SUPPRESSION OF MILD STEEL DEGRADATION IN H_2SO_4 MEDIUM USING COW BONE ASH - POLYANILINE COMPOSITE AS INHIBITOR: ELECTROCHEMICAL AND THERMOMETRIC STUDIES

ABSTRACT

This study is on the suppression of mild steel deterioration in H_2SO_4 medium using cow bone ash - polyaniline composite as inhibitor. The cow bone ash polyaniline composite was synthesized, and then characterized using Fourier transform infrared (FTIR) spectrophotometer. Electrochemical and thermometric studies were carried out in the deterioration control procedure. Result analyses showed that synthesized cow bone ash polyaniline composite (CBAPC) has C-H ring hydrogen, =C-O-C symmetric stretch, CH_2 plane scissoring, N=Q=N quinoid ring stretching, CH_2 asymmetric and symmetric stretching and N-H stretch as the variable functional groups. The presence of the heteroatoms with free electron pairs and substituent group indicates that synthesized composite will promote effective corrosion control capability. On the electrochemical analysis, cow bone ash polyaniline composite was identified as mixed-type form of inhibitor. It inhibited both cathodic and anodic reactions. Inhibitor added to the acid medium improved the magnitude of the impedance spectrum. Thermometric analysis revealed that reaction number decreased with increase in concentration of the inhibitor. Conversely, inhibition efficiency increased with increase in inhibitor concentration. Maximum inhibition efficiency of 93.41% was obtained in the deterioration control of mild steel in sulphuric acid using the cow bone ash – polyaniline composite. Good performance of the inhibitor was due to presence of heteroatoms and allied functional groups of CBAPC.

Keywords: Mild steel, H_2SO_4 medium, Cow bone ash, Polyaniline

1.0 Introduction

Mild steel is a metal that is useful in construction works. It has wide industrial applications. For instance, marine engineers used it to fabricate ships and boats, while automobiles engineers use it to fabricate tricycles, motorcycles and cars body parts. Mild steel are also used to fabricate agricultural equipments, pipes, gates, chairs and other metallic products. The quality of processed mild steel depends on the percentage of impurities contained in the processed form. Impurities alter surface structure of mild steel thereby making it susceptible to corrosion. Corrosion is a destructive attack of metal as a result of electrochemical activity between the metal and its environment. It is caused by oxidation and reduction reactions (Omyma and Shadia 2011). Also, metal corrodes due to its quest to return back to its original state. Typically, the process of returning to its original and stable state requires lowering of the Gibb's free energy of the metal. In any case, corrosion has devastating effects and consequences. As such, corrosion control scientist and engineers are tailoring a lot of efforts on corrosion control processes.

Corrosion control is a noble activity of environmental, technical, economical and aesthetical importance (Arthur et al, 2013). There are various ways to controlling corrosion, but one of the most recognized technique is inhibitor application (Kim et al, 2002; Onukwui and Omo`tioma, 2016). Corrosion inhibitor reduces or prevents corrosion by adsorbed on the metal surface. It can also happen by formation of protective layer (passive film) or barrier to oxygen or moisture. Several materials such as plant extracts, drugs, ionic liquids, polymer material (polyaniline) have been tested and identified as potential corrosion inhibitors (Omotioma and Onukwuli, 2015; Anadebe et al, 2018; Udeh et, 2021; Onukwuli et al, 2021). The cheapest is plant extract but the variation of its inhibition efficiency is worrisome. As a location dependent inhibitor, its efficiency may not be reliable. Ionic liquids and drugs are highly expensive, and may not be economically viable. On the other hand, polyaniline is cheap, good and efficient corrosion inhibitor Wu et al (2000), but environmental concern makes it not suitable for industrial application due to its non-biodegradability. Therefore, modification of its surface morphology is required to enhance its biodegradability. Wu et al (2000) synthesized polyaniline, PANi-clay nanocomposites with prolonged chain conformation of polyaniline. The composites showed a slim drop-off in conduction as compared with pure polyaniline. Yeh et al (2001) used PANi-MMT (montmorillonite) nanocomposites for deterioration security purposes for cold-rolled steel (CRS). They presented important transformation in corrosion resistance of the PANi coating on CRS with integration of clay. Non biodegradability of polyaniline poses a threat to the environment. Therefore, there is a compelling need to alter its nature by blending it with Cow bone ash, making the surface to open for better degradation and absorption. Consequently, this study seek to carry out electrochemical and thermometric studies of the corrosion control of mild steel in sulphuric acid using Cow bone ash - polyaniline composite as inhibitor.

