Eco-Friendly Corrosion Inhibition of Pipeline Steel Using Brassica oleracea

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1. Introduction

Steel pipes are widely used to transport industrial fluids. The operation of these pipes involves acid pickling, acid descaling, oil well acidification, and so forth. These operations result in increased corrosion damage due to the aggressive nature of industrial chemicals and environment. The application of chemical substances as corrosion inhibitors has received several research attentions [1–5].

The inside of pipelines is usually subject to a flow regime and injecting corrosion inhibitors is a practical method of corrosion control [6]. Corrosion inhibitors are mostly organic and inorganic in nature. Structurally, organic corrosion inhibitors consist of polar and nonpolar ends. The polar end, which consists of heteroatoms such as oxygen, nitrogen, and sulphur, is usually adsorbed on the electrovalent metal surface. The heteroatoms usually have extra outer electrons to fill or share with the vacant d-orbital of the metal [7–10].

There are environmental issues associated with the application of most inhibitors as some are toxic to the ecosystem. Plants extracts are eco-friendly and have been found to contain phytochemical constituents with similar characteristics to organic corrosion inhibitor; hence, their applicability as inhibitors has been reported [11–15]. The constituent compounds present in the plant biomass may antagonize or synergize to give the resultant corrosion inhibition efficiency [16–18]. The use of wastes from plants as corrosion inhibitors can be another way of extending the beneficial use of these plants and so enhance municipal waste management.

A lot of research has been carried out on the chemical composition of Brassica oleracea (BO) extract. Internal leaves of BO have shown high antioxidant capacity. Analysis of the methanoic extract of BO leaves using GC-MS identified 44 compounds that exhibited antimicrobial activity [22].

The present work aims at the development of eco-friendly corrosion inhibitor and proposing the use of parts of beneficial plants usually discarded as waste. The mechanism of non indirect proportionality between corrosion inhibitor concentration and percentage inhibition efficiency is proposed.

2. Experimental

2.1. Plant Collection and Extraction. The outer leaves of Brassica oleracea were washed and air-dried. The dried leaves were pulverized using an electric blender. About 500 g of the dried sample was soaked in 99% ethanol (analytical grade) in 1000 mL volumetric flask. Sufficient quantity of ethanol
Table 1: Chemical composition of pipeline steel (wt%).

<table>
<thead>
<tr>
<th>Element</th>
<th>C</th>
<th>S</th>
<th>P</th>
<th>Si</th>
<th>Mn</th>
<th>Al</th>
<th>Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>Composition (wt%)</td>
<td>0.47</td>
<td>0.005</td>
<td>0.003</td>
<td>0.24</td>
<td>1.44</td>
<td>0.01</td>
<td>Balance</td>
</tr>
</tbody>
</table>

was added to cover the surface of the sample. The flask was covered and left for 48 hours. The content of the flask was filtered and the filtrate concentrated using rotary evaporator. The dried residue was stored in an air tight analytical container. Appropriate quantities were subsequently weighed to make desired concentrations of the inhibitor solution.

2.2. Electrochemical Measurements. The electrochemical determinations were carried out using a conventional three-electrode cell with a platinum counter electrode, a saturated calomel electrode (SCE) coupled to a fine Luggin capillary as reference electrode. Pipeline steel was used as the working electrode (WE) and has the composition shown in Table 1. The WE was embedded in a Teflon holder using epoxy resin. The edges were sealed with hydrocarbon wax to expose an area of 1 cm². The WE was prepared before the experiment by polishing with different grades of emery paper (150, 400, 800, 1000, and 2000), cleaned with distilled water, degreased with acetone, dried, and stored in a moisture-free desiccator. All the experiments were carried out at open circuit potential (OCP) for 30 min to attain a stable potential, while the corrosive environment temperature was maintained using a thermostat water bath. The experiments were all carried out using a Perstet 2273 Advanced Electrochemical system. Each experiment was repeated three times to ensure reproducibility.

The potentiodynamic polarization measurement was started at the cathodic potential of −250 mV to anodic potential of +250 mV at a scan rate of 1 mV s⁻¹. Corrosion current density (Icorr), equilibrium corrosion potential (Ecorr), and other kinetic parameters were extrapolated using the power suite software. Corrosion inhibition efficiency was calculated from Icorr values by applying the following relationship:

\[ \eta_p (%) = \frac{I_{corr}^0 - I_{corr}}{I_{corr}^0} \times 100, \]  \hspace{1cm} (1)

where Icorr⁰ and Icorr are corrosion current densities in the uninhibited and inhibited systems, respectively.

The potentiodynamic polarization curve for pipeline steel in 0.5 M H₂SO₄ with and without concentrations of Brassica oleracea extract at 303 K.

