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Corrosion Kinetics of Mild Steel Coated with Titanium-Based Anti-corrosion Polyethylene Wax from Waste LDPE Water Sachets in Brine and Acidic Media

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Abstract

Corrosion of carbon steel remains a major global challenge across multiple industrial sectors, necessitating efficient and sustainable mitigation strategies. This study presents a novel titanium-based anticorrosion polyethylene wax (TAC-PEW) coating synthesized from discarded low-density polyethylene (LDPE) sachets sourced from sachet water industries. LDPE was pyrolyzed under optimal conditions of 450 °C for 35 min, yielding 60.77 % wax, which was subsequently blended with titanium and other additives to produce TAC-PEW. In acidic media, TAC-PEW provided substantial protection for mild steel with highest inhibition efficiency of 85.7 %. Kinetic analysis showed that the data fitted an exponential decay model with an exceptional correlation coefficient ($R^2 = 0.9999$) and a decay constant of 0.2529 hr^{-1}, indicating rapid suppression of the initial corrosion rate.TAC-PEW demonstrates dual environmental and industrial benefits by repurposing non-biodegradable plastic waste into a high-performance, sustainable coating for corrosion control in aggressive environments.

Keywords: TAC-PEW, Corrosion, Mild Steel, Inhibition, Kinetics

1. Introduction

Corrosion of carbon steel is a pervasive problem in numerous industries such as oil and gas, automotive, marine and ship building, manufacturing and industrial sectors, aerospace, among others, leading to substantial economic losses and safety concerns (Aljibori et al., 2024; Al-Amiery et al., 2024; Aljibori et al., 2023). Hence, the problem of carbon steel corrosion is a major challenge that cuts across many sectors. Mitigating corrosion-related issues requires the development of effective and sustainable protective coatings among other inhibitors (Al-Amiery et al., 2024). In recent years, there has been growing interest in utilizing waste materials for the production of innovative anticorrosion coatings (Thomas et al., 2022). This research paper focuses on investigating the application of a novel titanium-based anticorrosion polyethylene wax, derived from waste low-density polyethylene water sachets, for the protection of carbon steel substrates in aggressive environments such as brine and acidic media.

The development of advanced coatings with enhanced corrosion resistance properties is a complex task, requiring a deep understanding of the underlying corrosion kinetics (Thomas et al., 2022). Traditionally, experimental methods have been employed to assess corrosion behavior. However, these approaches can be time-consuming, resource-intensive, and limited in capturing the complex interplay of factors affecting corrosion (Al-Amiery et al., 2024). To overcome these limitations, computational modeling techniques have gained attention as valuable tools for analyzing, predicting, and understanding corrosion kinetics (Jia et al., 2022).

This study proposes the application of a Python-based predictive modeling approach to analyze and forecast the corrosion kinetics parameters of carbon steel coated with the novel titanium-based anticorrosion polyethylene wax (TAC-PEW). The computational framework integrates advanced statistical and data-driven algorithms to estimate optimal model parameters and generate model plots (Raschka et al., 2020). This method enables the development of a robust predictive framework for corrosion behavior, offering insights into the effectiveness of the coating in different environments.

The choice of waste low-density polyethylene water sachets as the precursor for the wax used in the formulation of the novel titanium-based polyethylene wax coating is driven by environmental and sustainability considerations. These sachets are a major source of plastic waste, particularly in regions with limited waste management infrastructure (Raschka et al., 2020). By transforming this waste material into a value-added product with anticorrosion properties, two significant challenges—waste management and corrosion protection—will be simultaneously addressed. The objectives of this research work are twofold. Firstly, to investigate the effectiveness of the enhanced titanium-based polyethylene wax coating in inhibiting corrosion of carbon steel in brine and acidic media. This evaluation involves experimental measurements of corrosion parameters, including corrosion rate and weight loss under controlled conditions. Secondly, to develop and apply Python-based computational models to analyze and predict corrosion kinetics based on the experimental data. This modeling approach enables the exploration of complex corrosion behavior patterns, facilitating the optimization of coating parameters for improved performance.

The outcomes of this research have significant implications for the corrosion protection industry. The utilization of waste low-density polyethylene water sachets for producing an enhanced titanium-based polyethylene wax coating not only contributes to waste management efforts but also offers a sustainable and cost-effective solution for corrosion prevention. The application of a Python-based predictive modeling approach provides a valuable tool for the accurate prediction of corrosion kinetics, enabling the development of advanced coating systems tailored to specific environmental conditions. Finally, this research paper explores the application of computational modeling for studying the corrosion kinetics of carbon steel coated with enhanced titanium-based polyethylene wax derived from waste low-density polyethylene water sachets in brine and acidic media. By combining innovative coatings for corrosion prevention with advanced predictive modeling for kinetic analysis, progress in corrosion protection strategies can be achieved, offering more durable and efficient solutions for various industries.

2.0 Materials and methods

2.1 Materials

The materials used include: Waste low-density polyethylene films (commonly known as pure water sachets (see Fig 1)) locally sourced within Ifite in Awka South Local Government Area (6.2116° N, 7.0714° E) of Anambra State, Nigeria, the mild steel (conforming to ASTM A36 specification (nominal composition: C ≤ 0.26 wt%, Mn 0.60–0.90 wt%, P ≤ 0.04 wt%, S ≤ 0.05 wt%, balance Fe) , titanium-dioxide (powdered form), alkyd resin, isopropyl alcohol, hydrochloric acid, brine, cobalt(II) naphthenate (commonly known as cobalt drier) and mixed dryer (a mixture of cobalt(II) 2-ethylhexanoate, zirconium(IV) 2-ethylhexanoate and calcium 2-ethylhexanoate), these materials were procured from a dealer at the bridge head market Onitsha, Anambra State, Nigeria.



Fig 1: Site of low-density polyethylene from sachet water industries

2.1.1 Sample preparation

The sachets from used sachet water were washed and sun dried, thereafter, the sachets were bleached using nitrocellulose to remove ink imprints. The recovered samples were allow to dry under room temperature and thereafter shredded and set for pyrolysis.

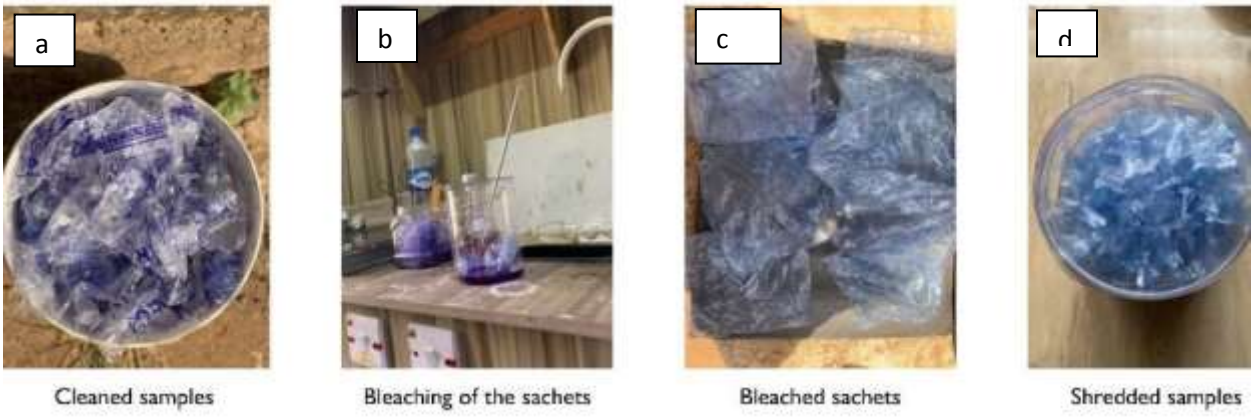


Fig 2: Sample preparation

2.2 Production of PEW

The pyrolysis experiment was carried out using SX-5-12 WIMCOM scientific muffle furnace.

