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Applications of Green Inhibitors of Sugarcane Bagasse and Garcinia Kola Fruit Pod for Mild Steel Natural Gas Pipeline Corrosion Inhibition in Acidic Medium

Teddy Ekimimosugha Jemine, Sylvia Igbafe, Adekunle Timisiriyu Adeniyi, Anselm Iuebego Igbafe[a]

Department of Chemical and Petroleum Engineering, Afe Babalola University, Ado-Ekiti, Ekiti State, Nigeria

[a]igbafeai@abuad.edu.ng

Abstract. *This study examined the effectiveness of sugarcane bagasse (SCB) and garcinia kola fruit pod (GKFP) extracts as green corrosion inhibitors on mild steel. Extracts of SCB and GKFP were obtained using ethanol in a solvent extraction and characterized physiochemically and phytochemically. Using central composite design (CCD) approach in design expert version 12, process variables of extract concentrations of 0.025 - 0.075 g per liter, exposure durations of 4 - 6 days and temperatures of 50 - 80 °C were varied for the evaluation of the gravimetric corrosion tests. Phytochemical analyses revealed the presence of alkaloids, flavonoids, glycosides, saponin, steroids, phenols, terpenoids, tannin and anthraquinones. FTIR analyses of the SCB and GKFP extracts indicated functional groups of phenols, hydroxyl, alcohols, carbonyl, esters, alkyl halides, aldehydes and alkenes. The best of the observed CCD findings on inhibition efficiencies were 92.11 and 90.20 % on SCB and GKFP extracts respectively with process conditions of inhibitor concentrations of 0.025 and 0.075 g/L of SCB and GKFP extracts respectively for temperature of 50 °C and exposure time 5 days. However, on overall analyses based on varying inhibitor concentrations, temperature range and duration of exposure, the optimal inhibition performance was 62.04 % with SCB and 64.35 % with GKFP. The most effective inhibitor is GKFP which yielded a higher inhibition efficiency under same operating conditions. bioactive compound acts as antioxidants in providing a reducing environment of the acidic reaction by which hydrogen ion in donated in the cause of the reaction. The investigation between the absence and presence of phytochemicals coupled with the components in both extracts from FTIR analyses revealed the significant participation of the bioactive agents of on the mild steel corrosion inhibition in acidic medium.*

Keywords: Sugarcane bagasse, Garcinia kola fruit pod, corrosion inhibitors, acidic medium mild steel

Introduction

Natural gas transported through pipelines in and out of petroleum production and process industries have always been bedeviled by corrosion. Corrosion is the degradation of metallic surfaces exposed to the certain surroundings. It brings infrastructural damages and most pipeline failures are attributed to this phenomenon. Pipelines have been the most reliable, safest, and efficient way to conveying crude oil and natural gas. Pipelines installations are mostly underground to avoid interruption with human activities [1]. Corrosion is an inevitable occurring event with a significant negative influence on high-cost processes or facilities comprising of metallic materials. This consequently makes it a problem of utmost resolution in all sectors of the oil and gas industries.

In order to control excessive corrosion rate, some approaches have been employed which include the use of inhibitors [2], [3]. Corrosion inhibitors are chemical compounds that are used to reduce the rate of corrosion on metallic materials when exposed to particular conditions, such as temperature, humidity, salinity and other acidic media. Corrosion inhibitors used especially in acidic environment range from compounds of chemical inhibition and bio-active chemical inhibition [4].

Studies have shown the need for improved inhibitors especially those of pure chemical synthesis which are relatively expensive, non-biodegradable and extremely toxic in comparison to natural inhibitors derived from agro-based materials which are safer and more environmentally friendly [5]–[8]. The use of natural or green inhibitors are more likely to provide less risks exposure to the environment, haven been synthesized from similar sources [9], [10]. GKFP extract is a pale brownish liquid which possesses antioxidant properties due to its phenolic and flavonoid content, in addition, other phytochemicals of significant value present such as tannins, saponins enhances it antibacterial properties in inhibiting their growth [11], [12]. SCB extract is pale yellowish also with added value due to their antioxidant activity as a result the presence of phenols, plant sterols and flavonoids [13]. Thus, this study was aimed at developing two green inhibitor types from SCB and GKFP extracts for the inhibition of mild steel in dilute hydrochloric acid medium. The objectives included the investigations of corrosion rate performances by gravimetric weight losses for varying temperatures, exposure or contact times and extracts concentrations as well as the examination of the bioactive ingredients of the green inhibitors from phytochemical components and functional organic groups analyses.

