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MATERIALS AND METHODS

As the research interest focusing on environmental friendly, bio degradable, biocompatible inhibitors, the present work was carried out to study the corrosion inhibition efficiency of some synthesized Chitosan Schiff bases. The outline of the work was sketched under following headings:

1) Synthesis of Chitosan Schiff bases
2) Characterization of Chitosan Schiff bases
3) Corrosion monitoring techniques
4) Adsorption Monitoring technique – Cyclic voltammetry technique
5) Surface analytical techniques
6) Theoretical studies – Quantum chemical calculations
7) Scale inhibition tests

3.1 Synthesis of Chitosan Schiff bases:

Table 3 - Chemicals used for the synthesis

Name of the chemical	Company
Chitosan (75% deacetylated)	Himedia
Salicylaldehyde	Avra synthesis
Vanillin	Avra synthesis
Thiophene 2- carboxaldehyde	Avra synthesis
Pyrrole carboxaldehyde	Avra synthesis
Acetone	Spectrum
Ethanol	Avra synthesis
Acetic acid	Merck

3.1.1 Selection of Inhibitors:

Chitosan is the most abundant naturally occurring biodegradable polymer recently received a considerable attention with properties like biocompatibility, hemocompatibility and metal binding ability. Chitosan normally extracted from exoskeletons of the crusteaceans like shrimps and crabs. Chitosan is a natural bio polymer composed of ß -D-glucosamine and N-acetyl-ß-D-glucosamine units with a 1, 4-linkage. Chitosan consists of two reactive groups' namely free amino group and hydroxyl group which can be modified for the desired properties. The free amino groups present in Chitosan offer a chemical modification in the polymer chain. One among the modification is the formation of Schiff base by the reaction of free amino group of Chitosan with an active carbonyl of aldehyde. The introduction of imine group (-HC=N) in the Chitosan matrix improves the anticorrosion performance and the film forming capability of the Chitosan derivative favors the longevity of the metal. As the ecological factor is considered, it would be beneficial to use environment friendly compound for the modification of polymer matrix. Taking all this into consideration, attempt of synthesizing Chitosan Schiff bases containing chelating group and aromatic ring for the application of corrosion protection is undertaken. Due to environmental concerns, the aldehydes such as salicylaldehyde, vanillin, thiophene-2-carboxaldehyde, pyrrole-3 carboxaldehyde used for the modification are also environment-friendly compounds.

- **Salicylaldehyde** – occurs rather frequently in nature; in flowers, roots, fruits and essential oils of cinnamonum cassia and of tobacco leaves. It is also used as flavouring agents.
- **Vanillin** – widely used in food production, pharmaceutics, cosmetics, etc.
- **Thiophene-2-carboxaldehyde** – an ecofriendly compound used in manufacturing of pharmaceuticals.
- **Pyrrole carboxaldehyde** – used as pharmaceutical intermediate.

3.1.2 Synthesis procedure of Chitosan Schiff bases:

Chitosan Schiff bases were synthesized by the simple condensation reaction between free amino group of Chitosan matrix and the active carbonyl group of aldehydes. The ratio of Chitosan and aldehydes was optimized as 1:1 for the synthesis procedure of four Chitosan Schiff bases. 1 g of Chitosan was dissolved in 1% of aqueous solution of acetic acid. 1% of selected aldehydes were dissolved in appropriate solvents for complete dissolution. The aldehyde solutions were added in drops to the Chitosan suspension with constant stirring at room temperature. The reaction was allowed to continue for 7 hours at room temperature. The yellow solution obtained was kept overnight. The product was precipitated using acetone, washed several times with acetone to remove unreacted aldehydes. The product was dried under vaccum and then weighed.

The percentage yield and Degree of deacetylation were calculated using the formulae

$$\% \, Yield = \frac{\text{Weight of Chitosan schiff base(g)}}{\text{Weight of Chitosan(g)+Weight of aldehyde(g)}} \text{ x } 100 \quad (1)$$

$$Degree\ of\ acetylation = \left(1 - \frac{\frac{C}{N} - 5.145}{6.861 - 5.145}\right) \square \, 100 \quad (2)$$

3.1.3. Solubility of Chitosan Schiff bases:

The solubility of the synthesized Chitosan Schiff bases was evaluated by dispersing the samples in different solvents viz., Water, DMF, DMSO, Acetone, Acetic acid and Methanol at room temperature.

