Electrophoresis Deposition of Tungsten oxide Nanoparticles for Corrosion Inhibition

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ABSTRACT
In the present research, electrophoretic deposition technique (EPD) was used to deposit tungsten oxide (WO₃) nanoparticles onto galvanized steel from a tungsten oxide ethanol suspension at various concentrations of (1.7×10⁻², 2.5×10⁻² and 3.4×10⁻² M) for corrosion protection application. The (WO₃) nano coating was used as a barrier layer for the corrosion protection of galvanized steel in saline solution. (WO₃) nanoparticles were characterized by measuring the Fourier transform infrared spectroscopy, UV-Visible and X-ray diffraction techniques. The morphology of the (WO₃) nanoparticles was investigated using Scanning Electron Microscopy (SEM), and Atomic Force Microscopy (AFM). Results indicated that (WO₃) nanoparticles layer was efficiently deposited onto galvanized steel using (EPD), also, the deposited nanoparticles film was found to be homogenous and smooth. (EPD) and the partial reduction of the (WO₃) nanoparticles occurred simultaneously under the applied electrical fields. Moreover, the anti-corrosion performance of the (WO₃) nanoparticles –EPD layers was characterized using Tafel polarization method. Polarization studies identified the coated (WO₃) nanoparticles behave as a mixed type inhibitor. Protection efficiencies data were increased as the (WO₃) nanoparticles concentrations and temperature increased, indicating chemisorption protection mechanism.

Keywords: Electrophoretic deposition, tungsten oxide, Galvanized steel, Corrosion, Saline medium

INTRODUCTION
Electrophoretic deposition (EPD) process is based on a suspension of particles that occurs without any reaction involved. In fact, the principal driving force for (EPD) is the charge and the electrophoretic mobility of the particles in the solvent under the influence of an applied electric field, with the drawback that the solvent should be organic in order to avoid water electrolysis (1). Metal oxides are an important class of materials, which benefit from the large electronegativity of oxygen to induce strong bonding with nearby atoms (2). At the same time, when compared with bulk materials, nanostructured metal oxides benefit from the spatial confinement, the large fraction of surface atoms, high surface energy, strong surface adsorption, and increased surface-to-volume ratio that greatly improves the performance of these materials (3). These properties have urged to prepare coatings of greater wear and tear resistance. The deposition of this materials can be accomplished by a variety of physical and chemical techniques but nowadays, electrodeposited metal oxides are generally used in both laboratories and industries due to the flexibility to control structure and morphology of the oxide electrodes combined with a reduced cost.
Tungsten oxide (WO₃) nanomaterial is good corrosion inhibitor because it possess many advantages such as high inhibition efficiency, low cost, low toxicity and easy production. The deposition of metal/metal oxide nanoparticles composites allowed advances on the protective coatings field. Sajjadnejad et al. improved the corrosion resistance of zinc by co-depositing (TiO₂) nanoparticles, while Zeng et al. incorporated (CeO₂) nanoparticles to improve the corrosion behavior of nickel coatings. Thus, there are no other reports in the literature known by the authors where (EPD) has been used for the deposition of (WO₃) nanoparticles as protective coatings films.

Zinc it is extensively used as a sacrificial protective coating for ferrous metal products (galvanized steel) and also as a material used in metallic structures submitted to outdoor exposure. Zinc is a very active metal so that it corrodes quickly in aqueous solutions. Zinc specimens exposed to an unpolluted dry atmosphere were quickly covered with a thin grey layer of (ZnO). A priority of this study was to increase common level of corrosion resistance of galvanized steel by developing different corrosion resistant layers on their surfaces. In this study electrophoretic deposition of tungsten oxide nanoparticles on galvanized steel surface were performed and the structure and corrosion behavior of coatings were investigated. The effect of the tungsten oxide nanoparticles content and temperature on corrosion behavior of coated steel in (3.5wt%) sodium chloride solution was evaluated by Tafel polarization method. FTIR spectrum, EDX, UV-Visible spectra, SEM and AFM images were also employed for investigating of the chemical composition, surface morphology and phase structure of coatings nanoparticles, respectively.

