Abstract

The toxicity of number of organic and synthetic compounds have led to the use of natural products as anticorrosion agents which are eco-friendly and harmless. Therefore, an attempt is made to use natural products as plant extracts to investigate the corrosion inhibition of Steel (St 37-2) in petroleum medium (obtained from Iraqi refinery) using electrochemical studies. The inhibition was performed by four plant extracts including *Cinnamon* stems, *Ficuscarica*, *Sweet clover* and *Tobacco* leaves depending on presence of coumarins in these plants. Ethanolic extracts were characterized by UV-Visible, FTIR, and HPLC, these techniques confirm the presence of coumarins through the band of absorption at λ_{max}=274nm in UV-Visible spectrum. FTIR spectra of plant extracts confirm appear the stretching of C=O group near 1699.34cm^{-1}. Retention time of coumarins near 2.342 min confirms the presence of coumarins through HPLC analysis.

Galvanostatic test was conducted on steel 37-2 in petroleum medium in absence and presence of four plant extracts at four temperatures (323, 333, 343 and 353 K) by adding four concentrations of coumarin including 10, 40, 70 and 100 ppm and four concentrations of each extract including 1, 3, 5 and 7 mL/L. Generally, the presence of plant extracts shifts the corrosion potentials toward either active or noble direction suggesting that the selected extracts are mixed-type inhibitors. Corrosion current densities were decreased confirming the inhibitive action of natural products under inhibitors at experimental conditions. Inhibition efficiencies IE% confirm that the four extracts act as anticorrosion agents. 1 mL/L is the best concentrations of *cinnamon* extract, 3 mL/L is the best concentrations of *ficuscarica* and *sweet clover* extracts, while7 mL/L is the best concentration of *tobacco* extract, the best efficiencies ranged between 71 to 87%.

FTIR of film formed on steel surface in petroleum medium in the presence of natural inhibitors indicated the decreasing in the intensity of the important peaks in plants because of formation of Fe^{2+}—plant extract complexes due to adsorption of the inhibitor on steel surface. Adsorption isotherms are usually used to describe the adsorption process, and the straight lines of plotting C_{inh}/θ against C_{inh} indicate that the plant extracts obey Langmuir adsorption isotherm with regression coefficient close to unity and in the range $0.996 \geq R^2 \geq 0.917$ for four plant extracts. The values of equilibrium constant of the adsorption-desorption process K_{ads} are relatively small indicating that the interaction between the adsorbed extract molecules and steel surface is physically adsorbed, which has been confirmed through the small values of free energy (ΔG^o_{ads})indicating the electrostatic interactions between the charged molecules and the charged metal surface as physical adsorption. Other thermodynamic function are also

calculated such as the enthalpy of adsorption (ΔH^o_{ads})using Gibbs–Helmholtz equation and the entropy of adsorption (ΔS^o_{ads}), the values of these two functions were negative indicating the exothermic adsorption process and the reduction in disordering which takes place on going from reactants to the activated complex. The apparent activation energies (E_a^*) for the corrosion process in absence and presence of plant extracts were evaluated from Arrhenius equation, and the increasing of activation energies in the presence of plant extracts refers to the adsorption of the organic molecules which occurs as the interaction energy between molecule and metal surface is higher than that between the H_2O molecule and the metal surface. Since, we get activation energies equal to 46.41, 13.14, 24.01 and 14.65 kJ.mol^{-1} corresponding to 1mL/L *cinnamon*, 3mL/L *ficuscarica*, 3mL/L *sweet clover* and 7mL/L *tobacco* extract respectively compared with activation energy of uninhibited medium 10.57 kJ.mol^{-1}, the highest activation energy was in a petroleum medium containing *cinnamon* extract.

Optical microscopies show a noticeable reduction in corrosion sites and corrosion products on the corroded surface after adding the inhibitors as compared with the case of corrosion in the petroleum medium without inhibitor especially in the presence of the best concentration of each inhibitor.

Finally, Atomic Force Microscopy displays the surface topography of un-corroded metal surface (polished steel surface as reference sample) which is8.39 nm. The slight roughness observed on the polished steel surface is due to atmospheric corrosion. AFM of corroded metal surface displays few pits in the absence of the inhibitor immersed in petroleum medium equal to 44.7 nm. These data suggest that steel surface immersed in petroleum medium has a greater surface roughness than the polished metal surface, which shows that the unprotected steel surface is rougher. This is due to the corrosion of the steel in the petroleum medium. AFM of steel surface after immersion in petroleum medium containing 1mL/L of *Cinnamon* extract, 3mL/L *Ficuscarica* extract, 3mL/L *Sweet clover* extract and 7mL/L *Tobacco* extract, gave roughness values Ra of 0.631, 4.13, 1.1 and 5.89 nm respectively. These parameters confirm that the surface is smoother especially with *cinnamon*. The smoothness of the surface is due to the formation of a compact protective film of Fe^{2+} – plant extract complex thereby inhibiting the corrosion of steel.