3.2 Characterization of Chitosan Schiff bases:

3.2.1 Elemental analysis:

The elemental composition of the synthesized Chitosan Schiff bases were analyzed and confirmed by using the instrument Elemental vario EL III.

3.2.2 UV- Visible and FTIR spectroscopic techniques:

The synthesized Chitosan Schiff bases were characterized using spectroscopic techniques- UV visible and FTIR. The UV-Visible spectra were recorded using Systronics double beam spectrophotometer in the range of 200-600 nm.The fundamental vibrations of Chitosan Schiff bases were identified using Fourier transform infrared spectroscopy (FTIR) (Schimadzu IR affinity 1) in the range of 4000-400 cm^{-1}.

3.2.3 Scanning Electron Microscopy (SEM):

The surface morphology of the Chitosan and Chitosan Schiff bases were analyzed using scanning electron microscopy (JEOL JSM-6490LA).

3.2.4 Thermal analysis:

The thermal degradation and stability of the Chitosan Schiff bases was determined using Thermogravimetric analyser (EXSTAR SII TG/DTA 6300). The samples were heated at 10 ^{o}C/min in a nitrogen atmosphere; Alumina was used as a reference material for thermal analysis.

3.3 Corrosion Monitoring Techniques:

3.3.1 Material preparation:

Corrosion studies (weight loss) were conducted with commercially available mild steel (MS) strips of dimension 5 cm x 1 cm x 2 mm and electrochemical studies carried out with of 1 cm^2 coupons fixed to a brass rod. The chemical composition of MS specimen was found to be C-0.106 %, Mn-0.196 %, P-0.027 %, Cr-0.022 %, S-0.016 %, Ni-0.012 %, Si-0.006 %, Mo-0.003 %, and remainder Fe. The mild steel specimens were mechanically polished, their surface was abraded with fine grade emery paper, degreasing in acetone and stored in desiccator at room temperature before conducting experiments.

3.3.2 Test solution:

The test solution (1M HCl) was prepared by diluting analytical grade of 36% HCl with double distilled water. Concentration of Chitosan Schiff bases (100 ppm, 300 ppm, 600 ppm, 900 ppm, 1200 ppm, 1500 ppm) were selected for the present work.

3.3.3 Weight loss Experiments:

The most accurate and simplest method of estimating the corrosion rate is weight loss analysis. Weight loss experiments were performed using standard ASTM procedure (***ASTM G1-3***).The pre-weighed mild steel specimens in triplicates were immersed in the test solution in absence and presence of various concentrations of inhibitor for 1-24 hours at room temperature. The experiments were also carried out for different temperatures (303-343 K) for the same concentration range. After the weight loss studies, the specimens were cleaned, dried and reweighed. The weight loss was taken to be the difference between the weight of the specimen after the immersion at a given time and original weight of the specimen. The specimens were weighed using Denver Balance.

From the obtained weight loss results, corrosion rate (CR) and inhibition efficiency (IE) was calculated as follows:

$$CR(mpy) = \frac{3.45\ X\ 10^6 X W}{ADt} \tag{3}$$

$$IE(\%) = \frac{Wo - W}{Wo}\ X\ 100 \tag{4}$$

where Wo and W are the weight loss (g) of the coupon in the absence and presence of inhibitor, A is the area of the coupon in cm^2, D is the density of the material in g/cm^3, and t is the time of exposure in hours.

3.3.4 Solution analysis-Spectroscopic techniques:

3.3.4.1 UV Spectrophotometric measurements:

Electronic absorption spectral studies were carried out to examine the possibility of the Fe- complex formation in the electrolytic solution. UV-visible spectra were recorded (Systronics double beam spectrophotometer) for the test solutions of inhibitors after the mild steel samples immersed in optimum concentration of Chitosan Schiff bases for 6 h.

