

CORROSION INHIBITION ASSESMENT OF SALICYLIDENE-2-AMINOPHENOL ON MILD STEEL USE IN FABRICATION OF AGRICULTURAL TOOLS AND MACHINES.

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ABSTRACT

An eco-friendly approach for synthesizing salicylalidene-2-aminophenol Schiff base (SAL2AP) in aqueous environments was studied. The synthesized Schiff base was analyzed through physicochemical method, including C H N elemental analyses. FTIR, Uv- visible, ¹HNMR, and ¹³C NMR spectroscopic techniques were used to ascertain chemical compositions of the Schiff base. The inhibitory properties of these Schiff base against mild steel corrosion in 1 M hydrochloric acid solutions at a temperature of 30°C was evaluated. Gravimetric technique was used to analyze the corrosion inhibition performance of SAL2AP Schiff base on mild steel. The results obtained from this study revealed the remarkable inhibitory potential of SAL2AP on mild steel corrosion in 1M HCl solution. The corrosion inhibition efficiency of SAL2AP Schiff base was found to increase with increasing concentration of SAL2AP, ultimately reaching an impressive maximum inhibition efficiency of 85.66 % at concentration of 1×10^{-3} mmol/dm³. The adsorption behavior of SAL2AP on mild steel followed the Langmuir isotherm model. The effect of increasing temperature of 40°C, 50°C, 60 °C, and 70 °C, and increase in immersion time on IE of SAL2AP was also studied. Decrease in IE was observed with increasing temperature and immersion time which is typical of physisorption adsorption process.

Keywords: Corrosion, Salicylidene-2-aminophenol, Schiff base, Inhibition efficiency, Mild steel.

INTRODUCTION

Mechanized agricultural practices play an important role in realizing many United Nation's sustainable development goals to reduce poverty, and hunger. (Sim and Kienzle, 2016). Agricultural mechanization aids in sustainable development of world food systems by increasing production output and reducing food wastage through the production chain (Kienzle *et al.*, 2013). Mechanized agriculture involves production, use, maintenance, and repair of machines used in production of crops and livestock (Kormawa *et al.*, 2018). The versatile application of mild steel (MS) In various engineering and industrial processes is due to its unique properties, such as ductility, toughness, weld ability, excellent mechanical workability, as well as its relatively low cost (Onu *et al.*, 2024).

Agricultural machines made of mild steel are prone to wear such as adhesive, abrasion, fatigue, erosion, and corrosion when exposed to corrosive chemicals and harsh conditions in the field. These conditions include: plant moisture, corrosive soils, pesticides, fertilizers, harvesting, and post-harvest processing (Aliboev, 2016). These factors lead to increase in consumption of energy, production losses, high cost of maintenance, and decrease in longevity performance of agricultural machines and tools. Corrosion is the surface disintegration of metals / alloys due to chemical or electrochemical reactions with its environment. Mechanical systems and all machines consists of moving parts from different materials including mild steel, hence corrosion poses a big challenge to industries. Therefore, corrosion mitigation, especially of mild steel which constitutes the greater parts of the machines becomes paramount (Wills and Walsh ,2006). The cost of corrosion in the world is about 2,505 billion dollars, which represents 3-4 % of gross national product (GNP). Effective corrosion control using coatings, corrosion inhibitors, and preventive maintenance is estimated to reduce this cost by 15- 35% (McMahon *et al.*, 2019). Corrosion inhibitor is a substance that when presented in the corrosion system at a suitable concentration, lowers the corrosion rate without altering the concentration of any corrosive agent. A good inhibitor is expected to possess some vital characteristics such as low cost, stability at a certain temperature, and more importantly, low environmental and health toxicity (Gamal *et al.*, 2023; Ebenso *et al.*, 2010). There is growing environmental and health concerns associated with the use of carcinogenic chromate based inhibitors as metallic corrosion inhibitors in aqueous systems, hence the need for eco- friendly inhibitors such as Schiff bases as an alternative for the toxic inhibitors cannot be over emphasized (Sinko, 2001, Okafor and Zhang, 2009; Xia *et al.*, 2020). A Schiff base is a nitrogen analogue of an aldehyde or ketone in which the C=O group is replaced by C=N-R group. It is synthesized by reacting an aldehyde with a primary amine (Alamshany and Aisha, 2019). Chemistry of Schiff bases and their metal compounds have wide range of scientific applications, such as in medicine, catalysis, and corrosion control. The presence of electron-rich heteroatoms i.e., (N, O, S, P), and aromatic rings in molecules of Schiff base makes them very reactive, and effective corrosion

