Original Article

Corrosion protection of mild steel in different aqueous media via epoxy/nanomaterial coating: preparation, characterization and mathematical views

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**ABSTRACT**

Corrosion rates of mild steel in different aqueous solutions at different operating conditions were studied by weight loss technique in the absence and presence of epoxy coating. It was found that corrosion rates increased with temperature and salt concentration and decreased with pH values. Presence of coating reduces the corrosion rates to significant values in acidic solutions. The performance of the coating was poor in saline solution. A magnesium oxide (MgO) nanoparticle was prepared via sol–gel method and the diagnosis was carried out by XRD technique. Maximum coating efficiency was 97% in acidic solution, while the lower one was 29.8% in saline solution in absence of nanoparticles. Nano scale MgO was used effectively with epoxy coating in saline solutions and improve the coating performance with maximum value of 93.7%. SEM test was also used to study the surface morphology. Several mathematical models were suggested to correlate the operating condition with corrosion rate. Polynomial interaction effect model was suitable to represent the data with a high correlation coefficient.

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1. Introduction

Failure of equipment due to corrosion is a main problem in the chemical and petrochemical industry. Mild steel is still the material most commonly used for pipes and other equipment parts. Mild steel pipes are widely used in oil transportation, and in their ways from oil fields to petroleum refineries passes across different environments. Many parameters and environmental factors influence the corrosion of pipe materials, such as, temperature, pH, salinity, etc. These factors play an important role in corrosion of construction materials. Corrosion can be minimized by changing the environmental factors that sometimes is hard to control, or by deal with pipe itself.

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2238-7854/© 2018 Brazilian Metallurgical, Materials and Mining Association. Published by Elsevier Editora Ltda. This is an open access article under the CC BY-NC-ND license ([http://creativecommons.org/licenses/by-nc-nd/4.0/](http://creativecommons.org/licenses/by-nc-nd/4.0/)).
Coating is one of the methods of corrosion control and epoxy coating represent the most important engineered polymers that drawn attention due to its wide applications including structural materials, tissue substitutes [1], anti-corrosion coatings [2] and flame retardant additives [3]. In material science, the combination of an organic phase (generally polymers) with inorganic particles has gained significant attention. Nano sized particles allow to improve the mechanical properties of polymer and various types of nanoparticles have been applied to prepare modified epoxy nanocomposites, which show enlarged application in specific areas [4–6]. Galliano and Landolt [7] studied the effect of reinforcement of epoxy coating by corrosion inhibiting additives. Two kinds of additives were used: organic and inorganic based materials. The results obtained show that corrosion inhibiting additives significantly modify and improve the characteristics of epoxy coatings. Xianming Shi et al. [8] studied the effect of epoxy coatings containing nanoparticles on steel substrates immersed in saline solutions. Steel corrosion resistance and microstructure of the coating matrix were significantly improved by addition of nanomaterial. In the review paper of Hanemann and Szabó [9], it was concluded that the addition of inorganic nanoparticles to polymers allows the alteration of the polymers physical properties as well as the application of new structures in the polymer matrix. In contrast to micron-sized fillers, the interface between the nanomaterial and the polymer matrix plays an important role due the large filler specific surface area. They also concluded that the most interesting nanoparticles are metals oxides with high applications in different fields. These nano oxides improve several composite properties that attributed to the large surface area of the filler and its interfacial polymer layer. Kotnarowska et al. [10] investigated the erosive wear kinetics of epoxy-polyurethane coatings modified with Al$_2$O$_3$ or silica nanoparticles. Modification of the epoxy with nano filler caused the significant increase of erosion resistance. Epoxy-polyurethane coatings in the presence of nanosilica showed the highest erosive wear resistance. Bezy and Fathima [11] analyzed the mechanical properties of epoxy resin with TiO$_2$ nanoparticles. Certain influence on mechanical properties was observed by addition of nanomaterial to epoxy. Tensile strength, flexural strength, and impact strength were improved in the presence of TiO$_2$. In the present work, nano MgO was prepared via sol–gel method and the corrosion rates of mild steel in different aqueous solutions at different operating conditions were studied by weight loss technique in absence and presence nano scale MgO with epoxy coating.