3.3.4.2 Atomic absorption spectroscopy

The amount of iron dissolved from both inhibited (1500 ppm of Chitosan Schiff bases) and uninhibited mild steel samples after immersing in 1M HCl for 6h was determined using a fully automated, computer controlled atomic absorption spectrometer (Shimadzu AA-7000).

3.3.5 Electrochemical Techniques:

Electrochemical measurements were performed using a conventional three electrode glass cell consisting of mild steel substrate of $1cm^2$ exposed area as working electrode, a platinum electrode as counter electrode and a saturated calomel electrode as reference electrode using Frequency Response Analyzer (Solartron 1280B) supported with corrware and Zplot softwares. Prior to each experiment the working electrode was polished with different grades of emery paper, rinsed with distilled water and then inserted to the glass cell. The working electrode was allowed to immerse in the electrolyte solutions for about 30 minutes to attain the steady state potential. Electrochemical tests were carried out for different concentrations of inhibitors at room temperature and at higher temperatures (303-343 K).

3.3.5.1 Potentiodynamic polarization Method (DC technique):

Potentiodynamic polarization curves were obtained from anodic potential of -0.1V to cathodic potential of -1 V versus open circuit potential at a sweep rate of 2 mV/s. The experiments were conducted in atmospheric conditions without any stirring. The anodic and cathodic curves of the Tafel plots were extrapolated to obtain corrosion current densities (I_{corr}). The inhibition efficiency was calculated using the equation,

$$IE(\%) = \frac{Iocorr - Icorr}{Icorr} X\, 100 \qquad (5)$$

where I_{ocorr} and I_{corr} are the corrosion current densities in the absence and presence of inhibitor, respectively. The polarization resistance R_p was determined from the slopes of the polarization curves of linear polarization region at the vicinity of the corrosion potential. The inhibition efficiency can be calculated using R_p values by,

$$IE(\%) = \frac{IoRp - IRp}{Rp} X\, 100 \qquad (6)$$

3.3.5.2 Electrochemical Impedance Spectroscopy (AC technique):

EIS measurements were carried out at a frequency range of 20 kHz to 0.1Hz by applying AC amplitude of 10 mV. The results were collected using Z plot software and interpreted with Z view software.

Impedance parameters such as solution resistance (Rs), polarization resistance (Rp), constant phase element (Yo) and Phase angle shift (θ) were obtained from fitting the experimental data to the equivalent circuit. The impedance parameters were used to calculate inhibition efficiency using the equations,

$$IE(\%) = \frac{Rp(inh) - Rp}{Rp(inh)} X\, 100 \qquad (7)$$

where Rp(inh) and Rp are the polarization resistance in presence and absence of inhibitor respectively.

4. Adsorption monitoring technique - Cyclic Voltammetric studies:

To examine the adsorption effect of Chitosan Schiff bases on the metal surface cyclic voltammetric studies were carried out using Bio-Logic SP-150 electrochemical system. Cyclic voltammetric experiments were performed using a potentiostat equipped with PC along with a three electrode cell consists of mild steel as working electrode with exposed area of 1cm^2, saturated calomel electrode as reference electrode and a platinum electrode as counter electrode as same used in polarization and EIS experiments. The cyclic voltammetry curves were recorded in the scan range of -1 to -0.2 V with scan rate of 50 mV/s. Though the effect of corrosion inhibitors were usually studied at low potential scan rates, the CV measurements were carried out in mentioned scan rate which could be the possible scan rate used for the present study.

5. Protective layer characterization:

5.1 Fourier Transform Infrared spectroscopy (FTIR):

The protective layer formed on the MS specimen after immersing 1M HCl along with 1500ppm of inhibitors for 6 hours was examined using Fourier transform infrared spectroscopy (FTIR) (Schimadzu IR affinity 1).

5.2 Scanning electron Microscopy- Energy Dispersive X-ray spectroscopy:

The surface morphology of the mild steel specimen was studied by scanning electron microscopy (SEM) using (JEOL JSM-6490LA). The energy of the acceleration beam employed was 30kV. The surface film formed on the mild steel substrate was examined by energy dispersive X-ray spectroscopy (EDX) system attached with SEM. The spectra were recorded on the samples immersed for a period of 6 h in 1M HCl in the absence and presence of optimum concentration of the inhibitors.