Pre-weighed shredded sachets samples were introduced into the burning chambers of the muffle furnace. The pyrolysis experiment was conducted at varying temperature (623K and 723K) and residence time of 35 minutes and 60 minutes (Dubdub & Al-Yaari, 2020). After the desired residence time, the resulting polyethylene wax (PEW) was allowed to cool to room temperature, collected and weighed.

The wax yield was estimated using Equation 1:

$$Y_w = \frac{X_2}{X_1} \times 100\% \qquad 1$$

where Y_w is the yield of wax in percentage, X_2 is the mass of the wax obtained from pyrolysis, and X_1 is the initial mass of the samples.

2.3 Characterization of PEW

The PEW was analyzed using Cary 630 FTIR spectrometer by Agilent Technology US to observe the functional groups present in PEW. Micrograph Analysis similar to Scanning electron microscopy (SEM) experiments was conducted to identify the physical morphology of the surfaces. The wax hardness was estimated using a durometer (ASTM D2240). The thermo-gravimetric analysis (TGA) on PEW was carried out using a NETZSCH thermo-gravimetric analyzer.



Fig 3: Polyethylene wax recovered from pyrolysis of waste sachets from sachet water industries

2.4 **Solvent Selection for TAC-PEW**

The choice of solvent was made between Xylene and isopropyl alcohol (IPA), both of which were used to dissolve the alkyd at ratio 1:1.5 for the solvent and the alkyd. The selection was based on the observed solubility in-terms of viscosity and consistency (Dubdub & Al-Yaari''2020).

2.5 Formulation of TAC-PEW

The TAC-PEW was formulated using different ratios of titanium dioxide, xylene, alkyd resin, mixed dryer and cobalt dryer. Varying mass of PEW was melted in a 250ml pyrex beaker using controlled temperature magnetic stirrer at 70 degree temperature. The desired volume of xylene was introduced as solvent and the mixture was allowed to stirrer for 20min. Thereafter, xylene was used as solvent. Different masses of alkyd resin were dissolved in the mixture. Another 20min residence tine was allowed to enhance the mixing consistency. Varying weights of titanium dioxide was introduced into the mixing vessel and other additives were added in proportions. Then the mixture was allowed to blend. Samples were analyzed and stored for corrosion inhibition efficiency experiment. Effect of solvent-titanum dioxide-PEW ratio in TAC-PEW coating formulation was evaluated.

2.6 Anti-corrosion efficiency experiment of the TAC-PEW coating

Four carbon steel samples were watched and allowed to dry; this was done to remove possible impurities. Thereafter, three of the samples were uniformly coated with the 10 ml of the TAC-PEW coating and were allowed to dry under room temperature for four hours. The one not coated was used as control. The samples were weighed and the initial samples weight recorded (approximately, the samples weight was constant 5.1 for the samples coated with TAC-PEW and 4.81 for the control). Each of the samples was introduced into 50 ml of dilute hydrochloric acid, brine and H_2O under different temperature conditions (however, for estimating the kinetics, corrosion rate dependence on time at 30ºC was used for this study). The samples were reweighed every 1 hr interval and the weight loss estimated. The corrosion rate was calculated using Equation 2

$$CR = \frac{K.m_{loss}}{A.t.\rho}. \qquad 2$$

where k is a constant $8.76 \cdot 10^4$ so that CR is in [mm/y], m_{loss} is the mass loss [g] of the metal ($m_0 - m_f$) in time t [hours], A is the surface area of the material exposed [cm^2], and ρ is the density of the material [g/cm^3] (ASTM, 2012)

2.7 Model description

2.7.1 Corrosion kinetic models for carbon steel

Corrosion kinetic models are mathematical representations that describe the rate of corrosion for a given material under specific conditions (Enikeev et al.,2020). These models help predict and understand the corrosion behavior of materials, allowing for better corrosion prevention and control. The data were modeled using four different corrosion kinetic models. These models include the linear mode l(Equation 3, parabolic rate model (Equation 4), exponential rate model (Equation 5) and Logarithmic rate model (Equation 6) (see Table 1).

Table 1: Corrosion kinetics model equations based on corrosion rate

Model	Mathematical Description	Constants	Equation No	References
Linear Rate Model	CR = Kt	K	3	Enikeev et al.,2020
Parabolic Rate Model	CR = k * √(t)	K	4	Tian et al.,2024
Exponential Model	CR = k * exp(-βt)	k and β	5	Tian et al.,2024
Logarithmic Model	CR= k * log(t)	K	6	Tian et al.,2024

2.8 Inhibition studies

The effectiveness of TAC-PEW in corrosion inhibition was studied using the weight loss of uncoated and coated steel in acidic medium. The inhibition efficiency is a measure of how well the TAC-PEW reduces the corrosion rate compared to the case without the coating. It was expressed as a percentage (Shwetha et al.,2024). The inhibition efficiency (IE) can be calculated using Equation 7

$$IE = \frac{CR_{uc} - CR_c}{CR_{uc}} * 100 \qquad 7$$

Where CR_{UC} is the corrosion rate of the control sample (uncoated steel), CR_C = corrosion rate of coated samples.

A higher inhibition efficiency value indicates better protection against corrosion by the TAC-PEW. Furthermore, the kinetics of corrosion inhibition was modeled using inhibition equations in Table 2 below.

Table 2: Corrosion inhibition kinetics model equations based on Inhibition efficiency

Model	Model Description	Equ. No	References
Linear Model	IE(t) = a + b * t	8	Castillo-Robles et al.,2024
Exponential model	IE(t) = a * exp(-b * t)	9	Castillo-Robles et al.,2024
The logistic model	IE(t) = a / (1 + exp(-b * (t - c)))	10	Castillo-Robles et al.,2024
Power Law Model	IE(t) = a * t^b	11	Castillo-Robles et al.,2024

2.9 Python coding sample for kinetic data modeling

The corrosion kinetics models in Table 1 were evaluated in Python using the data fitting, the data fitting techniques were provided by NumPy and SciPy libraries. The Numpy function was used to array the data and specify the model equation, thereafter; the curve fit function from SciPy fitted the data to the model, obtaining the kinetic model's parameters. The models's parameters were used to generate the curve while the data points were plotted along with the model curve using matplotlib. Thereafter CR prediction code were raised for coefficient validation and CR prediction and the correlation coefficient and error function values were evaluated using the experimental data set and the predicted data set. Plate 1 shows the kinetic model coding for the exponential decay corrosion kinetic model as a representative sample. Others coding for the models under consideration (Table 1) are presented as supplementary material. The codes represent a pathway for both the kinetic plot generation and evaluation of the optimal kinetic parameters. Furthermore, another set of codes were raised using the optimized coefficients and constants as data inputs for CR prediction as a means of validation. For the IE kinetics, curve fitting was first carried out using the curvefit function from SciPy to find the optimized coefficients. Thereafter, new sets of IE values were predicted using the fitted coefficients for a range of the set of t values, and then the model plot was raised using both the original data and the fitted curve to obtain the best fit model.

