Inhibitive Effect of Aqueous Extract of Aloe Vera and Sodium Molybdate-Zn\textsuperscript{2+} System on Carbon Steel

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ABSTRACT: The Inhibition efficiency (IE) of various concentrations of a SM(Sodium molybdate)-Zn\textsuperscript{2+}-Aloe vera system in controlling corrosion of mild steel immersed in well water was evaluated by a weight-loss study. The formulation consisting of 100 ppm of SM and 25 ppm of Zn\textsuperscript{2+} and 10ml of aloe vera extract showed 97\% IE. A synergistic effect was noticed between SM-Zn\textsuperscript{2+}-Aloe vera system. In the presence of aloe vera, SM-Zn\textsuperscript{2+} system has excellent inhibition efficiency. Polarization studies reveal that SM-Zn\textsuperscript{2+}-Aloe vera system functions as anodic inhibitor. AC impedance spectra suggest that a protective film is formed on the metal surface. FTIR spectra reveal that the protective film consists of Fe\textsuperscript{2+}-SM complex and Fe\textsuperscript{2+}-Aloe vera complex and Zn(OH)\textsubscript{2}.

KEYWORDS: Corrosion inhibition, Carbon steel, Sodium molybdate, Aloe vera, Synergistic effect.

I. INTRODUCTION

Plant extracts have become important as environmentally acceptable, readily available and renewable source for wide range of inhibitors. [1] In general, the plant extracts are of inhibitors with high inhibition efficiency and of non-toxicant. Several plant extracts [2-6] and eco-friendly inhibitors [7,8] attracted the researchers. Investigation of natural inhibitors is particularly interesting because they are non-expensive, ecologically friendly/acceptable and possess no threat to the environment. N.O. Eddy et al. [9] was studied the corrosion inhibition of ethanol extract of aloe vera on mild steel in acidic media. Sribharathy et al investigated the corrosion of mild steel in sea water by aloe vera extract [10]. Bo yong et al. Investigated the corrosion inhibition of mild steel in acidic media by garlic [11], [12] Yan Li et al. Berberine isolated an alkaloid from Captis studied for its anticorrosion effect for mild steel corrosion in H2SO4 medium. Curcumin have been investigated as corrosion inhibitors for a-brass in 2 M nitric acid solution [13]. Extracts of tobacco from twigs, stems, and leaves can protect steel and aluminium in saline solutions and strong pickling acids [14, 15]. Aqueous extracts of Eucalyptus leaves protect mild steel and copper in 1M HCl solution from corrosion [14, 16]. Extract of Hibiscus sabdariffa can be used as corrosion inhibitor for mild steel in 2M HCl and 1M H\textsubscript{2}SO\textsubscript{4} solution [14, 17]. El-Etre et al. investigated Khillah extract [18] for the corrosion inhibition of SX 316 steel in acidic media. Lawsonia extract [19] was studied for effect against acid induced corrosion of metals. Opuntia extract [20] was investigated for the corrosion of Aluminium in acid medium and vanillin [21] for the corrosion of mild steel in acid media. Fabrizio Zucchi and Ibrahim Hashi Omar [22] have found that Papua, Poinciana pulcherrima, Cassia occidentalis and Datura stramonium seeds, Calotropis procera, Azydracta indica and Auporpio turkiale sap are useful as acid corrosion inhibitors. Sethuraman and Bothi raja [23] have studied the acid extract of Datura metel as corrosion inhibitor for mild steel in acid medium. Quinine [24] has been studied for its anticorrosive effect of carbon steel in 1M HCl by Mohamed Ismail Awad. Anthony et al. has studied the effect of caffeine against chloride corrosion of carbon steel.[25] Corrosion inhibitors usually contain polar groups with atoms such as nitrogen, sulphur and oxygen. Correspondingly inhibitors include a wide list of organic and inorganic compounds [26].
The present work investigated the inhibition efficiency of an aqueous extract of plant material, Aloe vera, SM and Zinc System, in controlling corrosion of carbon steel (CS) immersed in well water in the absence and presence of inhibitor, using weight loss method. The protective film formed will be analyzed by Fourier transform infrared (FTIR) spectroscopy, potentiodynamic polarization and the alternating current (AC) impedance spectra and proposed a suitable mechanism of corrosion inhibition, based on the results of the above studies.

