Protection performance of orange oil distillates on low carbon steel in dilute acid electrolytes

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Abstract. Orange essential oil distillate (OOE) was studied for its inhibition performance on low carbon steel in 0.5 M H2SO4 and HCl aqueous electrolyte by electrochemical method and open circuit potential measurement. OOE performance was significantly proportional to it concentration with highest protection efficiency of 76.93% and 94.90% at optimal OOE concentration (10% OOE) in H2SO4 and HCl electrolyte. The performance of OOE at low concentration in H2SO4 was quite poor with inhibition efficiency values below 40%. OOE exhibited greater inhibition action in HCl solution with effective performance beginning at 4% OOE concentration compared to 6% concentration in H2SO4 electrolyte. Corrosion potential deviated basically in the anodic direction signifying the dominant inhibition effect to be through surface coverage of the steel surface. OOE exhibited mixed type corrosion inhibition. Open circuit potential graphs show OOE increases the thermodynamic fluctuation of the carbon steel in H2SO4 solution relative to the plots at 0% OOE, despite effective protection. In HCl, the open circuit potential plots were more electropositive relative to the plots at 0% OOE signifying decreased tendency to corrosion. Optical images of the carbon steel after evaluation with and without OOE significantly contrast each other.

1. Introduction
The corrosion dilemma is prevalent worldwide and accounts for a significant portion of the gross domestic product of countries. Most of the cost resulting from corrosion damage goes to maintenance and repair, replacement of damage parts and, corrosion control and monitoring techniques [1-3]. There are cases where damage due to corrosion of metallic parts results in leakage of toxic substances to the environment, injury to industry personnel due to industrial accidents, financial cost from plant shutdowns and unforeseen circumstances [4, 5]. One of the important focal points of material degradation is the universal utilization of carbon steels due to their inadequate corrosion resilience and inability to passivate against aqueous reactive species [6, 7]. Carbon steels are lowly priced, reusability, easily obtainable and desirable mechanical properties which can be easily altered to meet specific industrial requirements [8]. They are applied in petrochemical industry, automobile industry, mining industry, marine industry, desalination plants and energy generating industry. There are a number of effective methods of corrosion prevention and control. However, utilization of corrosion inhibitors remains the most competitive and proven method of corrosion control to extend the lifespan of carbon steels [9]. Chemical compounds of organic origin are widely used to enhance the corrosion resilience of carbon steel. They perform through evolution of a shielding film on the steel’s exterior. However, conventional inhibiting fluid derivatives are unsustainable due to the damage caused to the environment and personnel involved in their application [10-18]. Utilization of plant distillates for corrosion inhibition has seen increasing use of recent due to their non-toxic nature [19-24]. This manuscript assesses the protection performance of citrus sinensis oil distillate in aqueous H2SO4 and HCl aqueous electrolyte.
2. Experimental analysis
Orange essential oil distillate (OOE) was concocted in cubic concentrates of 2%, 4%, 6%, 8% and 10% per 200ml of 0.5 M H₂SO₄ and HCl solution. Low carbon steel (LCS) rods were sliced and partitioned into 6 test exhibits for each experimental study. Their general dimension is 0.7 cm radius and 0.7 cm length. The circular exterior ends of the rods were smoothened with coarse papers of different grits. Cu wires were attached to one end of the steel surface and mounted in prehardened resin before hardening after 5 minutes of encasement. Potentiodynamic polarization was executed with a potentiostatic instrument. The mounted LCS working terminal, Pt wire counter terminal and Ag/AgCl reference terminal were immersed within a container with the acid-inhibitor solution at specific inhibitor concentration per test. The electrodes are attached to the potentiostat-computer system to observe the output polarization plots from -1.2V to 0.5 V at sweep rate of 0.0015 v/s. Corrosion rate and other electrochemical parameters were gotten from the polarization test which were discussed in the subsequent sections. Open circuit potential measurement of the alloy in the aqueous acid/inhibitor electrolyte was executed with Digi-Ivy potentiostat for 4000 s at step potential of 0.1 V. Optical illustrations of the protected and corroded steel surface were obtained and assessed in the subsequent sections of the manuscript.