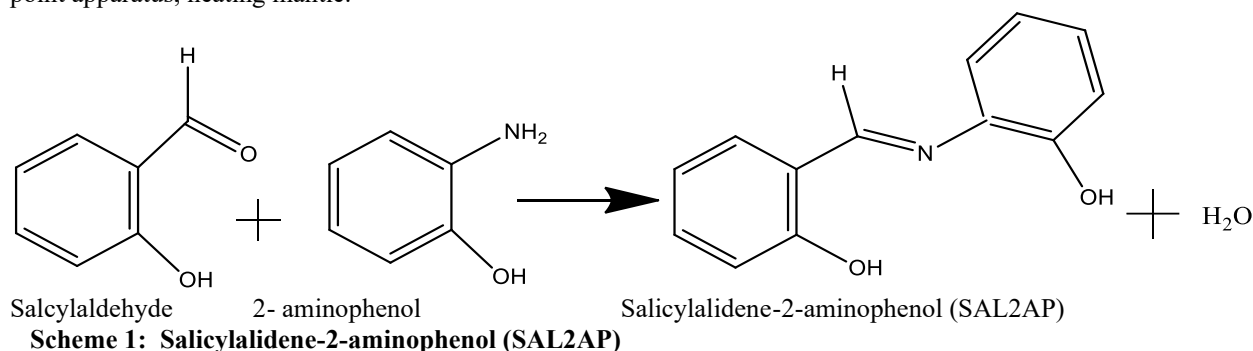
inhibitors. Schiff bases adsorb on the metal surface through their heteroatoms, forming protective films. (Akalezi *et al.*, 2020, Onu *et al.*, 2024, Oguzie *et al.*, 2010).

The objective of this present work is to synthesize, characterize, and assess the corrosion inhibition potentials of Salicylaldehyde-2-aminophenol Schiff base for inhibition of corrosion of mild steel, used in fabrication of agricultural machines and tools in acidic medium.

MATERIALS AND METHODS

Materials

All chemicals used are of analytical grade and used without further purification and were purchased from Sigma Aldrich. These included: Salicylaldehyde, 2-aminophenol, absolute ethanol, dimethyl sulfoxide, conc. HCl. Equipment used included: FTIR and Uv spectrophotometer, NMR spectrometer, elemental analyzer, thermometer, weighing balance, melting point apparatus, heating mantle.



Corrosion inhibition assessment

The experiment was carried-out at the Electrochemical Laboratory of Chemistry Department FUTO. The gravimetric method used follows similar approach by Akalezi *et al.*, 2020. Mild steel (MS) (with the composition of 0.24% carbon, 0.65% manganese, 0.6% Cr and 0.9 % Si respectively, and the remaining percentage is iron, was obtained from Engineering workshop of the Federal University of Technology Owerri, and was used as working specimen. The specimens were cut to sizes with dimensions (3.0 x 3.0 x 1.0) cm, with a hole at the middle of top edge for hanging. The surface of each specimen was prepared by wet grinding with 400 and 600 grit silicon carbide papers using deionized water, being degreased with high purity ethanol, rinsed with deionized water, and then dried before being introduced into the corrosive solution for testing. Gravimetric tests were performed by weighing cleaned and dried MS specimens before and after immersion in test solution of SAL2AP for 24 hours at different concentrations (0.2 mmol, 0.4 mmol, 0.6 mmol, 0.8 mmol, 1.0 mmol, 1.2 mmol, 1.6 mmol, and 2.0 mmol) at 30 °C. The experiment was also carried-out at varying temperatures such as 40 °C, 50 °C, 60 °C

Methods

1 M stock solution of the corrosive, HCl acid was prepared by appropriate dilution from the label. 0.1 M stock solutions of the Schiff base SAL2AP was prepared as stock solution, and serial dilutions prepared accordingly.