2. Experimental work

2.1. Metal preparation and procedure

Mild steel was used as working electrode. The chemical compositions of mild steel are listed in Table 1. Working electrode is shaped by dimensions of 2 cm × 3 cm × 0.2 cm with a surface area of about 13 cm$^2$. The cleaning procedure was as follows: the specimens were first degreased with analar benzene and acetone at 25 °C, and then annealed in a vacuum oven at 600 °C for 1 h and cooled to room temperature. Specimens were abraded in sequence under running tap water using emery paper of grade numbers 220, 320, 400 and 600, rinsed with running tap water followed by distilled water, dried with clean tissue, immersed in acetone and benzene, and kept in desiccator over silica gel bed until time of use [12]. The specimens were completely submerged in 250 cm$^3$ corrosion solution at pH 1, 2, and 3, temperatures 30, 40, 50, and 60 °C, and 1, 2 and 3% salt concentration for a period of 5 h in absence and presence of coating. After each experiment the specimens were washed with running tap water followed by distilled water, dried with clean tissue, immersed in acetone and benzene, and kept in desiccator over silica gel bed to dry, then weighed by high accuracy electronic balance.

2.2. Preparation of nanomaterials

Sol–gel method was used for preparation of MgO nanoparticles (NPs) [13,14]. Citric acid (C$_6$H$_8$O$_7$H$_2$O) was added to a solution of [Mg(NO$_3$)$_2$ 6H$_2$O] (magnesium nitrate hexahydrate) to make the molar ratio of citric acid to nitrate 1:2. The following steps were carried out:

1. 40 g of [Mg(NO$_3$)$_2$ 6H$_2$O] was dissolved in 60 ml of distilled water to yield 2.6 M solution.
2. 16.4 g of citric acid (as auto combustion fuel) was added to 60 ml of distilled water to yield 1.3 M solution.
3. The two solutions (steps 1 and 2 above) were mixed together in a magnetic stirrer for 30 min at room temperature. Few drops of ammonia solution were added to adjust to pH 7.
4. Mixing and graduated temperature rising up to 80 °C until sol–gel solution was obtained.
5. Dry gel (xerogel) was obtained after 40 min. The product was cooled and milled with a mortar to obtain a fine powder.
6. The calcination process of fine powder was done at 600 °C for 2 h to obtain the MgO nanoparticles.

The overall reaction is as follow:

\[ \text{Mg(NO}_3\text{)}_2 \cdot 6(\text{H}_2\text{O}) + \text{C}_6\text{H}_8\text{O}_7\text{H}_2\text{O} + \text{NH}_3 \rightarrow \text{Mgo} + 5.5\text{H}_2\text{O} + 6\text{CO}_2 + 1.5\text{N}_2 \]

2.3. Preparation of coating mixture and metal coating

The coating mixture was made by mixing epoxy resin (LUNA Coating Company-Turkish), polyamidoamine hardener, the

<table>
<thead>
<tr>
<th>Metal</th>
<th>Fe</th>
<th>C</th>
<th>Mn</th>
<th>Si</th>
<th>P</th>
<th>S</th>
<th>Cr</th>
<th>Mo</th>
<th>Ni</th>
<th>Al</th>
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</thead>
<tbody>
<tr>
<td>Compositions</td>
<td>Rem.</td>
<td>0.040</td>
<td>0.309</td>
<td>0.004</td>
<td>0.005</td>
<td>0.007</td>
<td>0.021</td>
<td>0.0009</td>
<td>0.010</td>
<td>0.004</td>
</tr>
</tbody>
</table>

Table 1 - Analytical chemical composition (wt.%) of mild steel alloy.
weight ratio of the epoxy resin to the hardener was 2:1. In the case of nano coating, the MgO nanoparticles were added at different concentrations (1, 2, and 3%). All the contents were blended using a speed mixer (H500 homogenizer form POL- EKO-APARATURA) for half an hour. Mild steel sheets were pretreated as mentioned above. The clean carbon steel substrate was dipped into the finally coating mixture for one time and then kept for 1 h sun light drying and then in an oven at 120°C for 1 h to allow full curing.