Theoretical Background

Corrosion is the deterioration of a metal or its alloy and consequent loss of the metal, due to direct chemical action or electrochemical reactions with its environment. It is a process which returns a metal into its natural state or a more chemically stable oxide. Metals are easily oxidized by losing electrons to oxygen and other substances in atmospheric air or in water. Similarly, oxygen atom is reduced by gaining electrons, to form an oxide with the metal. There are three theories of corrosion. These are the acid theory of corrosion, the dry or chemical theory of corrosion and wet or electrochemical theory of corrosion. The acid theory infers that corrosion of a metal is due to the presence of acids around it. On the other hand, dry corrosion is the transformation on the metal in contact with atmospheric gases such as oxygen, halogens, hydrogen sulphide, fumes of chemicals and oxides of sulphur and nitrogen and. It occurs mostly as oxidation reaction leading to oxide formation as a thin film on the metallic surface. The wet corrosion involves a reaction in aqueous or conducting electrolyte medium. It occurs when a metal comes in contact with a conducting liquid or two dissimilar metals are immersed or dipped partly in a solution which forms a kind of galvanic cell of which part of the metal surface acts as anode and the rest part as cathode. Oxidation at the anodic part takes place and results in corrosion at the anode, while reduction takes place at the cathode [14], [15].

Studies have shown the need for improved inhibitors especially those of pure chemical synthesis which are relatively expensive, non-biodegradable and extremely toxic in comparison to natural inhibitors derived from agro-based materials which are safer and more environmentally friendly [5]–[8]. The use of natural or green inhibitors are more likely to provide less risks exposure to the environment, haven been synthesized from similar sources [9], [10]. Garcinia kola (also called bitter kola) is a species of flowering plant belonging to the Mangosteen genus Garcinia of the family. It is found in West and East Africa. Its natural habitat is subtropical or tropical moist lowland forests. It is known for several medical applications. The fruit, seeds and bark of the plant have been used for centuries in folk medicine to treat ailments from coughs to fever. It grows as a shrub with diversity of organic components, including vitamins, proteins, terpenoids, sterols, flavonoids, phenols, enzymes, and amino acids. Sugarcane bagasse (SCB) is a fibrous residue remains after sugarcane juice is extracted from the plant. It is a major waste product of the sugarcane industry, and is used in energy generation when burned to generate heat and electricity for mills and others facilities [12], [13]. The existence of the kola pods of garcinia and sugarcane bagasse as an inhibitor has not been documented in literatures, especially for exposure in the acidic environment as was addressed in this paper.

GKFP extract is a pale brownish liquid which possesses antioxidant properties due to its phenolic and flavonoid content, in addition, other phytochemicals of significant value present such as tannins, saponins enhances it antibacterial properties in inhibiting their growth [11], [12]. SCB extract is pale yellowish also with added value due to their antioxidant activity as a result the presence of phenols, plant sterols and flavonoids [13]. Thus, this study was aimed at developing two green inhibitor types from SCB and GKFP extracts for the inhibition of mild steel in dilute hydrochloric acid medium. The objectives included the investigations of corrosion rate performances by gravimetric weight losses for varying temperatures, exposure or contact times and extracts concentrations as well as the examination of the bioactive ingredients of the green inhibitors from phytochemical components and functional organic groups analyses.

Materials and Methods

The materials used include GKFP collected from forest in Odigbo area and SCB obtained from sugar village at Agadagba-obon area, Ondo State, Nigeria. The reagents used in the various experiments were acetone ethanol hydrochloric acid sodium hydroxide, of all analytical grade chemicals by BDH and JHD chemicals.

Pulverized sugarcane bagasse and garcinia kola fruit pod preparation

100 grams each of SCB and GKFP, were sun dried separately for 24 hours, thereafter oven dried at 100 ^oC for 4 hours. The materials were then pounded using a mortar and pestle. The pounded materials were ground and sieved with a mesh size of 212 microns to small obtain fine particles [9].

Preparation of sugarcane bagasse and garcinia kola fruit pod extracts

10 grams each of the SCB and GKFP powder were weighed and steeped separately in 400 mL of ethanol for 72 hours in a round bottom flask throughout the extraction operation, to a mixture concentration of 0.025 g/L. Each powder mixture was filtered after the 72 hours. The filtrates were evaporated at 80^oC to concentrate the extracts by ethanol removal. With the need for effects of

varying extract concentrations, the procedure was repeated for 20 grams and 30 grams powder materials yielding 0.05 and 0.075 g/L respectively.

Characterizations of extract inhibitors

The phytochemical components of the synthesized extract inhibitors of SCB and GKFP were analyzed using standard technique described elsewhere [16]. The nature of functional groups and chemical bonds of the organics and inorganics of the synthesized extract inhibitors of SCB and GKFP were obtained by the Fourier transform infrared spectroscopy analysis, by molecular fingerprinting known standard compounds and used to screen scanned samples for the various components. It provides the type of bonding as inhibitors are adsorbed on metal surfaces.

