ISSN No:-2456-2165

Determination of the Anti-corrosive Activity of Chitosan on Mild Steel Using Gravimetric and Electrochemical Methods

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Abstract:- The anti-corrosive activity of chitosan (CT) on mild steel in HCl solutions was determined using gravimetric and electrochemical methods such linear polarization resistance (LPR), electrochemical impedance spectroscopy (EIS) and potentiodynamic polarization (PDP) methods. The gravimetric measurements indicated that the inhibition efficiencies of CT 47.62 - 64.25%. The LPR results gave the experimental inhibition efficiency of CT to be 67.46-97.85 % while potentiodynamic polarization resistant method was 56.19 - 89.09%. The EIS measurements indicated 78.45 - 90.96 % as an inhibition efficiencies of CT.

I. INTRODUCTION

Corrosion of metals remains one of the major problems in industry which has attracted much investigation and research (Abiola *et al*., 2007; Arora *et al*., 2007). Although several methods are available for protecting metals against corrosion attack, the utilization of inhibitors is an excellent protective method against corrosion (Mwakalesi et al 2023, Nkuzinna et al 2014). However, environmentalists have expressed serious concerns over the employment of several corrosion inhibitors due to the fact that they are toxic, non-biodegradable, scares and expensive (Kadhum et al 2022, Dalhatu et al 2023). Interestingly, chitosan (CT) (fig. 1) a naturally occurring amino polysaccharide commonly found in crustaceans and insects performs optimally as an active inhibitor of corrosion because of the ability of its amino and hydroxyl groups to form very strong coordination bond to the surface of metals (Dalhatu et al 2023, Chen et al 2022). This fact underscores the need for environmentally friendly corrosion inhibitors such as chitosan (CT) (Fig.1) to be applied as corrosion inhibitors. Therefore, this work is designed to determine the corrosion inhibitory activity of CT using gravimetric and electrochemical methods.

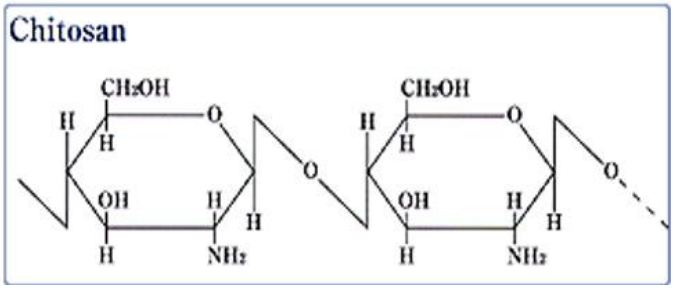

Fig 1: Structure of Chitosan

II. MATERIALS AND METHODS

A. Materials

The mild steel was purchased from Ken Johnson Nigeria Limited, Uyo, Akwa Ibom State, Nigeria. For weight loss determination, the sheet of mild steel was fragmented into coupons of 5 x 4 cm size and 2 x 1.5 cm dimension for electrochemical experiments. This was followed by the polishing of the coupons with emery paper starting with the coarsest and then the finest (600) then washed with ethanol, cleaned with acetone and stored in a desiccators. The chitosan was supplied by Prof. Lee. D. Wilson of the Department of Chemistry, University of Saskatchewan, Saskatoon, Canada.

B. Experimental

➢ *Weight Loss Experiment*

For weight loss measurement, a coupon of mild steel previously weighed was totally immersed in a beaker containing the test solution (250 ml). The content of the beaker was placed in a water bath at 30 °C. There was a repetition of the experiment at 40, 50 and 60°C and the sample weight was measured before immersion with Scaltec high precision balance (Model SPB31) at every 24 hours interval. After the removal of each sample from the solution, the sample was washed in a NaOH solution containing aluminium dust followed by drying in acetone before re-weighing is carried out. The weight difference for a duration of 168 hours was considered the total

weight loss. The inhibition efficiency (%η) for CT was calculated with the formula (Yurt *et al*., 2004)

,

$$\%I = \left(1 - \frac{W_1}{W_2}\right) \times 100 \quad 2.1$$

$$Corrosion\ rate\ (mpy) = \frac{W}{At} \quad 2.2$$

➢ *Electrochemical measurements*

A cylindrical pyrex vessel with a cap containing five openings was used as the electrochemical cell, closed. Three out of the five openings were used for the electrodes- a mild steel having of 0.28 cm^2 surface area in 2 M solution of HCl, while saturated calomel electrode (SCE) served as the electrode of reference and a platinium plate of surface area, 1 cm^2 was used as the counter electrode.