2.4. Surface morphology analysis

The SEM model AIS2300C (Angstrom Advanced, USA) was employed to carry out SEM analysis. The diagnosis of nanomaterial present with epoxy coat on the metal surface was studied by XRD technique and energy dispersive X-ray spectroscopy (EDX).

3. Results and discussion

3.1. Structural analysis

XRD patterns of the MgO nanoparticles (commercial and prepared) are shown in Fig. 1. It can be noticed that all the patterns exhibit diffraction peaks around (2θ = 42.8°, 62.1°, 78.4° and 109.6°) referred to (200), (220), (400) and (420) favoring directions respectively. These values are in good agreement with the International Center of Diffraction Data (ICDD) card number (00-045-0946). The strongest peak occurs at 2θ = 42.8° which is referred to (200) plane. The positions of the peaks and the presence of more than one diffraction peak lead to the conclusion that the samples are polycrystalline in nature, and the diffraction peaks of the prepared MgO nanoparticles were matched well with these peaks of the cubic crystalline structure. It can be noticed that 2θ for MgO nanoparticles (commercial) less compared with 2θ for MgO nanoparticles (prepared) as shown in Table 2. In addition, any other impure diffraction peaks were not detected from the XRD patterns for all samples, which indicated that the MgO nanoparticles commercial and prepared one are pure. The average crystallite size and micro strains induced in the films can be determined using Williamson–Hall (W–H) formula shown below [15]:

\[
\beta_{hkl} \cos \theta = \left( \frac{K \lambda}{D_{av}} \right) + 4S \sin \theta
\]

where \( \beta_{hkl} \) is full width of half maximum, \( D_{av} \) is the average crystallite size, \( k \) is constant and was assumed to be equal to 0.9, \( \lambda \) is wavelength for Cu target for XRD instrument, \( \theta \) is Bragg’s angle for all peaks, and \( S \) is the micro strain in the film. If \( \beta_{hkl} \cos \theta \) is plotted with respect to \( 4 \sin \theta \), strain and crystallite size can be calculated from the slope and y-intercept of the fitted line respectively as shown in Fig. 2. The average crystallite size for all films is also calculated for (200) direction by Scherrer formula by using the relation [16]:

\[
D_{av} = \left( \frac{K \lambda}{\beta \cos \theta} \right)
\]

It is observed that the crystallite size for the MgO nanoparticles (commercial and prepared) value of these results agree qualitatively with the results of crystallite size obtained by Williamson–Hall method as shown in Table 3. No significant difference could be observed between the XRD patterns of the prepared MgO nanoparticles and the commercial MgO. The micro strain in the samples is induced during the growth of samples by varying displacements of the atoms with respect to their reference lattice position [1]. Values of micro strain in MgO nanoparticles (prepared) were negative, which indicates the occurrence of compression in the lattice and in MgO nanoparticles (commercial) were positive, which indicates the occurrence of dispersion in the lattice. The texture coefficient \( T_c \) represents the texture of a particular plane, in which greater than unity values imply that there are numerous of grains in that particular direction. The texture coefficients \( T_c(hkl) \) for sample have been calculated from the X-ray data using the well-known formula [17]:

\[
T_c(hkl) = \frac{I(hkl)/I_0(hkl)}{N_l^{-1} \sum I(hkl)/I_0(hkl)}
\]

where \( I(hkl) \) is the measured intensity, \( I_0(hkl) \) taken from the (ICDD) card data, \( (N_l) \) is the reflection number and (hkl) is Miller