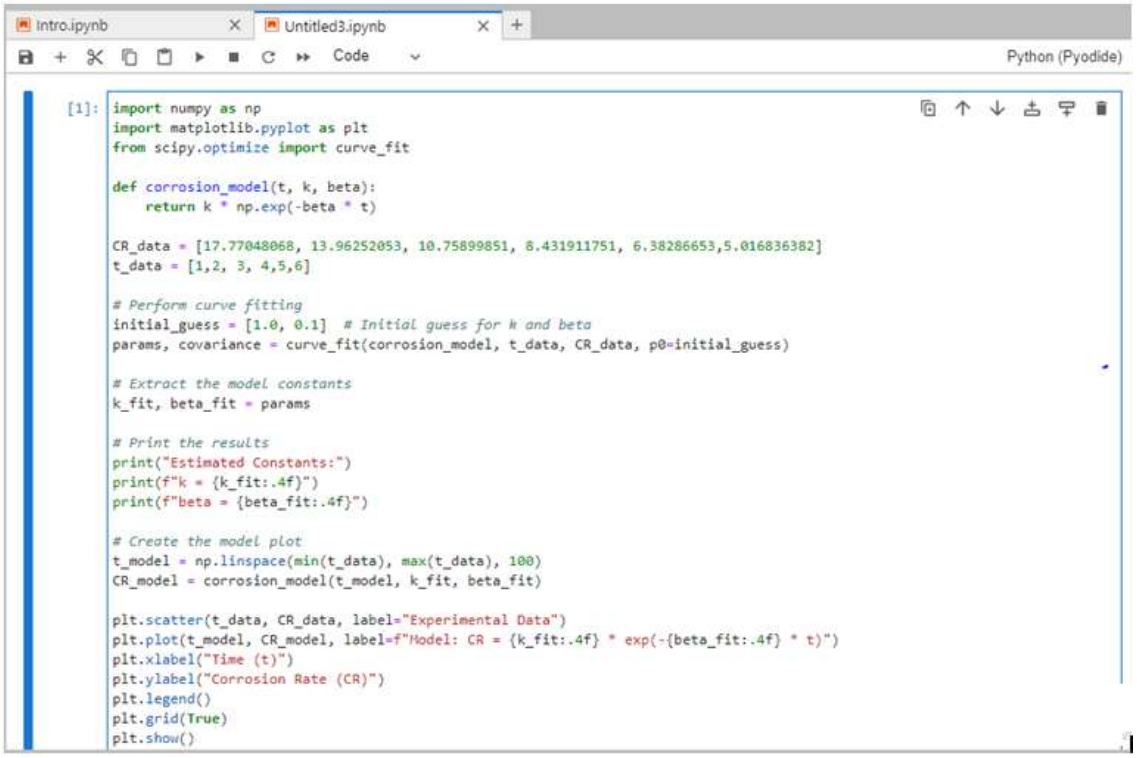


Plate 1: coding for exponential kinetic model

2.10 Model Error analysis

The statistical error functions utilized include the coefficient of correlation, non-linear chi-squared and standard deviation.

$$R^2 = \frac{\sum_{i=1}^{n}(I_{e.cal} - I_{e.exp})^2}{\sum_{i=1}^{n}(I_{e.cal} - I_{e.exp})^2 + (I_{e.cal} - I_{e.exp})^2} \quad (12)$$

$$Chi\ squared = \sum \frac{(I_{e.exp} - I_{e.cal})^2}{I_{e.exp}} \quad (13)$$

$$SD = \sqrt{1/(N-1)\sum_{i=1}^{N}(\frac{I_{e\ exp} - I_{e\ pred}}{I_{e\ exp}} - AARE_{)^2}} \quad (14)$$

3.0 Result and Discussion

3.1 Pyrolysis of waste sachets

Waste sachets from sachet water packaging typically consist of low-density polyethylene (LDPE) and other additives such as pigments, stabilizers, and plasticizers. During pyrolysis, the degradation of the LDPE began at about 473K (200°C), and the reaction was completed at 723K (450°C). At this temperature, there were release of volatile organic compounds (VOCs) which was detected from the off odor. However, as reported by other researchers, the exact temperature at which LDPE starts to degrade varies depending on various factors such as the grade and additives in the LDPE, the heating rate, and the heating medium (Felgel-Farnholz et al.,2023), Table 3 indicates wax yield relative to the initial weight of the shredded polyethylene (PE) feed to the pyrolysis system at 350ºC and 450ºC (reference temperatures were choosen based on best temperatures reported by previous studies(Felgel-Farnholz et al.,2023)). The weight loss resulting from the thermal degradation (difference between the initial weight and product weight) must have occurred due to some major breakdown processes during pyrolysis. The sachet water packaging LDPE, a long-chain polymer of ethylene monomers break down in the presence of heat resulting to formation of smaller molecules (Bamps et al.,2023). The chemical reactions responsible for this degradation and wax formation include: random scission, chain unzipping and possibly dehydrogenation (Dai et al.,2022). During this process, chemical bonds along the chain or at the end of the molecule are broken randomly (Mishra et al.,2023), resulting in definite fragmentation into hydrocarbons or formation of shorter hydrocarbon chains (as is the case with chain unzipping). Also, possible removal of hydrogen atoms from the polymer chains which will likely result to formation of unsaturated hydrocarbon. Table 2 shows the effect of temperature on the wax yield. At lesser temperature (350ºC) the wax production took more heating time but as temperature increased the wax yield increased from 54.44% to 60.7 and reduction in the heating time from 55min to 35min.

Table 3: Effect of pyrolysis temperature on the wax yield

Pyrolysis Temperature (°C)	Heating time (minutes)	Weight of raw material (g)	Weight of wax produced (g)	Yield (%)
450	35	146.628	89.108	60.77
350	55	40.052	21.776	54.44

The same tendencies were also reported by Ullah et al.,2022, where the optimum wax yield from pyrolysis of polyethylene was obtained at a slightly higher temperature (65ºC) with a lower operation time. This may be because at higher temperatures, the thermal decomposition of waste materials are faster, resulting to shorter heating times. However, increasing the temperature above 450oC was reported to have negative effect on the wax yield as the volatility of the pyrolysis products tend to increase which can result in loss of yield due to evaporation. Hence, the optimum yield of wax is as a result of the balance between the thermal decomposition rate and the volatility of the gaseous products (Ullah et al.,2022).

3.2 Characterization of Polyethylene Wax

A comprehensive characterization of the wax gives valuable insight into the properties and composition of the wax. Furthermore, it can also aid in understanding the potential applications and properties of the LDPE-derived wax for various industrial and commercial purposes (Valizadeh et al.,2024).

3.2.1 Physical appearance: The wax obtained was light brown in color and showed glossy appearance. The wax materials were solid at room temperature and relatively brittle. The appearance can be attributed to the pyrolysis condition and resulting changes in the molecular structure during the pyrolysis process (Valizadeh et al.,2024).

3.2.2 Hardness: The shore D hardness test results for the two wax samples obtained at 350 and 450 degrees Celsius reported in Table 4 is in agreement with the results reported by previous researchers (Nwapa et al.,2020; Czarnecka-Komorowska; et al.,2020)

Table 4: shore D hardness test response

Temperature	350ºC	450ºC
Hardness (shore)	84.33±0.5	89.5±0.5

A higher shore value indicates a harder wax, which may be preferable in applications that require durability and resistance to deformation. However, a softer wax may be more suitable for applications that require flexibility and malleability. Also, in a case where the wax would be used for coating, it is intended to provide a high gloss finish, then a wax with a higher hardness may be preferred. On the other hand, if the coating is intended to provide better scratch resistance, then a wax with a lower hardness but higher flexibility may be preferred (Wagle et al., 2021). For the production of anti-corrosive coating (TAC-PEW) as undertaken in this study, LPDE-wax of higher hardness was preferred based on the specific need and requirement of durability, wear resistance, scratch resistance, improved barrier properties, among others.

3.2.3 Fourier Transform Infrared Spectrometry (FTIR)

FTIR analysis carried out on the polyethylene wax obtained at 350°C and 450°C to study their chemical functional group resulting from the molecular structure adjustment following the pyrolysis process. The results as seen in Figures 4 and 5 are almost similar. The strong and sharp peak was observed at 719.4cm-1 belonging to CH2 rocking band. It is attributed to the rocking motion of CH2 groups within the crystalline regions of the LDPE-wax sample. This peak is a common feature in FTIR spectra of polyethylene-based materials and is particularly prominent in samples with a higher degree of crystallinity. The prominent peak at 1357.4cm-1 is often associated with the asymmetric bending vibration of CH3 groups. The presence of this peak indicates the existence of methyl (CH3) groups in the LDPE-wax. Methyl groups contribute to the structure of the aliphatic hydrocarbon backbone of the polymers and are common in LDPE-wax. The peak at 1718.3 cm^-1 is commonly associated with the carbonyl (C=O) stretching vibration. The presence of a peak at 1718.3 cm^-1 suggests the existence of carbonyl groups in the LDPE-wax. Carbonyl groups are typically found in compounds such as esters, ketones, aldehydes, and carboxylic acids. Their presence in the FTIR spectrum of LDPE-wax may indicate traces of foreign component or impurities, which may have resulted from the bleaching of the inscription ink from the waste sachet water packaging using nitrocellulose before the pyrolysis.