5.3 Atomic Force Microscopic analysis:

The surface morphology of the mild steel specimen was investigated by Atomic force microscopy was performed using AFM -A.P.E. Research Italy (A-100). After the immersion of Mild steel specimens in inhibited and uninhibited solution for 6 hours, the specimens were cleaned with distilled water, dried and then used for AFM.

5.4 Contact angle measurements:

The most Interesting technique used to study the formation of adsorptive layer on the surface of the mild steel is contact angle measurements. The contact angle measurements on the mild surfaces after 6 hours of immersion in solution with and without Chitosan Schiff bases were performed on a Goniometer instrument equipped with a camera for imaging. The deionized water under static conditions was employed to determine the contact angle. The measurements were repeated for three times for each sample and the average values are reported.

5.5 X-ray photon spectroscopy (XPS):

X-ray photoelectron spectroscopy (XPS) technique was carried out to detect the chemical composition of the adsorbed film on the mild steel surface. For this technique, the mild steel sample after immersing in Chitosan salicylaldehyde Schiff base for about 6 hours of immersion by following the procedure as in weight loss technique, with the mild steel of 1 cm^2 exposed area. X-ray photoelectron spectroscopy spectrum was recorded by XPS K-alpha (Thermofisher Scientific,UK).

6. Theoretical studies- Quantum Chemical Calculations:

The relationship between the inhibition ability of Chitosan Schiff bases and their quantum chemical parameters were established by theoretical calculations using Austin model 1 (AM1) and parametric method 3 (PM 3) in Hyperchem 7 software.

Density functional theory (DFT) has found wide applicability in the analysis of the characteristics of the inhibitor/metal surface mechanisms and in the description of the structure nature of the inhibitor on the corrosion process. Gas phase geometry optimization and quantum chemical calculations were performed using Density functional theory (DFT) and the 6-311G (d,p) basis set. Becke's Three parameter Hybrid Functional together with the Lee- Yang- Parr correlation functional theory (B3LYP) was selected for the calculations using Gaussian 03 program package. Schematic structures were drawn using the Chem draw package version while optimized structures were drawn using the gaussView5 program. Quantum chemical parameters and Mulliken charges were determined from the software so as to determine the actives sites responsible for the inhibition performance of the Chitosan Schiff bases.

7. Scale inhibition test

7.1 Static scale Inhibition experiment

Scale inhibition efficiency was tested by "calcium carbonate deposition method" as reported by **Zeng and Yan, 2013**.The Principle was to determine the concentration of Ca^{2+}ions by standard EDTA titration after heating the test samples with and without scale inhibitors. and The scale inhibition efficiency (SIE) was calculated using the equation,

$$I.E = \frac{\mathrm{Vs-Vb}}{\mathrm{Vi-Vb}} \times 100 \qquad (8)$$

where Vb and Vs are the concentration of calcium ions present in the sample without and with scale inhibitor and Vi was the initial concentration of calcium ions present in the test sample. Figure 5 represents the calcium ions precipitated in initial, blank and sample solutions.

7.1.1 Test samples:

Following the standard procedure used in Oilfield industries, the static evaluation test for qualifying the scale inhibiting properties of the polymers was conducted. The solutions for the evaluation of the scale inhibition performance of the polymers were prepared as shown in Table 4.

Table 4 – Brine concentration and experimental conditions for scale inhibition test

Scale Test	Brine Concentration (g/L)	Conditions
$CaCO_3$	NaCl – 50, $CaCl_2$ – 14.80, $NaHCO_3$ – 1.864	Inhibitor dosage – 100, 200, 300, 400,500ppm Bath time – 4h, 6h, 8h,10h, 12h Bath temperature – 60°C, 65°C, 70°C, 75°C, 80°C

Synthetic water samples are prepared by mixing the salt solutions as mentioned in the standard procedure. The brine solutions were added to the partition bottles in the specified amount as given in Table 5. The bottles with the brine solutions were closed tightly and placed in the thermostat for static evaluation test. After the test conditions, the precipitate settled down in the bottle was filtered using Whatmann filter paper. The supernatant solution was used for EDTA titration for the estimation of Ca^{2+} ions.