| Table 2 – X-ray diffraction data of MgO nanoparticles (commercial and prepared). |
|---------------------------------|---------|---------|---------|
| Sample                        | 2θ      | d_{hkl} (Å) | (hkl)   |
| MgO (JCPDS 00-045-0946)       | 42.916  | 2.1056   | (200)   |
|                                | 62.302  | 1.4890   | (220)   |
|                                | 78.628  | 1.2157   | (222)   |
|                                | 109.760 | 0.9417   | (420)   |
| MgO commercial                | 42.807  | 2.1107   | (200)   |
|                                | 62.177  | 1.4711   | (220)   |
|                                | 78.491  | 1.2175   | (222)   |
|                                | 109.601 | 0.8601   | (420)   |
| MgO prepared                  | 42.882  | 2.1072   | (200)   |
|                                | 62.243  | 1.4903   | (220)   |
|                                | 78.519  | 1.2172   | (222)   |
|                                | 109.605 | 0.9426   | (420)   |

indices. The texture coefficient is calculated for crystal plane (200) of the MgO nanoparticles (commercial and prepared). Value of texture coefficient was greater than 1, which indicates the abundance of grains in the (200) direction. The above results are in good agreement with the work of Rao et al. [18] for XRD pattern of MgO nanoparticles. Peaks were absorbed at 36°, 42°, 62°, 74°, and 78° along with miller indices values (111), (200), (220), (311) and (222), respectively. Goryczka et al. [19] prepared nano MgO powder by sol–gel method. The nano powder was characterized via XRD. The estimated crystallite size, calculated form Williamson–Hall method, equals to 5 nm.

3.2. Corrosion rate data

The corrosion of mild steel in different operating conditions was studied by weight loss measurements. The corrosion rate of mild steel was determined using the relation:

\[
C_k = \frac{\text{Weight loss (g)}}{\text{Area (m²) } \times \text{Time (day)}}
\]  

(4)

\(C_k\) is corrosion rate (g/m²·day) and symbol as gmd. The percentage coating efficiency (%IE) was calculated at optimum conditions using the relationship:

\[
\%\text{IE} = \frac{C_{k}^{0} - C_{k}^{1}}{C_{k}^{0}} \times 100
\]

(5)

\(C_{k}^{0}\) and \(C_{k}^{1}\) are the corrosion rates in absence and presence of coating, respectively [12]. Tables 4–6 collect the corrosion rate data at different conditions. Tables 4–7 collect the obtained results. It is clear that corrosion rate increased with temperature, acidity and salinity and presence of coating lower the corrosion rate values.

3.3. Effect of temperature and thermodynamic parameters

The effects of temperature on the corrosion of mild steel in different aqueous solutions were shown in Figs. 3–7. Corrosion rate increased with temperature increase. The corrosion reaction of mild steel is generally accompanied with different corrosion products and rise in temperature typically accelerates the corrosion reactions, resulting in progressive dissolution of steel. The increase in the rate of steel corrosion with increasing corrosive media temperature may be due to several reasons; increasing solution temperature leads to decreasing viscosity with a consequent increase in oxygen diffusivity, which leads to increase the rate of mass transfer of dissolved oxygen to the cathode surface, then increasing the corrosion

Fig. 2 – The W–H analysis of nano MgO ((A) commercial and (B) prepared).

Table 3 – XRD results of MgO nanoparticles (commercial and prepared).

<table>
<thead>
<tr>
<th>Samples</th>
<th>MgO commercial</th>
<th>MgO prepared</th>
</tr>
</thead>
<tbody>
<tr>
<td>2θ (deg)</td>
<td>42.8072</td>
<td>42.8828</td>
</tr>
<tr>
<td>hkl</td>
<td>(200)</td>
<td>(200)</td>
</tr>
<tr>
<td>d (Å)</td>
<td>2.11079</td>
<td>2.10724</td>
</tr>
<tr>
<td>(FWHM) (rad)</td>
<td>0.0067</td>
<td>0.0101</td>
</tr>
<tr>
<td>D (nm) W–H</td>
<td>19.2</td>
<td>13.4</td>
</tr>
<tr>
<td>D (nm) Scherrer</td>
<td>22.2</td>
<td>14.7</td>
</tr>
<tr>
<td>Micro strain S (W–H)</td>
<td>+7.4 x 10^{-4}</td>
<td>-4.5 x 10^{-4}</td>
</tr>
<tr>
<td>Lattice constants a₀ (Å)</td>
<td>4.22158</td>
<td>4.21448</td>
</tr>
<tr>
<td>Tₜ</td>
<td>1.955</td>
<td>1.863</td>
</tr>
</tbody>
</table>

