

SUPPRESSION OF MILD STEEL DEGRADATION IN H₂SO₄ 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 H₂SO₄ medium using cow bone ash - polyaniline composite (CBAPC) as inhibitor. The CBAPC was synthesized, and then characterized using Fourier transform infrared spectrophotometer. Electrochemical and thermometric studies were carried out in the deterioration control procedure. Result analyses showed that synthesized CBAPC has C-H ring hydrogen, =C-O-C symmetric stretch, CH₂ plane scissoring, N=Q=N quinoid ring stretching, CH₂ 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, CBAPC was identified as mixed-type 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 CBAPC. Maximum inhibition efficiency of 93.41% was obtained by the thermometric technique. Good performance of the inhibitor was due to presence of heteroatoms and allied functional groups of CBAPC. Thus, synthesized cow bone ash polyaniline composite (CBAPC) should be applied as inhibitor for suppressing mild steel degradation in H₂SO₄ medium. This research report is important to research community because it provides the basis for conversion of cow bone (which is often regarded as waste) to useful product (corrosion inhibitor). It established the effectiveness of the cow bone ash - polyaniline composite in suppressing corrosion of mild in acid medium.

Keywords: Mild steel, H₂SO₄ medium, Cow bone ash, Polyaniline

1.0 Introduction

Mild steel is a metal that is highly 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 is also used to fabricate agricultural equipment, 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 [1]. 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 [2, 3]. There are various ways to controlling corrosion, but one of the most recognized techniques is inhibitor application [4, 5, 6]. Inhibitors of various kinds have been used for corrosion inhibition of metals [7, 8, 9]. The inhibitors were found to reduce or prevent corrosion by adsorption process. It also happened 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 [10, 11, 12, 13, 14, 15, 16]. 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 [17], 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 [17] 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 [18] 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 cow bone ash were mixed together to form a solution with vigorous stirring for 4hrs. The clay was dispersed in the solution using an ultrasonic bath. The suspension was left in the air for about 30 min. for the cow bone ash to swell. 5% ammonium persulfate ((NH₄)₂S₂O₈) 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 H₂O to remove residual oxidant. The produced composite was dried to a constant weight in an oven under vacuum at 100°C, after which it was ground, measured and stored for later use. This method employed in this experiment followed the procedure used by Zhu [19].

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 obtained high spectral resolution data over a wide spectra range. Fourier transform (a mathematical process) converted the raw data into concrete spectrum. Analyses of the various FTIR produced peaks were carried out so as to determine the appropriate functional groups in accordance with the procedure of previous reports [10, 20].

2.4 Study of Electrochemical Behaviour.

Potentiodynamic polarization (PDP) and electrochemical impedance spectroscopy (EIS) were used for the electrochemical experiments in accordance with the method used by Anadebe et al [21]. EIS was used to watch the electrochemical charges with critical understanding of physical processes taking place at the mild steel/ H₂SO₄ interface. Potentiostat/galvanostat 263 electrochemical system workstation aided the studies, with conventional three-electrode corrosion cell. A graphite rod and a saturated calomel electrode (SCE) functioned as counter and reference electrodes, respectively. The mild steel sample fixed in epoxy resin with a surface area of 1 cm² exposed to the test solution, was used as the working electrode. The measurements were done in aerated and unstirred media at the end of 1800 s of immersion, which allowed the open circuit potential (OCP) to attain steady state [21, 22, 23, 24]. Temperature was fixed at 30±1 °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) [19].

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

$i_{corr(uninh)}$ 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 [10, 25] was embraced in this work. The measurements were performed using water bath with thermostat set at 30 °C. The temperatures of the vessel containing the mild steel and the test solution were recorded on a regular basis until it got to a steady temperature value. The reaction number (RN) was evaluated from Equation (2):

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

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

Equation (3) was used to determine inhibitor efficiency:

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

RN_{free} and RN_{add} represent 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 [10].

