SPECIMEN FORMAT FOR THESES OF MONTH

Faculty	:	**Science**
Department	:	**Chemistry**
Branch/ Area:	:	**Polymer science and Corrosion science**
Sub Subject Heading:	:	
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Title of the thesis	:	**Eco-friendly Chitosan Schiff bases for Enhanced Corrosion Resistance of Mild Steel in Acid Medium and Calcium Carbonate Scale Inhibition**
(i) In Roman Script		-
(ii) In roman Script		-
Nomenclature of Degree:	:	
Month & Year of Enrolment:	:	**July 2013**
Month & Year of Registration:	:	**July 2013**
Month &Year of Submission:	:	**April 2017**
Month &Year of Award	:	**January 2018**
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Abstract within 300 words:

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 theactive 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 313-343K with different concentrations (100-1500ppm). Inhibition efficiency of the inhibitors increased with increase in concentration of all the studied concentration within the range of 100-1500ppm. All the Schiff base inhibitors showed better inhibition performance of around 90% at the concentration of 1500ppm.

Potentiodynamic polarization analysis revealed that Chitosan Schiff bases behaved as a mixed type inhibitor. The protective film formed on the metal was stable till 323K 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 ΔQ-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 –HC=N and –OH groups of Chitosan Schiff bases and also the presence of Mulliken charges on the heteroatoms. 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 $CaCO_3$ 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 $CaCO_3$ 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 $CaCO_3$.

i) Major objectives :

- To synthesize environment friendly Chitosan Schiff bases with multiple functional groups and hetero atoms.
- To confirm the formation of imine groups in the polymer matrix using Elemental analysis, UV, FT-IR Spectroscopy and to determine the thermal stability of the Chitosan derivatives using thermo gravimetric analysis (TGA/DTA).
- To evaluate the corrosion inhibition performance of Chitosan Schiff bases on mild steel in 1M HCl at various times, concentration and temperature by weight loss and electrochemical methods.
- To monitor the adsorption behaviour of the Chitosan Schiff bases on the mild steel surface by cyclic voltammetric studies and to calculate the thermodynamic adsorption parameters using adsorption isotherms.
- To confirm the protective layer formation on the metal surface using surface analytical techniques.
- To determine the relationship between inhibition ability of Chitosan Schiff bases and their quantum chemical parameters using theoretical calculations.

- To propose a mechanism for adsorption of Chitosan Schiff bases with supporting evidences
- To explore the applicability of polymers as scale inhibitors in synthetic water samples.

ii) Findings:

- The yield of synthesized Chitosan Schiff bases was about 60-65% since the degree of deacetylation is 76.99% by which substitution of aldehydes in the Chitosan matrix may not be possible at 100%.
- The elemental and spectral studies (UV and FTIR) confirmed the incorporation of aldehyde groups in the Chitosan backbone. The increase in C/N ratio from elemental analysis and the presence of imine vibrations in the FTIR spectra of Chitosan Schiff bases clearly evident the formation of Schiff base in the polymer matrix.
- The thermal stability of the Chitosan Schiff bases were found to be lesser than the native Chitosan which may be due to the anchoring of aldehyde groups into the Chitosan matrix.
- The weight loss technique revealed that all the studied Schiff base polymers exhibited 90% IE for the concentration of 1500ppm at 12 hours of immersion. Schiff base polymers showed a consistent inhibition performance up to 333K with a slight decline at 343K.
- The performance of the Schiff bases was analyzed by estimating Fe^{2+} ions in the solution left after weight loss experiments using AAS studies. The results are in agreement with weight loss results. The UV analysis of the above solution proved the formation of Fe-complexes in the solution.
- The parallel nature of the Tafel curves obtained in the potentiodynamic polarization method suggested the activation controlled mechanism of inhibition. The reduction in cathodic, anodic current densities and corresponding current density (I_{corr}) and also negligible E_{corr} values collectively suggested Chitosan Schiff bases as mixed type inhibitors.
- From the results of impedance measurements, a single semicircle representation of the Nyquist plot corresponding to one time constant in the Bode plot implies that the metal dissolution process is controlled by a single transfer process. The diameter of the semicircle in the Nyquist plot and the magnitude of the Bode modulus increased with increasing concentration of the inhibitors that suggested the formation of a

protective layer on the metal surface. The impedance |*Z*| as well as the phase shift (θ) of mild steel increased with increase in concentration because of the adsorption of inhibitor molecules on the active sites of the metal surface.

- Basic information on the interaction of the inhibitor molecules and the metal surface was provided by adsorption isotherms. The best fit was obtained with Temkin isotherm with R^2 close to unity for all the investigated inhibitors. The larger K_{ads} values suggested the greater inhibition efficiency and more stable protective layer with better inhibition performance. The ΔG_{ads} values are negative and greater than 40kJ mol^{-1}, ΔH_{ads} values are positive and greater than 100kJ mol^{-1} indicated the chemical mode of adsorption of the inhibitors. Similarly, the values of ΔS_{ads} confirmed the orderly arrangement of inhibitor molecules.
- The adsorption of Chitosan Schiff bases on the mild steel surface was explained by cyclic voltammetric studies. The absence of redox peaks and also the existence of strong droop in presence of inhibitors suggested the protective layer formation. The reduction in Q (charge accumulation) with immersion time confirmed the effective adsorption of Schiff base polymers on the metal surface.
- The formation of protective layer on the metal surface was confirmed using SEM, EDX, AFM, contact angle measurements, FTIR and XPS techniques. SEM technique revealed the extensive coverage of polymeric clusters on the metal surface. The atomic percentage of elements observed from the EDAX spectrum indicated the presence of nitrogen and sulphur atoms that confirmed the formation of protective layer on metal surface. AFM studies revealed a homogeneous film formation by the inhibitors on the metal surface. The film formation was further confirmed by the increase in hydrophobicity (increased contact angle) of the metal surface exposed to inhibitor solution. The main confirmation of the Fe-inhibitor bonding was confirmed by FTIR and XPS analysis. Both the technique revealed the presence of Fe-N bonding.
- Quantum chemical calculations viz., semi-empirical and DFT methods were employed to identity the active adsorption sites responsible for the inhibition. Both the studies revealed that imine group and hydroxyl group on the Schiff base polymers as electron donating sites with high E_{HOMO}. Moreover, the presence of Mulliken charges on the hetero atoms of the inhibitors also suggested the coordinating sites responsible for the inhibition.

- Based on the experimental and theoretical results, the plausible mechanism for the inhibition action of Chitosan Schiff bases was proposed with some supporting evidences.
- The Chitosan Schiff bases are found to be capable of inhibiting $CaCO_3$ scale formation in synthetic water samples. 400ppm concentration of inhibitors with 6 h of bath time and at 65^{o}C of bath temperature effectively inhibited the scale formation. The changes in the crystal morphology were studied using SEM analysis and the thermal stability of the scale crystals were analyzed using TGA analysis.

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