Mild steel specimen preparation

Mild steel sheet metal of known composition was partitioned into coupons of 30 by 30 by 1.5 mm specified dimension, cleaned and polished mechanically using emery papers of grit levels between 100 and higher grades of silicon carbide to reveal the glossy, shiny surfaces. The coupons surfaces were degreased of oils and organic contaminants using absolute ethanol and dried in acetone and was store in desiccators to avoid contamination and re-oxidation. The gravimetric analyses of weight differential of the mild steel before and after corrosion were evaluated.

Mild steel corrosion test

The mild steel sample specimens were soaked in 200mL of 1M HCl (corrosive medium) in three separate vessels. In two of the vessels were each introduced 0.1M NaOH to the extracts (inhibitors) concentrates of SCB and GKFP, while the third vessel contains no NaOH. The 0.1M NaOH acts as pH modifier to the extracts in acidic solution. Each experiment was conducted on batch process over a specified conditions and duration. The central composite design in design expert version 13, was applied to three factor variables: extracts concentrations (0.025 – 0.075 g/L), metal-acid contact times (96 – 144 hr) and exposure temperatures (50 – 80^{o}C) in fifteen experimental runs to conduct batch corrosion experiments. Each experiment was conducted in the presence and absence of the inhibitors by gravimetric method to determine metal weight losses followed by the evaluation of corrosion rate (CR) and inhibition efficiency (IE) [17]

$$CR(\mathrm{mm/yr}) = 87.6\left(\frac{\Delta W}{\rho A t}\right) \tag{1}$$

$$IE\ (\%) = \left(1 - \frac{CR_i}{CR_{wi}}\right) x\ 100 \tag{2}$$

where ΔW is mild steel weight losses in mg, ρ is density of the mild steel g/cm^3, A is surface area in cm^2, t is exposure time in hr, CR_i corrosion rate with inhibitor present and CR_{wi} corrosion rate without inhibitor present.

Results and Discussion

Phytochemical analysis on both sugarcane bagasse and garcinia kola fruit pod

In **Table 1**, the qualitative and quantitative values of nine bioactive components were observed in the extracts of the SCB and the GFKP. The bioactive chemicals are all antioxidants which contribute similar functions in providing a reducing environment of the acidic reactions to take place in which hydrogen ion in donated in the cause of the reaction. The qualitative presence of the varieties of phytochemicals in both inhibitor types are indicative of a good corrosion inhibitor in line with literatures [9]–[11]. The only difference is on the quantity or amount of each observed component. The alkaloids and tannin in both extracts were dominating with triple pluses indicating high presence, while flavonoids, glycosides and saponins were moderately present and steroids, phenols, terpenoids and anthraquinones were barely present and hence were most likely of least significant effect on the mild steel corrosion rate inhibition [9]–[11]

Table 1. Qualitative and quantitative phytochemical compounds in SCB and GFKP extracts

Bioactive constituent	**SCB Observation**	**SCB (mg/L)**	**GFKP Observation**	**GFKP (mg/L)**
Alkaloids	+++	8.30±0.04	+++	8.55±0.05
Flavonoids	++	2.04±0.02	++	2.42±0.02
Glycosides	++	0.04±0.02	++	0.08±0.01
Saponins	++	5.20±0.03	++	5.33±0.02
Steroids	+	0.20±0.02	+	0.26±0.00
Phenols	+	0.63±0.01	+	0.88±0.01
Terpenoids	+	0.40±0.02	+	0.58±0.02
Tannin	+++	8.88±0.03	+++	8.28±0.05
Anthraquinones	+	1.20±0.02	+	1.42±0.02

Where +++ implies highly present,
++ implies moderately present
+ implies slightly present

FTIR analysis on both sugarcane bagasse and garcinia kola fruit pod

The FTIR spectrum analysis of *SCB and GKFP* extracts are presented in **Figures 1** and **2**. The chemical species were observed in the wavelength bands of 3499.14cm^{-1} to 622.18cm^{-1} for the SCB and 3985.1cm^{-1} to 1108.5cm^{-1} for the GKFP inhibitors respectively, by comparing the values with the standard IR data spectra. On one hand (Figure 1), the SCB inhibitor peaks wavelengths (cm^{-1}) were 3499.14; 3000.07; 2905.71; 1692.06; 1501.16; 1298.00; 1150.90; 1099.25; 900.04; 622.18 which could be attributed to functional groups comprising of OH (compounds like carbohydrates, fatty acids, proteins, lignin units, cellulose, and absorbed water), C-H (such as alkane groups and aliphatic acids), carboxyl groups in starch OH-C=O, the C-O stretching vibration is present, carbonyl C=O stretching vibration, which constitutes carbonyl and carboxylate groups in lignocellulose compounds, C–H stretching vibrations of celluloses, hemicelluloses, and lignin. Also, esters C-O stretching vibrations in the carboxyl-containing compounds lignin and phenols, alcohols to C–O bond in acids, alcohols, and phenols, carbonyl group C-O stretching vibrations and alkanes C-H bonding [18], [19].