EXPERIMENTAL

Solutions Preparation
(35g of NaCl) ( Sigma Aldrich) was dissolved in (1000 mL) distilled water to prepare (3.5% of NaCl) solution. Tungsten oxide nanoparticles (99.9% purity, Sigma Aldrich) was prepared in different concentrations (1.7×10⁻², 2.5×10⁻² and 3.4×10⁻²) M by dissolving an appropriate amount of it in (100 mL) of absolute ethanol to prepare coating solutions and few amount of iodide is added to these solutions in order to increase their conductivity.

Electrophoresis Deposition of Emulsion (Coating Samples)
Electrophoresis deposition of tungsten oxide nanoparticles on galvanized steel specimen was carried out by using direct current D.C voltage power supply (0 – 15 V). (150 ml) covered beaker contain two slit with distance between them equal to (1cm) was used and the electrical circuit was connected by ammeter, respectively, to measure the current generated between the poles. Meanwhile, Stainless steel rode used as inert electrode in deposition process cell and galvanized steel specimen was catch by tong made of stainless steel. The deposition of specimens occurs at various time and finally, the specimens were thermally dried in an oven at 100 °C for 2 min. Following the above mentioned (EPD) procedure a thick film was coated on galvanized steel to ensure a uniform coating of the (WO₃NP) film.

Electrochemical Studies
Electrochemical measurements were performed by using three-electrode potentiodynamic polarization technique that are respectively, Saturated Calomel Electrode (SCE) as a reference electrode, a platinum electrode as an auxiliary electrode and galvanized steel alloy as a working electrode. M Lab (WENKING MLab multichannel and SCI-MLab system for corrosion measurement obtained from Bank Electronics-Intelligent controls GmbH, Germany 2007) is an instrument with high-tech for electrochemical measurements. M-Lab is worked by computer desktop Window XP.

The protection efficiency (%IE) of tungsten oxide in inhibiting galvanized steel corrosion in (3.5%) NaCl solution was determined from the equation:

\[ IE(\%) = \left\{ \left( \frac{i_{\text{corr}}^c - i_{\text{corr}}}{i_{\text{corr}}^c} \right) \times 100 \right\} \]

Where, (iₘcorr) and (i₉corr) are respectively the corrosion current density for blank and coated galvanized steel with various (WO₃)NP coating concentrations at the same temperature. The surface coverage (θ) of
galvanized steel by (WO$_3$)NP is estimated by using this relation (9):

$$
\theta = \left( \frac{% \text{IE}}{100} \right)
$$

**Characterization**

Commercial (WO$_3$) nanoparticles were analyzed by Fourier transform infrared spectroscopy (FTIR), the spectrum was recorded in the range of (400-4000 cm$^{-1}$). The crystal structure was characterized by using X-ray diffraction (XRD) through employing a XPERT-PRO X-ray diffractometer with CuK$\alpha$ ($\lambda=1.5406$) radiation using a tube voltage and current of (40kv) and (30mA) respectively. Scanning Electron Microscope (SEM) – (SIGMA HV – Carl Zeiss with Bruker Quantax 200 – Z10 EDS Detector) and Atomic Force Microscopy (AFM), were used to measure the surface morphology and atomic compositions of the (WO$_3$) nanoparticles. The compositions of particles were further confirmed by (EDX) analysis. The UV–Visible spectrum of the examined nanoparticles was recorded in the range (200–800 nm) using a Varian, Cary 5000 with a scanning rate of (600nm/min).

**RESULTS AND DISCUSSION**

**Polarization Measurements**

Figures 1a, b, c and d illustrate the polarization curves for corrosion of galvanized steel in (3.5%) NaCl solution for blank and various concentrations of (WO$_3$)NP coatings at different temperatures (293, 298,303,308 and 313)K. Electrochemical parameters as corrosion current density ($i_{corr}$), corrosion potential ($E_{corr}$), cathodic (bc), and anodic (ba) Tafel slopes are given in Table 1.