The presence of this group suggests the need to thoroughly wash the sachets properly after bleaching. The peak at 1461.1 cm-1 is attributed to the symmetric stretching vibration of CH2 groups. Like the peak at 719.4 cm^-1, it indicates the presence of CH2 groups in the LDPE-wax. The intensity and position of this peak can provide information about the arrangement and interactions of CH2 groups in the material. The CH2 group peaks are characteristic of the aliphatic hydrocarbon backbone of LDPE, which is primarily composed of C-C and C-H bonds. The presence of CH2 groups and the crystalline regions in the LDPE-wax are typical features of the polymer. Also, prominent peaks of intensity 94.5 and 93.7 found at 965.4 and 909.4 cm-1, `respectively both indicate the presence of CH2 groups as well and are consistent with the molecular structure of the polymer. LDPE is composed of repeating units of ethylene monomers, and the FTIR spectrum reflects the characteristic vibrational modes of these molecular units (Boronat et al.,2024). Another prominent peak was observed at 1047.4 cm^-1 is likely associated with the asymmetric stretching vibration of C-O-C (carbon-oxygen-carbon) groups. This type of peak strongly suggests the presence of polyethylene glycol (PEG) in the LDPE-wax. PEG is a polymeric compound derived from ethylene glycol and is often used as an additive or plasticizer in various polymer formulations, including LDPE. Hence, this group is expected in LDPE-wax FTIR spectrum. Two others peaks of low intensity were observed at 2914.8cm-1 and 2847.7cm-1 are still related to the vibrational modes of CH2 and CH3 groups, which are abundant in LDPE (Low-Density Polyethylene) and are part of its aliphatic hydrocarbon backbone.

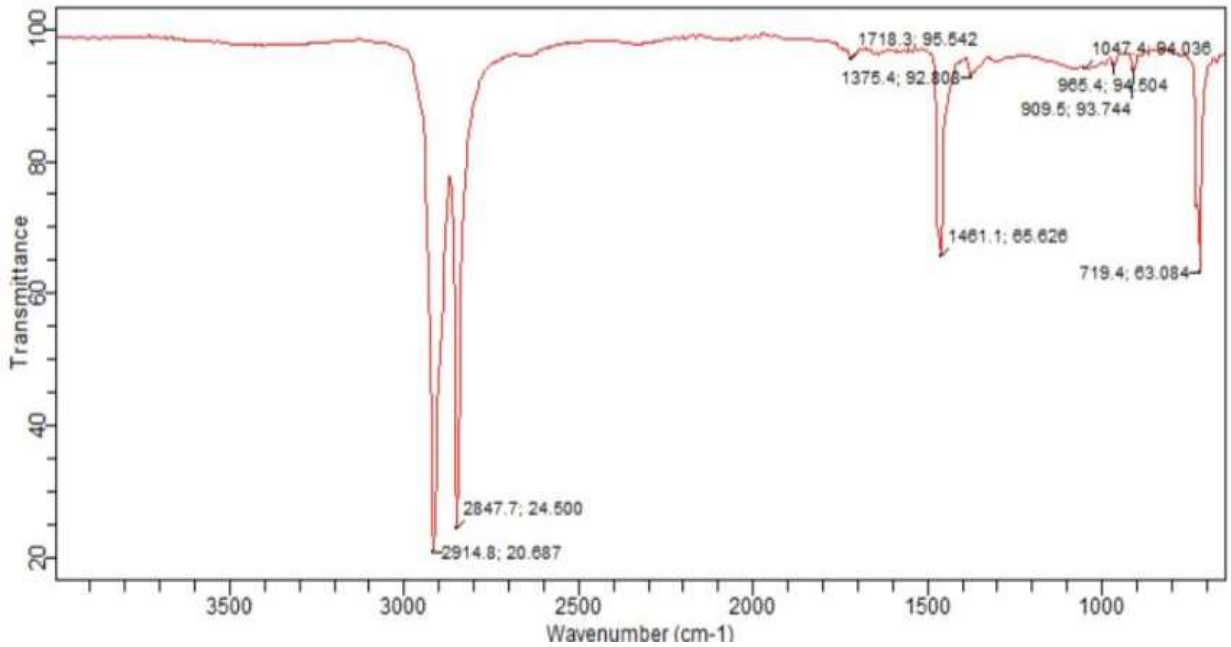


Figure 4: FTIR for wax produced at 450 °C

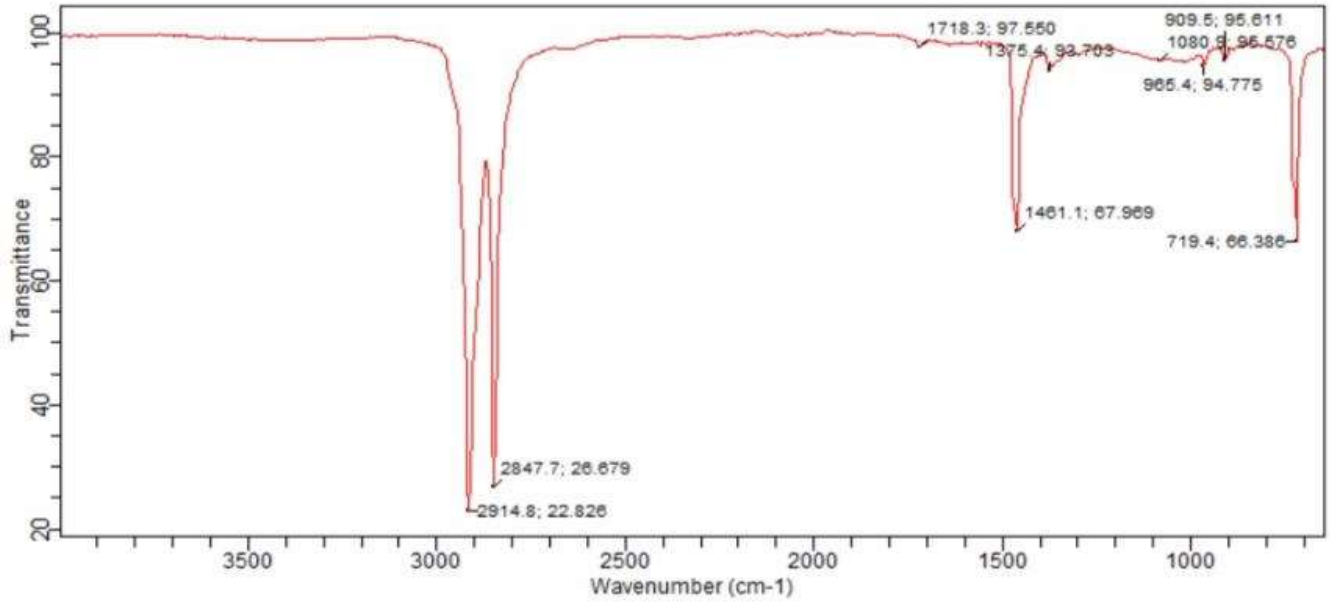
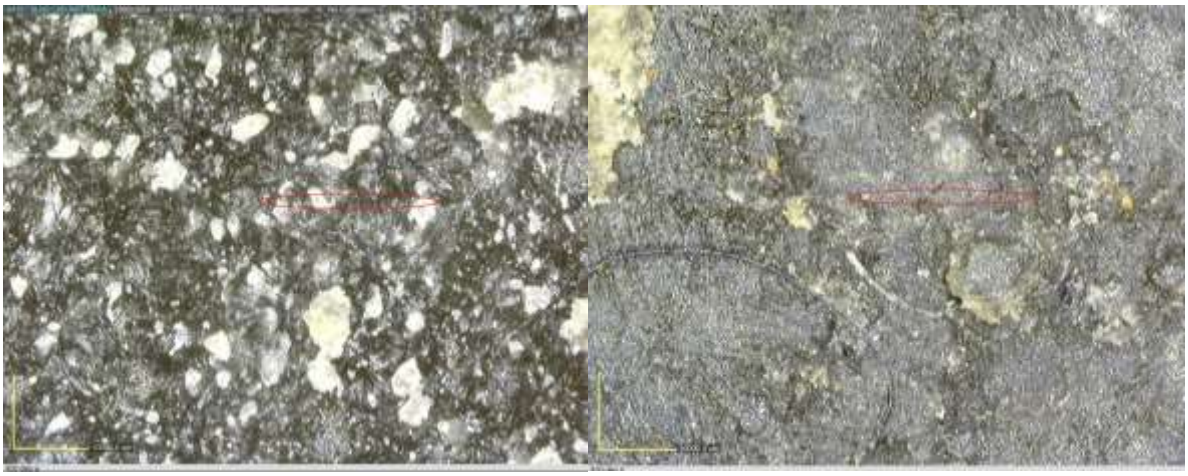


