**ABSTRACT**

In the present work, two macrocyclic compounds namely 5,6,11,12-tetramethyl-1,2,4,7,8,10-hexaazacyclododeca-4,6,10,12-tetraene-3 ,9-dithione (TMCD) and 5,6,11,12- tetraphenyl- 1,2,4,7,8,10-hexaazacyclododeca-4 ,6,10,12-tetraene-3 ,9-dithione (TMPD) have been synthesized and for the first time reported as inhibitors against the corrosion of aluminium in 1 M hydrochloric acid. The synthesized compounds were characterized using H-1 NMR and C-13 NMR. The corrosion inhibition behaviour of TMCD and TMPD was studied using gravimetric measurements, electrochemical impedance spectroscopy and potentiodynamic polarization studies. The surface analysis was carried out using AFM and SEM. Theoretical studies on the adsorption behaviour of inhibitor were carried out using the Density Functional Theory method. A detailed study of the effect of temperature and the influence of immersion time is presented using weight loss technique. Potentiodynamic polarization study proves that the corrosion inhibition efficiencies of TMCD and TMPD at 400 mg L–1 concentration are 97.30% and 89.71% respectively. Both the inhibitors behaved as mixed type but exhibit cathodic predominance. The results of EIS-Nyquist plots show inductive behavior at low frequency characteristic of the electrochemical behaviour of aluminium. The increase in polarization resistance with concentration suggests the adsorption and corrosion inhibition behaviour for both TMCD and TMPD. The AFM studies reveal a considerable decrease in surface roughness in the presence of inhibitors compared to blank sample and the SEM images show a highly smooth surface of the metal sample in the presence of inhibitors. The Fukui functions, global softness and Mulliken charges reveal that the sites for electrophilic attack are the hetero atoms. The frontier molecular orbital energies, the molecular orbital energy gap and the other quantumchemical parameters corroborated the experimental observations and suggested a better performance of TMCD compared to TMPD molecule.