

RESEARCH ARTICLE

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Synthesis of hydroxylated fatty amide from underutilized seed oil of *Khaya senegalensis*: a potential green inhibitor of corrosion in aluminum

Adewale Adewuyi^{1*}  and Rotimi A. Oderinde²

Abstract

Background: Corrosion is a serious problem all over the world. Most currently used approach to control corrosion have short comings which necessitates the search for novel materials that are green, cheap, from renewable source, and eco-friendly that can be used to combat this problem of corrosion control.

Method: *Khaya senegalensis* fatty hydroxylamide (KSFA) was synthesized from *K. senegalensis* seed oil via simple reaction route involving esterification, transesterification, hydroxylation, and amidation reaction. KSFA was characterized using Fourier-transform infrared (FTIR), nuclear magnetic resonance (¹HNMR), CHN elemental analyzer, particle size distribution (PSD), X-ray diffractometer, zeta potential, thermogravimetric analysis (TG), thermogravimetric-mass spectrometer (TG-MS), and scanning electron micrograph (SEM) coupled with energy dispersion spectroscopy (EDS). Inhibitory effect of KSFA on corrosion of aluminum (Al) in 0.5 M HCl was studied at different concentrations of KSFA and temperatures using weight loss method.

Result: Result from gas chromatography (GC) revealed oil of *K. senegalensis* to predominantly contain C18:1 (68.46%) fatty acid. Hydroxyl and amide functional groups present in KSFA were confirmed by FTIR and ¹HNMR. TG analysis revealed loss in mass around 80–190, 200–450, and above 450 °C while TG-MS revealed five different masses with *m/z* values 16, 17, 18, 28, and 44. Corrosion inhibition capacity of KSFA was by surface adsorption, which is spontaneous, and physisorption and described by Langmuir isotherm. The corrosion inhibition efficiency of KSFA increased with increase in its concentration while its corrosion rate reduced with increase in concentration.

Conclusion: The inhibition efficiency of 90.43% exhibited by KSFA and the fact that KSFA was synthesized via non-hazardous process from a renewable sourced biomass is an indication that KSFA is a potential green and efficient inhibitor of corrosion in aluminum. KSFA is simple to use as an inhibitor and easy to prepare.

Keywords: Adsorption, Aluminum, Corrosion inhibitors, *Khaya senegalensis*, Seed oil

Background

Corrosion of metal can be described as an electrochemical process involving the oxidation of anode coupled with a reduction reaction. During this process, metal is in contact with water or moisture in the atmosphere, and at such, the metal is the anode while the water is the electrolyte (Aylward and TJV 2002). This simply

describes what happens during the corrosion of metals. This has had several negative impacts on equipment, structures, and several appliances made of metals or containing metals. The deterioration of materials caused by corrosion is a serious concern, which has enormous economic implications. Al is an important metal that has found several domestic and industrial applications. Al is known to resist corrosion due to its low electrode potential and ability to form a protective oxide (Al₂O₃) film. Despite of its ability to form a protective oxide film, Al is still susceptible to pitting corrosion; a process

* Correspondence: walexy62@yahoo.com

¹Department of Chemical Sciences, College of Natural Sciences, Redeemer's University, Mowe, Osun state, Nigeria

Full list of author information is available at the end of the article

which is initiated in the presence of anion such as chloride which is capable of penetrating its protective oxide film (Gustafsson 2011; Li et al. 2013). The stability of the protective oxide is pH dependent and it is only stable within the pH range of about 4 to 8; the stability gets altered at pH less than 4 or at pH higher than 8. As a result, this exposes the Al to damage via corrosion. The cost of replacing Al because of corrosion is expensive (Eddy et al. 2015). Although some methods have been used in time past to control corrosion of metals, some of them still suffer from certain drawbacks such as toxicity, high cost, and efficiency (Lecante et al. 2011; Deshpande et al. 2014; Wei et al. 2015; Taghavikish et al. 2017). However, the use of biomass, which is biodegradable, non-toxic, readily available, and green as corrosion inhibitors, has the potential of circumventing this drawback.

Presently, efforts are made to develop novel materials that are green, cheap, renewable, and recyclable to meet the unprecedented demands for eco-friendly chemicals. Some of these eco-friendly chemicals may have the ability of being corrosion inhibitors and as such contributing significantly to sustainable development. The use of inhibitors is a well acceptable method for the protection of metal against corrosion, mostly in acidic media (Tawfik 2015). Most corrosion inhibitors are organic compounds containing heteroatoms (nitrogen, oxygen, and sulfur) and or π -electrons in their structures; the presence of which determines the efficiency and mechanism of operation of these inhibitors (Kokalj et al. 2010; Yadav et al. 2015). These heteroatoms and π -electrons are considered to achieve the inhibition by interacting with the metal surface which results in the formation of an inhibitive surface film (Sastri 2011), although this inhibition mechanism has not been clearly understood (Kokalj et al. 2010; Yadav et al. 2015).