Fig. 3 – Variation of corrosion rate of mild steel with temperature at different pH values in absence of coating.
rate. On the other hand, the decrease in solution viscosity with increasing temperature improves its conductivity with a consequent increase in corrosion current and the rate of steel dissolution [20]. In general, the effect of temperature can describe according to Arrhenius equation (Eq. (6)) [20]. Activation energies ($E_a$) were calculated from the Arrhenius plots ($\log(C_a)$ against the reciprocal absolute temperature) as shown in Fig. 8 [21].

$$C_R = A \exp \left( -\frac{E_a}{RT} \right)$$  \hspace{1cm} (6)

where $A$ is frequency factor, $T$ is the absolute temperature, $R$ is the universal gas constant. Table 8 shows the values of activation energy in presence and absence of coating. Activation energy gives information about how much energy needed to cross the barrier from reactants to products, in other words, it represent the minimum energy needed to start the corrosion reaction. In acidic solution and absence of coating, the values of $E_a$ lower than the values in presence of coating which attributed to lower corrosion rate values. In saline solution, the values of $E_a$ are approximately the same and the presence of coating has insignificant effect on reaction rate.

### 3.4. Effect of pH

The effects of pH on the corrosion of mild steel in different aqueous solutions were shown in Table 4. Corrosion rate increased with pH decrease in both absence and presence of coating. This may be attributed to the presence of hydrogen ion. The spontaneous dissolution of iron can be described by

<p>| Table 4 – Corrosion rate as a function of temperature and pH in absence and presence of coating. |</p>
<table>
<thead>
<tr>
<th>No.</th>
<th>Temp. (°C)</th>
<th>pH</th>
<th>Corrosion rate (gmd) Without coat</th>
<th>With coat</th>
<th>Coating efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>30</td>
<td>1</td>
<td>65.76</td>
<td>1.98</td>
<td>97</td>
</tr>
<tr>
<td>2</td>
<td>40</td>
<td>1</td>
<td>90.216</td>
<td>3.55</td>
<td>96</td>
</tr>
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<td>3</td>
<td>50</td>
<td>1</td>
<td>190.66</td>
<td>7.104</td>
<td>96.3</td>
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<tr>
<td>4</td>
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<td>1</td>
<td>410.232</td>
<td>28.44</td>
<td>93.1</td>
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<tr>
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<td>2</td>
<td>49.34</td>
<td>1.32</td>
<td>97.3</td>
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<td>67.99</td>
<td>2.21</td>
<td>96.7</td>
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<td>7</td>
<td>50</td>
<td>2</td>
<td>102.2</td>
<td>3.55</td>
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<tr>
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<td>60</td>
<td>2</td>
<td>288.8</td>
<td>15.09</td>
<td>94.7</td>
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<tr>
<td>9</td>
<td>30</td>
<td>3</td>
<td>22.76</td>
<td>0.88</td>
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<tr>
<td>10</td>
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<td>3.01</td>
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<td>3</td>
<td>103.07</td>
<td>11.54</td>
<td>88.8</td>
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</table>

<p>| Table 5 – Corrosion rate as a function of temperature and salt concentration. |</p>
<table>
<thead>
<tr>
<th>No.</th>
<th>Temp. (°C)</th>
<th>Salt concentration (%)</th>
<th>Corrosion rate (gmd) Without coat</th>
<th>With coat</th>
<th>Coating efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
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<td>4.87</td>
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<td>29.8</td>
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</table>