Table 5 – Quantity of brine solutions used for the scale inhibition tests

Brine solutions	Initial 1	Initial 2	Blank1	Blank2	Sample 1	Sample 2
$CaCl_2$	50	50	50	50	50	50
Distilled water	1	1	1	1	-	-
$NaHCO_3$	-	-	50	50	50	50
NaCl	50	50	-	-	-	-
Scale inhibitors	-	-	-	-	Required amount	Required amount

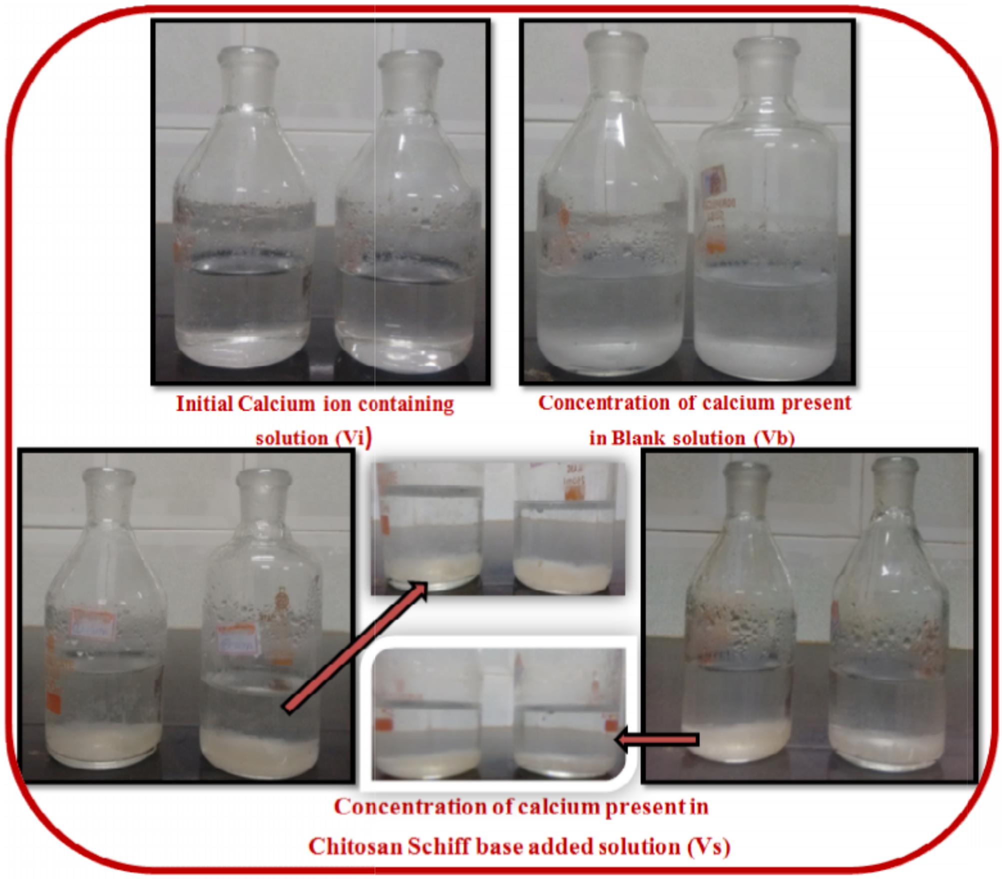

Figure 5 – Photographic representation of calcium ions precipitation in studied solutions.

7.2 Characterization of the scale crystals

The morphology of the scale crystal $CaCO_3$ in the presence and absence of Chitosan Schiff bases was characterized using SEM analysis. The thermal behaviour of the $CaCO_3$ scale crystal was analyzed using thermo gravimetric analyzer (EXSTAR SII TG/DTA 6300) to study the thermal difference between the crystals formed before and after the scale inhibition tests.