Biodegradable aquatic waste-fish scales as corrosion inhibitor for mild steel in acid medium

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ABSTRACT

Corrosion control methods, especially the use of inhibitors, have gained monumental importance in the present scenario of expunging corrosion and the quest for eco-friendly reasons continues. To arrive at an inexpensive non-toxic, eco-friendly inhibitor formulations the present study on the use of aquatic waste – fish scale extract has been carried out by the classical weight loss measurements and electrochemical polarization measurements. The acid extract could bring out a maximum of 96.5% inhibition of mild steel corrosion in 0.5M H₂SO₄. The extract was temperature resistant. Thermodynamic parameters of the corrosion process were calculated from temperature study. The absorptive behaviour of fish extract in acid solution may be approximated both by Langmuir and Temkin type isotherms. The results obtained by Tafel, Linear polarization resistance and impedance spectroscopy have been correlated with the classical weight loss measurements. Values of Tafel constant bₐ and b₈ confirmed that the fish scale extract acts like mixed type inhibitor. The fish scale extract in H₂SO₄ medium efficiently inhibits the corrosion and proved to be zero cost inhibitor, eco-friendly, non-toxic and highly economical.

Key words: Biodegradable aquatic waste-fish scales, corrosion inhibitor.

INTRODUCTION

The serious consequences of the corrosion process have become a problem of worldwide significance. In addition to our everyday encounters with this form of degradation, corrosion causes plant shutdowns, waste of valuable resources, loss or contamination of product, reduction in efficiency, costly maintenance, and expensive over-design. It can also jeopardize safety and inhibit technological progress.

Metals and its alloys are exposed to the action of acids in industry¹. Processes in which acids play a very important part are acid pickling, industrial acid cleaning, cleaning of oil refinery equipment, oil well acidizing and acid descaling¹,². The exposures can be most severe but in many cases, corrosion inhibitors are widely used in industry to prevent or to reduce the corrosion rates of metallic materials in these acid media²,³.

Because of the toxic nature and high cost of some chemicals currently in use, it is necessary to develop environmentally acceptable and less expensive inhibitors. Natural products can be considered as a good source for this purpose⁴. The possible replacement of some expensive chemicals as corrosion inhibitors for metal in acid cleaning process by naturally occurring substances of plant origin has been studied by Hosary and Salem⁴. Natural products of plant origin contain different organic compounds e.g. alkaloids, lignin, tannins, amino acids, pigments and most are known to have inhibitive action⁴-⁸. Ekpe et al.,⁵ and Saleh et al.,⁹ used the aqueous extracts of some plant parts (fruits, fruit shell, leaves, seeds) as corrosion inhibitors for some metals.
The natural inhibitors studied have been found to be highly eco-friendly and possess no threat to the environment. The present work is a commencement made to study the inhibition potential of aquatic waste (fish scale) for mild steel in sulphuric acid medium.

**MATERIAL AND METHODS**

**Preparation of the specimens and inhibitor**
Locally available mild steel of chemical composition, Carbon 0.081, Manganese 0.296, Silicon 0.016, Phosphorous 0.032, Sulphur 0.014, Chromium 0.021, Molybdenum 0.019, Nickel 0.016, and remaining Iron was cut into pieces of area 5×1 cm². The specimens were polished mechanically, degreased, cleaned successively in deionized water, dried, stored in a dessicator and used for all studies. The experiment was carried in 0.5M sulphuric acid because it is one of the most commonly and widely used acid in industries. The fish scales were collected from a nearby fish stall and dried. About 25g of the scales was weighed and refluxed in 500ml of 0.5 M sulphuric acid for 3hrs. It was kept overnight and filtered to get 5% extract.

**Physico chemical method (Weight loss method)**
The Mild Steel coupons were weighed in Denvar balance. The weighed samples in triplicate were immersed in 100 ml of acid solution (with and without inhibitor) for a specific time viz., ½ hr, 3hr, 6hr, and 24hr. The specimens were removed and washed with saturated sodium bicarbonate solution and water, dried and reweighed.

The experiments were also performed with different concentrations of inhibitor (0.05%-0.5%) and at various temperatures such as 303K, 313K, 323K, 333K, and 343K.

The inhibitor efficiency is estimated by

\[ IE = \frac{W_0 - W}{W_0} \times 100 \]

Where, \( W_0 \) and \( W \) are the weight losses without and with the addition of inhibitors.

**Potentiodynamic polarization and electrochemical impedance measurements**
The corrosion monitoring techniques like
- Potentiodynamic polarization (Tafel polarization)
- Electrochemical impedance spectroscopy (EIS) methods have been used in the present investigation. For both the techniques, solartron Electrochemical Measurement Unit (1284Z) model was used with a software package of Z plot and Corrware. The system includes a potentiostat, personal computer and Frequency Response Analyser.