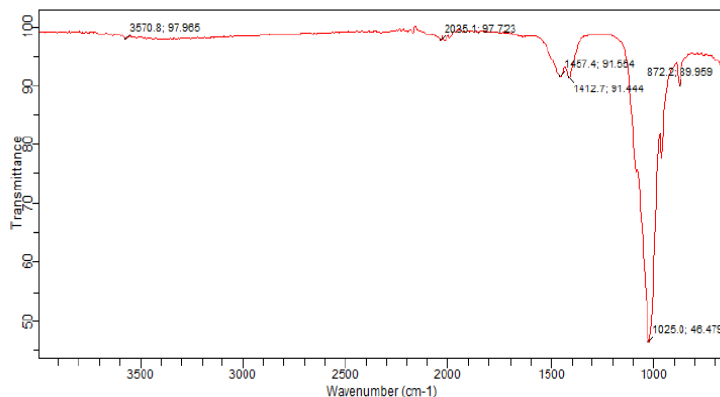


Figure 1: FTIR spectrum of activated cow bone ash

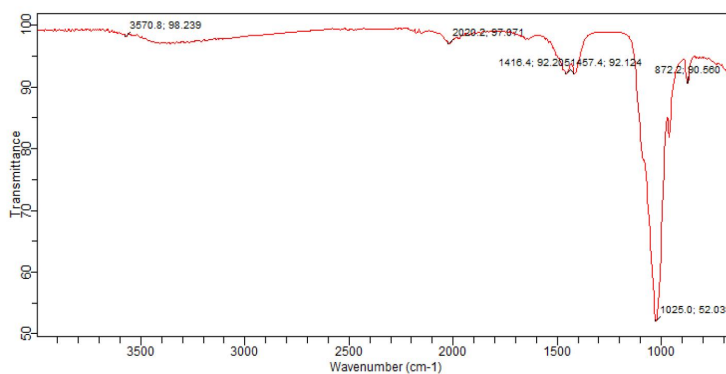


Figure 2: FTIR spectrum of cow bone ash - polyaniline composite

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 N-H stretch, Secondary amine stretching

3.2 Electrochemical Results of the corrosion inhibition studies

Potentiodynamic polarization (PDP) results 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 [24] and Omotioma and Onukwuli [10], mixed-type inhibitor is helpful in regulating anodic and cathodic forms of corrosion. It agreed with the work of Reda et al [15], where the data revealed that the inhibitor system enhances polarization resistance. The effectiveness of the inhibition performance relied on the adsorption of inhibitor molecules at the mild steel/H₂SO₄ interface.

Electrochemical impedance (EI) 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 H₂SO₄ 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 [13, 21]. 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 depressed 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) [12, 24, 26]. Impedance spectroscopy reveals relevant information relating to electrode kinetics, surface properties and adsorption mechanism. The middle of this depressed semicircle was lightly shifted below the real axis [11, 12]. In Table 2, electrochemical parameters of CBAPC for the deterioration control of mild steel in H₂SO₄ were presented. Inhibition efficiencies of 76.3% and 57.4% were obtained at inhibitor concentrations of 0.7g/L and 0.5g/L respectively. It align with the report of Kaseb et al [9], where it was stated that inhibitory effectiveness of Aloe ferox Mill extract rose with the increase in concentration. Good performance of the CBAPC may be due to presence of heteroatoms and other related functional groups in the molecular composition.