Synthesis of SAL2AP Schiff base

SAL2AP was synthesized by the method of Onu *et al.*, 2024, by the condensation reaction between salicylaldehyde and 2-aminophenol. 3.58 g (0.02 moles) of 2-aminophenol dissolved in 100 ml of ethanol was added to 4.0 g (0.02 moles) of salicylaldehyde in 100 ml of ethanol. The mixture was concentrated by heating to half of its volume and allowed to cool. The wine-red colored crystals obtained were filtered, washed with ethanol, recrystallized from ethanol and dried in a desiccator. The percentage yield of SAL2AP is 88 %.

and 70 °C to study the effect of increased temperatures on inhibition efficiency of SAL2AP inhibitor. The MS specimen was immersed, and retrieved periodically in presence and absence of solutions of SAL2AP for four (4) weeks to study effect of immersion time on inhibition efficiency, I.E. The experiments were carried out in duplicate and average values were obtained. The degree of surface coverage (θ), and the inhibition efficiency IE (%) were calculated at different concentrations using the following equations:

$$IE\% = \frac{w_0 - w_i}{w_0} \times 100 \quad (1)$$

Where w_0 and w_i are initial and final weight of MS before and after immersion respectively.

$$\theta = \frac{IE}{100} \quad (2)$$

RESULTS AND DISCUSSIONS

Characterization of SAL2AP Schiff base

Table 1 shows the color, pH, percentage yield, melting point, molecular compositions, and molecular weight of the synthesized Schiff base SAL2AP.

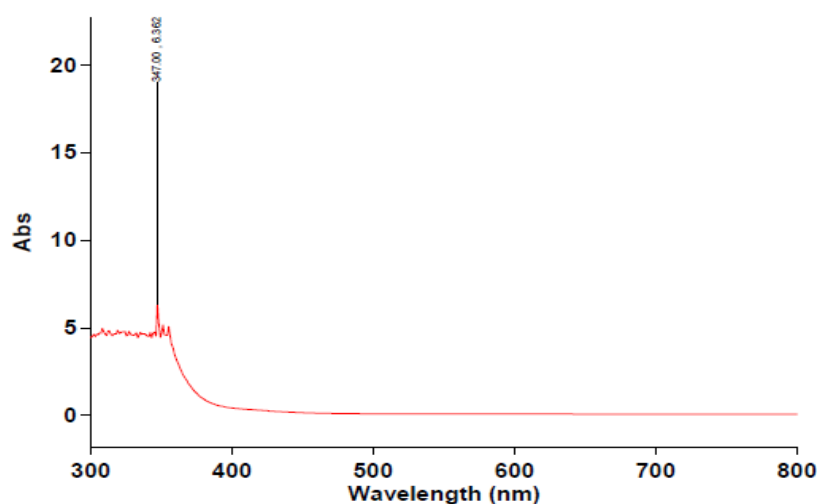
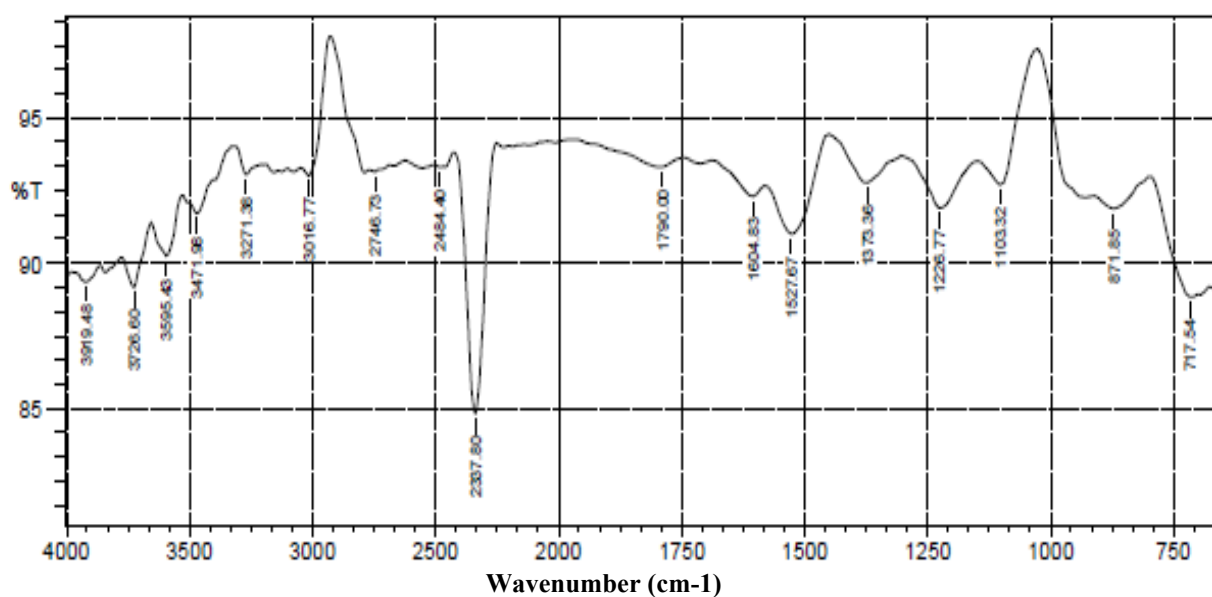
Table 1 Physical characterization of SAL2AP