II. EXPERIMENTAL

2.1. Preparation of plant extract and specimens

An aqueous extract was prepared by grinding 10 g of fresh extract of aleo vera gel, filtering and making up to 100 ml using double distilled water. Carbon steel specimens (0.0267% S, 0.06% P, 0.4% Mn, 0.1% C and the rest iron) of dimensions 1.0 cm x 4.0 cm x 0.2 cm were polished to a mirror finish and degreased with trichloroethylene.

2.3. Weight loss method

Carbon steel specimens were immersed in 100 ml of the well water, containing various concentrations of the inhibitor (sodium molybdate) in the absence and presence of ZnO for 3 days. The weights of the specimens before and after immersion were determined using a Digital Balance Model AY 62 SHIMADZU. The corrosion products were cleaned with Clarke’s solution. It can be prepared by dissolving 20 gms of Sb2O3 and 50 gms of SnCl2 in one litre of Conc. HCl of specific gravity (1.9)[27]. The corrosion IE was then calculated using the equation.

\[ \text{IE} = 100 \left[1 - \frac{W_{2}}{W_{1}}\right] \% \]

where \( W_{1} \) is the corrosion rate in the absence of inhibitor and \( W_{2} \) is the corrosion rate in the presence of inhibitor.

Corrosion rate was calculated using the formula

\[ \text{W} = \text{weight loss in milligrams} / \text{D} \times \text{A} \times \text{T} \]

\( \text{D} \) = density of specimen = 7.87 gm/cm³

\( \text{A} \) = area of specimen = 10cm² and \( T \) = exposure in hours = 72 hrs.

2.4. Potentiodynamic Polarization

Polarization studies were carried out in a CHI-electrochemical work station with impedance model 660A. It was provided with IR compensation facility. A three-electrode cell assembly was used. The working electrode was carbon steel. A SCE was the reference electrode. Platinum was the counter electrode. From polarization study, corrosion parameters such as corrosion potential (Ecorr), corrosion current (Icorr), Tafel slopes anodic = bₐ, and cathodic = bₐ were calculated and a linear polarization study was done. The scan rate (V/S) was 0.01. Hold time at (E corrosion) was zero and quiet time (s) was two.

2.5. AC Impedance Spectra

The instrument used for polarization study was used to record AC impedance spectra also. The cell set up was also the same. The real part (Z’) and imaginary part (Z”) of the cell impedance were measured in ohms at various frequencies. Values of charge transfer resistance (Rₓ) and the double layer capacitance (Cdl) were calculated. AC impedance spectra were recorded with initial Ecorr = 0, high frequency (Hz) = 1x10⁵, low frequency (Hz) = 1, amplitude (V) = 0.005, and quiet time (s) = 2.

2.6. Synergism Parameter

The synergism parameter can be calculated by using the equation indicates the synergistic effect existing between the inhibitors [28-30]. \( S_{t} \) value is found to be greater than one suggesting that the synergistic effect between the inhibitors is \( S_{t}=1-I_{1}\%+2 /1-I_{1}\%I_{2}\% \), where \( I_{1} \) = inhibition efficiency of substance 1, \( I_{2} \) = inhibition efficiency of substance 2, \( I_{1+2} \) = combined inhibition efficiency of substance 1 and 2. If synergistic effect exists between the inhibitors, \( S_{t} \) value will be greater than one.
2.7. Analysis of Variance (F-Test)
An F-test was carried out to investigate whether the synergistic effect existing between inhibitor systems is statistically significant [31]. If F-value is greater than 5.32 for 1,8 degrees of freedom, the synergistic effect proves to be statistically significant. If it is less than 5.32 for 1,8 degrees of freedom, it was statistically insignificant at a 0.05 level of significance.