3. Results and discussion
3.1. Potentiodynamic polarization
Potentiodynamic polarization graphs of LCS in OOE/H₂SO₄ and OOE/HCl solution at exact OOE concentration are shown in Fig. 1(a) and (b). Outputs from the test is shown in Table 1. Results in Table 1 shows OOE strongly influenced the corrosion of LCS in both acids. However, general observation of the results shows OOE exhibited higher efficiency in HCl solution compared H₂SO₄ solution. The higher inhibition efficiency in HCl solution is because of the higher dissociation and reaction potential of H₂SO₄ in H₂O as against HCl where H₂SO₄ releases two protons whereas HCl releases on proton. Secondly the size of Cl⁻ ions is much smaller than the corresponding SO₄²⁻ ions as such the reaction effect of Cl⁻ ions tends to be limited as against the general surface deterioration caused by the action of SO₄²⁻ ions. Effective inhibition performance was attained at 4% OOE concentration in HCl compared to 6% OOE concentration in H₂SO₄. Nevertheless, the progressive rise in OOE inhibition efficiency analogous to OOE concentration depicts the protection effect of the oil distillate is concentration dependent wherewith surface coverage of the steel surface by the inhibiting ions suppresses the oxidation of the steel. Optimal inhibition efficiency of 76.93% was attained at 5% OOE concentration in H₂SO₄ and 94.90% at 5% concentration in HCl. Variation of corrosion potential values analogous to the potential at 0% OOE shows OOE exhibits mixed type inhibition reaction mechanism. This is proven from the variation of the inclines of the anodic-cathodic polarization plots where significant decrease in the slopes occurred with increase in OOE concentration. However, the cathodic plots in Fig. 1(b) shows at 6% - 10% OOE concentration shows dominant cathodic inhibition effect whereby the O₂ reduction and H₂ evolution reactions are hindered.

3.2. Open circuit potential measurement
Open circuit potential (OCP) plots for LCS corrosion in H₂SO₄ and HCl solution at 0%, 2% and 10% OOE concentration are shown in Fig. 2(a) and (b). The plots in Fig. 2(a) shows OCP at 0% OOE is more electropositive than the plots at 2% and 10% OOE concentration. The plot at 0% OOE started at -0.478 V and sharply deviated electropositively to -0.450 V at 400 s before gradually progressive in the same direction. The plots at 2% and 10% OOE transited from onset to electronegative potentials culminating at -0.475 V and -0.499 V at 4000 s. The negative shift at 2% and 10% OOE shows that OO increases the thermodynamic tendency LCS to corrode despite effective inhibition performance at 10% OOE concentration. The phenomenon is probably due to lateral interaction effect among inhibitor molecules which strongly influences their inhibition performance. This is evident in the significant potential transient at 10% OOE concentration. The OCP graphs in Fig. 2(b) shows the plot at 2% OOE is more electropositive than the plots at 0% and 10% OOE concentration despite gradual progression to electronegative values coupled with visible potential transients. The potential fluctuations signify contentious adsorption among OOE ionic species and Cl⁻ ions in the electrolyte.
Table 1. Outputs from potentiodynamic polarization of LCS in 0.5M H₂SO₄ and HCl solution at exact OOE concentration (n=1)

| Sample | OOE Conc. (%) | LCS Cₑ (mm/y) | OOE Iₑ (%) | C₁ (A) | C₁ (A/cm²) | Cₚ (V) | Rₛ (Ω) | Bₑ (V/dec) | Bₛ (V/dec) |
|--------|----------------|----------------|-------------|--------|-------------|--------|--------|------------|------------|
| A      | 0              | 9.47           | 0           | 9.38E-04 | 8.30E-04   | -0.429 | 17.40 | -7.203     | 1.451      |
| B      | 2              | 7.58           | 19.95       | 7.51E-04 | 6.64E-04   | -0.427 | 29.49 | -7.503     | 0.138      |
| C      | 4              | 6.12           | 35.35       | 6.06E-04 | 5.36E-04   | -0.402 | 43.26 | -10.480    | 2.969      |
| D      | 6              | 3.52           | 62.82       | 3.49E-04 | 3.08E-04   | -0.390 | 75.64 | -7.943     | 1.054      |
| E      | 8              | 2.84           | 69.97       | 2.82E-04 | 2.49E-04   | -0.420 | 91.24 | -2.475     | 4.046      |
| F      | 10             | 2.18           | 76.93       | 2.16E-04 | 1.91E-04   | -0.428 | 118.80| -6.364     | 9.240      |