2.0 Materials and Method

2.1 Cow bone (animal bone) sample preparation

The Cow bone was washed thoroughly with water to remove the unwanted materials. Then, the sample was heated in the furnace at 600°C for 2hrs. The animal bone ash was prepared by burning the bone in a muffle furnace at 600°C for 2hrs. After cooling in desiccators, the weighed clay and animal bone ash were stored in nylon bags for use in synthesis of the inhibitor.

2.2 Synthesis of cow bone ash polyaniline composite

200mls of 0.2M aniline and 200g of samples (ABA Clays) was mixed together to form a solution with vigorous stirring for 4hrs. The clay was dispersed in the solution using an ultrasonic bath. The suspension will be left in the air for about 30 minutes for the clay to swell. 5% Ammonium persulfate ($(NH_4)_2S_2O_8$) was added to the aniline-samples mixture in a drop-wise manner and stirred for 48 hours before filtration. The precipitated powder was collected with a Buchner funnel and rinsed with 1000 mL distilled water to remove residual oxidant. The resulting composite was dried to a constant weight in an oven under vacuum at

100°C, after which it was grounded, weighed and stored in vials for later use. This method was employed by zhu (2003).

2.3 Inhibitor's Characterization.

The functional groups of the animal bone ash (cow bone ash) and the cow bone ash polyaniline composite were determined. Fourier transform infrared spectrophotometer (Cary 630, Agilent Technologies USA) was used to determine the functional groups of the inhibitor. The FTIR spectrophotometer concurrently collected high spectral resolution data over a wide spectra range. Fourier transform (a mathematical process) converted the raw data into actual spectrum. Analyses of the various FTIR produced peaks were carried out so as to determine the appropriate functional groups (Furniss et al, 1989; Omotioma and Onukwuli, 2015).

2.4 Study Of Electrochemical Behaviour.

Electrochemical (potentiodynamic polarization and electrochemical impedance spectroscopy) studies were carried out according to the method used by Anadebe et al (2019). Electrochemical tests were conducted using a potentiostat/galvanostat 263 electrochemical system workstation, with conventional three-eletrode corrosion cell. A graphite rod and a saturated calomel electrode (SCE) were used as counter and reference electrodes, respectively. A mild steel specimen fixed in epoxy resin with a surface area of 1 cm^2 exposed to the test solution, served as the working electrode. Electrochemical measurements were carried out in aerated and unstirred solution at the end of 1800 s of immersion, which allowed the open circuit potential (OCP) to attain steady state (Oguzie et al, 2010; Ihebrodike et al, 2011; Al-Otaibi et al, 2014; Anadebe et al, 2019). Temperature was fixed at 30±1 ^{0}C. Polarization studies were performed in the range of ±250 mV versus corrosion potential at a scan rate of 0.333 mV/s. The inhibition efficiency was determined using Equation (1).

$$IE\ \% \ = \frac{i_{corr(uninh)} - i_{corr(inh)}}{i_{corr(uninh)}} \times 100 \qquad (1)$$

$i_{corr(uninh)}$ and $i_{corr(inh)}$ denotes the corrosion current density values without and with inhibitor respectively.

2.5 Study of Thermometric Method of Corrosion Control

The thermometric study method used by past researchers (Mabrouk et al, 2011; Eddy et al, 2012; Omotioma and Onukwuli, 2015) was embraced in this work. The measurements were performed using water bath with thermostat set at 30 ^{0}C. The temperatures of the vessel containing the mild steel and the test solution were recorded on a regular basis reaching a steady temperature value. The reaction number (RN) was evaluated from Equation (2):

$$RN = \frac{T_m - T_i}{t} \qquad (2)$$

T_m and T_i are the maximum and initial temperatures (in ^{0}C) respectively, and t is the time in minutes elapsed to reach T_m.