For potentiodynamic polarization studies, the experiments were carried out over a potential range of -200mV to +200mV with respect to reference electrode and its current response was measured at a scan rate of 2mVsec⁻¹.

Impedance measurements were carried out at corrosion potential. The A.C. amplitude of 10mV was applied and the frequency was varied from 10 kHz to 100 mHz. The real and imaginary parts of the impedance were plotted as Nyquist plot. From the Nyquist plots and Bode plots, the Charge Transfer Resistance (\( R_{ct} \)) and Double Layer Capacitance (\( C_d \)) values were calculated.

**RESULTS AND DISCUSSION**

**Weight loss measurements**
The effect of various concentration of fish scale extract on the corrosion of mild steel is shown in fig1. The results indicate that the efficiency of the extract increases with increase in extract inhibitor concentration. Maximum inhibition efficiency of 96.5% was noticed at 24 hrs with 0.5% concentration. The inhibition efficiency progressively increased with rise in period of immersion upto 24 hrs. Increase in inhibition effect with increase in concentration of the extract infer that, the inhibition may be due to the increase in the adsorption of the extract constituents on the metal surface, resulting in decrease in dissolution of mild steel.

There is gradual increase in inhibition efficiency upto 3hrs and after that there is enhancement in inhibition efficiency up to 24hrs. The inhibition efficiency at 6, 12, 24 hrs are more
or less same indicating the optimum period of immersion for maximum inhibition efficiency as 6hrs.

The mild steel samples are exposed to 0.5M H₂SO₄ at specific temperatures (303K, 313K, 323K, 333K, 343K, and 353K) for 30 minutes. As per the results from table-1 it can be said that the performance of the extract increased at all concentrations with temperature upto 333K. The maximum inhibition efficiency of 91% was observed with 0.5% concentration at 323K. Increase in inhibition efficiency with temperature can be explained due to increase in the adsorption of inhibitor molecule on mild steel surface up to 323K.

**Adsorption isotherm**

In acid corrosion generally, it is assumed that inhibitors act through a process of adsorption

### Table 1: Influence of temperature on inhibition efficiency of fish scale extract

<table>
<thead>
<tr>
<th>Conc.(%)</th>
<th>303K</th>
<th>313K</th>
<th>323K</th>
<th>333K</th>
<th>343K</th>
<th>353K</th>
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<td>81.93</td>
<td>82.19</td>
<td>82.33</td>
<td>56.3</td>
<td>46.93</td>
<td>46.78</td>
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<td>0.05</td>
<td>82.47</td>
<td>83.28</td>
<td>87.1</td>
<td>63.53</td>
<td>49.92</td>
<td>47.88</td>
</tr>
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<td>1</td>
<td>87.26</td>
<td>86.73</td>
<td>87.69</td>
<td>63.8</td>
<td>56.55</td>
<td>51.33</td>
</tr>
<tr>
<td>0.15</td>
<td>85.62</td>
<td>89.73</td>
<td>89.12</td>
<td>71.71</td>
<td>61.22</td>
<td>59.19</td>
</tr>
<tr>
<td>0.2</td>
<td>84.53</td>
<td>90.6</td>
<td>89.24</td>
<td>76.13</td>
<td>60.91</td>
<td>52.3</td>
</tr>
<tr>
<td>0.3</td>
<td>86.31</td>
<td>91.18</td>
<td>92.12</td>
<td>76.67</td>
<td>67.15</td>
<td>57.82</td>
</tr>
<tr>
<td>0.4</td>
<td>84.32</td>
<td>90.69</td>
<td>92.12</td>
<td>79.75</td>
<td>68.13</td>
<td>63.22</td>
</tr>
<tr>
<td>0.45</td>
<td>83.77</td>
<td>91.03</td>
<td>91.03</td>
<td>81.09</td>
<td>66.73</td>
<td>66.82</td>
</tr>
<tr>
<td>0.5</td>
<td>83.7</td>
<td>89.7</td>
<td>90.99</td>
<td>81.9</td>
<td>72.65</td>
<td>66.08</td>
</tr>
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</table>