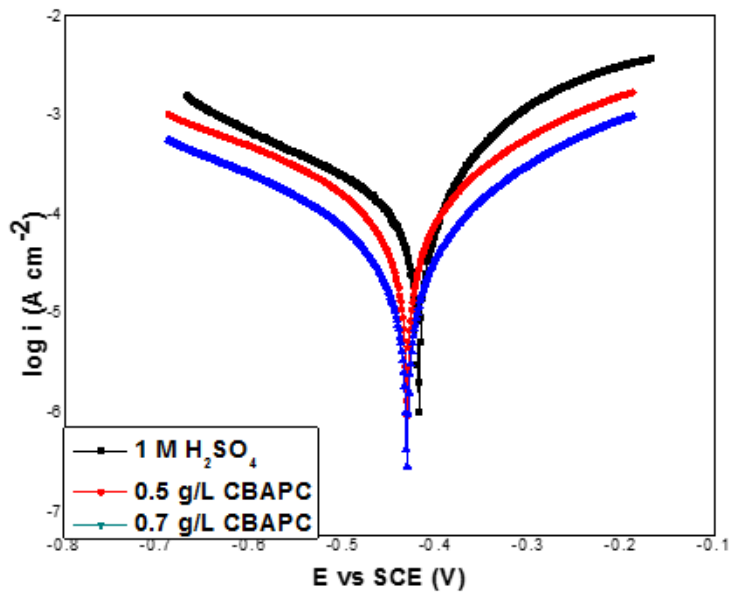


Figure 3: PDP curves of the study

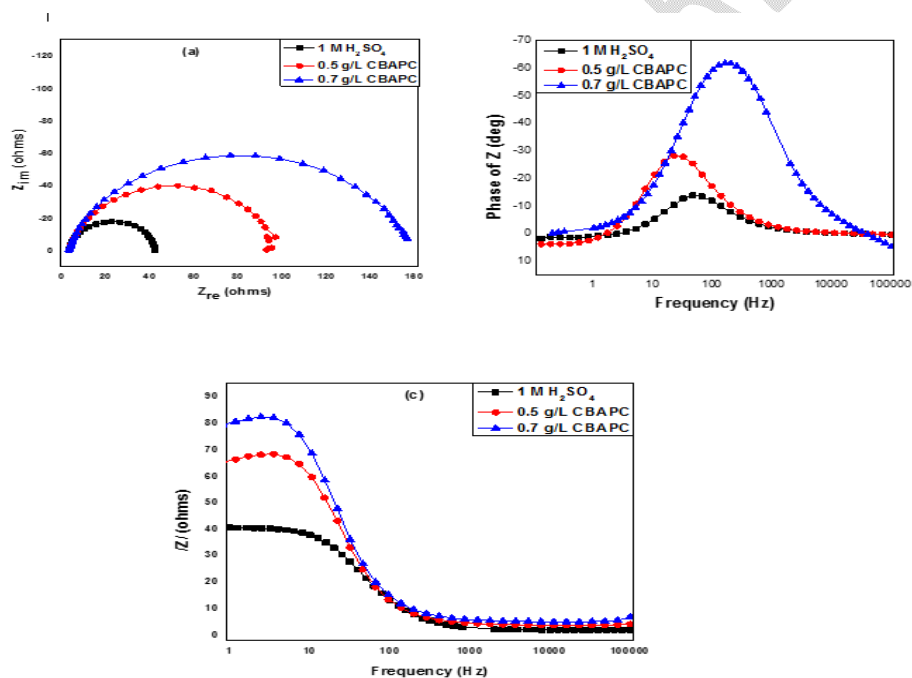


Figure 4: EI spectra for the absence and presence of CBAPC: (a) Nyquist (b) Bode phase angle plots and (c) Bode modulus plots

Table 2: Electrochemical parameters for corrosion suppression

System	E_{corr}	I_{corr}	IE (%)	R_{ct} (ohms)	N	IE (%)
1M H ₂ SO 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 CBAPC ranged from 0.1g/L - 0.9 g/L. Reaction number decreased with increase in concentration of the inhibitor. Conversely, inhibition efficiency increased with the rise in concentration of the CBAPC. This is in agreement with the report of Onukwuli and Omotioma [4]. 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, CH₂ plane scissoring, N=Q=N quinoid ring stretching, CH₂ 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. Synthesized cow bone ash polyaniline composite (CBAPC) should be applied as inhibitor for suppressing mild steel degradation in H₂SO₄ medium

Disclaimer (Artificial intelligence)

Author(s) hereby declare that NO generative AI technologies such as Large Language Models (ChatGPT, COPILOT, etc.) and text-to-image generators have been used during the writing or editing of this manuscript.

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