One of the prime goals of this study is to find a natural organic product that can efficiently retard acid corrosion of mild steel at low cost. Keeping this aim in mind, we have selected *Argemone Mexicana* (plant), *Chlorophytum Borivilianum* (herb) and *M. Paradisica* (peel) for corrosion studies. Various experiments have been conducted using several techniques, to assess the inhibition potential of inhibitors. The details are given below-

2.1 Preparation of the Extracts

Argemone Mexicana Extract- Leaves (100 gm) of *Argemone Mexicana* were carefully separated from the plant, washed thoroughly followed and dried on a tissue paper [Dash and Murthy, 2011]. Then, it was properly crushed in the grinder and 100 ml of water was added to make a solution. Thus prepared solution was kept on stirring for 48 hours. After prescribed time, the solution was filtered and the residue was again suspended in the double distilled water. The above mentioned procedure was repeated three more times for exhausted extraction. At the end, all the filtrates were pooled and dried in rotatory evaporator. The stock solution of the extract was prepared by dissolving 1 g of the dried residue in 1 ml of the distilled water and used as such for corrosion studies.

Chlorophytum Borivilianum Extract- The extract was prepared according to a standard method given by Kenjale et al [2007]. The roots of *Chlorophytum Borivilianum* were identified and collected from the field. Then, they were dried in sun light for one week and pounded in a grinder. Thus obtained powder (100 gm) was added to distilled water (600 mL) and kept on stirring for 3 hr. This aqueous solution was filtered and the above described process was repeated two more times for complete extraction. At the end, all

the filtrates were collected and dried in a vacuum oven for one day. An amount of 1 g of dried extract was soaked in 10 mL distilled water and used as such for the study.

Musha Paradisica (banana) Extract- Banana fruits (green color, raw) were purchased from the local market at Kaushambi, Uttar Pradesh, India. The fruits were thoroughly washed under running tap water, cleaned with paper towel, and then stored under the ambient conditions for one day. Afterwards, the peels were carefully removed from banana fruits (raw banana peel). Some of the fruits (purchased on first day) were put on drying for another eight days at room temperature, which was intentionally executed for ripening of the fruits (yellow). For over ripening of the fruits (yellowish brown), some of them were left as such for another three days. The peel tissues of raw, ripe, and overripe bananas were collected at the end, and boiled in distilled water for 10 minutes. Then, the peels were homogenized thrice with a mixture of acetone-water (70% acetone) at room temperature, using pre-chilled pestle and mortar for 48 h under shaking conditions. Thus prepared solutions were filtered and centrifuged in Beckman centrifuge machine (at 4 °C) for 10 min at 15,000×g. The obtained extracts were concentrated with the help of a rotary evaporator and dried in a vacuum oven for one whole night. An amount of 1 g of the concentrated powder was dissolved in 10 mL distilled water and used without any further purification for corrosion studies.

2.2 Preparation of Test Coupons

Test specimens were cut from a mild steel sheet into desired dimension of the samples, i.e., 1×5×0.03 cm^3 and 1×1×0.03 cm^3 for weight loss and electrochemical studies, respectively. Prior to corrosion experiments, the test coupons were prepared by grinding

them with emery paper of grade 1/0 to 6/0, successively and cleaning them with AR grade acetone along with distilled water. The following composition of mild steel was used in all the experiments (Wt %): C-0.16, Mn-0.032, Si-0.18, S-0.026, P-0.03 and rest Fe.

2.3 Corrosive Solutions

AR grade 35% HCl and AR grade 98% were used as corrosive media. The required concentration of HCl and H_2SO_4 solutions were prepared by appropriate dilution of stock acids with double distilled water. A 100 mL of each acid was used for corrosion experiments.