### Table 2: Kinetic and thermodynamic parameters of adsorption of fish scale extract on mild steel in 0.5M H₂SO₄

<table>
<thead>
<tr>
<th>Conc. (%)</th>
<th>Activation of energy (Ea) KJ/mol</th>
<th>Free energy of adsorption (ΔG) KJ/mol</th>
<th>Heat of adsorption (ΔH) J/mol</th>
<th>Entropy change (ΔS) KJ/mol</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>303</td>
<td>313</td>
<td>323</td>
<td>333</td>
</tr>
<tr>
<td>blank</td>
<td>68.1</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>0.05</td>
<td>73.2</td>
<td>21.45</td>
<td>22.20</td>
<td>22.94</td>
</tr>
<tr>
<td>0.15</td>
<td>75.4</td>
<td>19.80</td>
<td>20.59</td>
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</tr>
<tr>
<td>0.2</td>
<td>73.3</td>
<td>19.72</td>
<td>20.25</td>
<td>21.12</td>
</tr>
<tr>
<td>0.3</td>
<td>71.4</td>
<td>18.64</td>
<td>20.25</td>
<td>20.73</td>
</tr>
<tr>
<td>0.35</td>
<td>68.9</td>
<td>17.25</td>
<td>19.55</td>
<td>20.00</td>
</tr>
<tr>
<td>0.4</td>
<td>69.0</td>
<td>17.38</td>
<td>19.23</td>
<td>20.18</td>
</tr>
<tr>
<td>0.45</td>
<td>66.3</td>
<td>16.64</td>
<td>18.73</td>
<td>19.82</td>
</tr>
<tr>
<td>0.5</td>
<td>64.8</td>
<td>16.24</td>
<td>18.53</td>
<td>19.12</td>
</tr>
<tr>
<td></td>
<td>61.8</td>
<td>15.96</td>
<td>17.86</td>
<td>18.83</td>
</tr>
</tbody>
</table>
on the metal surface. In the present study, the plot of \( \log \theta / 1 - \theta \) vs. \( \log C \) (Fig. 2) gave straight line indicating that the system obeyed Langmuir adsorption isotherm.

**Energy of activation**

The data obtained from weight loss measurements were plotted in accordance to Arrhenius equation. Log \( CR = (-Ea/2.303RT) + \text{constant} \) Where \( CR = \text{corrosion rate} \)

\( Ea = \text{activation energy} \)

\( R = \text{gas constant} \)

\( T = \text{absolute temperature} \)
The activation energies for corrosion process are estimated from the slopes of lines of Arrhenius plot and given in Table 2. From the table it is understood the energy of activation changes in the presence of the inhibitor.

For adsorption inhibitors the observed rate shows not only the effect of temperature on the metal dissolution, but also, the variation of surface coverage with temperature at constant concentration. Accordingly the energy of activation, changes in the present study. The energy of activation decreased in the presence of inhibitor. The lower value of activation energy at higher concentration of the inhibitor is explained as the likely specific interaction between iron and the inhibitor molecules.

**Thermodynamic and kinetic parameter**

From the table 2 it is noted that the values of $\Delta G$ are found to be negative in presence and absence of inhibitor. This indicates a strong interaction between the metal surface and the inhibitor molecules and spontaneous adsorption of inhibitor on the surface of the mild steel\(^1\). From the plots of $\Delta G$ vs. T the values of $\Delta H$ and $\Delta S$ are calculated from intercepts and slopes respectively. The values of $\Delta H$ and $\Delta S$ indicate that the system is enthalpic and entropic controlled.

**Electrochemical measurements**

Linear polarization measurements, Tafel intercept method and electrochemical impedance measurement carried out for mild steel acid corrosion in the presence of fish scale extract. Electrochemical studies will be helpful to predict the nature of inhibitor and to predict a suitable mechanism for inhibition process. The values of corrosion kinetic parameters – corrosion current ($E_{corr}$), corrosion current density ($I_{corr}$), Tafel slopes ($b_a$ and $b_c$), linear polarization resistance ($R_p$) are recorded in the table 3.

**Potentiodynamic studies**

From Potentiodynamic studies, the polarization curves obtained in the presence and absence of fish scale are depicted in the fig. 3. The results indicate a considerable reduction in $I_{corr}$ values in the presence of the inhibitor. Thus confirms the inhibitive nature of the fish scale and also the adsorption of fish scale on metal surface. The values of inhibition efficiency are found to be increasing.

![Polarisation curves of MS in the presence of fish scales extract in acid medium](image-url)
with increase in concentration of inhibitor. Around 78% of inhibition was obtained with 0.5% concentration. No significant change in Ecorr values in the presence of inhibitor indicates the mixed nature of the inhibitor. Tafel constant $b_a$ and $b_c$ are found to be changing with the concentration of the inhibitor. Polarization curves obtained in the presence of the inhibitor also reveals that the fish scale under investigation is controlling the metal dissolution reaction as well as hydrogen evolution reaction. It can be concluded from the results obtained that the fish scale acts as a mixed inhibitor.