<p>| Table 6 – Corrosion rate as a function of temperature and salt concentration and pH. |</p>
<table>
<thead>
<tr>
<th>No.</th>
<th>Temp. (°C)</th>
<th>pH</th>
<th>Salt concentration (%)</th>
<th>Corrosion rate (gmd) Without coat</th>
<th>With coat</th>
<th>Coating efficiency (%)</th>
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<td>1</td>
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<td>887.11</td>
<td>97.34</td>
<td>89.1</td>
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</table>
Fig. 4 – Variation of corrosion rate of mild steel with temperature at different pH values in presence of coating.

Fig. 5 – Variation of corrosion rate of mild steel with temperature at different salt concentration values in absence of coating.

Table 7 – Corrosion rate as a function of temperature and salt concentration in presence of nano-coating.

<table>
<thead>
<tr>
<th>No.</th>
<th>Temp. (°C)</th>
<th>MgO nanoparticles (%)</th>
<th>Salt concentration (%)</th>
<th>Without coat</th>
<th>With nano coat</th>
<th>Corrosion rate (g/m²)</th>
<th>Nano coating efficiency (%)</th>
</tr>
</thead>
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<tr>
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anodic dissolution reaction (Eq. (7)) accompanied by the corresponding cathodic reaction (Eq. (8)) of hydrogen evolution:

\[ \text{Fe} \rightarrow \text{Fe}^{2+} + 2e^- \]  \hspace{1cm} (7)

\[ 2\text{H}^+ + 2e^- \rightarrow \text{H}_2 \uparrow \]  \hspace{1cm} (8)

As the cathodic reaction increased the anodic one is also increased and vice versa. Presence of oxygen in acidic solution raises the cathodic reaction which leads to increasing the anodic dissolution of steel:

\[ \text{O}_2 + 4\text{H}^+ + 4e^- \rightarrow 2\text{H}_2\text{O} \]  \hspace{1cm} (9)

While in neutral and basic solutions the cathodic reaction may be written as:

\[ \text{O}_2 + 2\text{H}_2\text{O} + 4e^- \rightarrow 4\text{OH}^- \]  \hspace{1cm} (10)

Similar results were obtained by Li et al. [22] that effect of pH, chloride ion concentration and temperature on the corrosion behavior of steel. The surface conditions are determined and significantly influenced by these variables. The protection of the passive film is enhanced with increasing the pH and decreasing Cl\textsuperscript{-} concentration and solution temperature.

3.5. Effect of salt concentration

As shown in Table 5, corrosion rate increased with salt concentration. It was suggested that the presence of Cl\textsuperscript{-} ions in the solution can work as a catalyst for oxidation of steel via formation of FeCl\textsubscript{3}\textsuperscript{-} complex, which is unstable and can be drawn into solution and react with OH\textsuperscript{-} ions to form Fe(OH)\textsubscript{2}. This produces chloride ions back into solution and consumption of OH\textsuperscript{-} ions, as shown below [23]:

\[ 2\text{Fe} + 6\text{Cl}^- \rightarrow 2\text{FeCl}_3^- + 4e^- \]  \hspace{1cm} (11)

\[ \text{FeCl}_3^- + 2\text{OH}^- \rightarrow \text{Fe(OH)}_2 + 3\text{Cl}^- \]  \hspace{1cm} (12)

The electron obtained in oxidation reaction can be consumed in cathodic sites. The presence of chloride ions can destroy the passive film that may be formed on steel surface. The small size Cl\textsuperscript{-} ion penetrates through the passive layer to the positively charged metal cation destroying the protective function of the passive film. Steel highly affected by the deterioration of the passive film [24].