- *Polarization Measurement*

Mild steel was immersed in a test solution for 30 minutes in order to obtain a steady state open-circuit potential (E_{op}). The polarization measurement was determined using the polarization curve which was recorded under potentiodynamic polarization conditions and air atmosphere controlled by a pentium 4 computer. After establishing the open circuit potential, dynamic polarization curves were gotten at a scan rate of 1 mV/s in the potential range of -0.25 to 0.25 V. Tafel extrapolation method was used to arrive at corrosion current (i_{corr}) values. The inhibition efficiency was calculated with the equation,

$$IE = \frac{i^0_{corr} - i^{ihb}_{corr}}{i^0_{corr}} \times \frac{100}{1} \quad 3.4$$

- *Electrochemical impedance spectroscopy measurement*

The measurements relating to electrochemical impedance spectroscopy measurements were carried out over a frequency domain range of 10 - 100, 000 Hz at 303 K using amplitude of 5mV RMS peak to peak with alternating current (ac) signal at the open circuit potential and at air atmosphere. The data on impedance were gotten with Nyquist plots and the polarization resistance R_p, was obtained.

$$R_p = R_{ct} + R_d + R_a + R_f \quad 3.5$$

III. RESULTS AND DISCUSSION

A. Gravimetric Method

Figs 1 to 4 showed plots for the weight loss variation with time for mild steel corrosion in 0.1 M HCl at varied concentrations of chitosan (CT) at 303, 313, 323 and 333 K, respectively.

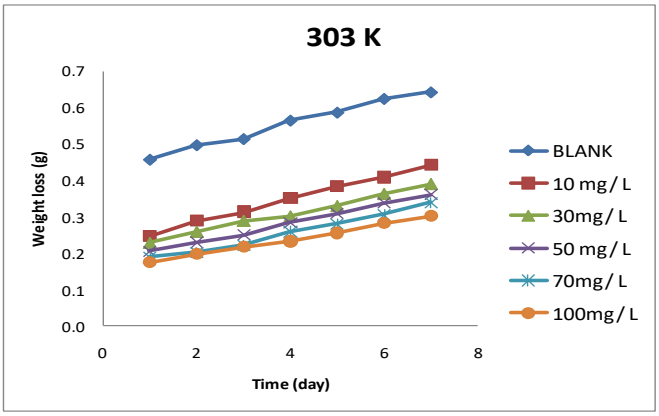

Fig. 1: Weight loss variation with time for mild steel corrosion in 0.1 M HCl in the absence and in the presence of various concentrations of CT at 303 K

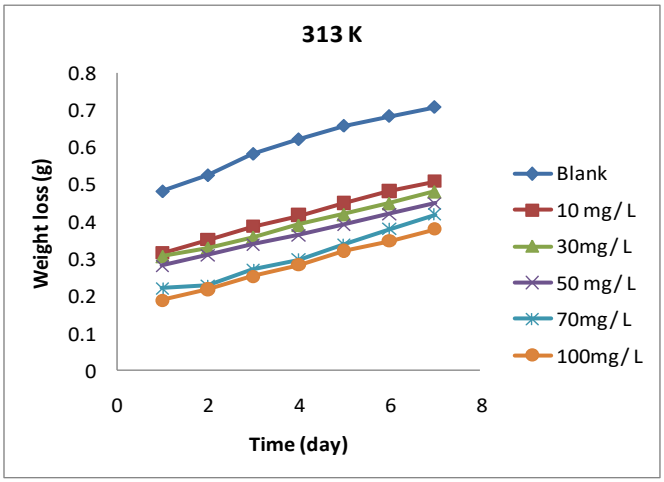

Fig. 2: Weight loss variation with time for mild steel corrosion in 0.1 M HCl in the absence and in the presence of various concentrations of CT at 313 K

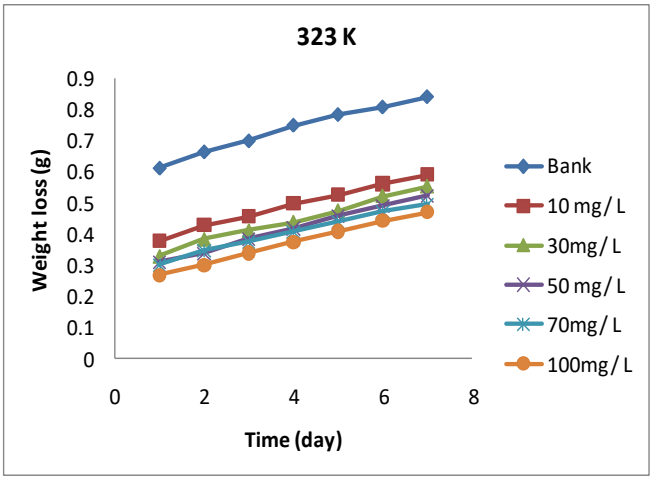

Fig. 3: Weight loss variation with time for mild steel corrosion in 0.1 M HCl in the absence and in the presence of various concentrations of CT at 323 K