Compound	Molecular Formular	Color	Yield (%)	Melting point (°C)	pH	% composition			Molecular Weight (g/mol)
						C	H	N	
SAL2AP	C ₁₃ H ₁₁ NO ₂	Wine -red	88	91	6	71.32 (72.44)	4.83 (4.82)	7.34 (7.40)	213

Analysis of Uv Electronic Spectrum and FTIR Spectrum of SAL2AP

Figures 1 and 2 show the UV and FTIR spectra of SAL2AP respectively. The UV spectrum shows maximum absorbance observed for SAL2AP Schiff base at 347 nm, attributed to $n \rightarrow \pi^*$ transition due to the transition of non-bonding electrons of the nitrogen

atom of the azomethine to the antibonding pi (π^*) orbital of the azomethine group. FTIR spectrum of SAL2AP in Figure 2, shows characteristics vibrational signals due to functional groups such as: $\nu(\text{C}=\text{N})$ at 1604 cm^{-1} , $\nu(\text{C}-\text{O})$ at 1226 cm^{-1} , $\nu(\text{OH})$ at 3471 cm^{-1} , and $\nu(\text{C}-\text{H})$ at 3016 cm^{-1} . This further confirms the formation of the Schiff base.

**Figure 1. UV Spectrum of SAL2AP****Figure 2. FTIR Spectrum of SAL2AP**

Proton (^1H) and Carbon (^{13}C) NMR of Schiff base SAL2AP

^1H NMR of SAL2AP, (Figure 3) showed key vibrations due to proton (H) of azomethine group ($\text{HC}=\text{N}$), a singlet, at $\delta = 8.91$ ppm, singlet due to proton, H (OH) of aminophenol and aldehyde moiety at $\delta = 9.68$ ppm, and 13.18 ppm respectively. ^{13}C NMR shows vibration due to azomethine carbon at $\delta = 163.65$ ppm (Figure 4). These characteristics vibrational frequencies give credence to the formation of the Schiff base.