3.6. Corrosion control via coating

Tables 4–6 collect the corrosion rate data in the presence of coating. Corrosion rate falls due to the formation of coating barrier layer between the metal surface and corrosive solution. In Table 4, MgO nanoparticles free epoxy coating reduces the corrosion rate significantly with maximum protection coating efficiency of 97%, while in saline solution (Table 4) the presence of coating has a limited effect on corrosion rate as compared with acidic one. Interaction between acidic and saline solution was also evaluated at aggressive conditions (Table 5, pH 1 and 3% salt concentration). Coating performance was better than saline condition alone with average protection efficiency of 86.9%. These results indicate that the epoxy coating is more resistant to acidic conditions than the saline media. Fig. 9 shows the variation of coating efficiency at different conditions in absence of nano materials. The barrier performance of coatings can be improved by the combination of inorganic filler particles [25]. These particles increase

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3.7. Scanning electron microscopy (SEM) investigations

The SEM mild steel surface in the absence and presence of the epoxy coating (with and without nanoparticles additives) is shown in Fig. 11 at seven corrosion conditions (3% salt concentration and 60 °C). Fig. 11a and b represent the SEM of the mild steel surface in the absence of coating before and after immersion in corrosive media respectively. The comparison between these two figures can show the damage due to corrosion. However, in the presence of coating (Fig. 11c), the surface morphology is remarkably improved, but the coated surface is damaged due to corrosive environment (Fig. 11d). Addition of nanoparticles to epoxy coating have a significant effect as shown in Fig. 11e, the mild steel surface is covered with clear and smooth layer which isolates the metal from the corrosive environments. The effect of corrosion is shown in Fig. 11f.

3.8. EDX analysis

Energy dispersive X-ray spectroscopy (EDX) spectrum of the energy versus relative counts of the detected X-rays is obtained and evaluated for qualitative and quantitative determinations of the elements as shown in Fig. 12. The strong peaks observed in the spectrum related to magnesium (Mg) and oxygen (O). The elemental constitution of MgO nanoparticles with two major peaks was found to have weight...
percentage of 56.7 of Mg and 43.30 of oxygen, and 49.32 of Mg and 50.68 of oxygen for spectrum (1,2) respectively as shown in Fig. 10. The prepared MgO nanoparticles have atomic percentage at 46.29 of Mg and 53.71 of oxygen and 39.04 of Mg and 60.96 of oxygen for spectrum (1,2) as shown in Fig. 10 also. This confirmed the formation of MgO nanoparticles in all the three process. The EDX results indicate that no other element but (Mg) and (O) were present in pure MgO nanoparticles.

3.9. Mathematical and statistical modeling

Mathematical formulas can be used as a powerful method for data representation. Several mathematical models were suggested in the present work to represent the corrosion rate data. The models are divided into two sets. Linear and polynomial models. The linear models are:

\[
y = \alpha + \sum_{i=1}^{n} \beta_i x_i + \sum_{i=1}^{n} \epsilon_i \quad (13)
\]

Linear-Logarithmic model

\[
y = \alpha + \sum_{i=1}^{n} \beta_i \log x_i + \sum_{i=1}^{n} \epsilon_i \quad (14)
\]

Logarithmic-Linear model

\[
\log y = \alpha + \sum_{i=1}^{n} \beta_i x_i + \sum_{i=1}^{n} \epsilon_i \quad (15)
\]

The second-order polynomial model was also suggested. This model takes into account the individual effect of each variables and the interaction between them.

Polynomial-individual effect model

\[
y = \alpha + \sum_{i=1}^{n} \beta_i x_i + \sum_{i=1}^{n} \beta_i x_i^2 + \sum_{i=1}^{n} \epsilon_i \quad (16)
\]