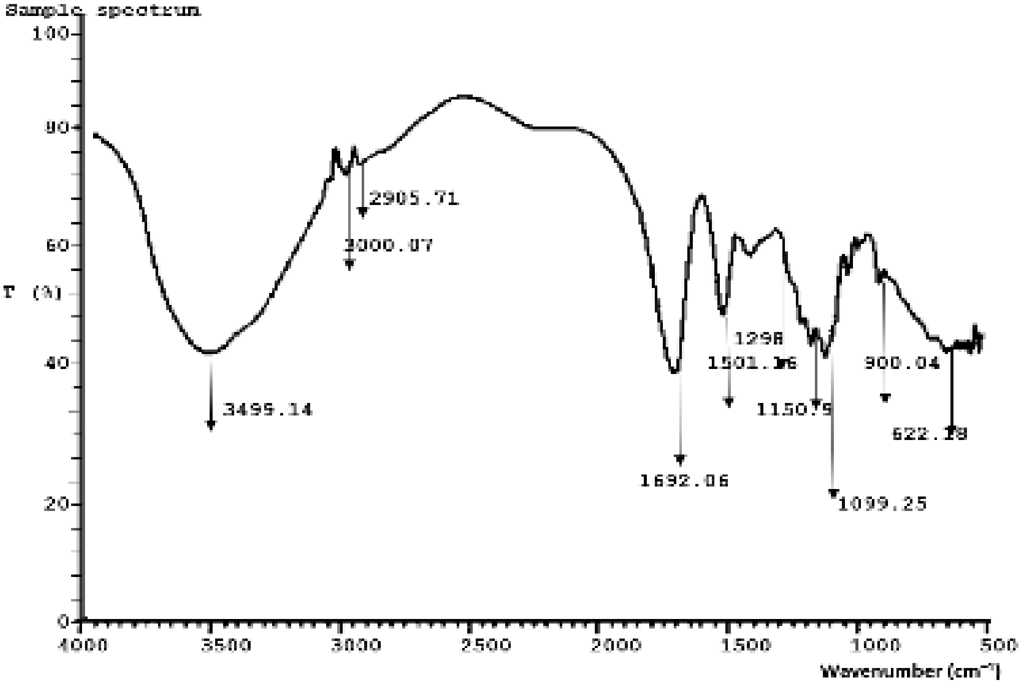


Figure 1. Sugarcane bagasse extract FTIR spectrum analysis

On the other hand (**Figure 2**), the GKFP inhibitor peaks wavelengths (cm^{-1}) were 3985.1; 3691.3; 3467.8; 3120.3; 2986.3; 1967.5; 1856.2; 1329.6; 1108.5 of compounds with functional groups comprising of OH (phenol, hydroxyl groups), C=O (aldehydes), C=C stretching (alkenes), $CH(CH_3)_2$ (alkyl groups), O=C-O-C (esters) and aromatics C-H bond. Phenol and hydroxyl groups (O–H stretching vibration of intermolecular hydrogen bonding due to the hydroxyl functional group such as in the tannoids), alkenes (C=C stretching vibrations within aliphatic and aromatic compounds), alkyl halide C-I symmetric stretching mode of vibration), esters group (O=C-O-C stretching vibration due to either ester groups), alkyls ($CH(CH_3)_2$ stretching vibration due to alkyls group), aldehyde group (C=O stretching vibration, which constitutes carbonyl and carboxylate groups in lignocellulose compounds), alkane (C–H- stretching vibrations of aromatic blend), esters (lignin and phenols, which contain carboxyl groups, exhibit C-O stretching vibrations) and inorganic nitrogen (N) (with bio-bonding) [18], [19].