2.4 Characterization of Inhibitors

The selected inhibitors (extracts) were characterized by UV-Vis spectroscopy, FTIR spectroscopy and HPLC techniques. The details of the characterization processes is given below-

2.4.1 UV-Visible Spectroscopy: The optical properties of the extracts were tested by Perkin Elmer, Lambda 25, UV/VIS spectrometer (Figure 1). A 20 µL of each extract was dropped in 2.5 mL of distilled water and thus prepared solutions were individually examined by the spectrometer in the wavelength range of 200-900 nm. The obtained results (peaks) were calibrated with the standard database and possible electronic transactions of the molecules were proposed. Furthermore, Uv-vis spectroscopy was also used to access the details the adsorption process. For this, the specimens (size: $1\times5\times0.03$ cm^3) were separately dipped in the solutions containing HCl and H_2SO_4 acid (100 mL) with optimum concentration of the extracts. After 1 hour, the test coupons were drawn out and precisely cleaned with distilled water. Afterwards, the samples were dip-washed twice in distilled water and then allowed to be immersed for half an hour in the solution followed by smooth rubbing of the steel surface. These solutions,

containing traces of the organic matters of the extracts, were examined again and the results were compared with the spectrum of pure extracts.

Figure 2.1 Perkin Elmer Lambda 25 Uv-vis Spectrometer

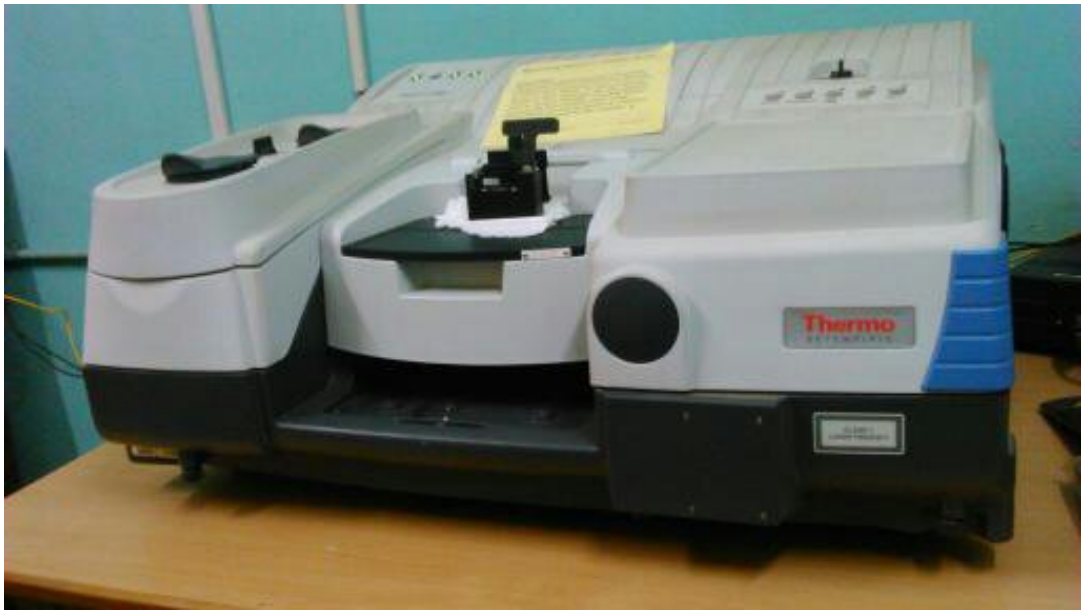

Figure 2.2 Thermo Scientific, Nicolet 6700, FTIR Spectrometer

2.4.2 Fourier Transform Infrared Spectroscopy: FTIR spectroscopy was used for structural characterization of the extracts and identification of functional groups present in the extracts. The experiments were performed on Thermo scientific, Nicolet 6700 (Figure 2), using 100 µL of inhibitors. The extracts were characterized in transmittance mode in region of 800-4000 cm^{-1} (wave numbers), using special attachments provided with the machine for liquid samples. Presence of functional groups were investigated and identified by comparison with standard peaks of the groups.

2.4.3 High Pressure Liquid Chromatography:

Figure 2.3 HPLC Instrument (METROHM) for chromatographic analysis

The chromatographic analysis of the inhibitors was executed on HPLC, Metrohm limited, (Figure 3): column, C-18, ODS, 300mm×4.6mm; mobile phase (binary mode), 0.05 M acetonitrile: water and methanol: water in ratio of 80:20; flow rate, 0.15 mL/ min; the temperature of column was set at 38˚C. Prior to start experiments, the extracts were

filtered by PTFE syringe filter (dia-0.45 mm), Whatman (made in U.K.). For analysis, an amount of 100 µl of each extract was injected into HPLC instrument through a syringe. The chemical molecules of the extracts were identified by comparison of their experimental retention times with standard retention times of pure compounds.