![Potentiodynamic polarization curve for pipeline steel in 0.5 M H₂SO₄ with different concentrations of Brassica oleracea extract at 303 K.](image)

2.3. Surface Morphology. Surface morphology studies were carried out using Oxford x-Max scanning electron microscope (SEM). The test pipeline steel coupons were prepared as described for the electrochemical experiment above. A coupon was immersed in 0.5 M sulphuric acid while the second coupon was immersed in a solution of 0.5 M sulphuric acid with 0.1 g/L Brassica oleracea extract for 8 hours. The coupons were retrieved, rinsed, dried, and subjected to SEM examination.

2.4. Fourier Transform Infrared Spectroscopy. The pipeline steel specimens were immersed in 0.5 M sulphuric acid with 0.1 g/L Brassica oleracea extract for 24 hours. The steel samples were taken out and dried. The nature of the surface film formed and the presence of functional groups in the Brassica oleracea extract in the corrosion product were tested by Magna-IR 560 Spectrometer ESP Nicolet with the aid of KBr disc provided by the instrument. These were compared with the FTIR of Brassica oleracea extract [23].

3. Results and Discussion

3.1. Potentiodynamic Polarization. The polarization curves obtained for pipeline steel in 0.5 M H₂SO₄ with and without concentrations of Brassica oleracea extract at 303 K are presented in Figure 1. The kinetic parameters, corrosion potential (Ecorr), corrosion current density (Icorr), cathodic Tafel slope (βcath), anodic Tafel slope (βan), and inhibition efficiency (ηinh), associated with Figure 1 are presented in Table 2. From Figure 1, the presence of BO extract reduced the cathodic current, while Table 1 indicates a reduction in both the cathodic and anodic current with the resultant
Table 2: Potentiodynamic polarization parameters for pipeline steel in 0.5 M H₂SO₄ with and without different concentrations of Brassica oleracea extract at 303 K.

<table>
<thead>
<tr>
<th>Concentration (g/L)</th>
<th>Blank</th>
<th>0.01</th>
<th>0.1</th>
<th>1.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>Eff. (𝜂%)</td>
<td>96.80</td>
<td>98.31</td>
<td>93.48</td>
<td></td>
</tr>
<tr>
<td>Icorr (A/cm²)</td>
<td>1.47e⁻²</td>
<td>4.70e⁻²</td>
<td>2.48e⁻²</td>
<td>9.59e⁻²</td>
</tr>
<tr>
<td>βc (mV dec⁻¹)</td>
<td>324.72</td>
<td>141.03</td>
<td>132.19</td>
<td>195.58</td>
</tr>
<tr>
<td>βa (mV dec⁻¹)</td>
<td>343.22</td>
<td>68.20</td>
<td>50.63</td>
<td>74.89</td>
</tr>
<tr>
<td>Ecorr (mV versus SCE)</td>
<td>-442.69</td>
<td>-490.79</td>
<td>-484.56</td>
<td>-462.18</td>
</tr>
</tbody>
</table>

Figure 2: Potentiodynamic polarization curve for pipeline steel in 0.5 M sulfuric acid with and without different concentrations of Brassica oleracea extract at 313 K.

The corrosion inhibition efficiency of Brassica oleracea reached a value of 98.31% at 0.1 g/L within the experimental condition. The inhibition efficiency later decreased to 93.48% at the concentration of 1.0 g/L. From Table 2, BO can be classified as a mixed type inhibitor because it was able to reduce both the cathodic and anodic current. This trend has been reported by other researchers [24, 25]. Also, Table 2 indicates a change in Ecorr, less than 85 mV. An inhibitor is classified as an anodic-type or cathodic-type inhibitor when the change in Ecorr is greater than 85 mV [24–26].

Figure 2 presents the potentiodynamic polarization curve for pipeline steel in 0.5 M H₂SO₄, with and without concentrations of Brassica oleracea at 313 K. The parameters for Figure 2 are presented in Table 3. The anodic inhibiting effect appears to become more pronounced with rise in temperature. The shift in the Ecorr, though still less than 85 mV, was shifted more towards the anodic region. There was a further reduction in the value of the corrosion current density and consequent increase in corrosion inhibition efficiency to 99.63% at 313 K.

Figures 3 and 4 present the plot of pipeline steel in 0.5 M H₂SO₄ with and without concentrations of Brassica oleracea extract at 333 K, respectively. Tables 4 and 5 present the extracted kinetic parameters from Figures 3 and 4, respectively. The optimal inhibition performance of the extract was recorded at 0.1 g/L extract concentration at 313 K. This may be attributed to the optimization of the bonding interaction of the molecular components of Brassica oleracea with the metal surface d-orbitals. The multi-phytochemical components of BO extract gave the highest inhibition efficiency and surface coverage at 0.1 g/L and 313 K. It may be assumed that this is the condition for optimal corrosion inhibition performance and surface coverage. At other experimental conditions, optimal metal-inhibitor bonding may not have been attained because of stearic hindrance.