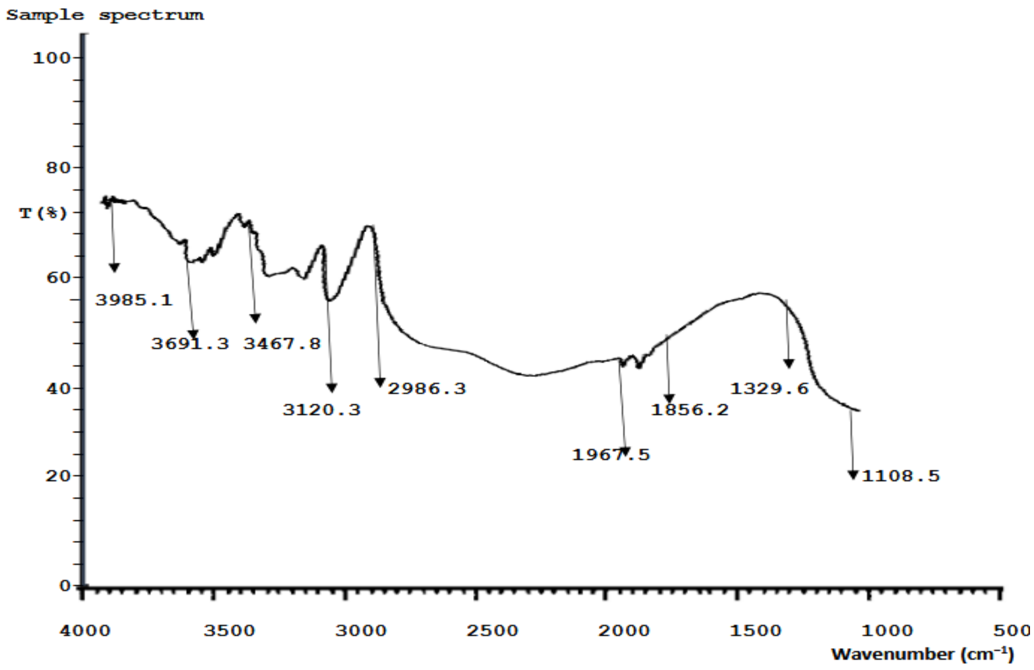


Figure 2. Garcinia kola fruit pod extract FTIR spectrum analysis

The design of experiments outcomes for the inhibition efficiencies by SCB and GFKP are summarized in **Figure 3**. Corrosion rate inhibition efficiency on mild steel were very highest at SCB inhibitor concentration of 0.025 g/L over a period of 5 days at 50 oC compared to the best observed with GKFP inhibitor concentration of 0.075 g/L at the same contact time and temperature (**Figure 4**). Consequently, higher SCB inhibitor's concentrations had little effect on the inhibition efficiency.

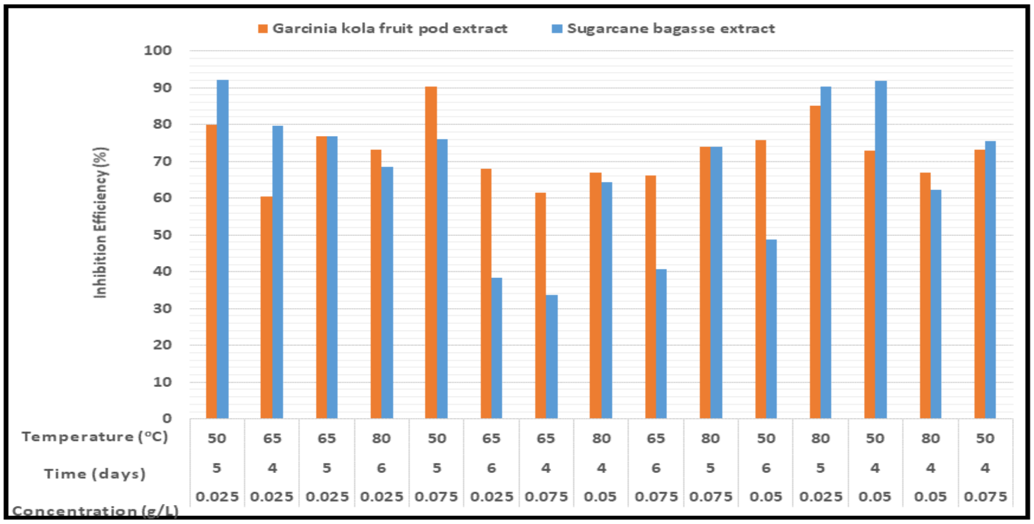
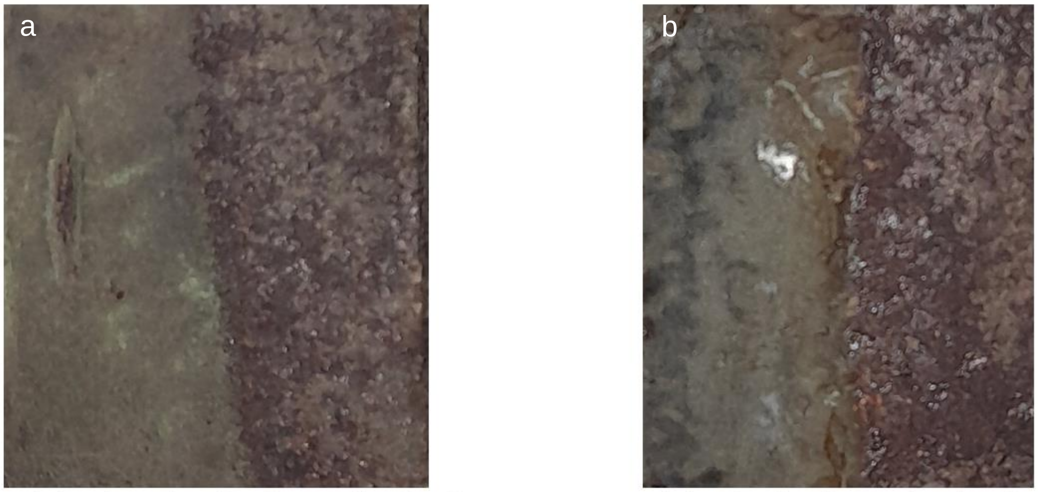