2.5 Assessment of Corrosion Inhibition

Corrosion inhibiting capacity of inhibitors were investigated by three well known techniques-

2.5.1 Weight Loss Measurements: Weight loss test is a classical method to measure inhibitor's ability to protect metals in corrosive environments. According to this method, corrosion rate of a metal is directly proportional to its weight lost in a corrosive media. To conduct weight loss experiments: mild steel test coupons were prepared, weighed and then immersed in conical flasks containing 100 mL of corrosive solutions with different concentration of inhibitors, at room temperature (26±1° C) for 5 hours. After the exposure time, metal strips were collected and washed with double distilled water. The samples were dried in an oven for quarter an hour at 30° C, and weighed again in electronic balance (METTLER TOLEDO, Sensitivity ±0.1 mg). In order to consider the effect of inhibitor on acid corrosion of steel, the difference in weight of the samples (in absence and presence of the extracts) were calculated. Accordingly, various parameters such as corrosion rate, surface coverage and inhibition efficiency, were calculated by the equations given under section 1.10 (introduction). To achieve high accuracy, three set of mild steel strips were arranged for each concentration of inhibitor and average weight

loss values were reported. A schematic diagram is shown in Figure 4 to explain the weight loss experiment.

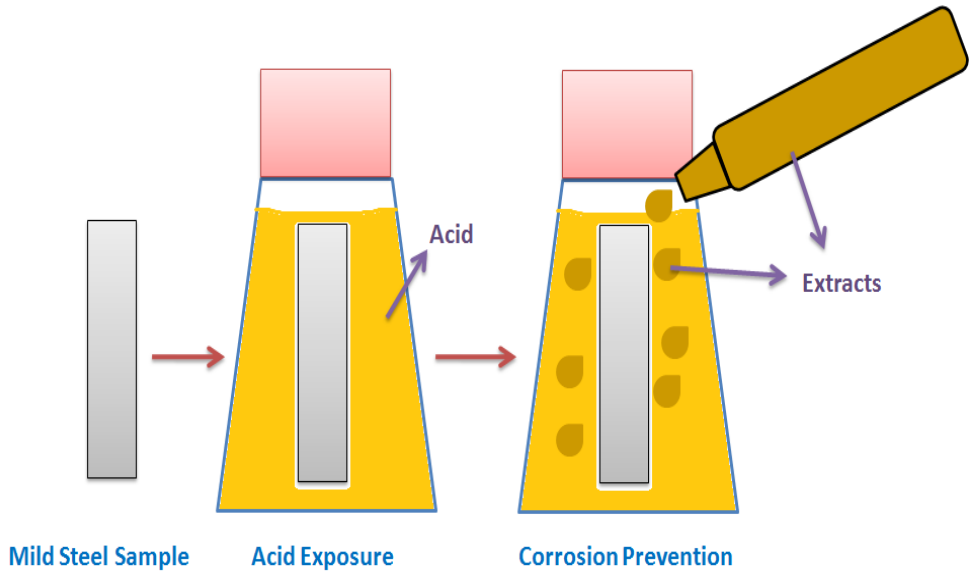

Figure 2.4 Schematic illustration of weight loss measurements technique

Adsorption Study: To know the adsorption behavior of inhibitors, surface coverage (θ) values (obtained from weight loss method) were plotted against concentration (C) of inhibitors. This process was performed according to different isotherms. For Langmuir isotherm, a graph was plotted between C/θ and C; for Temkin isotherm, a graph was plotted between log C and θ; for Frumkin isotherm, a graph was plotted between log (θ/(1-θ)) × C and θ. For all the isotherms, regression coefficient values were obtained. The isotherm with highest regression coefficient was selected as the most suitable adsorption isotherm to describe metal-inhibitor interaction.