Equation (3) was used to determine inhibitor efficiency.:

$$IE\% = \left(1 - \frac{RN_{add}}{RN_{free}}\right) * 100 \qquad (3)$$

RN_{free} and RN_{add} reprsent the reaction number values for the mild steel corrosion in free and inhibited H_2SO_4 media respectively.

3.0 Results and Discussion

3.1 Functional groups of the cow bone ash and cow bone ash – polyaniline composite

Spectra of cow bone ash and cow bone ash – polyaniline composite are given in Figures (1) and (2) respectively. The peaks of the transmittance versus wave length represent the functional groups. The identified functional groups are outlined in Table 1. The prevailing functional groups of the cow bone ash are; C-H ring hydrogen, silicate Si-O bond stretching, =C-O-C sym, CH_2 plane scissoring, CH_2 asymmetric and symmetric stretching, N-H stretch and OH bending stretching. Presence of silicate Si-O bond stretching, =C-O-C and N-H stretch is an indication that the cow bone ash can blend and alter the surface morphology of the polyaniline for enhanced inhibitive characteristics. The synthesized cow bone ash polyaniline composite has C-H Ring hydrogen, =C-O-C sym, CH_2 plane scissoring, N=Q=N quinoid ring stretching, CH_2 asymmetric and symmetric stretching and N-H stretch as the primary functional groups. The presence of heteroatoms with free electron pairs and substituent group indicates that the synthesized composite will promote effective corrosion control capability (Omotioma and Onukwuli, 2015).

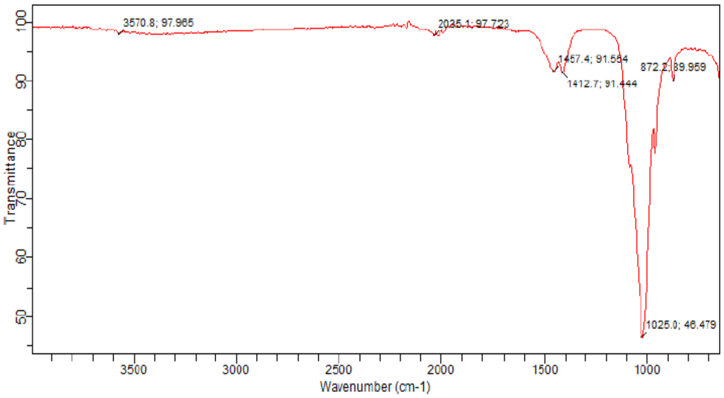

Figure 1: FTIR spectrum of activated cow bone ash

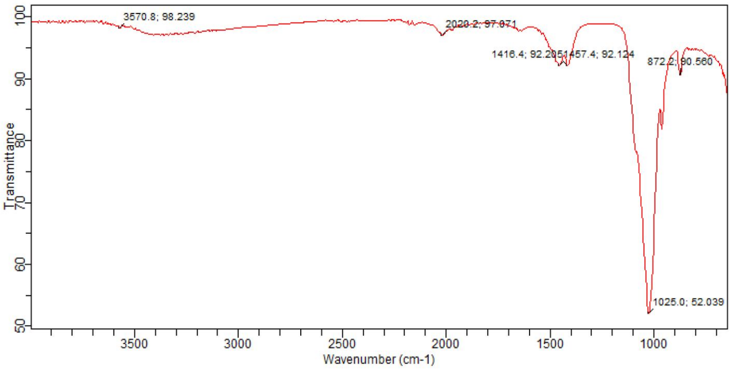

Figure 2: FTIR spectrum of cow bone ash - polyaniline composite

Table 1: FTIR absorption peaks and the functional groups of the composite

	Peak assignment	
Peak position (cm-1)	Cow bone ash (Animal bone ash)	Cow bone ash - polyaniline composite
872.2	C-H ring hydrogen	C-H Ring hydrogen
909.5-1118.2	Silicate Si-O bond stretching, =C-O-C sym	=C-O-C sym
1457.4	CH_2 plane scissoring	CH_2 plane scissoring, N=Q=N quinoid ring stretching
2009.0-2158.1	CH_2 asymmetric and symmetric stretchings	CH_2 asymmetric and symmetric stretchings
3203-3697.5	N-H stretch, OH bending stretching	N-H stretch, Secondary amine