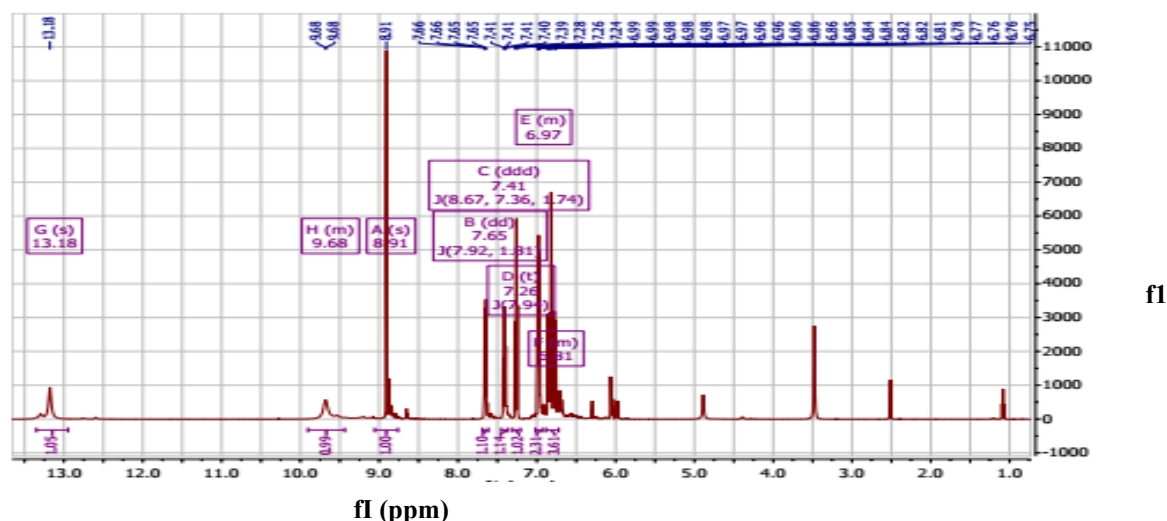


Figure 3. Proton NMR of SAL2AP

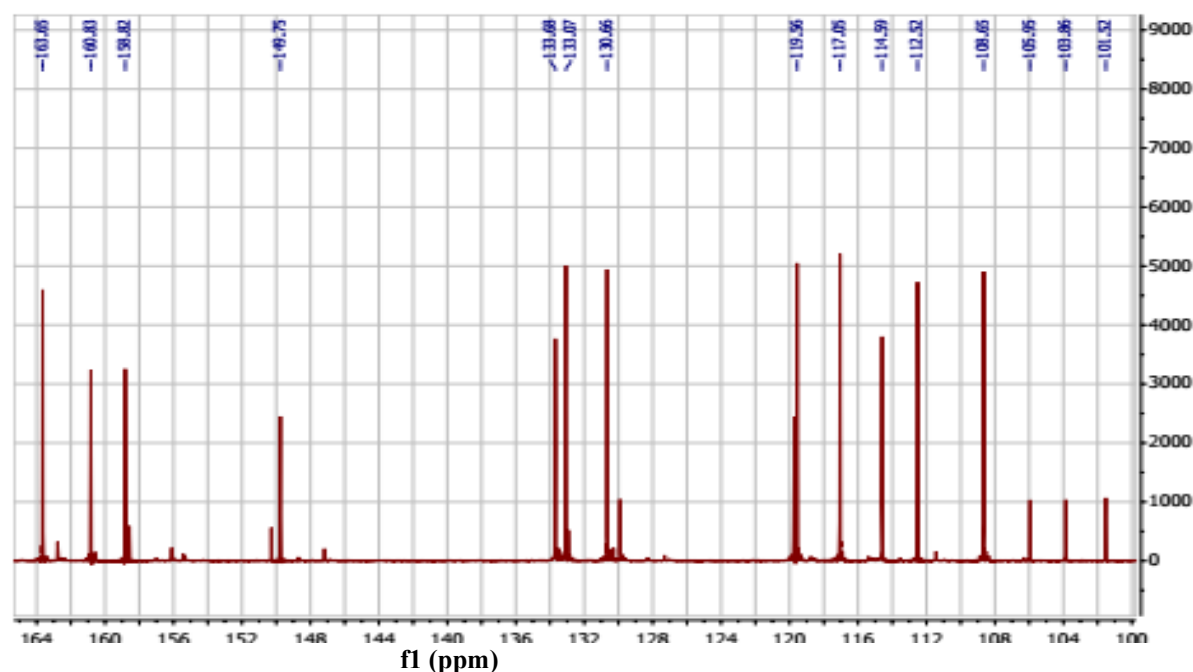


Figure 4 Carbon NMR of SAL2AP

Corrosion Inhibition Test Analysis

The corrosion inhibition potentials of SAL2AP Schiff base was determined chemically by gravimetric method. Table 2 shows the following parameters: inhibition efficiency, IE of SAL2AP in 1.0 M HCl, and 10% DMSO in the absence and different concentrations of SAL2AP at room temperature (303K), surface coverage (θ) and C/θ . It could be observed that IE increased with increase in concentration (C) of SAL2AP (Figure 5), and surface coverage (θ) (Figure 6). Figure 5 represents the trend

of IE with concentration after 24 hr. immersion time, and confirms that IE of SAL2AP is concentration dependent. This observation can be attributed to the increase in surface coverage with increase in concentration of SAL2AP due to the adsorption of more inhibitor molecules on the mild steel surface while forming a protective film. The adsorbed film blocks the corrosion active sites thereby creating a barrier between the mild steel surface and the aggressive solution which prevents degradation of the mild steel (Oguzie *et al.*, 2010). The decrease in IE