Temperature study: The behavior of inhibition efficiency of inhibitors was investigated in temperature range of 30˚-60˚ C. The study was performed with the help of by Arrhenius equation (activation energy) and Transition state equation (entropy and enthalpy). For

activation energy, a graph was plotted between ln C_r and 1/T; for enthalpy and entropy, a graph was plotted between ln (C_r/T) and 1/T. The values of activation energy, enthalpy and entropy were obtained from the slope and intercept values of the curves.

Effect of Acid Concentration: To know the effect of change in acid concentration on inhibition potential of inhibitors, weight loss experiments were conducted in 1-5 M HCl and 0.5-2.5 M H_2SO_4 solutions (highly consumed mineral acids). The inhibition efficiencies and corrosion rates were calculated by weight loss measurements. Thus the values of inhibition efficiency and corrosion rate was obtained for each concentration and compared with the values in alone HCl and H_2SO_4 solution.

2.5.2 Electrochemical tests: All the electrochemical experiments were conducted in a three neck cell that includes Ag-AgCl as a reference electrode, platinum foil as a counter electrode and mild steel sample as a working electrode. The corrosion inhibition testing of the inhibitors were executed by an electrochemical work station CHI 7041C, CH instruments, USA (Figure 5). Before starting the experiments, the electrochemical system was run for 10 minutes at open circuit conditions to attain steady open circuit potential. A mixture of 100 mL acids and different concentrations of the extracts were used as test solutions for the study.

To know the Tafel polarization behavior of inhibitors, an over potential voltage was applied in the range of -250 mV vs Ag-AgCl to +250 mV vs Ag-AgCl at a scan rate of 0.5 mV s^{-1}. The response of mild steel (in absence and presence of the extracts) was analyzed with the help of CHI 7041C software. Corrosion current density (I_{corr}) and equilibrium corrosion potential (E_{corr}) values were obtained by using the software, and inhibition efficiency s was calculated at different concentrations of inhibitors by the equation number 12 (section 1.10).

Figure 2.5 CH Instruments (CHI7041C) for electrochemical measurements

The electrochemical impedance spectroscopy (EIS) test was performed using 5 mV alternating current signals in the frequency range of 0.1 MHz to 10 mHz. The impedance spectra were investigated for the charge transfer resistance and the double layer capacitance values, and inhibition efficiency was calculated at various inhibitor concentrations with the help of the equation number 11 (section 1.10).

2.6 Surface Morphology Examination

Generally, corrosion inhibitors retard corrosion through adsorption of their chemical molecules on metal surface. This indicates that an inhibitor greatly affect surface chemistry of an electrode along with interface (metal-acid) chemistry. Thus, it is obvious to examine the change in morphology of metals surface in absence and presence of inhibitors. Two well known techniques were employed for this purpose-

2.6.1 Scanning electron Microscopy: This technique focus on the interaction of electrons with a substrate and provide surface images based on that interaction. Surface

morphology of the test samples were recorded by scanning electron microscope SUPRA 40, Carl Zesis, Germany (Figure 6). For this test, mild steel samples (area- 1 cm^2) were immersed in acid solutions with and without inhibitors. After 3 hours, the specimens were picked out, washed with distilled water and then dried in an oven. Thus obtained samples were mounted in SEM instrument and the surface images were captured.

Figure 2.6 Scanning Electron Microscope, SUPRA 40, Carl Zeiss, Germany

2.6.2 Atomic Force Microscopy: Atomic force microscopy is a valuable tool to access the details of corrosion process at the nano level. AFM not only provide surface morphology of the samples (qualitative) but also give surface roughness value (quantitative), which effectively reflect the changes. For this study, prepared mild steel samples were immersed in acid media without and with optimum concentration of inhibitors. After one hour, the specimens were drawn out, cleaned with distilled water followed by wiping with tissue paper, and dried in an

oven for 10 minutes. Afterwards, the samples were investigated in semi contact mode by AFM-STM, model Pro 47, NT-MDT, Russia, using Si_3N_4 tips (Figure 7).

Figure 2.7 Atomic Force Microscope, model Pro 47, NT-MDT, Russia