Figure 3. Optimum conditions assessment for the SCB and GFKP extracts corrosion rate inhibition by DOE outcomes on mild steel

However, these outstandingly high inhibition efficiencies of 92.11 and 90.08 % with by SCB and GFKP respectively, are strong indicators of the effect the presence of alkaloids and tannin in both extract inhibitors on the mild steel specimen. In addition, the observed compounds in SCB were OH (Hydroxyl group), C-O (Alcohol group), CH (Alkane), C-O-C (Carbonyl group) and C-H bond. Consequently, the absorption brought on by hydroxyl group confirms the present of carbohydrate and lignin, C=C stretching and C-H bond which makes the extract most likely a good corrosion inhibitor. Likewise, the compounds observed in the GKFP include OH (phenol, hydroxyl group), C=O (Aldehyde), C=C (Alkene), $CH(CH_3)_2$ (alkyls group), O=C-O-C (Esters) and Aromatic C-H bond. Their absorption brought on by hydroxyl group presence as well as C=C stretching and C-H bond makes the extract a good corrosion inhibitor.



Corroded steel sample surface @ 0.025g/L, 5 days @ 50°C (Left side: SCB inhibitor protected; Right side: Unprotected)

Corroded steel surface @ 0.025g/L, 5 days @ 50°C (Left side: GKFP inhibitor protected; Right side: Unprotected)

Figure 4. Corroded mild steel sample surfaces showing protection by (a) SCB with smooth extracts covering and (b) GFKP with rough extracts covering

Regression numerical modelling for the inhibition efficiency

Equation 3 depicts a generalized second-order regression model

$$\hat{y} = \widehat{\beta_o} + \widehat{\sum_{i=1}^{k} \beta_i}\, x_i + \widehat{\sum_{i=1}^{k} \beta_{ii}}\; x_i^2 + \sum_{i=1}^{k} \sum_{j=i}^{i=1} \widehat{\beta_{ij}}\; x_i x_j \qquad (3)$$

where x_i and x_j (development variables) and βs are the tuning parameters. In this study, the interactions have been designed to optimize the system's inhibitors concentration, contact time and temperature circumstances for the use of SCB and GKFP corrosion inhibitions.

Modelling for the inhibition efficiency of SCB extract on mild steel

The analysis of variance findings indicates that when a model's p-value is less than 0.01, it is deemed significant, therefore since the use of SCB extract inhibition efficiency gave p-value of <0.0002 the model is significant. In addition, only six out of nine components were significant with p-values less than 0.01. Model components reduction enhances the model if it has a lot of unnecessary terms. Therefore, the only significant components of this model are concentration, contact time, concentration-time interaction, time-temperature interaction, squares of time and temperature. That is A, B, AB, BC, B^2, and C^2. Thus, the numerical model with interactions among the significant varying using SCB extract inhibitor is given by equation (4). The data set were effectively fitted in a second-order generalized quadratic model with a coefficient of determination R^2 equals 0.9905.

$$IE(\%) = 66.04 - 9.33A - 9.18B - 1.66C + 11.34AB - 0.74AC + 13.47BC - 1.21A^2 \\ -16.06B^2 + 18.98C^2 \tag{4}$$

The predicted R^2 of 0.8567 is in reasonable agreement with the adjusted R^2 of 0.9733; that is the difference being less than 0.2 (**Figure 4a**). Adequate precision measures the signal to noise ratio. A ratio greater than 4 is desirable. Hence a ratio of 22.03 in this study, indicates an adequate signal with no noise interferences.

Modelling for the inhibition efficiency of GKFP extract on mild steel

The findings of the analysis of variance indicates that a model is significant when the p-value is less than 0.01, therefore, since the GKFP extract inhibition efficiency model gave p-value of <0.0001, the model is significant. In addition, only four components were significant with p-values less than 0.01. Model reduction may enhance model if it has a lot of unnecessary terms. Therefore, the only significant components are temperature, temperature-concentration interaction, squares of time and temperature. That is C, AC, B^2, and C^2. The numerical model with interactions among varying factors of temperature, concentration, and time with using GKFP as an inhibitor is given by equation (5). The data set were effectively fitted in a second-order generalized model with a coefficient of determination R^2 equals 0.9934.

$$IE(\%) = 65.61 - 32.39A + 1.59B - 12.62C - 0.91AB - 10.06AC + 0.27BC - 16.12A^2 \\ -14.11B^2 + 4.20C^2 \tag{5}$$

The predicted R^2 of 0.8938 is in reasonable agreement with the adjusted R^2 of 0.9815; that is the difference being less than 0.2 (**Figure 4b**). Adequate precision measures the signal to noise ratio. A ratio greater than 4 is desirable. Hence a ratio of 31.4 in this study, indicates an adequate signal. This model can be used to navigate the design space.