III. RESULT AND DISCUSSION

3.1. Analysis of Result of the weight loss method
The physicochemical parameters of well water are given in Table 1. The inhibition efficiency (IE) of sodium molybdate (SM)-Zn\(^{2+}\)-Aloe vera in controlling corrosion of carbon steel immersed in well water for a period of 3 days in the absence and the presence of inhibitors is given in Table 2. In order to examine the role of Aloe vera in the ternary inhibitor formulation, experiments were conducted with Aloe vera alone, SM, and with Zn\(^{2+}\) + Aloe vera in a wide concentration range.

Table 1. Physico-Chemical Parameters of Well Water

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>8.38</td>
</tr>
<tr>
<td>Conductivity</td>
<td>3110µmhos/cm</td>
</tr>
<tr>
<td>Chloride</td>
<td>665 ppm</td>
</tr>
<tr>
<td>Sulphate</td>
<td>14ppm</td>
</tr>
<tr>
<td>TDS</td>
<td>2013ppm</td>
</tr>
<tr>
<td>Total hardness</td>
<td>1100ppm</td>
</tr>
</tbody>
</table>

Table 2. Corrosion Rate (CR) and IE of Carbon Steel in Well Water, in the Absence and the Presence of Inhibitors and IE Obtained by Weight-Loss Method

<table>
<thead>
<tr>
<th>SM ppm</th>
<th>Zn(^{2+}) ppm</th>
<th>Aloe vera ml</th>
<th>IE %</th>
<th>CR mmy</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>0</td>
<td>-</td>
<td>0.1174</td>
</tr>
<tr>
<td>0</td>
<td>0</td>
<td>0</td>
<td>28</td>
<td>0.0950</td>
</tr>
<tr>
<td>0</td>
<td>25</td>
<td>0</td>
<td>5</td>
<td>0.1115</td>
</tr>
<tr>
<td>0</td>
<td>0</td>
<td>10</td>
<td>32</td>
<td>0.0798</td>
</tr>
<tr>
<td>100</td>
<td>25</td>
<td>0</td>
<td>40</td>
<td>0.0704</td>
</tr>
<tr>
<td>100</td>
<td>25</td>
<td>2</td>
<td>55</td>
<td>0.0528</td>
</tr>
<tr>
<td>100</td>
<td>25</td>
<td>4</td>
<td>65</td>
<td>0.0410</td>
</tr>
<tr>
<td>100</td>
<td>25</td>
<td>6</td>
<td>73</td>
<td>0.0316</td>
</tr>
<tr>
<td>100</td>
<td>25</td>
<td>8</td>
<td>83</td>
<td>0.0199</td>
</tr>
<tr>
<td>100</td>
<td>25</td>
<td>10</td>
<td>97</td>
<td>0.0003</td>
</tr>
<tr>
<td>100</td>
<td>0</td>
<td>10</td>
<td>58</td>
<td>0.0493</td>
</tr>
<tr>
<td>0</td>
<td>25</td>
<td>10</td>
<td>47</td>
<td>0.0622</td>
</tr>
</tbody>
</table>

The synergistic effect in the SM- Zn\(^{2+}\)-Aloe vera system is evident from the data in Table 2. The Zn\(^{2+}\) ion acts as one synergist and Aloe vera acts as the other. From the data in Table 2, it is seen that at relatively higher concentrations of both SM, Zn\(^{2+}\) and Aloe vera, 97% IE was obtained. However, such an efficiency is not obtained with combinations of SM and Aloe vera, even at relatively high concentrations. Thus, it may be concluded that Zn\(^{2+}\) is the primary synergist and Aloe vera is the secondary synergist and both play a significant synergistic role in inhibiting corrosion. Hence, the highest IE is obtained at such low concentrations of each of the components in the ternary inhibition formulation.

