Corrosion inhibition of mild steel by Capsicum annuum fruit paste

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Summary The anti-corrosive property of Capsicum annuum fruit paste (CFP) on mild steel was investigated. Weight loss and SEM analysis showed that the aqueous and ethanolic solutions of CFP exhibits excellent corrosion inhibition in 2 M HCl. Contact angle, surface atomic composition and FTIR studies verified the presence of an organic film on the mild steel surface. The FTIR spectra also indicated the formation of active compound-Fe complex. CFP thus shows potential as an inexpensive environment friendly corrosion inhibitor for mild steel.

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Introduction

Protection of steel from acid corrosion has become increasingly important in various industries. The toxicity of most status quo corrosion inhibitors has increased the need for environment friendly ones (Rani and Bharathi Bai, 2011). Plant based polar organic compounds containing heteroatoms and ring structures have been widely explored (Selvi et al., 2009; Souza et al., 2014; Africa, 2008; Fouda et al., 2014; Saratha and Vasudha, 2010) and have proven to be effective.

Capsicum annuum (chili pepper) fruit has a high concentration of alkaloids called capsaicinoids (Wesolowska et al., 2011) and other polar molecules like ascorbic acid (Marin et al., 2004) hence making it a strong candidate in anti-corrosion studies.

In this study, we explored the corrosion inhibitory properties of CFP as a solution and as dried coat in acid. Weight loss method and SEM were used to study the inhibition efficiency. Contact angle, EDS and FTIR studies were done to analyse the protective film.

Materials and methods

Preparation of the corrosion inhibitor solution

200 g of fresh green chili fruit was washed and ground using a mixer grinder till a paste of even consistency was obtained. The paste was squeezed and filtered through a double layered muslin cloth to obtain the liquid part. This liquid extract was used as the inhibitor solution.
Preparation of the metal samples

Mild steel coupons (0.035% S, 0.05% P, 0.60 Mn, 0.15% C and the rest iron) of dimensions 20 mm \( \times \) 40 mm \( \times \) 3 mm were polished with Ajax emery paper grade 120 and washed with distilled water. Samples for the analysis were prepared by immersing these coupons in solutions of 30 ml 2 N HCl, 10 ml inhibitor solution with 10 ml of distilled water or 10 ml of 95% ethanol for the weight loss, SEM and EDS studies and only distilled water for FTIR and contact angle studies. The coupons were subsequently removed from the solution washed with distilled water and dried.

Weight-loss method

The polished coupons were initially weighed using a Shimadzu electronic balance-BL220H and immersed in solutions as described above. The reference coupons were immersed in the acid without the inhibitor solution. The treated and dried coupons were then weighed after the stipulated time.

Inhibition efficiency (IE) were calculated using the following equations,

\[
IE = 100 \left( 1 - \frac{W_2}{W_1} \right) \%
\]

\( W_1 \) — weight loss in the absence of the inhibitor solution (reference) (mg); \( W_2 \) — weight loss in the presence of the inhibitor solution (test) (mg).

For the anti-corrosive coating tests the metal pieces were immersed in the inhibitor solution on a plate and placed in a hot air oven for 24 h till all the liquid was evaporated leaving behind a coat on the metal coupons. The coupons were then weighed and immersed in a solution containing 30 ml of 2 N HCl. Polished coupons were immersed in the acid as reference. The weight loss was determined for 1, 4 and 7 days of incubation.

Contact angle measurements

Sessile drop contact angle measurements were used to confirm the formation of the organic film (Souza et al., 2014). The contact angle was measured by placing 100 \( \mu \)L of distilled water on metal pieces immersed in acid with and without the inhibition solutions for 24 h.

Analysis of the protective film

The surface morphology and atomic compositions (from EDS) of the samples were analyzed using a Zeiss Ultra 55 FE-SEM machine. FTIR study was done to analyze the nature of the protective film formed on the mild steel surface (Kalaivani et al., 2009). FTIR spectrum of the inhibition solution, inhibition solution mixed with ferrous sulphate and the film formed on the metal surface was obtained in their original state using ATR-FTIR by the Perkin Elmer Frontier FTIR Spectrum 10 instrument.