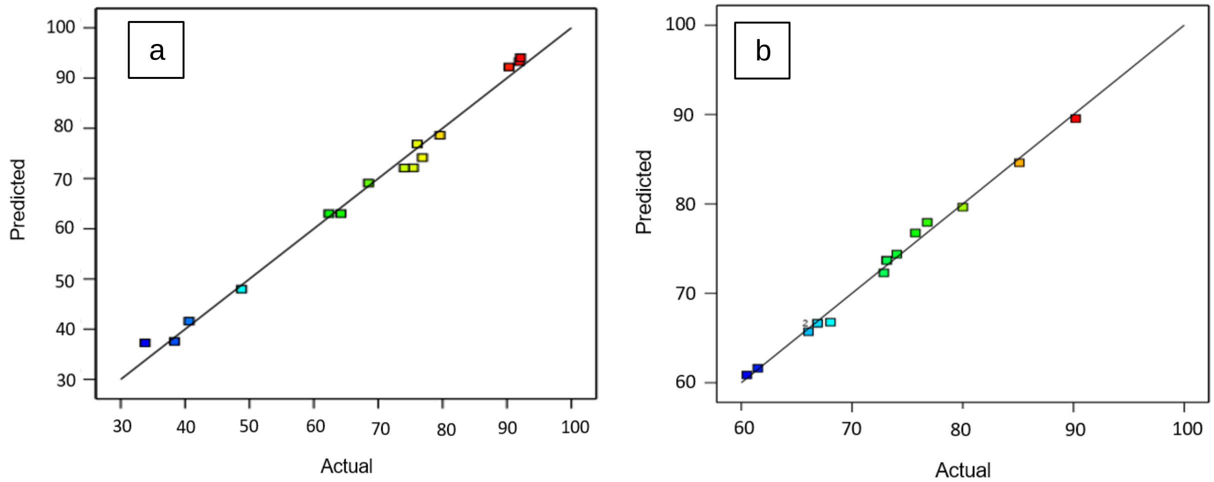
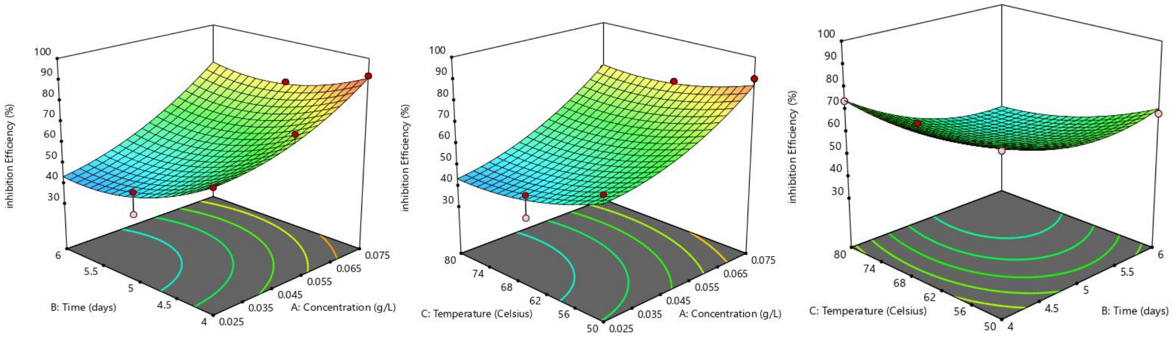


Figure 5. Predicted vs actual inhibition efficiencies on mild steel: (a) SCB extract; (b) GKFP extract

Inhibition efficiency with SCB and GKFP extracts

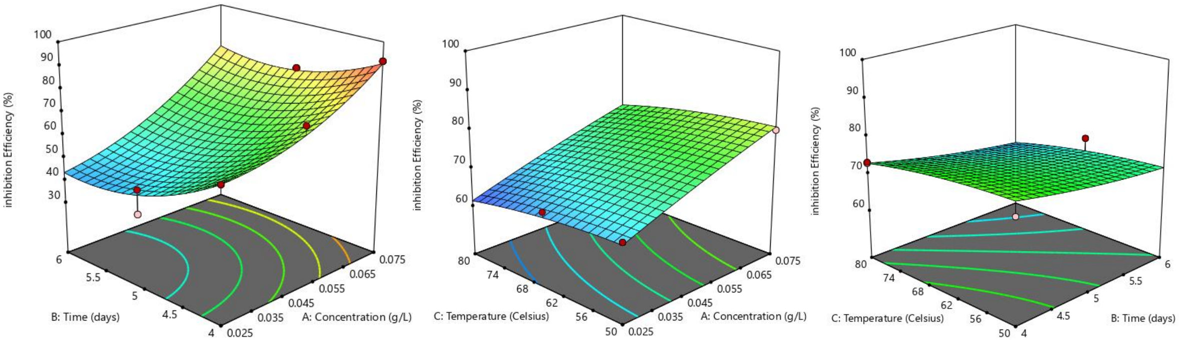
The loss in weight of the sample which is rate of metal dissolution within its area over specific time period for varying temperatures of medium were carried out. The variations of dissolution rate unprotected and protected solutions which indirectly reflect the protection performance of the inhibitors are provided in Figures 5a to c and 6a to c for the SCB and GKFP respectively, with varying inhibitor concentration and exposure temperature and time.