Data obtained show that the presence of (WO$_3$)NP coating caused an alteration in the corrosion potential ($E_{corr}$) of galvanized steel and the range of shifting is toward more negative potentials with increasing temperature and into lower negative potentials with increasing concentration of coated inhibitor (Table-1). This is interpreted on the basis of the decreasing corrosion feasibility in the existence of (WO$_3$)NP and also by its increasing concentration of the coating, this indicated that coated (WO$_3$)NP affects anodic reaction rather than cathodic one.
Fig. 1: Polarization curves for galvanized steel corrosion in (3.5%) NaCl for blank and coated with various tungsten oxide nano particles coating concentrations at different temperatures in the range (293-313)K.

At a constant (WO₃)NP coating concentration, (E_{corr}) values moved to more negative potential with increasing temperature. Thus, corrosion became more feasible with the rise of temperature (Table 1). The corrosion rate as reflected in the values of the corrosion current density (i_{corr}) at constant tungsten oxide coating concentration were increased with the rise of temperature. On the other hand, (i_{corr}) data decreased with increasing tungsten oxide concentration and this behavior may be attributed to the better corrosion protection of (WO₃)NP film on steel surface. Therefore Tafel discussion of (WO₃)NP illustrates the restricted mobility of electrolyte ions to the steel surface in saline medium. This is indicative that (WO₃)NP coating reflects the remarkable anticorrosion properties for steel alloy. Therefore, The increasing of the concentration of coating (WO₃)NP leads to an increase of the protection efficiencies (%IE) due to good adhesion property of (WO₃)NP coating and strong compact adsorbed films is formed on the surface of the galvanized steel with increase of the temperature. This implies the increase in surface coverage (θ) with increase in the coating concentration. Thus, The maximum inhibition efficiency (77%) was achieved at the highest (WO₃)NP coating concentration of (3.4 ×10⁻² M) and at (313K).

Values of Tafel slopes (cathodic and anodic) are varied at all (WO₃)NP coating concentrations and temperatures as shown in table 1. These results refer to the variation of the rate-determining step from charge transfer process to either chemical deposition or to electrochemical desorption in the cathodic reactions and also to the variation of this step in dissolution reaction of galvanized steel alloy(10).

Table 1: Corrosion parameters of galvanized steel in (3.5%) NaCl for blank and coated with various tungsten oxide concentrations (1.7×10⁻², 2.5×10⁻² and 3.4×10⁻²) M at different temperatures in the range (293-313)K.

| Inh×10⁻² [M] | T [K] | E_{corr}[mV] | i_{corr}[µA/cm²²] | Tafel slope [mV/dec] | θ   | %IE |
|----------------|-------|--------------|------------------|----------------------|-----|-----|
|                |       |              |                  | -b_c     | +b_a |     |
| 0               | 293   | 608.1        | 52.78            | 95.5      | 71.4 | -   | -   |
|                 | 298   | 653.5        | 61.54            | 128.2     | 87.8 | -   | -   |
|                 | 303   | 677.6        | 71.82            | 130.4     | 105.3| -   | -   |
|                 | 308   | 707.7        | 79.73            | 114       | 118.8| -   | -   |
|                 | 313   | 731.9        | 96.91            | 128.1     | 107.5| -   | -   |
| 1.7             | 293   | 629          | 27.32            | 75.9      | 83.8 | 0.482| 48.22|
|                 | 298   | 666.4        | 30.66            | 84.3      | 91.5 | 0.501| 50.17|
|                 | 303   | 668.1        | 34.02            | 123.8     | 79.9 | 0.526| 52.63|
|                 | 308   | 676.2        | 37.40            | 202.4     | 81.5 | 0.530| 53.08|
|                 | 313   | 693.6        | 43.83            | 149       | 93.5 | 0.547| 54.77|
Kinetics of Corrosion