3.2. Synergism parameter
The values of synergism parameters are shown in Table 3. The values of S\(_i\) are greater than one, suggesting a synergistic effect. S\(_i\) approaches 1 when no interaction exists between the inhibitor compounds. When S\(_i\) >1, this points to the synergistic effect. In the case of S\(_i\)<1, the negative interaction of inhibitors prevails (i.e., corrosion rate increases).
Table 3. Synergism Parameter of Carbon Steel Immersed in Well Water in the Presence and Absence of Inhibitor

<table>
<thead>
<tr>
<th>SM+Zn²⁺ (I₁) IE (%)</th>
<th>Aloe vera (I₂) IE (%)</th>
<th>SM-Zn²⁺-Aloe vera (I₁⁺₂) IE (%)</th>
<th>S₁</th>
</tr>
</thead>
<tbody>
<tr>
<td>40</td>
<td>15</td>
<td>51</td>
<td>1.13</td>
</tr>
<tr>
<td>40</td>
<td>19</td>
<td>65</td>
<td>1.40</td>
</tr>
<tr>
<td>40</td>
<td>23</td>
<td>74</td>
<td>1.77</td>
</tr>
<tr>
<td>40</td>
<td>28</td>
<td>83</td>
<td>2.53</td>
</tr>
<tr>
<td>40</td>
<td>32</td>
<td>97</td>
<td>13.67</td>
</tr>
</tbody>
</table>

3.3. Analysis of variance (ANOVA)

F-test is used if the synergistic effect exists between inhibitors is statistically significant. The results are given in Table 4. Influence of various concentrations of Aloe vera (2, 4, 6, 8 and 10 ml) on the inhibition efficiencies of SM(100ppm)-Zn²⁺(25ppm) is tested in Table 4. The calculated F-value is 10.65. It is statistically significant, since it is greater than the critical F-value (5.32) for 1, 8 degrees of freedom at 0.05 level of significance. Hence, it is concluded that the inhibition efficiencies of the SM-Zn²⁺-Aloe vera system is statistically significant.

Table 4. Distribution of F Value between the Inhibition Efficiencies of SM-Zn²⁺ and SM-Zn²⁺-Aloe vera Systems

<table>
<thead>
<tr>
<th>Source of variance</th>
<th>Sum of squares</th>
<th>Degrees of freedom</th>
<th>Mean square</th>
<th>F</th>
<th>Level of significance of F</th>
</tr>
</thead>
<tbody>
<tr>
<td>Between</td>
<td>3630.48</td>
<td>1</td>
<td>3630.48</td>
<td>10.65</td>
<td>P&gt;0.05</td>
</tr>
<tr>
<td>Within</td>
<td>2726.50</td>
<td>8</td>
<td>340.75</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

3.4. FTIR spectra

FTIR spectra have been used to analyze the protective film formed on metal surface [32,33]. FTIR spectrum of pure sodium molybdate is given in Figure 2a. The Mo-O stretching frequency appears at 824 cm⁻¹. The active principle in an aqueous extract of Aloe Vera is shown in Figure 1. It contains phenolic -OH group and carboxyl (C=O) group.

Fig 1. Aloe Vera

A few drops of an aqueous extract of Aloe vera was dried on a glass plate. A solid mass was obtained. Its spectrum is shown in Figure 2b. The hydroxyl (-OH) group appears at 3312 cm⁻¹ and carboxyl group (C=O) appears at 1626 cm⁻¹. The FTIR spectrum of the protective film formed on the metal surface after immersion in the solution containing 10 ml of Aloe Vera, 100 ppm of SM and 25ppm of Zn²⁺ is shown in the Figure 2c. The MoO₄²⁻ stretching frequency of SM Shifted from 824 cm⁻¹ to 853 cm⁻¹. This suggests that MoO₄²⁻ of SM is coordinated with Fe²⁺ on the anodic sites of the metal surface, also resulting in the formation of Fe²⁺-MoO₄²⁻ complex.