(a) **(b)** **(c)**

Figure 6. (a) Inhibition efficiency at constant temperature; (b) at constant contact time; (c) at constant inhibitor concentration

Inhibition efficiency varies with SCB extract concentrations and inversely with temperatures and contact times (**Figure 6a-c**). The inhibition efficiency was peak on 92.11 % on the mild steel over a 4-day period (**Figure 6a**), which is also reflect as same at 50 ^oC (**Figure 6b**). Similarly, the least value of 33.7 % was observed at over a 6-day period at 80ºC. Summarily, inhibitor concentration of SCB has less effective with increasing temperature and time. In **Figure 6c**, the effects of time and temperature reveal a direct relationship on one another and inversely related to protection efficiency. In the same fashion, inhibition efficiency varies directly with GKFP extract concentrations and in reverse with temperatures and contact times (**Figure 6a-c**). The inhibition efficiency was peaked on 90.2 % on the mild steel over a 4-day period (**Figure 6a**), and 50 ºC **(Figure 6b**). However, the minimum was at 60.5 % over a 6-day period and 80ºC. Consequently, GKFP inhibitor concentration also showed less effect with increasing temperature and time. In **Figure 6c**, the effects of time and temperature revealed an indirectly relationship with protection.



(a) **(b)** **(c)**

Figure 7. (a) Inhibition efficiency at constant temperature; (b) at constant contact time; (c) at constant inhibitor concentration

The findings signify that SCB and GKFP are potential candidates for corrosion prevention for mild steel in acidic environments implying that the chemical reaction rates were impeded in the treated solution as against the unprotected solution. The findings revealed that the dissolution rates increase with increase in temperature and contact time on both the unprotected and protected solutions systems. Another observation was that inhibition efficiency decrease with increasing temperature and contact time because increase in temperature over a time lag results in disperse separation of the heterocyclic bonds of the SCB and GKFP extract molecules spread over the surface of the mild steel consequently minimizing the surface coverage. However, this takes a different turn with increasing concentration of SCB and GKFP extract inhibitors because of their increase in bioactive constituents on the metal surfaces [9]–[11]. Inhibition efficiency was maximum at a temperature of 50ºC, period of 4 days and concentration of 0.075gL with both inhibitor types, which indicates that mild steel dissolution and protection efficiency depend on the concentration of extract, temperature and length of exposure on the metallic material.

Optimized corrosion rate and conditions on the mild steel in using SCB and GKFP

On numerical scale the optimised rate of corrosion of mild steel on dilute HCl solution, using the SCB extract at 0.05 g/L over a period of 5 days at a temperature of 65 ºC yielded a protection efficiency of 62.95% (**Figure 8a**). while using the GKFP extract at 0.05 g/L within a period of 5 days at a temperature of 65 ^{o}C yielded an inhibition efficiency of 64.35% (**Figure 8b**). This confirms that GKFP had better inhibition on corrosion with it extract compared to SCB.

(a) **(b)**

Figure 8. Optimal scale on mild corrosion using: (a) SCB inhibitor; (b) GFKP inhibitor

Conclusions

Two green inhibitors have been synthesized from agro-based wastes (SCB and GKFP) for mild steel corrosion in dilute hydrochloric acid medium. The extracts of both materials contain phytochemical bioactive constituents of alkanoids, flavonoids, glycosides, saponins, steroids, phenols, terpenoids, tannin and anthraquinones as well as aromatic molecules including carbohydrates, fatty acids, proteins, lignin, lignocellulose, cellulose, hemicelluloses, absorbed water and esters. The gravimetric weight loss test of specimen with and without inhibitor extracts confirmed the indicated involvement of the phytochemicals and organics on the inhibition of the mild steel and further analyses revealed the potentials of GKFP optimal yield of 64.35 % over that of SCB with 62.04 %. GKFP extract demonstrated a better option for corrosion inhibitor for mild steel than SCB at the same concentrations and process conditions. The GKFP extracts is thus recommended for corrosion reduction treatment on mild steel natural gas pipes prior to being laid and during maintenance operations. A numerical model for each material type was developed and statistically significant at p-values less than 0.0002 and 0.0001, with adjusted coefficient of determination of 97.33 % and 98.15 % for SCB and GKFP respectively.

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