ISSN No:-2456-2165

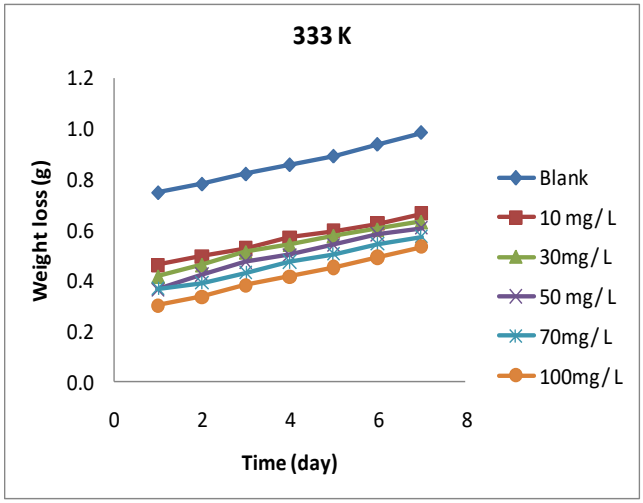

Fig. 4: Weight loss variation with time for mild steel corrosion in 0.1 M HCl in the absence and in the presence of various concentrations of CT at 333 K

The plots indicated that the inhibition of corrosion by CT was dependent on concentration, and corrosion worsened with increases in temperature. It can be deduced that mild steel corrosion in solutions of HCl obeys kinetic principles which requires that the rates of all chemical reactions increase with increases in temperature and within the period of time until the completion of reaction. The effects of CT on mild steel corrosion in solutions of HCl indicates inhibition and CT exhibited anti-corrosive effects on mild steel in HCL solutions. The extent of inhibition to a great level depended on the temperature and concentration of CT, therefore it is concluded that the inhibition efficiencies of CT for the corrosion of mild steel in solutions of HCl was dependent on the concentration of inhibitor and temperature of the corroding system. The corrosion rate values of mild steel and inhibition efficiencies of CT are represented in Tables 1.

Table 1: Inhibition efficiency and degree of CT for the corrosion of mild steel in 0.1 M HCl

C (mg/L)	303 K	333 K	303 K	333 K
10	47.62	37.13	37.26	32.45
30	53.92	40.35	45.96	35.70
50	57.36	44.43	40.74	38.54
70	59.86	48.14	42.28	41.68
100	64.25	53.09	46.56	45.94

B. Electrochemical Method

➢ *Electrochemical Impedance Method (EIS)*

The electrochemical impedance data for corrosion of mild steel in 0.1 M HCl in the absence and presence of CT is presented in Table 2. The observed electrochemical impedance (R) in the absence of CT was 58.24 Ωcm^2. In 10 – 100mg/L of CT, the electrochemical impedance (R_{CT}) increased from 270.2Ωcm^2 to 644.3Ωcm^2 while the percentage inhibition efficiency (%IE) increased from 78.45% to 90.96%. The sharp increase in electrochemical impedance as well as inhibition with increase in concentration of CT not only showed that CT inhibited mild steel corrosion in 0.1 M HCl but also corrosion rate inversely depended on electrochemical efficiency and inhibition efficiency. This corroborates the dependency of corrosion rate and inhibition efficiency on the concentration of inhibitor observed in the weight loss experiments.

Table 2: Electrochemical impedance parameters for mild steel corrosion in the presence of various concentrations of CT

C (mg/L)	N	R_{CT} (Ωcm^2)	%IE
Blank	0.88	58.24	-
10	0.87	270.2	78.45
30	0.87	524.2	88.89
50	0.86	573.08	89.84
70	0.84	622.2	90.64
100	0.84	644.3	90.96

According to the data, it is clear that adding the inhibitor to the acid solution causes the charge transfer resistance to increase and the constant phase element to decrease. The rise in double-layer thickness, which results in a better inhibitory efficiency by adsorption onto the metal/electrolyte interface, and/or a drop in the dielectric constant typically cause the fall in CPE values. The substitution of inhibitor molecules for water molecules on the electrode surface, as well as the increase in double layer thickness, may be responsible for the rise in Rct and the fall in CPE values.

➢ *Polarization Study*

Linear polarization resistant (LPR) and potentiometric polarization resistance (PPR) analysis were also carried out to understand the effect of CT on mild steel corrosion in solution of HCl at 303K. Results obtained for LPR are presented in Tables 3. The results obtained from this study, also confirmed that both CT is adsorption inhibitors because their inhibition efficiencies were found to increase with improved concentration.

Table 3: Linear polarization resistant (LPR) parameters for mild steel corrosion in 0.1 M HCl containing various concentrations of CT at 303 K

C (g/L)	R_p (Ω/cm^2)	%I (Fe/HCl)
Blank	17.32	-
10	53.22	67.46
30	69.23	74.98
50	83.99	79.38
70	130.41	86.72
100	806.50	97.85

It was also observed that corrosion current (I_{corr}) decreased while inhibition efficiency increased with increase in inhibitor concentration for CT. This showed that mild steel corrosion rate in 0.1 M HCl decreased with increase in the concentration of the indicators. This observation agrees with the result obtained in weight loss experiments. The corrosion currents (I_{corr})

obtained in the presence of CT were significantly lower than that obtained in the absence of the inhibitors. This implies that both CT inhibited the corrosion of mild steel in 0.1 M HCl.

IV. CONCLUSION

The results obtained from the experiments indicated that CT inhibited mild steel corrosion in solutions of HCl. The inhibition efficiencies of CT was found to be directly dependent on its concentrations and temperature. Electrochemical data showed that CT is a mixed type inhibitors since it inhibited both anodic and cathodic reactions.

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