Oleochemicals are chemicals obtained from plants and animals. They have found a wide range of domestic and industrial applications, which includes use as cosmetics, fuels, cleaners, lubricants, bioplastics, surfactants, and surface coatings. Oleochemicals synthesized from plant seed oil have the possibility of containing heteroatoms and or π -electrons in their structures, which presents them as potential inhibitors for corrosion control. They are possible replacements for petroleum-based chemicals, are eco-friendly, are biodegradable, and are from a renewable source. Therefore, the search for lesser-known or underutilized plant oil for oleochemical production has been of interest. *Khaya senegalensis* seed oil is an example of underutilized oil that can serve as feedstock for the production of oleochemicals.

K. senegalensis belonging to the plant family Meliaceae is probably the most distinctive of the species, which is the main source of African mahogany (Karigar et al. 2010), often planted as shade tree and sometimes for

beautification. The oil from the plant has been reportedly used as a fumigant in pest control in Asia and Africa (Bamaiyi et al. 2007). Okieimen and Eromosele (1999) reported the fatty acid content from the seed oil obtained from Eastern part of Nigeria as stearic acid (10.41%), palmitic acid (21.39%), oleic acid (64.62%), and unidentified acid (3.58%) while Karigar et al. (2010) reported the fatty acid from Indian sourced *K. senegalensis* seed oil as myristic acid (0.1%), palmitic acid (10.93%), stearic acid (7.77%), oleic acid (72.95%), and linoleic acid (7.92%). The high unsaturation of the fatty acid content of the seed oil was a pointer of π -electron system and that this oil can be modified for better production of oleochemicals, which could act as corrosion inhibitors.

In this light, the aim of this present work is to develop an Al corrosion inhibitor that is green, from a renewable source, and eco-friendly. To achieve this, we synthesized fatty hydroxylamide (an oleochemical) from the seed oil of *K. senegalensis* and also evaluated it for its corrosion inhibition capacity against Al in acidic medium.

Methods

Materials

The seeds of *K. senegalensis* were obtained from a garden in Ibadan, Oyo state, Nigeria. The seeds were air dried and ground into powder. Hydrogen peroxide, n-hexane, ethylenediamine, formic acid, sodium methoxide, and all other chemicals used were purchased from Sigma-Aldrich (Brazil). Oil was later extracted from the powdered seeds of *K. senegalensis* using n-hexane for 10 h in a soxhlet extractor.

Fatty acid composition

The oil of *K. senegalensis* was analyzed for its fatty acid composition as previously described by Adewuyi et al. (2014) with little modification. The fatty acids were determined as fatty methyl esters of the oil of *K. senegalensis*. Oil of *K. senegalensis* was refluxed at 70 °C for 3 h in 2% sulfuric acid in methanol to produce the methyl esters. Identification of the fatty acids, and their composition was carried out on a HP7820A gas chromatograph (Agilent) equipped with flame ionization detector. A SP2560 column (30 m \times 0.25 mm \times 0.20 μ m) was used for the analysis while keeping the injector and detector temperature at 250 °C and 260 °C, respectively. Oven temperature was also programmed at 120 °C with steady increase at 7 °C/min until this was finally increased to 240 °C. The carrier gas was hydrogen at a flow rate of 1.5 mL/min, and the volume of injection was 1 μ L. Data acquisition program EZChrom Elite Compact (Agilent) was used while identification of peaks was made by comparison with standards of fatty acid methyl esters C14-C22 FAME (Supelco cat no 18917).

Hydroxylated methyl esters from the seed oil of *K. senegalensis*

The seed oil of *K. senegalensis* was converted to methyl esters as previously described (Adewuyi et al. 2012) and later hydroxylated. Briefly, this was achieved by firstly esterifying the seed oil using 2% sulfuric acid in methanol at 70 °C for 2 h to convert the free fatty acid content of the oil to methyl esters. This was later transesterified using 1% KOH in methanol at 70 °C for 4 h. The product obtained was extracted with ethyl acetate, washed with distilled water until free of KOH, and passed over sodium sulfate, and ethyl acetate was removed using a rotary evaporator.

The methyl esters formed were finally hydroxylated using performic acid produced in situ (Adewuyi et al. 2013). Methyl esters of *K. senegalensis* (0.0482 mol) and formic acid (0.106 mol) were poured into a three-necked round-bottom flask; the mixture was gently cooled to a temperature of 15 °C. Hydrogen peroxide (0.407 mol) was further added dropwise to the mixture while the temperature of the mixture was later raised to 70 °C and the reaction was allowed to continue for 15 h. The mixture was cooled to room temperature, and the hydroxylated methyl esters were extracted from the product using ethyl acetate; this was washed severally with distilled water until acid free and passed over sodium sulfate. The hydroxylated methyl esters were separated from the ethyl acetate using a rotary evaporator.