3.2 Electrochemical Results of the corrosion inhibition studies

Potentiodynamic polarization result of mild steel in 1 M of sulphuric Acid in the absence and presence of cow bone ash – polyaniline composite (CBAPC) is shown in Figure 3. The curves revealed shifts in both anodic and cathodic sides. The suppression procedure influenced both the cathodic and anodic reactions, which suggests that CBAPC is a mixed-type inhibitor. According to the reports of Al-Otaibi et al (2014) and Omotioma and Onukwuli (2015), mixed-type inhibitor is helpful in regulating anodic and cathodic types of corrosion. Electrochemical impedance spectra are represented in Figure 4. The classes are three; Nyquist, Bode phase angle and Bode mag plots. In each of the plots, trend curves of uninhibited and inhibited H_2SO_4 with 0.5g/L and 0.7g/L CBAPC were displayed. Impedance spectra were measured at the respective corrosion potential, which were analyzed in terms of equivalent circuit. The displayed semi-circle is an indication that there is a charge transfer process occurring with charge transfer resistance in parallel with the interfacial capacitance (Anadebe et al, 2019; Udeh et al, 2021). The spectra effectively explained the semicircles in the complex plane.

Sufficient opposing charge movement has direct correlation with slow corrosion system. It was discovered that the semicircles were depressssed into real axis of the Nyquist plot as an outcome of the crudeness of the metal surface. The discovered discharge effect can be described by power law dependent capacity (regarded as constant phase element) (khaled, 2003; Onukwuli et al, 2021). EIS is an indispensable way of watching electrochemical charges with critical apprehension of physical processes happening at the mild steel/ H_2SO_4 interface. Impedance spectroscopy reveals relevant information relating to electrode kinetics, surface pr+operties and adsorption mechanism. The middle of this depressed semicircle was lightly shifted below the real axis (Anadebe et al, 2018). In Tables 4, electrochemical parameters of CBAPC for the deterioration control of mild steel in H_2SO_4 were presented. Inhibition efficiencies of 76.3% and 57.4% were obtained at inhibitor concentrations of 0.7g/L and 0.5g/L respectively. Good performance of the inhibitor may be due to presence of heteroatoms and other related functional groups in the molecular structure.

