TURNING WASTE PEONY LEAVES INTO GREEN CHEMICALS: AN EXPLORATORY STUDY

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A quick thank-you

- Center for Environmentally Sustainable Transportation in Cold Climates
- Michael Williams, EagleSong Family Peony Farm
- Ling Cao, Western Transportation Institute
- Mehdi Salih Shihb, Al-Nahrain University
- Eden Adele Havens, WSU
Highlights

• Chloride induced corrosion of metals results in significant cost and environmental footprint.

• A novel chemical/biological process for deriving “green” inhibitors was developed.

• The main active ingredient of the inhibitor was determined.

• A mixture of an adsorbed organic layer and a passive iron oxide layer induced by the organic materials significantly mitigated the corrosion of steel.
The Big Picture

• 20 million tons of deicing salt per year in the U.S.

• Corrosive for metallic component of vehicles

• **Annual costs: $2.8 B**

• 25-30% of these costs are preventable

• Corrosion mitigating strategies are much needed!
Why did we do this exploratory study?

- Corrosion inhibitors are proven to be effective in reducing the metallic corrosion and thus preserving the service life and performance of assets.
- Some agro-based inhibitors can offer additional benefits as ‘cryoprotectants’: reducing the freezing point!
- In place of petroleum-derived inhibitors, inhibitors from renewable resources are highly desirable: less toxic, readily available, bio-degradable, more cost-effective.
- Green inhibitors feature organic compounds containing heteroatoms such as P, S, N and O which can adsorb onto the metallic surface and form a protective layer.
Peony leaves derived solution

• In the State of Alaska alone, there are 58 peony farms that can produce about 200,000 peonies annually which after the flower season generate a substantial amount of peony leaves as waste.

• The up-cycling of this waste can benefit the environment and the economy.

• This work explores an innovative process to derive “green” chemicals from waste peony leaves (and stalks).
EXPERIMENTAL

Materials
- Carbon steel (C1010)
- 3.5% NaCl solution
- Peony leaves extract: using a zero-waste process

<table>
<thead>
<tr>
<th>Definition</th>
<th>Different concentrations of peony leaves derived solution</th>
</tr>
</thead>
<tbody>
<tr>
<td>Concentration</td>
<td>0 vol.%</td>
</tr>
<tr>
<td>Sample</td>
<td>PLS0</td>
</tr>
</tbody>
</table>

Methods
- Chemical analyses
- Electrochemical Measurements
- Surface analyses
- Water contact angle
Preparation of peony leaves extract

Urea + Ca(OH)$_2$ + NaOH + ground peony leaves powder + DI water

Adjusting pH above 11.5

Fast stirring then freezing at -13 °C

Partially frozen solution stirred again and simultaneously 500 mL DI water was added into it.

pH adjusted to 8.5 by adding HNO$_3$ and NaOH. Then, a mixture of KH$_2$PO$_4$, NaH$_2$PO$_4$.H$_2$O and MgSO$_4$.7H$_2$O was added to the solution to create a medium suitable for the growth of bacteria.

Bacillus Megaterium bacteria (NRRL B-14308) was added to the solution, which was subsequently placed in a shaker for 14 days.
RESULTS AND DISCUSSION

FT-IR spectroscopy
## FT-IR spectroscopy

<table>
<thead>
<tr>
<th>Wave number (cm(^{-1}))</th>
<th>Functional group</th>
<th>Bond</th>
<th>Frequency range (cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Broad peak</td>
<td><strong>alcohols</strong></td>
<td>O–H stretch</td>
<td>3500 to 3200</td>
</tr>
<tr>
<td>3427 and 3329</td>
<td>1°, 2° amines</td>
<td>N–H Stretch</td>
<td>3400–3250</td>
</tr>
<tr>
<td>2914</td>
<td>alkanes</td>
<td>C–H stretch</td>
<td>3000–2850</td>
</tr>
<tr>
<td>1674</td>
<td>carbonyls or alkenes</td>
<td>C=O stretch or – C=C– stretch</td>
<td>1760–1665 or 1680–1640</td>
</tr>
<tr>
<td>1595</td>
<td><strong>aromatics</strong></td>
<td>C–C stretch (in–ring)</td>
<td>1600–1585</td>
</tr>
<tr>
<td>1456</td>
<td>alkanes</td>
<td>C–H bend</td>
<td>1470–1450</td>
</tr>
<tr>
<td>1362</td>
<td>alkanes</td>
<td>C–H rock</td>
<td>1370–1350</td>
</tr>
<tr>
<td>1149</td>
<td><strong>phosphine oxides</strong></td>
<td>P=O bond</td>
<td>1210–1140</td>
</tr>
<tr>
<td>1032</td>
<td>aliphatic amines</td>
<td>C–N stretch</td>
<td>1250–1020</td>
</tr>
<tr>
<td>787 and 706</td>
<td>alkyl halides</td>
<td>C–Cl stretch</td>
<td>850–550</td>
</tr>
</tbody>
</table>
Liquid chromatography - mass spectroscopy (LC-MS)

