{ads} = -RT \ln (55.5 K)$$  \hspace{1cm} (7)

where, $T$ is the experimental temperature in Kelvin (298 K), $R$ is the molar gas constant (8.314 J. K$^{-1}$.mol$^{-1}$) and value (55.5) is the concentration of water in the solution mol/L [25,26].

Adsorption free energy in the case of cells with and without diaphragms are given in Table-3. It is found that all values are negative which indicate that the adsorption of the inhibitor occurs spontaneously and more positive than -40 KJ/mol indicating that the inhibitors are physically adsorbed on the metal surface [28]. The values lie in the range of 9.95-11.42 KJ/mol for cell without diaphragm and 12.54-12.66 KJ/mol for cell with diaphragm. These results indicate that the cell with diaphragm has higher efficiency for adsorption of polymers molecules than the cell without diaphragm because it has higher negatively values of adsorption free energy. The stability of a passive layers of polymers on carbon steel surface was found in the following order:

- Cellulose acetate > Carboxymethyl cellulose sodium salt (CMC) > Chitosan > Starch

**SEM micrographs of carbon steel:** Scanning electron microscope (SEM) examination of anodic corrosion of metals has widely studied [29,30]. This is important to indicate if these inhibitors are efficient or not by study the behaviour of polymers molecules on carbon steel surface.

The SEM analysis (Fig. 4a) shows the morphology of carbon steel as a raw material. The surface is rough and uneven and large number of pits with large size and high depth distributed over the surface are seen (Fig. 4b) shows the morphology of carbon steel in blank solution. Only a slight difference in the surface morphology was observed in which cavities and small pits are represented clearly. Fig. 4c and 4f show slightly roughness and more homogenous surface. Deep cavities are eliminated by filling up, also, grain boundaries are decreased gradually. This behaviour may be due to involvement of starch and chitosan molecules in the cavities of steel surface so appear more uniform than blank. According to Fig. 4d and 4e the metallic surface seems to be uniform, smooth, bright and almost not affected by corrosion. Morphology in micrograph (Fig. 4g) appear uniform, smooth and bright more than Fig. 4e. This seems to be due to adsorption of starch increases because of the increase in concentration.

Fig. 4h show the SEM micrograph for steel surfaces at the higher temperatures (45 °C) it shows uniform, smooth and bright surface to some extent more than at lower temperature (25 °C).

It is found that the presence of polymers molecules make a passive layer act as protective film on carbon steel surface and improve the surface morphology on it. So these polymers act as a good corrosion inhibitors.

**Isokinetic temperatures relationships:** Thermodynamic treatment and activation energy were studied [31-33] and the data has been obtained as shown in Table-4. Energy of activation $\Delta G'$ can be obtained by the equation:

$$\Delta G' = \Delta H' - T \Delta S'$$  \hspace{1cm} (8)

The changes in either, or both, the enthalpy or the entropy make change in the rate within a reaction series. The correlation between $\Delta H'$ and $\Delta S'$ is a linear relationship may given as:

$$\delta \Delta H' = \beta \delta \Delta S'$$  \hspace{1cm} (9)

The operator, $\delta$, concerns difference between any two reactions in series. Substituting from the eqn. 8, we obtain:

$$\beta \delta \Delta S' = \delta \Delta G' + T \delta \Delta S'$$  \hspace{1cm} (10)

It is follows that when $\delta \Delta G'$ = zero, then $\beta = T$. In other words, the slope in a linear plot of $\Delta H'$ versus $\Delta S'$ is the temperature at which all reactions that conform to the line occur at the same rate. $\beta$ is therefore known as the isokinetic temperature.
The isokinetic plot of $\Delta H^*$ and $\Delta S^*$ for different concentrations of the polymers under study.

The temperature less than 298 K indicate that the rate of the reaction is entropy control (starch) in case of cell without diaphragm which is greater than 298 K indicate enthalpy control reaction (cellulose acetate, CMC and chitosan in case of cell without diaphragm and all compounds in case of cell with diaphragm) [31].

### Estimation of percentage inhibition of different polymers using weight loss method:

The free dissolution of carbon steel in 8 M $\text{H}_3\text{PO}_4$ in the presence and absence of polymers were used followed by measuring the loss in weight at 25 °C. From weight loss data, the corrosion rate ($\text{g m}^{-2} \text{h}^{-1}$) was calculated for different concentrations of the polymers. Loss in weight per area cm$^2$ ($W_i$) can be calculated from the following relation:

$$ W_i = \frac{W_o - W_t}{A} \quad (11) $$

where $W_o$ is the original weight (mg) of carbon steel specimen. $W_t$ is the weight after immersion in test electrolyte and $A$ is the surface area in cm$^2$.

The corrosion rate (CR) can be calculated from the following equation:

$$ CR = \frac{W_o - W_t}{A \cdot t} \quad (12) $$

where $t$ is the immersion time in (day).

The percentage inhibition efficiency (IE %) over the exposure time was calculated according to the following equations:

$$ \text{IE} (\%) = \frac{CR_{\text{un}} - CR_{\text{in}}}{CR_{\text{un}}} \quad (13) $$

where $CR_{\text{un}}$ and $CR_{\text{in}}$ are the corrosion rate (mg m$^{-2}$ day$^{-1}$) without and with the inhibitor, respectively [34]. The results indicated that the percentage inhibition efficiency of polymers on carbon steel surface was founded in the following order:

Cellulose acetate > Carboxymethyl cellulose sodium salt (CMC) > Chitosan > Starch

Table-5 shows the values of the percentage inhibition efficiency and the corrosion rate obtained from weight loss measurements of carbon steel in presence of different concentrations of the used polymers in 8 M $\text{H}_3\text{PO}_4$ solution.
These Tables show that an increase in the inhibitor concentration results in an increase of the inhibition efficiency in phosphoric acid solution and this can be attributed to the adsorption of the inhibitors on the carbon steel surface [34].

Inhibition efficiency increases with increasing the immersion time. This indicates that the stabilization of passive film of the inhibitors on the carbon steel surface [34].


Forced convection mechanism: Forced convection mechanism were applied using rotating carbon steel cylinder and using a cell with diaphragm which make support to the stabilization of passive layer of polymers as a corrosion inhibitors on carbon steel surface was found in the following order: cellulose acetate > Carboxymethyl cellulose sodium salt (CMC) > Chitosan > Starch.

forced convection mechanisms were applied and we obtained that the flow in system were turbulent flow.

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### REFERENCES