**Linear polarization resistance methods**

Linear polarization Resistance values in presence and absence the inhibitors are tabulated in the table-3 increase in $R_p$ values with increase in concentration of the fish scale understudy indicate

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![Impedance behaviour of MS in the presence of Fs extract](image1)

![Impedance behaviour of MS in the presence of Fs extract](image2)

![Impedance behaviour of MS in the presence of Fs extract](image3)
Table 3: Electrochemical, corrosion parameters and Impedance parameters for mild steel in the presence of fish scale in 0.5M H₂SO₄

<table>
<thead>
<tr>
<th>Conc. of inhibitor (%)</th>
<th>Ecorr (milli Volts/dec)</th>
<th>IcorrX (10⁻⁴ Amp/dec)</th>
<th>be (mV/dec)</th>
<th>I.E. %</th>
<th>RP Oh m/cm²</th>
<th>I.E. %</th>
<th>RctOh m/cm²</th>
<th>I.E. %</th>
<th>Cdl x10⁻⁵</th>
<th>Surface coverage θ</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>543</td>
<td>30.8</td>
<td>157</td>
<td>83</td>
<td>135</td>
<td>-</td>
<td>8.6</td>
<td>-</td>
<td>15.1</td>
<td>19.9</td>
</tr>
<tr>
<td>0.1</td>
<td>467</td>
<td>9.3</td>
<td>28</td>
<td>137</td>
<td>71.2</td>
<td>-</td>
<td>15.1</td>
<td>-</td>
<td>19.9</td>
<td>0.55</td>
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<tr>
<td>0.15</td>
<td>467</td>
<td>8.8</td>
<td>130</td>
<td>98</td>
<td>71.1</td>
<td>-</td>
<td>15.1</td>
<td>-</td>
<td>19.9</td>
<td>0.55</td>
</tr>
<tr>
<td>0.25</td>
<td>465</td>
<td>8.2</td>
<td>121</td>
<td>82</td>
<td>73.2</td>
<td>-</td>
<td>15.1</td>
<td>-</td>
<td>19.9</td>
<td>0.55</td>
</tr>
<tr>
<td>0.35</td>
<td>463</td>
<td>7.0</td>
<td>31</td>
<td>45</td>
<td>77.0</td>
<td>-</td>
<td>15.1</td>
<td>-</td>
<td>19.9</td>
<td>0.55</td>
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<td>0.5</td>
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<td>27</td>
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<td>15.1</td>
<td>-</td>
<td>19.9</td>
<td>0.55</td>
</tr>
</tbody>
</table>

The effective inhibitive action of the inhibitor. The maximum inhibition efficiency using $R_p$ values was found to be 78%.

**Electrochemical impedance spectroscopy**

Electrochemical impedance spectroscopy measurements are carried out in the presence and absence of fish scale and the values of $R_p$ and $C_{dl}$ are given in the table 3. From the table it is clear that $R_p$ increases with increase in concentration of inhibitor. The semicircle obtained for the present system indicates that the adsorption of inhibitors molecule are charge transfer controlled. Maximum inhibition efficiency using $R_p$ values is found to be at 81% at 0.3% concentration using $C_{dl}$ values the surface coverage was found to be 0.55.

**Mechanism of inhibition**

A corrosion inhibitor is a substance which when added in small amount to an environment, normally corrosive to a metal or alloy in contact with effectively reduces the corrosion rate.

According to Machu¹⁰ the inhibitors function by getting uniformly adsorbed over the entire metal surface. Mann¹¹ has suggested that the organic compounds get adsorbed through the polar unit present in them.

In the present study with fish scale extract has proved it to be an effective inhibitor for mild steel in acid media. The fish scale contains proteins, minerals such as CaCO₃, Mg(PO₄)₄, etc along with fat. During the extract preparation the proteins would have been hydrolysed into amino acid. The nitrogen, sulphur and oxygen atoms present in the amino acids contain lone pair of electrons. According to Hackerman (1954) the adsorption of the inhibitor molecules on the metal surface is through the unshared pair of electrons present on the hetero atoms.

Numerous studies has proved the synergistic effect of cations and anions during corrosion inhibition¹³. The cations and anions present in the extract would have helped to improve the performance of the extract.

Most of the constituents present in the extract can be adsorbed on the mild steel giving rise to such inhibition. It is hard to decide which of these constituents is responsible for this inhibition. It may be one or more or even all of them acting in synergism.

The acid extract of aquatic waste –fish scale could bring out a maximum of 96.59% inhibition efficiency and extract was temperature resistant. Optimum time of immersion for inhibition was found to be 6hrs. The inhibitor used in the current study followed Langmuir adsorption isotherm. Increase in Rp and Rct values and decrease in Icorr and Cdl values confirm that the inhibition process is by adsorption. Values of Tafel constant $ba$ and $bc$ confirm that the fish scale extract acts like mixed type inhibitor. The fish scale extract plays a major role in reducing the metal dissolution as well as hydrogen evolution and protect the mild steel surface from corrosion.

3. L.I. Antropov, Theoretical Electrochemistry, Moscow.