observed afterwards could be attributed to desorption of SAL2AP molecules from the mild steel surface. The presence of heteroatoms, ie (N and O), and aromatic rings in the molecules of SAL2AP, enables the interaction between the Fe of mild steel and SAL2AP inhibitor. These heteroatoms are electron-

rich, and donates electrons into the d- orbital of Fe in mild steel, enabling the formation of a protective film via this reaction. The film adheres to the surface of the mild steel, thereby mitigating corrosion. Optimum I.E of 85.66 % is observed at concentration of 1.0×10^{-3} mmol/ dm³

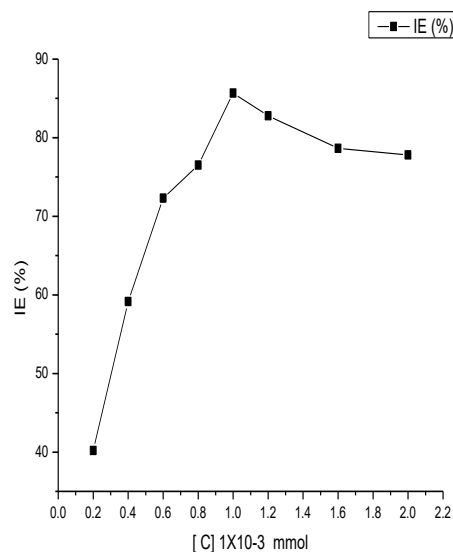


Fig. 5 IE vs concentration (C) (24hr immersion time)

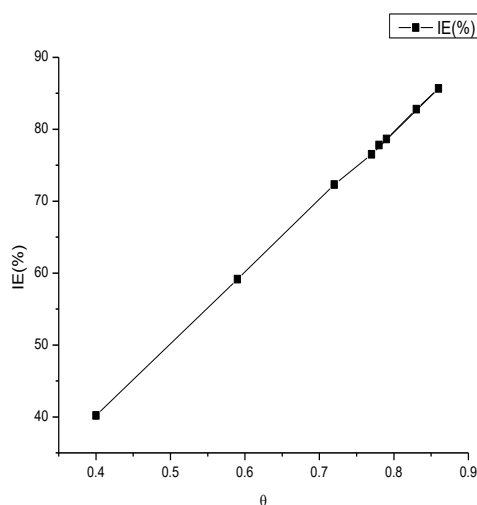


Fig. 6 IE vs surface coverage (Θ)

Table 2 Variation of IE with concentration

[C] of SAL2AP 1X 10 ⁻³ (mmol/dm ³)	I.E% of SAL2AP	θ	C/ θ
0.2	40.21	0.40	0.5
0.4	59.14	0.59	0.6
0.6	72.32	0.72	0.83
0.8	76.50	0.77	1.04
1.0	85.66	0.86	1.16
1.2	82.79	0.83	1.45
1.6	78.66	0.79	2.03
2.0	77.81	0.78	2.56