Figure 5: FTIR for wax produced at 350 °C

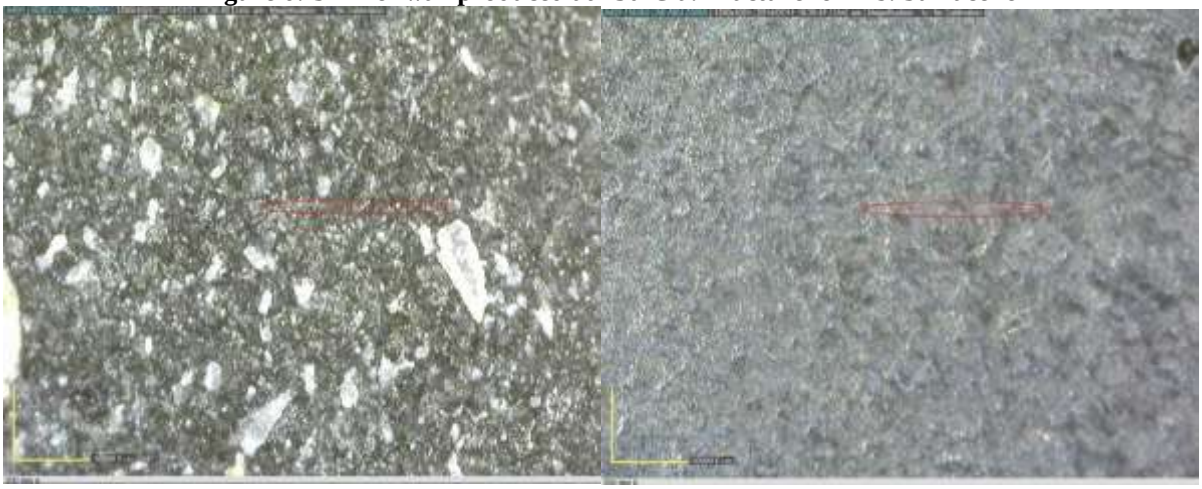
3.3.4 Microscopic examination

The morphological structures of the polyethylene wax obtained at 350°C and 450°C were viewed under microscope. The micrograph analysis of both samples, which presents the optical view of the samples show both the fracture and form surfaces of the wax as seen in Figures 6 and 7. The images reveal that the external surface of the polyethylene obtained at 450°C was very irregular and full of larger cavities with different shapes and sizes compared to that of the polyethylene wax obtained at 350°C. The two surfaces are covered with patches of grey and white. Smaller pores were detected on polyethylene wax obtained at 350°C, whereas large pores were clearly seen on the surface of the polyethylene wax obtained at 450°C. The well-developed pores resulted in larger surface area and more porous structure (Yetgin et al.,2021). Polyethylene wax obtained at 450°C has heterogeneous pore distribution. Higher temperature is believed to be responsible for the pore development in the polyethylene wax obtained at 450°C.



(a) **(b)**

Figure 6: SEM of wax produced at 450°C a. Fracture form b. Surface form

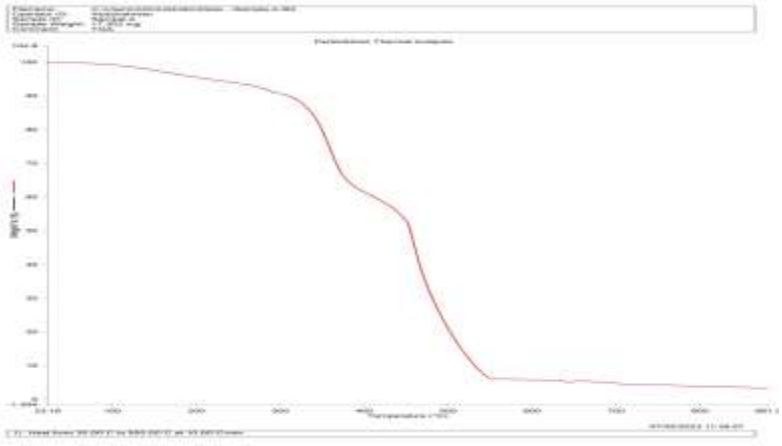


(a) **(b)**

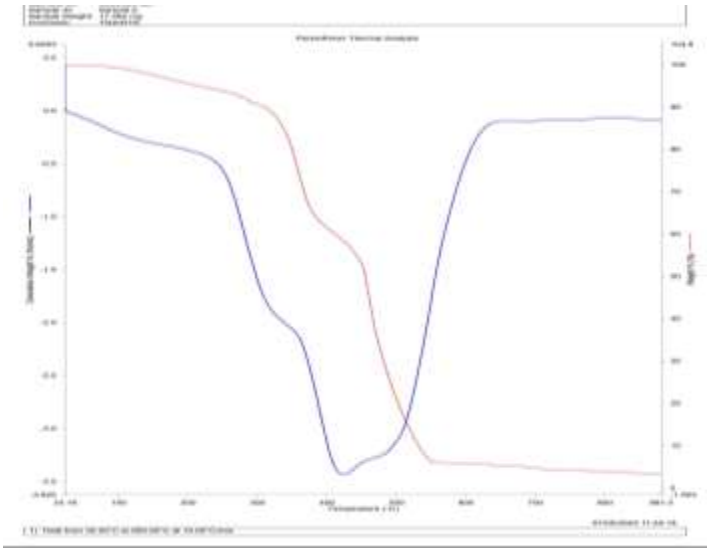
Figure 7: SEM of wax produced at 350°C a. Fracture form b. Surface form

3.3.5 Thermogravimetric Analysis (TGA)

Thermogravimetric analysis was intended to show the relationship between temperature and mass change of the wax. The expected result will aid the understanding of the mechanism of thermal decomposition.



(a)



(b)

Figure 8: TGA of Wax produced 450°C a. TGA curve b. TGA-DTA curve

The TGA curve in Figure 8a shows the percentage weight loss of the polyethylene wax as a function of increasing temperature. DTA (Differential Thermal Analysis) is a thermal analysis technique used to measure the difference in temperature between the wax sample and a reference material when both are subjected to identical thermal conditions. In this case, the DTA results are combined with the TGA results to produce a TGA-DTA curve as represented in Figure 8b. From the TGA curve, it is seen that there is an initial weight loss of about 0.034% at a temperature of 23.19°C, which may be due to evaporation of any moisture present in the sample. Further increase in temperature, increases the weight loss of the wax, indicating that the wax is undergoing decomposition. The TGA-DTA curve shows that the thermal degradation of the wax took places between 350 and 500°C. Since chemical bonds break more easily at higher temperatures, as temperature rises, a large amount of volatile matter evaporates. The graph shows a broad endothermic peak at around 400-500°C, which may be associated with the decomposition of the wax and indicating a major phase transition or reaction during the heating process. It was found that the wax almost degraded completely, the residue was 3.272% at the final temperature of 881.3°C, which may be attributed to the presence of residual carbon in the sample. From the TGA and DTA results, it could be reported that the polyethylene wax has good thermal stability up to about 500°C, with a gradual weight loss as the temperature increases. This suggests that the wax can be used in high-temperature applications without significant thermal degradation (Yetgin et al.,2021). Based on Fig 8b,