The phenolic -OH stretch shifted from 3312 cm⁻¹ to 3385 cm⁻¹. The C=O stretching shifted from 1626 cm⁻¹ to 1613 cm⁻¹. These shifts confirm the formation of Fe²⁺-Aloe Vera complex on the anodic sites of the metal surface [34, 35]. The Zn-O stretching frequency appears at 569 cm⁻¹ and the stretching frequency due to -OH appears at 3385 cm⁻¹. Therefore, it is concluded that Zn(OH)₂ is formed on cathodic sites of the metal surface [36].
3.6. Analysis of polarization curves

The polarization study has been used to investigate the formation of protective film on metal surface [37-41]. The polarization curves of carbon steel immersed in well water in the presence and absence of inhibitors are shown in Figure 3. The corrosion parameters are given in Table 5. When carbon steel is immersed in well water environment, the corrosion potential is −763 mV vs SCE. When 10 ml of Aloe vera and 100 ppm of SM and 25 ppm Zn2+ are added to the well water, the corrosion potential shifts to the cathodic side (−713 mV vs SCE). This suggests that this formulation controls the anodic reaction predominantly. Both the anodic and cathodic Tafel slopes are shifted in the presence of the inhibitor. However, a shift of 120 mV in the anodic Tafel slope (bₐ) is much higher as compared to a shift of 77 mV in the cathodic Tafel slope for the blank and SM (100ppm)-Zn2+ (25 ppm)- Aloe vera (10ml) formulations. Thus, it can be concluded that this inhibitor formulation acts as an anodic inhibitor. When carbon steel immersed in well water, the corrosion current, I_corr is 3.92x10⁻⁵ A/cm². When SM (100ppm)-Zn2+ (25 ppm)- Aloe vera (10ml) is added to well water, the Corrosion Current decreases to 2.010 x10⁻⁵ A/cm². The significant reduction in corrosion current indicates a decrease in corrosion rate in the presence of the inhibitor. Linear polarization resistance (LPR) value increases from 496.9 Ω cm² to 1584.8 Ω cm². This indicates that protective film formed on the metal surface. [42-48].

Table 5. Corrosion parameters of carbon steel immersed in various test solutions

<table>
<thead>
<tr>
<th>System</th>
<th>E_corr</th>
<th>bₐ</th>
<th>bᵣ</th>
<th>LPR cm²</th>
<th>I_corr A/cm²</th>
</tr>
</thead>
<tbody>
<tr>
<td>Well Water (WW)</td>
<td>-763</td>
<td>148</td>
<td>64</td>
<td>496.9</td>
<td>3.92 x 10⁻⁵</td>
</tr>
<tr>
<td>WW + SM (100ppm) + Zn²⁺ (25ppm) + Aloe vera (10ml)</td>
<td>-713</td>
<td>268</td>
<td>141</td>
<td>1584.8</td>
<td>2.010 x 10⁻⁵</td>
</tr>
</tbody>
</table>

Fig. 2. FTIR Spectrum (a) Pure sodium molybdate (b) Pure Aloe vera (c) Film formed on metal surface after the immersion in well water containing 100ppm SM - 25ppm of Zn²⁺ and 10ml Aloe vera

Fig. 3. Polarization curves of carbon steel immersed in various test solutions: a) Well water b) Well water containing 100 ppm of sodium molybdate and 25 ppm of Zn²⁺ + 10ml of Aloe vera
3.7. Analysis of AC Impedance spectra

AC impedance spectra have been used to detect the formation of the film formed on the metal surface. If a protective film is formed, the Charges transfer resistance increases and double layer capacitance value decreases [49-51]. The AC Impedance spectra of carbon steel immersed in various solutions are shown in Fig 4 to 5. The Nyquist plots are shown in Fig 4. The Bode plots are shown in Fig 5. The AC Impedance parameter, namely charge transfer resistance ($R_t$) and double layer capacitance ($C_{dl}$) are given in Table 6.