Variation of IE with immersion time and temperature

Bar charts in Figures 7 and 8 show variation of I.E with immersion time and temperature respectively. IE is observed to decrease with increase in immersion time and temperature. This is suggestive of physical adsorption of the inhibitor molecules on mild steel surface. It could be explained that over time, and with increasing temperature, there is desorption of the adsorbed molecules of the inhibitors from the mild steel surface. This situation arises due to electrostatic interaction between the inhibitor- molecules and the Fe of the mild steel, typical of physisorption adsorption process. This is suggestive of the absence of strong chemical bond between the inhibitor molecules and Fe (Oguzie *et al.*, 2004). This situation exposes the mild

steel to attack by the corrosive acidic medium, thereby decreasing I.E.

Adsorption isotherm

Basic information on the interaction between inhibitor and the metal surface can be provided by the adsorption isotherm. For this purpose, the values of the surface coverage (θ) at the different concentrations of the Schiff base were used to test for the best fit isotherm including Frumkin, Langmuir, and Temkin model. However, the best fit was obtained with the Langmuir isotherm. According to the Langmuir, θ is related to the inhibitor concentration, C by the equation.:

$$C/\theta = 1/K_{ads} + C \quad (3)$$

where K_{ads} is the equilibrium constant of the adsorption process, which describes the binding strength of the inhibitor molecules on the mild steel surface.

Figure 9 and Table 2 shows the dependence of the fraction of the surface coverage C/θ as a function of inhibitor concentration (C). The expected linear relationship is observed with a strong correlation coefficient ($R^2 = 0.998$) for SAL2AP. The value of the regression coefficient R^2 established the validity of this approach. The almost unity slope for the inhibitor suggests that the adsorbed inhibitor molecules formed a monolayer on the steel surface and there is no interaction among the adsorbed Schiff base molecules. The intercept of the linear plot

enables the derivation of the equilibrium constant of the adsorption process, K_{ads} . Value for K obtained equals to 6.13 mol / L. K value > 1 , suggests a stronger binding interaction between the inhibitor molecules (adsorbate) and the surface of the mild steel (adsorbent). This indicates a more efficient adsorption process. Invariably, more molecules of the inhibitor adhere to the mild steel surface, blocking the corrosion active sites on the mild steel thereby protecting the mild steel surface from the aggressive solution.