Demethoxyisogemichalcone C

Ganodermic acid TQ

1-docosanoyl-glycero-3-phosphate
Linear polarization resistance (LPR)

\[
\mathbf{\text{Corrosion rate (mpy)}} = \frac{0.13 \times \mathbf{i}_{\text{corr}} \times E.W.}{\rho}
\]

\[
\mathbf{i}_{\text{corr}} = \frac{\beta_a\beta_c}{2.3(\beta_a + \beta_c)} \frac{1}{R_p}
\]

0, 1, 2, 3 vol. % into 3.5 wt. % NaCl
LPR measurements reveal great potential

• The inhibition effect was still outstanding in the presence of 2 and 3 vol.% PLS even after 16 days of steel immersion.

• Such sustained inhibition is highly desirable, making this green inhibitor a promising candidate for formulating long-lasting inhibitor packages.
Potentiodynamic polarization (PDP)

C1010 steel after 16-d immersion in NaCl solution containing 0 to 3 vol.% PLS
• Anodic reactions for steel corrosion induced by chloride in near-neutral pH solutions:

\[ \text{Fe}^{2+} + 2\text{Cl}^- \rightarrow \text{FeCl}_2 \]

\[ \text{FeCl}_2 + 2\text{H}_2\text{O} \rightarrow \text{Fe(OH)}_2 + 2\text{H}^+ + 2\text{Cl}^- \]

\[ 6\text{FeCl}_2 + \text{O}_2 + 6\text{H}_2\text{O} \rightarrow 2\text{Fe}_3\text{O}_4 + 12\text{H}^+ + 12\text{Cl}^- \]

• The main cathodic reaction in the presence of sufficient dissolved oxygen:

\[ \text{O}_2 + 2\text{H}_2\text{O} + 4\text{e}^- \rightarrow 4\text{OH}^- \]
PDP measurements reveal probable mechanism of corrosion inhibition

- The addition of PLS shifted the cathodic current density to the passive direction and the corrosion potential ($E_{corr}$) to a more negative value. This is likely due to the adsorption of organic molecules on the cathodic active sites of steel surface.

- In the NaCl solutions containing PLS at various concentrations, the anodic branch of the polarization curve featured a current plateau, which is ascribed to desorption of strongly adsorbed inhibitor from the metallic surface.
Electrochemical impedance spectroscopy (EIS)

Nyquist plots for C1010 steel after 16-d immersion in NaCl solution containing 0 to 3 vol.% PLS.
EIS measurements confirm great potential

- The protection response of carbon steel was modified by the presence of different concentrations of PLS, and the surface impedance increased with the inhibitor concentration.

- These loops are not perfect semi-circles and such deviation is attributable to frequency dispersion by the roughness or non-homogeneity of the working electrode surface caused by corrosion attack.
Z_{CPE} = \frac{1}{Y_0(j\omega)^n}

C_{dl} = (Y_0 R_{ct}^{1-n})^{1/n}

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>Rs (Ω cm²)</th>
<th>Rf (Ω cm²)</th>
<th>Qf (Ω cm²)</th>
<th>R_{ct} (Ω cm²)</th>
<th>Q_{dl}</th>
<th>C_{dl} × 10^{-4} (F cm²)</th>
<th>IE %*</th>
</tr>
</thead>
<tbody>
<tr>
<td>PLS0</td>
<td>2.2</td>
<td>4.5</td>
<td>6.1 × 10^{-5}</td>
<td>0.96</td>
<td>2610</td>
<td>13.7</td>
<td>0.67</td>
</tr>
<tr>
<td>PLS1</td>
<td>2.8</td>
<td>388.3</td>
<td>29.1 × 10^{-5}</td>
<td>0.85</td>
<td>3739</td>
<td>6.9</td>
<td>0.62</td>
</tr>
<tr>
<td>PLS2</td>
<td>2.9</td>
<td>103.5</td>
<td>9.3 × 10^{-5}</td>
<td>0.94</td>
<td>4780</td>
<td>4.4</td>
<td>0.58</td>
</tr>
<tr>
<td>PLS3</td>
<td>2.5</td>
<td>454.9</td>
<td>8.2 × 10^{-5}</td>
<td>0.95</td>
<td>7628</td>
<td>2.5</td>
<td>0.61</td>
</tr>
</tbody>
</table>