Polynomial-interaction effect model

Fig. 11 – SEM of mild steel surface at severe corrosion conditions of 3% salt concentration and 60 °C. (a) Steel before corrosion. (b) Steel after corrosion. (c) Coated steel before corrosion. (d) Coated steel after corrosion. (e) Nano coated steel before corrosion. (f) Nano coated steel after corrosion.
where $y$ is corrosion rate (gmd), $x_1$ is temperature (°C), $x_2$ is corrosive solution concentration (wt.% for saline solution and pH for acidic one), $x_3$ is MgO nanoparticles concentration (wt%), $n$ is number of variables, $\epsilon$ is standard error, $\alpha$ and $\beta$ are constants. Mathematical modeling can be used as a tool of predicting corrosion rate as a function of different variables [27,28]. Eqs. (13)–(17) can be expanded and regression has been carried out to evaluate the coefficients of these equations. STATISTICA 7 software was used to estimate the coefficients. This software was based on Levenberg–Marquardt non-linear estimation least squares method. Maximum number of iteration was 1000, confidence level 95%, and convergence criterion was $1 \times 10^{-6}$. The expanded equations can be rewritten as:

$$y = \alpha + \sum_{i=1}^{i=n} \beta_i x_i + \sum_{i=1}^{i=n} \beta_i x_i^2 + \sum_{i=1}^{i=n} \beta_i x_i^3 + \epsilon_{\text{total}}$$

(17)

The numerical values of these coefficients, standard errors, and correlation coefficients were evaluated. Eqs. (10a)–(12a) represent the corrosion rate data with low correlation coefficients ($R^2 = 0.202, 0.255$ and 0.181 respectively). While Eqs. (13a) and (14a) were more accurate ($R^2 = 0.783$ and 0.915 in absence of coating respectively). Generally, correlation coefficient up to 0.30 indicates a poor relationship and is of uncertain validity; between 0.50 and 0.70 indicates a significant relationship and is of practical importance; while above 0.90 means a strong relationship [28]. Therefore, polynomial interaction effect model was selected to represent the corrosion rate data and the following equations were obtained:

$$C_R = 199.1 - 16.5T + 115.2pH + 0.35T^2 + 5.9pH^2 - 3.7TpH$$

($R^2 = 0.915$ without coating)

$$C_R = 31.5 - 1.9T + 2.4pH + 0.3T^2 + 1.4pH^2 - 0.22TPH$$

($R^2 = 0.928$ with coating)

$$C_R = -5.1 + 0.32T + 4.8S_C - 0.0012T^2 - 0.58S_C^2 - 0.33TS_C$$

($R^2 = 0.901$ without coating)

$$C_R = -3.01 + 0.18T + 0.85S_C - 0.0005T^2 - 0.28S_C^2 - 0.019TS_C$$

($R^2 = 0.887$ with coating)


\[ C_k = -6.8 + 0.13T + 2.9N_C + 2.45C + 7 \times 10^{-4}T^2 - 0.15N_C^2 + 0.02S_C^2 - 0.052T N_C - 0.667 S_C \]

\( R^2 = 0.967 \) with nanocoating

where \( C_k \) is corrosion rate (gmd), \( T \) is temperature (°C), \( S_C \) is salt concentration (wt.%), and \( N_C \) is MgO nanoparticles concentration (wt.%). The above equations can be used for quick estimation for corrosion rate at different operating conditions.

4. Conclusion

Corrosion rate of mild steel was evaluated as a function of temperature, pH, and salt concentration in absence and presence of epoxy coating. The following points were concluded form present study:

1. Epoxy coating was very powerful in acidic solution with coating efficiency approach 97%.
2. In saline solution the performance of coating was poor.
3. MgO nanoparticles were syntheses using sol–gel method. XRD studies show a good agreement between prepared and commercial nano MgO.
4. MgO nanoparticles were added to improve the efficiency of coating to a significant level in saline solution with a maximum coating efficiency of 93.7%.
5. SEM test was also used to study the surface morphology that showed lower damages in presence of coating.
6. It was found that the effect of temperature on corrosion process follow Arrhenius equation. Activation energy values were higher in the presence of coating.
7. Several mathematical models were suggested to correlate the effect of different variables on corrosion rate. Polynomial interaction effect model was suitable to represent the data with a high correlation coefficient.

Conflicts of interest

The authors declare no conflicts of interest.

Acknowledgement

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REFERENCES