The dependence of \((i_{\text{corr}})\) values on temperature was examined by plotting \(\log (i_{\text{corr}})\) versus \((1/T)\) for the blank and \((\text{WO}_3)\text{NP}\) coated galvanized steel in saline solution in accordance with the Arrhenius equation (11):

\[
\log i_{\text{corr}} = \log A - \frac{E_a}{2.303RT}
\]

where \((i_{\text{corr}})\) stands for the rate of corrosion at temperature \((T)\). Activation energy \((E_a)\) and the pre-exponential factor \((A)\) data were obtained from the slopes and intercept respectively \(\log (i_{\text{corr}})\) versus \((1/T)\) plots as shown in Figure 2, and data obtained are tabulated in table 2. It is clear that the correlation between \(\log (i_{\text{corr}})\) and \((1/T)\) in the absence and presence of different concentrations of the coated \((\text{WO}_3)\text{NP}\), fit with straight lines in all cases. The increase the concentration of the \((\text{WO}_3)\text{NP}\) leads to a decrease of the calculated temperature coefficient \((E_a)\), indicating that the protection efficiency increase as the temperature increase and chemisorptive adsorption is more probable (12). A high value of \((E_a)\) is connected with a high value of \((A)\) and the reverse is also true where \((E_a)\) is lower for the inhibited solution than for the uninhibited solution. This behavior was discussed on the basis that \((\text{WO}_3)\text{NP}\) are firmly held on the metal surface, sometimes by chemisorptions as a result of which a surface film of the reaction product is formed and the surface area of the metal covered by inhibitor molecules increases as temperature rises (13). Hence a chemisorptive mode of adsorption is more likely.

![Fig.-2: log \(i_{\text{corr}}\) versus \(1/T\) of galvanized steel corrosion in (3.5%) NaCl solution for blank and coated with various tungsten oxide concentrations.](image)

Enthalpy \((\Delta H^\ddagger)\) and entropy \((\Delta S^\ddagger)\) of activation were calculated from the transition state of a replacement formulation of Arrhenius equation that expressed as (14):
Where N is the Avogadro number, h is the Planck's constant. $\Delta H^*$ and $\Delta S^*$ values were obtained respectively, from the slope and intercept of the plot of $(\ln(i_{corr}))$ against $(1/T)$ as show in Fig.3. The calculated $\Delta H^*$ values are positive and they decrease on increasing the (WO$_3$)NP coated concentration indicating that corrosion process is endothermic$^{(15)}$. Otherwise, $\Delta S^*$ data are negative and negativity increased with increasing (WO$_3$)NP coated concentration. The negative values of $\Delta S^*$ reveal that the activated complex in the rate determining step represents association rather than the dissociation step, this means a decrease in disorder take place$^{(16, 17)}$.

![Fig.-3: Plots of ln $(i_{corr}/T)$ versus (1/T) for galvanized steel in (3.5%) NaCl solution for blank and coated with various tungsten oxide concentrations.](image)

Table 2: Activation energy ($E_a$), enthalpy ($\Delta H^*$), and entropy ($\Delta S^*$) of activation for the corrosion of Galvanized steel in 3.5% NaCl solution for blank and coated with various tungsten oxide concentrations.

| Concentration (M) | $E_a$ [kJ.mol$^{-1}$] | $A \times 10^{28}$ [molecule.cm$^{-2}$.s$^{-1}$] | $\Delta H^*$ [kJ.mol$^{-1}$] | $\Delta S^*$ [J.K$^{-1}$.mol$^{-1}$] |
|-------------------|------------------------|---------------------------------|-----------------|-----------------|
| 0.017            | 22.47                  | 3.220                           | 19.95           | 285.55          |
| 0.025            | 17.43                  | 0.210                           | 14.90           | 281.29          |
| 0.034            | 15.54                  | 0.094                           | 13.02           | 287.90          |
| 0.040            | 7.020                  | 0.002                           | 4.52            | 319.98          |