* IE% = \left[1 - \frac{R_{ct (uninhibited)}}{R_{ct (inhibited)}}\right] \times 100
Adsorption isotherm

Frumkin isotherm

\[ y = 3.1323x - 1.0329 \]
\[ R^2 = 0.9886 \]

Inhibitor Concentration, \( C \)

\[
\log \left( \frac{\theta C}{1 - \theta} \right) = 2\alpha \theta + 2.303 \log K
\]
\[
\Delta G_{ads}^0 = -2.303RT \log (C_{solvent}K)
\]
Adsorption isotherm reveal the type of adsorption

• The Frumkin isotherm is an extension of the Langmuir isotherm in describing certain adsorption phenomena. It accounts for non-ideal interactions of both insoluble-soluble (1-2) and/or soluble-soluble (2-2) components.

\[ \Delta G_{\text{ads}}^0 \] was estimated to be \(-14.56 \text{ kJ mol}^{-1}\). This negative value indicates that the adsorption process occurred spontaneously. Since the absolute value of \( \Delta G_{\text{ads}}^0 \) is less than 20 kJ mol\(^{-1}\), this suggests physical adsorption in which electrostatic interaction occurs between inhibitor molecules and metal surface.
**Digital Photos**

- The steel coupon exposed to uninhibited salt brine (PLS0) was partially covered by orange rust.

- The surface layer in the 3.5 wt.% NaCl with higher inhibitor concentrations (e.g., PLS at 3 vol.% ) was more uniform and complete.

The surface morphology of steel coupons after 16-d continuous exposure to various inhibitor/NaCl solutions.
FESEM micrographs of the surface layer

More porous rust

More compact corrosion product layer
XRD patterns of the surface layer

Intensity (a.u.)

2θ (degree)

- PLS3
- PLS2
- PLS1
- PLS0

Symbols:
- ◆ NaCl
- □ Fe
- ♣ γ-FeOOH
- ● Fe3O4
EDS results of the surface layer

PLS0

O  F  Fe

PLS3

adsorption of inhibitor molecules
Phosphate based compounds have a higher negative charge density than amine based ones; as such, they can form stronger and more stable bonds with the metallic surface.
XPS results for PLS3 steel coupon

Phosphorous peaks

all of the $\text{Fe}_3\text{O}_4$ phase and some of the $\gamma$-FeOOH were converted to $\gamma$-Fe$_2$O$_3$
SEM micrographs of as-washed steel surface after 16-day immersion in 3.5% NaCl solution with PLS at (a) 0 vol.%, (b) 1 vol.%, (c) 2 vol.%, and (d) 3 vol.%. The scale in all images represents 100 μm.
Water contact angle & surface free energy

- Contact angle
- Surface free energy

Sample Name:
- PLS0
- PLS1
- PLS2
- PLS3
The inhibition efficiency increased with increasing the concentration of peony leaves extract, from 0% to 3 vol.%. Used at 3 vol.%, this green inhibitor exhibited a good inhibition efficiency of 65.8% after 16 days of steel immersion time.

The adsorption of organic molecules follows the Frumkin adsorption isotherm through the physical adsorption in which electrostatic interaction occurs between inhibitor molecules and metal surface.
CONCLUDING REMARKS (II)

- The peony leaves extract is a cathodic inhibitor that blocks the cathodic active sites on the surface of carbon steel, while acting as a catalyst in converting Fe3O4 and γ-FeOOH to γ-Fe₂O₃.

- The corrosion inhibition by peony leaves extract was mainly due to the adsorption of 1-docosanoyl-glycero-3-phosphate molecules, as active ingredient, which induces the formation of γ-Fe₂O₃ as a passive layer on the steel. It also increases the hydrophobicity of the surface through the adsorption of the fatty acid chain of phospholipid compound.
Ongoing Research

Questions?

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