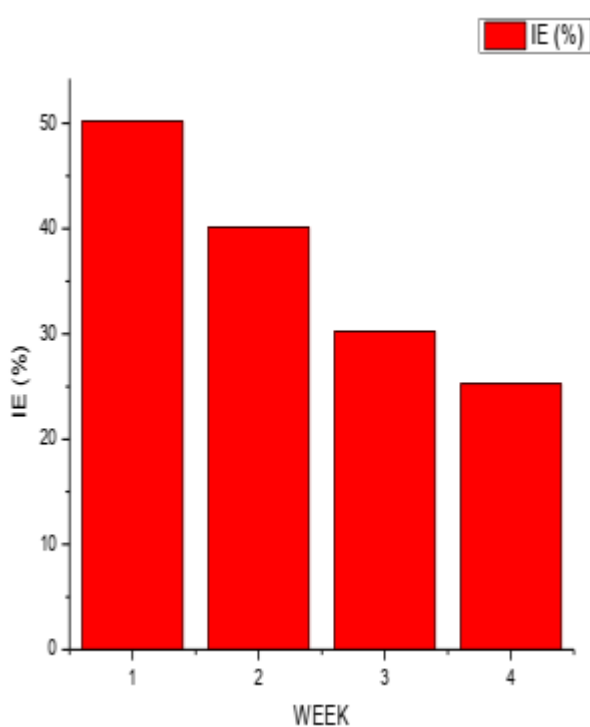


Figure 7. Variation of IE with Immersion Time

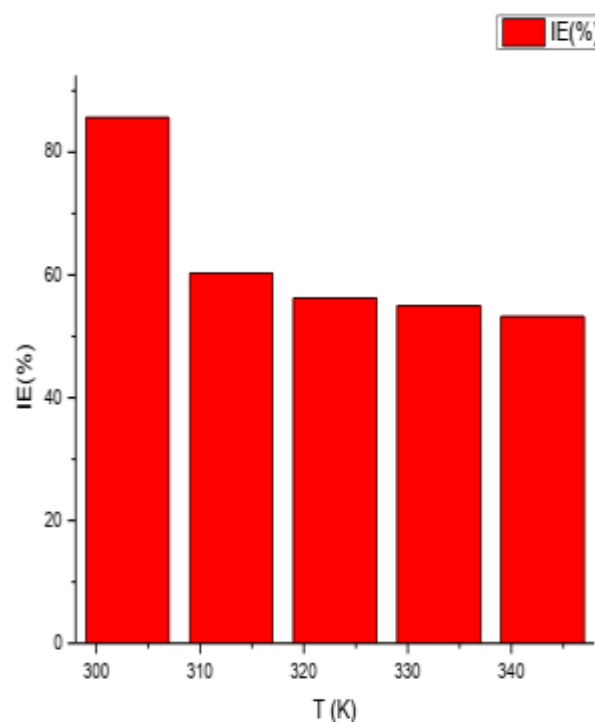


Figure 8. Variation of I.E with Temperature

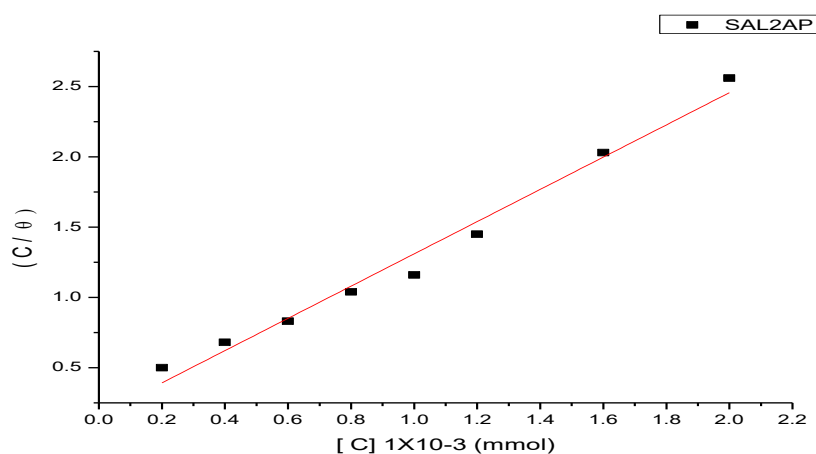


Figure 9. Langmuir Adsorption Isotherm for SAL2AP

CONCLUSION

The Schiff base Salicylidene-2-aminophenol (SAL2AP) has been successfully synthesized and characterized by physicochemical and spectral techniques. The inhibitory performance of SAL2AP in 1 M HCl on mild steel was evaluated. SAL2AP exhibited an impressive inhibitory performance on mild steel, recording an optimum inhibition efficiency of 85.66 % at 1.0×10^{-3} mmol /dm³ after 24-hour immersion time. Inhibition efficiency, IE of SAL2AP increased with increase in concentration of SAL2AP and surface coverage. However, a decrease in IE was observed with increase in immersion time and temperature, which is suggestive of the physical adsorption process of inhibitor molecules on mild steel surface. Langmuir adsorption isotherm best describes the adsorption process with R² value of 0.998.

RECOMMENDATION

Considering the physical adsorption process of the inhibitor molecules on the mild steel surface which led to decrease in IE over time and with increasing temperature, incorporating nano- metal oxides such as Al₂O₃ and ZnO into the molecule of SAL2AP will enhance its inhibition efficiency on mild steel used in fabrication of various agricultural machines, tools and equipment for extended period of time. As well as increase its stability to function better under high temperatures, and in presence of corrosive chemicals used for agricultural practices.

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