3.4 Solvent Selection for TAC-PEW production

The choice of solvent was made between the two most reported mineral solvents: Xylene and isopropyl alcohol (Zolghadr et al.,2021). Preference was based on the virtual consistency of the obtained mixture and the viscosity after dissolution of same quantity of alkyd resin in the solvents. The viscosities of the mixture obtained are presented as Table 5**.**

Table 5: Solubility of Alkyd Resin in Xylene and IPA respectively

Solvent	Solvent ratio	Alkyd resin ratio	Viscosity (mPa.s)	Consistency/Uniformity
IPA	1	1.5	54	Low
Xylene	1	1.5	66	High

For the anti-corrosion coating, solvent that returns a better mixing and high viscosity is needed. Table 5 shows the choice solvent as xylene with viscosity of 66mPa.s and high uniformity. This consistency is due to the fact that alkyd resins have a higher solubility in aromatic solvents such as xylene than in aliphatic solvents or other polar solvent such as Isopropyl alcohol (IPA)(Ifijen et al.,2022. Polar solvents are better suited for dissolving polar

materials. The mixture ratio with xylene also gave a more uniform and consistent mixture with a higher viscosity as seen in Table 5.

3.5. Effect of varying major components (titanium dioxide and wax) in preparing TAC-PEW on the corrosion rate of carbon steel

The ratio of titanium-dioxide was varied while other components were kept constant to study the influence of titanium dioxide on reduction of corrosion rate of carbon steel in acidic medium. The TAC-PEW was formulated using the variables ratio in Table 6. The corrosion reduction effect of the TAC-PEW coated on a carbon steel of 1.4 by 1.2 by 0.04 inches immersed in 0.2N of HCL after 4h are shown also in Table 6.

The results in Table 6, shows that increasing the ratio of titanium dioxide in the TAC-PEW formulation resulted in a decrease in weight loss and subsequently decrease in CR of the coated carbon steel samples acidic medium. The trend therefore suggested that the higher the ratio of titanium dioxide, the better the anti-corrosion properties of the coating. This can be attributed to the fact that titanium dioxide is a well-known corrosion inhibitor and has been widely used in anti-corrosion coatings. The increased presence of titanium dioxide in the coating likely provided more corrosion protection to the underlying steel surface, resulting in less weight loss of the samples.
However, there may be an optimal ratio of titanium dioxide in the TAC-PEW formulation beyond which further increases may not lead to significant improvements in anti-corrosion properties, and may even result in decreased coating flexibility; however, that will be reported under variables optimization, which is outside the scope of the present studies.

Table 6: Effect of varying titanium dioxide weight in formulation of TAC-PEW

Ratio	LDPE-Wax (g)	Alkyd resin (g) (Best ratio)	Xylene (g) (Best ratio)	Titanium dioxide (g)	Cobalt dryer (g)	Weight loss (g) in 0.2N HCl after 4 h	CR(g/m²·h)
1:1.5:1:**1**:0.2	1	1.5	1	**1**	0.2	0.32	19.34
1:1.5:1:**1**:0.2	1	1.5	1	**2**	0.2	0.23	13.90
1:1.5:1:**3**:0.2	1	1.5	1	**3**	0.2	0.19	11.48

The effect of the LDPE-wax quantity was also studied using 3g of titanium dioxide, other parameters were also held constant at 1.5g of alkyd resin, 1g of solvent and 0.2g of cobalt dryer making a ratio of (x:1.5:1:3:0.2), with x representing the ration for the LDPE-Wax.

Table 7: Effect of varying titanium dioxide weight in formulation of TAC-PEW

Ratio	Wax (g)	Alkyd resin (g)	Xylene (g) (Best ratio)	Titanium dioxide (g) (Best ratio)	Cobalt Dryer	Weight loss	CR (g/m²·h)
1:1.5:1:3:0.2	**1**	1.5	1	3	0.2	0.23	13.90208
2:1.5:1:3:0.2	**2**	1.5	1	3	0.2	0.22	13.29764
3:1.5:1:3:0.2	**3**	1.5	1	3	0.2	0.32	19.34202

It can be observed from Table 6, that coating with the 2:1.5:1:3:0.2 wax, alkyd resin, solvent, titanium oxide and cobalt dryer ratio had the least weight loss, while the coating with the 3:1:1:3:0.2 ratio had the highest weight loss. Hence, it shows that increasing the amount of wax in the mixture initially led to a slight increase in the coating's resistance to acid corrosion and finally to a decrease as the weight loss increased. This trend may be due to overloading of the coating with wax which can decrease the availability of active ingredients such as the titanium dioxide and alkyd resin, leading to a reduction in their protective properties (Zolghadr et al.,2021). Also, high wax content can lead to a more brittle coating which makes the coating more susceptible to cracking and exposing the underlying carbon steel to the corrosive medium. Hence, it is always pertinent to optimize the wax quantity for specific applications so that the desired level of corrosion protection would be achieved with the right balance of the active ingredients.

3.6 Final TAC-PEW formulation and corrosion inhibition test

The final TAC-PEW formulation was done using for wax, alkyd resin, xylene, titanium dioxide and cobalt dryer ratio of 2:1.5:1:3:0.2 respectively. The result of the rapid corrosion inhibition test carried out using six different steel of each 1.4 by 1.2 by 0.04 inches in 1N of HCl, water and in brine are reported in Table 8. The weight loss recorded in water and brine was relatively insignificant. This must have resulted from the short period of time the steel was exposed to those media. However, the acidic medium provides a harsher environment needed to rapid corrosion test. Furthermore, Table 8 shows the results of the inhibition efficiency (IE) with respect to time. A higher inhibition efficiency percentage indicates that the inhibitor is more effective at suppressing the targeted process. This suggests that the inhibitor is capable of significantly reducing the corrosion impact. The table below show significant inhibition index. The least inhibition efficiency was recorded at 1hr, while the highest was at 5hr with 87.5% inhibition efficiency. This shows that the TAC- PEW coating was effective. The high corrosion efficiency of TAC-PEW can be attributed to the mechanism of the corrosion inhibition of the TAC-PEW components. The titanium dioxide presents in TAC-PEW functions as a barrier and a passivator, preventing the direct contact of the metal surface with acid. Furthermore, Titanium dioxide is amphoteric, it acts as a pH buffer in a corrosive environment, maintaining a more neutral pH at the metal surface. These phenomena can suppress the acidic attack that accelerates corrosion. In addition, the PEW combined with the alkyd resin forms an enhanced adhesion and uniform film formation. This uniformity ensures that the titanium dioxide particles are evenly distributed and provide consistent corrosion inhibition.

PEW are often chemically inert and stable materials (Zolghadr et al.,2021). Hence, in most cases do not readily react with corrosive substances and is capable of protecting the metal from chemical/acid attack. In an extreme case, the wax due to its inert nature act as a sacrificial layer that undergoes any corrosive attack instead of the underlying metal. It was virtually observed that the coating layer was not depleted during that test time. This is consistent with the combined stability of the alkyd resin, PEW and titanium dioxide. This enhanced stability helped to maintain the TAC-PEW protective barrier's effectiveness under the exposed acidic environmental conditions.