Characterization Techniques of WO$_3$ nanoparticles

**Ultraviolet-Visible studies (UV-Visible)**
The optical measurement of the (WO$_3$) nanoparticles was carried out at room temperature by using UV–visible absorbance spectrophotometer. The recorded absorbance spectra of (WO$_3$)nanoparticles are shown in Figure 4. As it can be seen, all samples exhibit a clear absorption edge in the UV-Vis region, which correspond to the fundamental absorption of (WO$_3$)semiconductor.
Fourier Transform Infrared Spectrum (FTIR)

FT-IR spectroscopy is a very informative measurement for studying the functional groups. Figure 5 shows the infrared spectra of both (WO₃)NPs. The stretching vibrational mode of the terminal (W═O) bond produce a band at 945 cm⁻¹ (18,19). The broad absorption peak at 817 cm⁻¹ is assigned to (O=W–O) stretching vibration. The peak at 3441 cm⁻¹ attributed to (O–H) stretching vibration, and the bending vibration of adsorbed water molecules are located at 1635 cm⁻¹ (20).

X-ray Diffraction Spectroscopy (XRD)

Fig. 6 displays the XRD pattern of (WO₃) nanoparticles. The result shows all the diffraction peaks indexed to tetragonal phase of (WO₃) as per the JCPDS data card (ICSD 089092, JCPDS 89-8764; with space group P4/nmm). No peaks of any other phase or impurities were observed from the XRD patterns. Strong and sharp diffraction peaks also indicate a good crystalline sample.
8

Fig.-6: XRD pattern of (WO₃) nanoparticles

Scanning Electron Microscopy (SEM)
SEM is a useful technique to determine the morphology and particle size of the samples. Fig. 7 shows SEM image of pure (WO₃) nanoparticles. It is clearly observed that sample shows rod.

Fig.-7 SEM image of (WO₃) nanoparticles

Fig.-8 EDX Spectrum of (WO₃) nanoparticles
The chemical composition of (WO₃) nanoparticles were determined by EDAX analysis. Figure 8 shows the EDAX spectra for pure (WO₃). No other element except W and O has been detected which shows that particles are free of impurities.

Atomic Force Microscopy (AFM)
AFM is a powerful technique to investigate the surface morphology at nano to micro scale in addition to the statically determining the particles size distribution. More uniform grains may lead to more protective results. The three dimensional AFM morphology and the average diameter for (WO₃) NPs are shown in Figure 9.

Fig.-9 - AFM image of (WO₃) nanoparticles.
The results of AFM provide evidence for the excellent surface quality of (WO₃) NPs films in terms of low values of roughness. The origin of the surface roughness and the observed wavy character is due to the film morphology as a result of grain structure as indicated by the AFM. Analysis using AFM suggests that the growth of (WO₃) NPs films does not proceed in layer-by-layer or continuous fashion but occurs by island growth.

CONCLUSION
The use of electrophoretic deposition for nanostructured metal oxide films has been growing due to the versatility of this method in different applications and materials. In the present research, the coatings in which (WO₃) NPs were deposited on galvanized steel and the effect of the amount of (WO₃) NPs on the coatings morphology and its corrosion behavior were studied. Based on the obtained results, the use of nanoparticles of tungsten oxide improved the corrosion resistance of coatings. The fabricated composite coating that its plating solution contains (0.034M) nanoparticle has the lowest corrosion rate between all coatings. SEM observations showed that before corrosion tests the surfaces of galvanized steel coated tungsten oxide nanoparticles was completely smooth and homogeneous by absorption of the corrosive agents had action as a barrier against corrosive environment. The use of nanoparticles of tungsten oxide also created a uniform surface. High crystallinity of (WO₃) NPs have been detected. Scanning Electron and Atomic Force microscopy confirms the nano like morphology.

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