| Sample | OOE Conc. (%) | LCS Cₑ (mm/y) | OOE Iₑ (%) | C₁ (A) | C₁ (A/cm²) | Cₚ (V) | Rₛ (Ω) | Bₑ (V/dec) | Bₛ (V/dec) |
|--------|----------------|----------------|-------------|--------|-------------|--------|--------|------------|------------|
| A      | 0              | 5.52           | 0           | 5.47E-04 | 4.84E-04   | -0.453 | 47.18 | -6.646     | 13.15      |
| B      | 2              | 2.76           | 49.92       | 2.74E-04 | 2.42E-04   | -0.445 | 61.19 | -5.807     | -0.064     |
| C      | 4              | 2.19           | 60.41       | 2.16E-04 | 1.92E-04   | -0.458 | 83.81 | -5.140     | 4.930      |
| D      | 6              | 0.34           | 93.83       | 3.37E-05 | 2.99E-05   | -0.461 | 761.40| -7.394     | 10.500     |
| E      | 8              | 0.34           | 93.86       | 3.35E-05 | 2.97E-05   | -0.458 | 766.00| -5.107     | 11.180     |
| F      | 10             | 0.28           | 94.90       | 2.79E-05 | 2.47E-05   | -0.458 | 820.80| -5.130     | 10.730     |

The plot at 0% OOE shifted to electropositive values, but its final potential is more electronegative than the final value at 2% OOE concentration due to the inhibition effect of protonated OOE molecules aided by the electronegative steel surface due to initial adsorption by Cl⁻ anions. The plot at 10% OOE concentration in Fig. 2(b) exhibited similar plot configuration to the plot at 10% concentration in Fig. 2(a) due to reasons earlier discussed. Nevertheless, despite effective inhibition performance by OOE on LCS, OOE increases the thermodynamic instability of LCS surface and its tendency to corrode due to instability of the protected steel surface.
Figure 2. Open circuit potential graphs of LCS corrosion in (a) H$_2$SO$_4$ solution and (b) HCl solution at 0%, 2% and 10% OOE concentration

3.3. Optical microscopy study
Optical illustrations of LCS prior to corrosion, after in H$_2$SO$_4$ and HCl solution without OOE and after corrosion from the electrolytes in the presence of OOE are laid out from Fig. 3 to 5(b). Severe deterioration is visible on LCS surface in Fig. 4(a) and (b) due to the absence of OOE to counteract the degenerative reactions of SO$_4^{2-}$ and Cl$^-$ anions in the acid media. As a result, LCS surface was oxidized undergoing anodic dissolution. The degree of deterioration is greater on Fig. 4(a) which contrast to Fig. 4(b) because of the higher dissociation constant of H$_2$SO$_4$ in H$_2$O compared to HCl. The images in Fig. 5(a) and (b) significantly differs to the images earlier discussed due to suppression of the reduction-oxidation reaction mechanism. The mild surface deterioration on the images [Fig. 5(a) and (b)] is due to preadsorbed corrosive species on the steel surface which increased its ionization potential and electronegativity before subsequent attraction of cationic OOE molecules unto the steel which blocked further diffusion of corrosive species.

Figure 3. Optical illustration of LCS before corrosion

Figure 4. Optical image of LCS after corrosion without OOE from (a) H$_2$SO$_4$ solution and (b) HCl solution
The oil distillate of AA1070 analysis of AA1070

Figure 5. Optical image of LCS after corrosion from (a) H2SO4/OOE solution and (b) HCl/OOE solution

4. Conclusion
Orange essential oil distillate sufficiently stifled the degeneration of the carbon steel in H2SO4 and HCl aqueous electrolyte. The oil distillate exhibited higher efficiency at all concentrations in HCl solution compared to H2SO4 solution were effective performance occurred at higher concentrations of the distillate. The distillate exhibits mixed type protection characteristics with dominant cathodic inhibition effect at higher distillate concentrations in HCl solution. The morphology of the alloy after corrosion in the electrolyte in the absence of the distillate showed severe deterioration compared the improved morphology with the distillate. Corrosion potential measurement showed the distillate induced the thermodynamic instability of the steel in both acids despite effective corrosion inhibition performance.

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