Table 8: Weight loss of coated carbon steel samples in water, brine and acidic media (initial weight 4.87g)

Time (hour)	Control	Control brine	Control acid	Weight loss in water	Weight loss in brine	Weight loss in 1.0N HCl	CR for uncoated Steel ($g/m^2 \cdot h$)	CR coated steel ($g/m^2 \cdot h$)	IE (%)
1	0.00	0.00	0.49	0.02	0.01	0.20	15.9	6.9	56.51
2	0.00	0.00	0.77	0.01	0.0	0.11	4.38	4.2	81.27
3	0.00	0.00	0.89	0.0	0.02	0.12	3.18	0.53	83.33

4	0.00	0.00	0.93	0.01	0.03	0.15	2.99	0.59	80.00
5	0.00	0.00	0.88	0.0	0.02	0.16	2.55	0.32	87.50
6	0.00	0.00	0.83	0.01	0.02	0.11	1.45	0.27	81.81

3.7 Kinetics modeling of the corrosion rate data for TAC-PEW in acidic medium

The experimental data from the rapid corrosion test carried out in acidic medium for the un-coated steel, modeled using the kinetic models (Table 1) through sets of python codes (see supplementary materials) yielded kinetic model results as discussed below. Figs 8-10 show the graphical representation of the alignment of the experimental data to the corrosion kinetic models considered. It was observed that the corrosion rate data fitted well with exponential kinetic models much better than other models. Hence, as time (t) increases, the corrosion rate (CR) decreases exponentially. The exponential decay behavior shows that the initial corrosion rate is relatively high, but it decreases rapidly over time. The coefficient of correlation (R2) of 0.999 and standard deviation of 4.9 are indications that the model (Equation 15) generated is reliable for further predictions. Collectively, the constants, 'A' and 'B' define the behavior of the corrosion kinetics in the exponential model. The value of 'A' (scaling factor) represents the initial corrosion rate, while the value of 'B' determines how quickly the corrosion rate decreases as time (t) progresses. Hence, A and B can help to quantify the initial corrosion rate and the rate of decay of the corrosion process, providing valuable insights into the corrosion behavior and the effectiveness of corrosion inhibitors or protective measures. The model and experimental scaling factor of 22.97 and 17.78, respectively confirmed that the initial corrosion rate (IE) at time =0 or the decay rate at the beginning of the corrosion process is relatively high. The value of B found to be 0.2529 also indicates rapid decay since the corrosion rates were measured and reported in per hour basis.