3.2. Impedance Spectroscopy. Figures 5(a), 6, 7, and 8 present the electrochemical impedance EIS Nyquist plots for pipeline steel in 0.5 M H₂SO₄ with and without concentrations of
Brassica oleracea extract at 303, 313, 323, and 333 K, respectively. Researchers have used EIS to investigate the corrosion inhibition mechanism at the metal/electrolyte interfaces, since it provides information on the resistive and capacitive behavior at the interface [26–28].

The Nyquist plots show a series of depressed semicircles with center under the real axis. This behavior is characteristic of solid electrode, indicating frequency distribution of impedance data and results from roughness and heterogeneous nature of solid electrodes [29, 30]. Figures 5(a), 6, 7, and 8 are characterized by double time constants, the high frequency capacitive loop, and the low frequency inductive loop. The high frequency capacitive loop is attributed to the charge transfer process (charge transfer resistance $R_{ct}$) of the corrosion reaction. The $R_{ct}$ of an alloy is usually a composite value, but steel is an alloy predominated by iron, so its $R_{ct}$ is governed mainly by the dissolution of iron [31]. Researchers have attributed the low frequency inductive loop to surface relaxation due to adsorption of reaction intermediates [32, 33] and hydrogen [34] on the oxide film on the electrode.

The equivalent circuit shown in Figure 5(b) was used to analyze the impedance response in Figure 5(a). The circuit parameters of the oxide film can be represented as a parallel circuit of resistor and capacitor as in the impedance plot. In a nonideal situation, the capacitance is replaced by a parallel arrangement of two resistors in a series relationship to another resistor, an inductor, and a constant phase element. The impedance ($Z_{CPE}$) of CPE can be represented as follows [36]:

$$Z_{CPE} = Y_0^{-1} (j\omega)^{-n},$$  (3)

where $Y_0$ is a proportional factor and $n$ has the meaning of a phase shift. When $n = 0$, CPE represents a resistance, when $n = 1$, a capacitance, when $n = -1$, an inductance, and when $n = 0.5$, a Warburg element, $\omega$ is the angular frequency (rad s$^{-1}$), and $j^2 = -1$ is a imaginary number. The double-layer capacitance ($C_{dl}$) can be calculated from

$$C_{dl} = Y_0 (\omega'')^{n-1},$$  (4)

where $\omega''$ is the frequency at which the imaginary part of the impedance has a maximum.

The pattern of the impedance plot with and without varying concentrations of BO extract is similar suggesting that BO does not change the mechanism of corrosion under the experimental conditions. The impedance parameters such as the $R$ and $R_{ct}$ at 303 K were determined using the ZSimWin software by fitting to the equivalent circuit model $R(QR(LR))$ and presented in Table 6. Figure 5(c) presents a plot of the ZSimWin plot of experimental and computer data for the impedance response of pipeline steel in 0.5 M H$_2$SO$_4$ with 0.1 g/L BO. The plot shows that the impedance data of BO is well fitted into the model.

Table 6 indicates that the value of the charge transfer resistance increased with increase in Brassica oleracea extract concentration getting to peak in 0.1 g/L concentration. This is almost in agreement with the potentiodynamic polarization result. The slight difference in IE% of both methods can be attributed to change in the exact time of carrying out both measurements because corrosion potential changes with time. Also the value of CPE decreased reaching a minimum of $4.5 \times 10^{-5}$ at 0.1 g/L. Both trends suggest that the surface roughness of pipeline steel in the presence of the extract inhibitor decreased due to adsorbed Brassica oleracea extract on the pipeline steel surface. These increased the inhibitor film at the metal-acid interface thereby inhibiting the corrosion of pipeline steel in sulphuric acid environment [36, 37].

Figure 9 presents the Nyquist plot for time effect of pipeline steel in 0.5 M H$_2$SO$_4$ with 0.1 M g/L Brassica oleracea extract at 333 K.
extract for six days. The high frequency semicircle increased in diameter for the first four days before decreasing and increasing on the fifth and sixth day, respectively. The increase in the charge transfer resistance between day one and day four indicates an increased adsorption of *Brassica oleracea* extract with time. This implies that BO extracts increase in its corrosion inhibition efficiency with time.