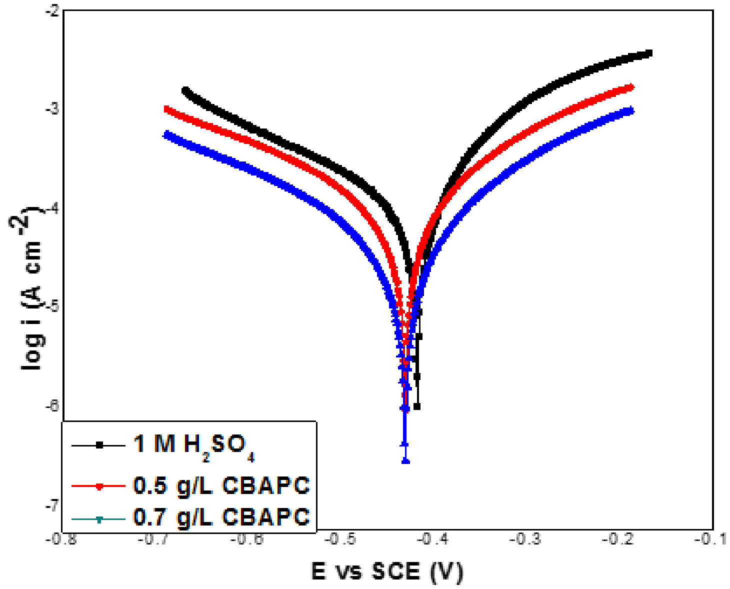

Figure 3: Potentiodynamic polarization curves of the study

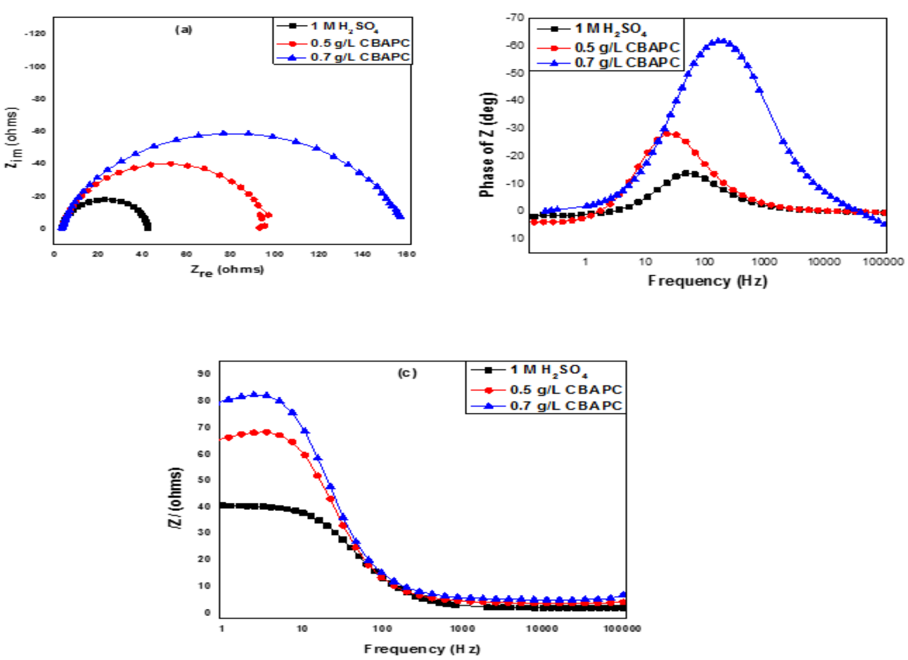

Figure 4: Electrochemical impedance spectra for the absence and presence of CBAPC: (a) Nyquist (b) Bode phase angle plots and (c) Bode modulus plots

Table 2: Electrochemical parameters for corrosion suppression

System	E_{corr}	I_{corr}	IE (%)	R_{ct} (ohms)	N	IE (%)
1M H_2SO_4	-424.8	196.9		42.5	0.89	
0.5 g/L CBAPC	-477.3	75.8	61.5	98.8	0.88	57.4
0.7 g/L CBAPC	-454.6	38.3	80.5	179.6	0.89	76.3

4.2 Thermometric Results

Effect of inhibitor concentration on the reaction number (RN) and inhibition efficiency (IE) for the mild steel in the sulphuric acid is given in Table 3. The value of the reaction number was determined as a function of the ratio of change in temperature to the maximal time reached. The concentration of the inhibitors ranged from 0.1 to 0.9 g/L. Reaction number decreased with increase in concentration of the inhibitor. Conversely, inhibition efficiency increased with increase in inhibitor concentration. This is in agreement with the findings of Onukwuli and Omotioma (2016). Maximum inhibition efficiency of 93.41% was obtained in the deterioration control of mild steel in Sulphuric acid using the cow bone ash – polyaniline composite (CBAPC).

Table 3: Effect of inhibitor concentration on the RN and IE

Inhibitor conc. (g/L)	RN	IE (%)
0.0	0.4112	
0.1	0.1470	64.26
0.3	0.0972	76.35
0.5	0.0603	85.33
0.7	0.0271	93.41
0.9	0.0312	92.42

Conclusion

From the analyzed results of the study of corrosion suppression, the conclusions of this study are follow:

The synthesized cow bone ash polyaniline composite (CBAPC) has C-H ring hydrogen, =C-O-C sym, CH_2 plane scissoring, N=Q=N quinoid ring stretching, CH_2 asymmetric and symmetric stretches and N-H stretch as the main functional groups. The presence of heteroatoms with free electron pairs and substituent group indicates that the synthesized composite will promote effective corrosion control capability.

On the electrochemical analysis, cow bone ash polyaniline composite was identified as mixed-type inhibitor. It inhibited both cathodic and anodic reactions. Addition of inhibitor to the acid medium increased the magnitude of the impedance spectrum.

Thermometric analysis revealed that reaction number decreased with increase in concentration of the inhibitor. Conversely, inhibition efficiency increased with increase in inhibitor concentration. Maximum inhibition efficiency of 93.41% was obtained in the deterioration moderation of mild steel in sulphuric acid using the cow bone ash – polyaniline composite. Good performance of the inhibitor was due to presence of heteroatoms and allied functional groups in the molecular structure of CBAPC.

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