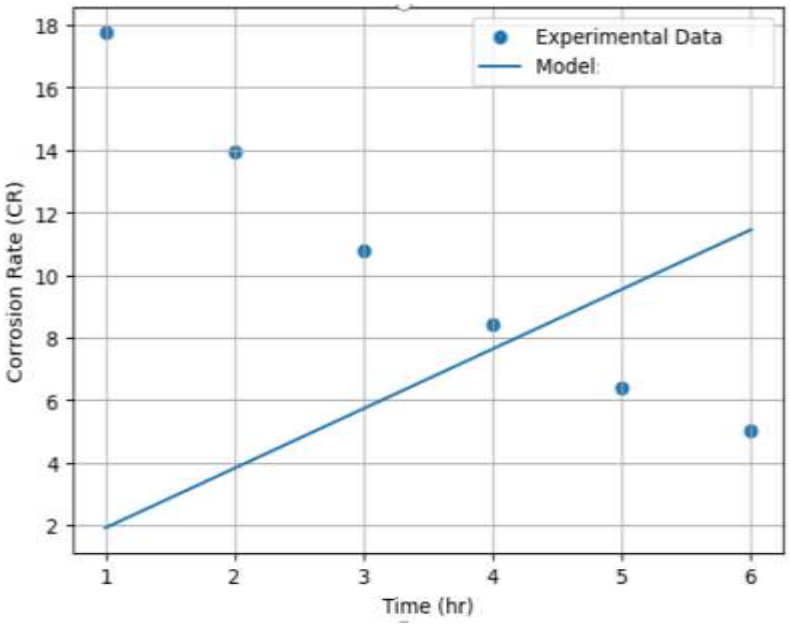


Fig 9 Linear kinetic models

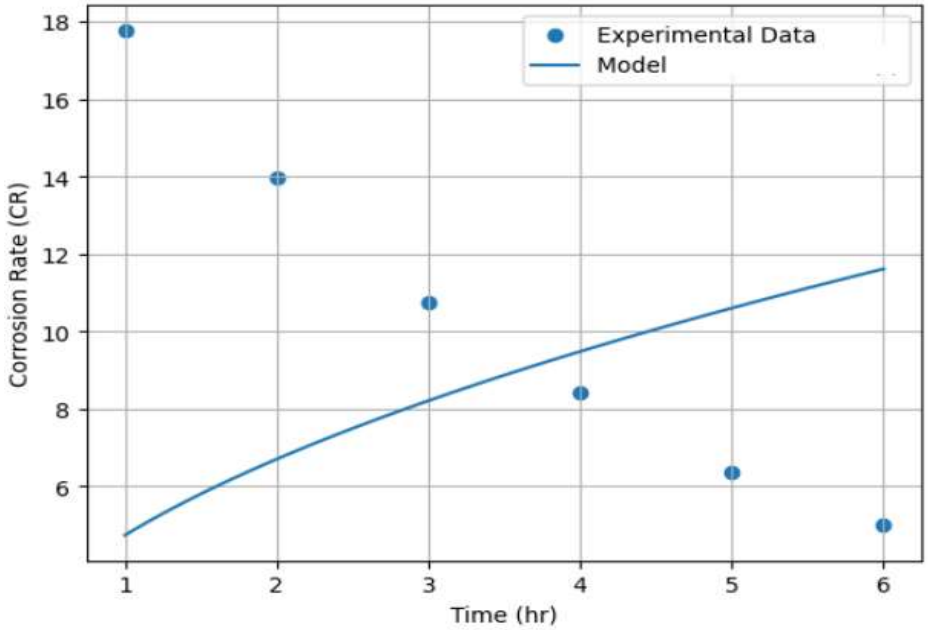


Fig 10 Parabolic kinetic model plot

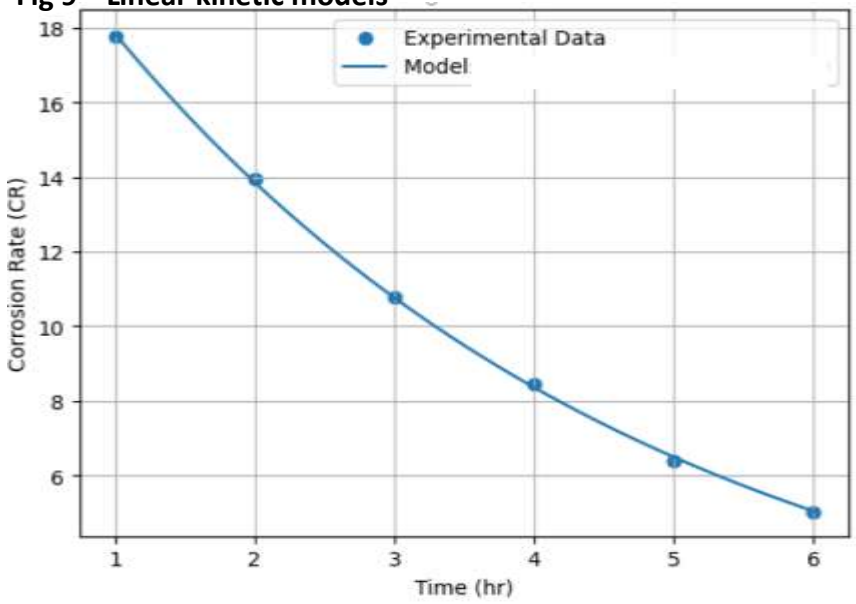


Fig 11 Exponential kinetic model plot

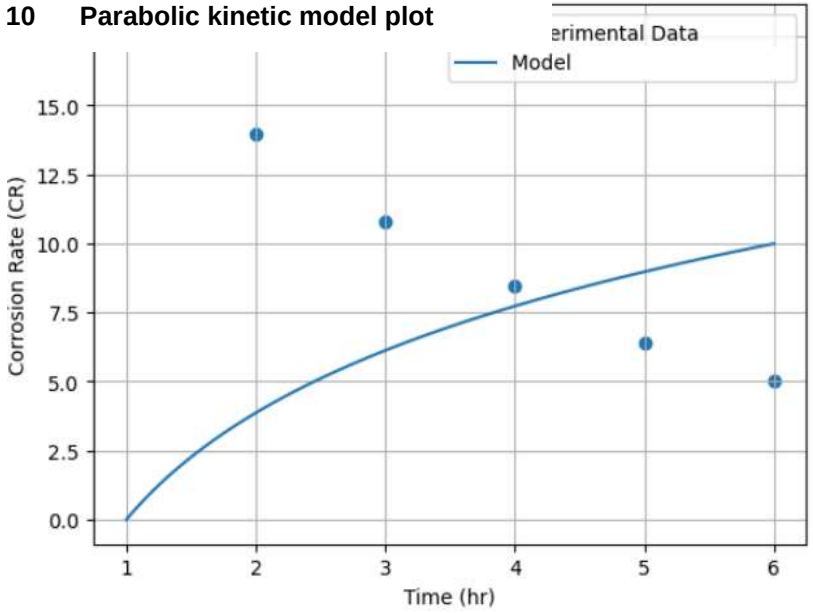


Fig 12 Logarithmic kinetic model plot

Table 9: Comparison of models predicted CR and experimental CR

Time (hr)	Linear Model CR	Parabolic model CR	Exponential model CR	Logarithmic model CR	Experimental CR
1	1.9090	4.7417	15.53	0.0000	15.9
2	3.8179	6.7058	5.43	3.8635	4.38
3	5.7269	8.2129	4.21	6.1234	3.18
4	7.6358	9.4835	3.27	7.7269	2.99
5	9.5448	10.6029	2.54	8.9707	2.55
6	11.4538	11.6149	1.42	9.9869	1.45

CR= 10.4175*(exp(-0.2529*t)) 15

Based on Equation 15, the extrapolated annual cummulative corrosion of 41.9gm^{-2}yr^{-1} and the annual average rate of 4.70×10^{-3}gm^{-2}h^{-1} were obtained.

3.8 Kinetics modeling of the corrosion inhibition efficiency data for TAC-PEW in acidic medium

Table 10: Comparison of models predicted IE and experimental IE

Time (hr)	Linear Model IE	Power Law Model IE	Exponential model IE	Logarithmic model IE	Experimental IE
1	71.8	68.20	72.53	80.64	56.51
2	75.3	75.64	75.60	80.64	81.27
3	78.8	80.36	78.80	80.64	83.33
4	82.4	83.90	82.14	80.64	80.00
5	85.9	86.74	85.61	80.64	87.50
6	89.5	89.14	82.23	80.64	81.81

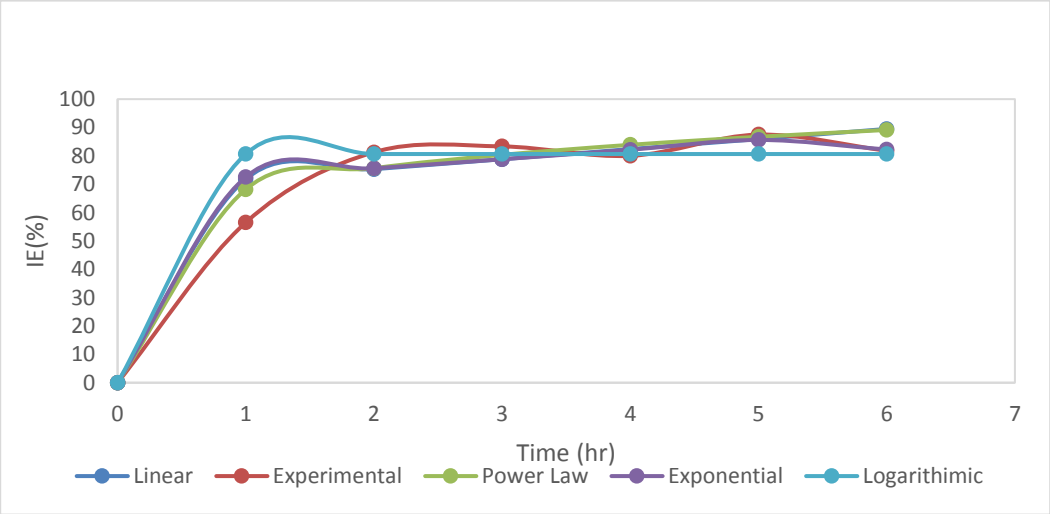


Fig 13: Comparison of experimental and model predicted inhibition efficiency of TAC-PEW coating

Table 11 shows the kinetic models fit with the corrosion rate data. It can be observed that the exponential models excellently described the corrosion rate data. the kinetic studies show the nature of corrosion of the steel in acidic medium without coating with TAC-PEW protective film. The exponential model suggest that the rate of corrosion increases over time exponentially which may be attributed to the breakdown of particles at the surface of the steel as it becomes increasingly reactive with the medium. This can be attributed to formation of corrosion product which in-turns induced further reactions. The magnitude of the exponential model's constant (K - 68.20) showcases the initial dynamics and the acceleration rate of the corrosion process. The K of this magnitude infers very rapid initial corrosion rate which is an indication that the medium was very aggressive. The positive β constant implies that the corrosion rate declines exponentially with time, inferring that the aggressive attack slows down as time progresses. This could be attributed to the fact that corrosion product layer must have been formed on the steel surface which

will provide temporal inhibition or due to the depletion of the corrosive species within the medium. Furthermore, the inhibition efficiency of TAC-PEW coating was evaluated via the study of the inhibition kinetics.

Table 11: Kinetic models parameters and error functions

Corrosion kinetic parameters						
Linear Model	**K**		**R^2**	**SD**	**X^2**	
	1.909		**-0.96**	4.483363301	2.03215E-34	
Parabolic Rate Model	**K**					
	4.74		-0.99853	3.797642	0.00011	
Exponential Model	**K**	B				
	68.20	**0.25**	0.999855	4.590512	1	
Logarithmic Model	**K**					
	5.57		**0.7**	**5.6343**	**0.231**	
Inhibition Kinetic model Parameters						
Parameters	**a**	**B**	**c**	**R^2**	**SD**	**X^2**
Linear	**19.02**	3.53	-	0.61601	8.469693	0.420794
Exponential model	**69.59**	**-0.04**	-	0.930591	10.77312	0.916929
The logistic model	80.64	38.00	-78.66	0.8	38.80356	0.215796
Power Law Model	68.20	0.15	-	0.748767	8.891774	0.646348

The TAC-PEW inhibition data in Table 11 shows the least inhibition efficiency (IE) of 59.18% at 1hr and the highest efficiency of 86.75% at the 5th hour. This infers that TAC-PEW provides excellent inhibition against corrosion of the steel. The highly significant initial inhibition efficiency and the subsequent rapid increase in rate after the initial suggests that there was a strong interaction between steel surface and TAC-PEW producing a robust barrier against the corrosive agents. Furthermore, it was observed that the overall efficiency was consistently high, which infers that the coating can sustain its protective ability on the steel over an extended period. Slight but continuous variation or fluctuations after the initial inhibition efficiency may be attributed to either environmental factor, partial degradation of coating or surface dynamics. The inhibition efficiency data followed exponential model as well, this can be seen virtually from Fig 13, with strong correlation coefficient (R2 value) in Table 11. The exponential model constant a and b were found to be 69.59 and 0.04 respectively. The constant "a" being theoretical inhibition efficiency supports the claim of strong interaction between the TAC-PEW and the steel surface, while low "b", show the rate at which inhibition efficiency decreases over time. Hence low "b" as obtained is desirable. It shows that the strength of TAC-PEW in protecting the steel surface does not deplete rapidly.

4.0 Conclusion

This work successfully created and tested a titanium-based anti-corrosion polyethylene wax (TAC-PEW) coating made from waste LDPE water sachets. The coating displayed good corrosion inhibition efficacy in acidic environments, with a peak value of 86.7%, as validated by robust kinetic modeling in Python. The exponential decrease of corrosion rate and inhibition efficiency demonstrates TAC-PEW's long-term effectiveness in safeguarding carbon steel. This approach solves key environmental and industrial corrosion control challenges by recycling waste materials into high-performance coatings. The findings serve as a solid platform for further optimization and large-scale TAC-PEW applications in a variety of industries.

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