Results and discussion

Weight-loss experiment results

The inhibition efficiency of both the aqueous and ethanolic solutions of the inhibitor solution increased with the immersion period and reached a maximum of 94% on the 4th day. The increase suggests that the protective film on the metal surface either increases with the incubation time or remains largely unaltered (Table 1).

The coated samples showed considerably high IE in acid even after 7 days of incubation suggesting the formation of a very stable protective film (Table 2).

<table>
<thead>
<tr>
<th>Table 1</th>
<th>Time of immersion versus IE. A — CFP added with distilled water, E — with 95% ethanol.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Time (days)</td>
<td>1A</td>
</tr>
<tr>
<td>IE</td>
<td>85.24</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Table 2</th>
<th>Time of immersion versus IE for the coated sample.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Time (days)</td>
<td>1</td>
</tr>
<tr>
<td>IE</td>
<td>96.48</td>
</tr>
</tbody>
</table>

Contact angle measurements

The figure shows the contact angle of the water drop with the steel surface under various conditions. The contact angle of the reference coupon is seen at 51° which decreases to 31° when incubated in the acid. The contact angle of the coupon immersed along with the inhibitor solution increases to 59°. This decreased wettability and increased hydrophobic nature suggests the formation of an organic film over the steel surface by the active compounds in CFP (Souza et al., 2014) (Fig. 1).

Surface analysis

The morphology of the steel surfaces before and after incubation in 2 N HCl with and without inhibitor solutions is shown in the figure. The metal immersed in the acid without the inhibitor solution shows intense corrosion with a highly rough surface. Corrosion pits formation is clearly observed. The metals immersed in the solution containing the inhibitor solution showed no surface roughness suggesting minimal corrosion. A smooth surface is observed, very similar to the reference coupon, with the marks observed being left only from the polishing. Complete coverage of the metal surface by the protective film without any cracks or gaps can be observed in the images (Fig. 2).

The surface atomic composition of carbon and oxygen of the metal coupon immersed in the aqueous (22.45% C,
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18.48% O, and rest iron) and ethanolic (19.85% C, 14.72% O, and rest iron) solution of the inhibitor solution was much higher than that of the reference (12.73% C, 9.25% O, and rest iron). This result confirms the presence of an organic film over the metal surface.

Analysis of the FTIR spectra

In the FTIR spectrum of the CFP it is was observed that the major polar functional groups present are hydroxyl group and the amide carbonyl group. The OH stretching frequency and the amide carbonyl group stretching shifts from 3306 cm⁻¹ to 3285 cm⁻¹ and 1634 cm⁻¹ to 1635 cm⁻¹ respectively, when CFP is complexed with Fe²⁺. The OH and carbonyl stretching frequency of the film formed on the metal coupons shifts from 3306 cm⁻¹ to 3182 cm⁻¹ and 1634 cm⁻¹ to 1622 cm⁻¹ respectively. The presence and shift of the stretching frequencies of the functional groups confirms the formation of active compound-Fe²⁺ complex on the metal surface (Rajendran et al., 2001).

Conclusion

The corrosion inhibition efficiency of CFP on mild steel immersed in 2N HCl increases with increasing incubation time. The dried CFP coat gives IE in excess of 90% even after 7 days of incubation in acid. The contact angle and EDS measurements verify the formation of a protective organic film over the mild steel surface when incubated in the inhibitor solution. The surface micrographs showed a corrosion-free morphology with continuous coverage of the protective film. The FTIR studies on the film showed peak maximums in the regions of hydroxyl (3182 cm⁻¹) and carbonyl (1622 cm⁻¹) functional groups. Formation of the active compound-Fe²⁺ complex was confirmed from the peak shifts. Capsicum annuum (chili pepper) fruit can thus be concluded as a promising candidate for the development of eco-friendly corrosion inhibitors.

References