When carbon steel is immersed in aqueous solution containing well water, the $R_t$ value is 79.71 ohm cm$^2$ and $C_{dl}$ value is 5.21 x $10^{-8}$ F cm$^{-2}$. When the SM (100ppm)-Zn$^{2+}$ (25 ppm)- Aloe vera(10ml) is added to the well water the $R_t$ value increases from 79.71 ohm cm$^2$ to 247.12 ohm cm$^2$ and $C_{dl}$ value decreases from 5.21x10$^{-8}$ F cm$^{-2}$ to 1.679x10$^{-8}$ F cm$^{-2}$. Further there is increase in impedance log(Z ohm$^{-1}$), value from 2.007 to 2.543. This accounts for the high inhibition efficiency of SM-Zn$^{2+}$ and Aloe vera system and a protective film is formed on the mild steel surface. This is also supported by the fact that for the inhibitor system the phase angle increases from 29.33° to 38.04°.

**Table 6.** Impedance parameter of carbon steel in well water in the absence and presence of inhibitors, obtained by AC Impedance method

<table>
<thead>
<tr>
<th>System</th>
<th>$R_t$ (ohm cm$^2$)</th>
<th>$C_{dl}$ (F cm$^{-2}$)</th>
<th>Impedance, log(Z ohm$^{-1}$)</th>
<th>Phase angle</th>
</tr>
</thead>
<tbody>
<tr>
<td>Well water (WW)</td>
<td>79.71</td>
<td>5.21x10$^{-8}$</td>
<td>2.007</td>
<td>29.33°</td>
</tr>
<tr>
<td>WW + SM + Zn$^{2+}$ + Aloe vera</td>
<td>247.12</td>
<td>1.679x10$^{-8}$</td>
<td>2.543</td>
<td>38.04°</td>
</tr>
</tbody>
</table>

**Fig. 4.** Nyquist plots of carbon steel immersed in various test solution a) Well water b) Well water + 100ppm SM + 25ppm Zn$^{2+}$ + Aloe vera

**Fig. 5.** Bode plots of carbon steel immersed in various test solution

Well water b) Well water + SM (100ppm) + Zn$^{2+}$ (25ppm) + Aloe Vera
IV. MECHANISM OF CORROSION INHIBITION

In order to explain the experimental results, the following mechanism of corrosion inhibition is proposed. The mechanistic aspect of the inhibition of carbon steel in well water by SM-Zn²⁺ and Aloe vera can be explained in terms of complexation and adsorption.

- Before immersion of carbon steel in well water environment, SM, Zn²⁺ and Aloe vera-Zn²⁺ form complexes, viz., Zn²⁺-SM, Zn²⁺-Aloe vera, and Zn²⁺-SM-Aloe vera. These complexes are in equilibrium in the solution with free Zn²⁺, SM, and Aloe vera ions.

- When carbon steel is immersed in this solution, the Zn²⁺-SM, Zn²⁺-Aloe vera complexes diffuse from the bulk of the solution towards Metal surface.

- On the metal surface Zn²⁺-SM-Aloe vera complex is converted in to Fe²⁺-SM complex and Fe²⁺-Aloe vera complex on the anodic sites. Zn²⁺ is released.
  \[ Zn^{2+} + SM + Aloe vera + Fe^{2+} \rightarrow Fe^{2+} \text{Aloe vera, Fe}^{2+} - SM + Zn^{2+} \]

- The released Zn²⁺ combines with OH⁻ to form Zn(OH)₂ on the cathodic sites.
  \[ Zn^{2+} + 2OH^- \rightarrow Zn(OH)_2 \downarrow \]

- Thus the protective film consist of Fe²⁺-SM complex and Fe²⁺-Aloe vera complex and Zn(OH)₂↓

V. CONCLUSIONS

- The formulation consisting of 100 ppm of SM and 25 ppm of Zn²⁺ and 10ml of Aloe vera showed 97% Inhibition efficiency.
- A synergistic effect was noticed between SM-Zn²⁺-Aloe vera system.
- In the presence of Aloe vera-SM-Zn²⁺ system has excellent inhibition efficiency.
- FTIR spectrum reveal that the protective film consists of Fe²⁺-SM complex and Fe²⁺-Aloe vera complex and Zn(OH)₂↓
- Polarization studies reveal that SM-Zn²⁺-Aloe vera functions as an anodic inhibitor.
- AC impedance spectra suggest that a protective film is formed on the metal surface.

REFERENCES

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