

## Abstract

Chitosan, a versatile biopolymer was modified into its Schiff base derivatives using four different aldehydes viz., salicylaldehyde, Vanillin, thiophene- 2-carboxaldehyde, pyrrole 2- carboxaldehyde. Chitosan Schiff bases (ChSSB, ChVSB, ChTSB, ChPSB) were synthesized by condensing the active carbonyl group of aldehydes with free amino groups of Chitosan. The synthesized Chitosan Schiff bases were characterized using Elemental, spectral (UV, FTIR) and SEM analysis to confirm the incorporation of aldehydes onto the Chitosan backbone through imine linkages. The thermal stability of the Chitosan Schiff bases was analyzed by thermogravimetric analysis. The corrosion inhibition performance of Chitosan Schiff bases was explored for mild steel in 1M HCl solution using weight loss, electrochemical impedance spectroscopy and potentiodynamic polarization methods at room temperature and at higher temperature range of 313-343 K with different concentrations (100-1500 ppm). Inhibition efficiency of the inhibitors increased with increase in concentration of all the studied concentration within the range of 100-1500 ppm. All the Schiff base inhibitors showed better inhibition performance of around 90% at the concentration of 1500 ppm.

Potentiodynamic polarization analysis revealed that Chitosan Schiff bases behaved as a mixed type inhibitor. The protective film formed on the metal was stable till 323 K and then tend to desorb at higher temperatures. Electrochemical impedance spectroscopy analysis (EIS) revealed an increase in polarization resistance due to the adsorbed inhibitor molecules. The temperature effect on the inhibition process was also tested by constructing Arrhenius plot and Transition plot. The data obtained from the temperature studies of weight loss technique were fitted to various isotherms and the best fit was found to be Temkin isotherm for all the studied Chitosan Schiff bases. Thermodynamic parameters of adsorption were calculated which indicated the chemisorptive nature of adsorption of the Schiff base polymers. The adsorption behaviour of the Chitosan Schiff bases on the metal surface was monitored by cyclic voltammetric studies. The reduction in  $\Delta Q-t$  plot after the addition of Schiff base inhibitors indicated the reduction in corrosion rate. The Schiff base derivatives showed a better inhibition performance by forming a protective layer on the metal surface.

Surface morphology of the metal was examined by FTIR, scanning electron microscopy atomic force spectroscopy and contact angle measurements. These studies confirmed the presence of a protective layer on the metal surface. The inhibition

mechanism of the inhibitor molecules was proposed in the light of the quantum chemical calculations using semi empirical (AM1 and PM3) methods and DFT method. The quantum chemical results showed the location of HOMO orbitals on the  $\text{-HC=N}$  and  $\text{-OH}$  groups of Chitosan Schiff bases and also the presence of Mulliken charges on the hetero atoms. This clearly confirmed the formation of strong bond through chemical interaction with the empty d- orbitals of the metal atom with the inhibitor molecules. The scale inhibiting potential of the synthesized Schiff base derivatives for  $\text{CaCO}_3$  scale was also investigated by static experiments and SEM analysis. The experimental results revealed the better scaling efficacy of the synthesized inhibitor and SEM analysis confirmed the morphological change of  $\text{CaCO}_3$  crystals in the presence of inhibitor. Thus, the synthesized Chitosan Schiff bases can be suggested as better corrosion inhibitor for the mild steel in acid medium and also as anti-scalant for  $\text{CaCO}_3$ .