3.3. Corrosion Surface Morphology. Figure 10 presents image of the corrosion surface morphology of pipeline steel immersed in (a) 0.5 M H$_2$SO$_4$ and (b) 0.5 M H$_2$SO$_4$ with 0.1 g/L BO extracts after 8 hours of immersion. The sulfuric acid aggressively corroded the sample in Figure 10(a) causing a rougher surface. The contrast was noticed in the sample in Figure 10(b) with smoother surface. The sample in Figure 10(b) surface is attributed to the ability of *Brassica oleracea* extract to form an adsorbed film on the surface of pipeline steel which was absent in Figure 10(a) sample. This is in agreement with the impedance results. The slight damage in sample in Figure 10(b) might have occurred due to the following reasons. (a) It has been proposed that the water molecules first get adsorbed at the metal/electrolyte interface before the inhibitor molecules displace them to get adsorbed at the metal surface [38]. The change in potential by the time the water molecules are at the surface of the metal without BO is a potential stage of corrosion damage. This could also be explained to result from the differential in the rate different molecules in the extract get adsorbed.
and stabilize at the surface due different molecular properties. (b) Since the inhibition efficiency is not 100%, it could have corroded in the presence of BO extract.

3.4. Fourier Transform Infrared Spectroscopy Spectra. The FTIR spectra of Brassica oleracea corrosion product from pipeline steel surface presented in Figure 11 were compared with those of Brassica oleracea previously reported [23]. The FTIR spectrum of Brassica oleracea is similar to the FTIR of Brassica oleracea film on pipeline steel surface, in range of 500–3500 cm$^{-1}$ indicating the presence of similar functional groups. It has peaks at 3330, 1635, 1418, and 1054 cm$^{-1}$. These peaks show the presence of –OH, –COOH, –NH, and C=O groups, respectively. The deviations are attributed to the formation of complex between iron and functional groups present in the BO extract. Similar deviation has been previously reported [39].

The [Fe-BO extract functional groups]$^{2+}$ may be a stable complex adsorbed on the pipeline steel surface, forming covalent or coordinate bonds between the anionic components of BO extracts and vacant Fe d-orbital. The metal-inhibitor bond usually leads to corrosion inhibition through
Table 6: Impedance parameters for pipe steel in 0.5 M H₂SO₄ with and without various concentrations of BO extract.

<table>
<thead>
<tr>
<th>Conc. (g/L)</th>
<th>Rs (Ωcm²)</th>
<th>R′ (Ωcm²)</th>
<th>R_ind (Ωcm²)</th>
<th>CPE Y₀ (S·secⁿ/cm²)</th>
<th>n</th>
<th>L (Hcm²)</th>
<th>%η</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>2.37</td>
<td>5.29</td>
<td>16.3</td>
<td>0.00028</td>
<td>0.97</td>
<td>6.97</td>
<td>—</td>
</tr>
<tr>
<td>1.0</td>
<td>2.96</td>
<td>38.93</td>
<td>78.88</td>
<td>0.00019</td>
<td>0.88</td>
<td>34.46</td>
<td>86.64</td>
</tr>
<tr>
<td>0.1</td>
<td>2.97</td>
<td>265.20</td>
<td>1283</td>
<td>0.000045</td>
<td>0.92</td>
<td>3372</td>
<td>98.04</td>
</tr>
<tr>
<td>0.01</td>
<td>2.98</td>
<td>102</td>
<td>1724</td>
<td>0.00012</td>
<td>0.93</td>
<td>7193</td>
<td>94.90</td>
</tr>
</tbody>
</table>

Figure 10: SEM micrograph of (a) pipeline steel in 0.5 M H₂SO₄ and (b) pipeline steel in 0.5 M H₂SO₄ with 0.1 g/L Brassica oleracea extract.

Figure 11: FTIR spectra of BO surface film.

adsorption [40]. Also, the Fe-BO extract functional groups complex may be a soluble complex leading to a catalytic effect, thus accelerating corrosion. The plant extract biomass is composed of many chemical compounds with a probability of both mechanisms operating concurrently. The inhibiting effect of Brassica oleracea can be attributed to the resultant effect of both corrosion accelerating and retarding mechanisms. The corrosion retarding mechanism through stable complex formation dominates at increasing concentration till a critical concentration is reached where formation of soluble complex dominates. This trend has been previously reported [18].

4. Conclusion

The extract from BO showed excellent corrosion inhibition characteristics for pipeline steel corrosion in acidic environment. The anticorrosion activities of BO plant extract are attributed to its multiconstituents. The resultant interaction between the multiconstituents of BO accounts for its high inhibition performance.

The extract of BO is a mixed-type corrosion inhibitor for pipeline steel in 0.5 M H₂SO₄. The inhibition of BO is through the formation of an adsorbed corrosion retarding complex of Fe and molecular components in BO [Fe-BO molecules] and an unstable soluble corrosion accelerating complex.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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