Synthesis of KSFA

Fatty hydroxyl amide was produced by reacting ethylenediamine with *K. senegalensis* hydroxyl methyl esters at a molar ratio of 6:1 (ethylenediamine to hydroxy methyl esters) in the presence of sodium methoxide (2% by weight of ethylenediamine and hydroxyl methyl esters) as catalyst. This was carried out in a round-bottom flask equipped with a thermometer and stirrer. The flask and its content was placed in an oil bath at a temperature of 120 °C and stirred for 18 h. The formation of KSFA was monitored with FTIR and ¹HNMR. On completing the reaction, the product was cooled and dissolved in diethyl ether in a separating funnel. The ether phase was washed severally with distilled water and passed over sodium sulfate. The ether phase left after washing with distilled water was finally concentrated using a rotary evaporator, which gave rise to a yellow solid product. The reaction equations are shown in Scheme 1.

Characterization

FTIR

The FTIR spectra of the starting material (oil) and final product (KSFA) were recorded using FTIR (Perkin Elmer, spectrum RXI 83303). The samples were blended

with KBr, pressed into pellets, and analyzed in the range of 400–4500 cm⁻¹.

¹HNMR

¹HNMR spectra of starting material (oil) and final product (KSFA) were obtained using a 400 MHz Bruker Advance DRX 400 NMR spectrophotometer in CDCl₃ containing some amount of TMS as internal standard.

CHN elemental analysis and particle size distribution

Elemental analysis was achieved using Perkin Elmer series II CHNS/O analyzer (Perkin Elmer, 2400, USA). Zeta potential analyzer (DT1200, Dispersion technology) was used to obtain the surface potential and particle size distribution, KSFA was made into powder form and the zeta potential analyzer was operated at 25 °C.

X-ray diffraction, TG and TG-MS analysis

The structural information was obtained using X-ray diffractometer (XRD-7000X-Ray diffractometer, Shimadzu) with filtered Cu Kα radiation operated at 40 kV and 40 mA. The XRD pattern was recorded from 10 to 80 °C of 2θ/s with a scanning speed of 2.00° of 2θ/min while TG analysis was carried out on DTG-60 (Shimadzu, C30574600245) under nitrogen atmosphere. The TG-MS (NETZSCH thermobalance model STA 449 F3 coupled with mass spectrometer NETZSCH Aëolos model QMS 403C with EI and quadrupole analyzer) was carried out in an argon flux of 20 mL min⁻¹ at a temperature range of 40–1000 °C and heating rate of 5 °C min⁻¹.

SEM

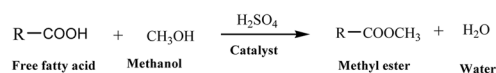
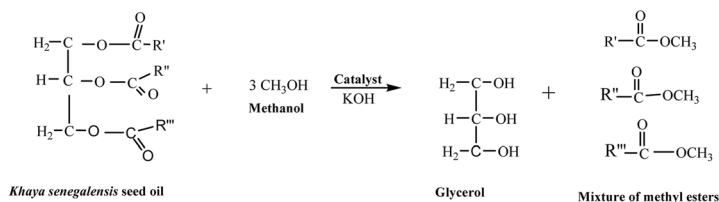
Surface morphology of samples was carried out using SEM (JEOL JSM-6360LV, Japan) coupled with EDS (Thermo Noran, 6714A-ISUS-SN, USA).

Corrosion study

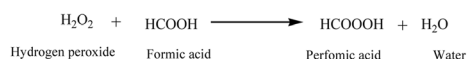
The Al sheets used in this study were 0.6 mm in thickness and were mechanically pressed cut into 3 × 3 cm coupons. Al sheets were degreased using ethanol; they were dried in acetone, and later stored before their use in corrosion studies. The corrosion process was initiated using HCl (0.5 M) while KSFA was used as the corrosion inhibitor. Concentrations of KSFA ranging from 5 × 10⁻⁵ to 1 × 10⁻³ mg/L were prepared using 0.5 M HCl as solvent to study the inhibitory capacity of KSFA during corrosion initiated by the 0.5 M HCl. The 0.5 M HCl solution was used as control while the other solutions prepared containing KSFA were used as test solution.

The corrosion taking place at the surface of the Al metal was studied using the procedure for weight loss determination of corrosion rates. Weight loss was determined by total immersion at room temperature using

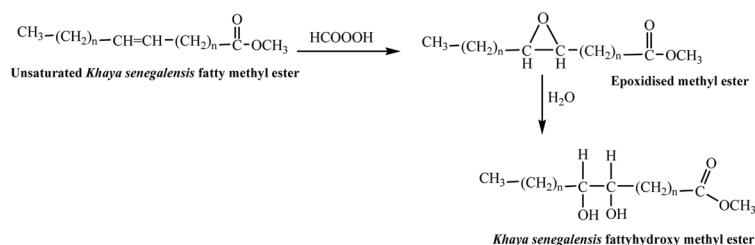
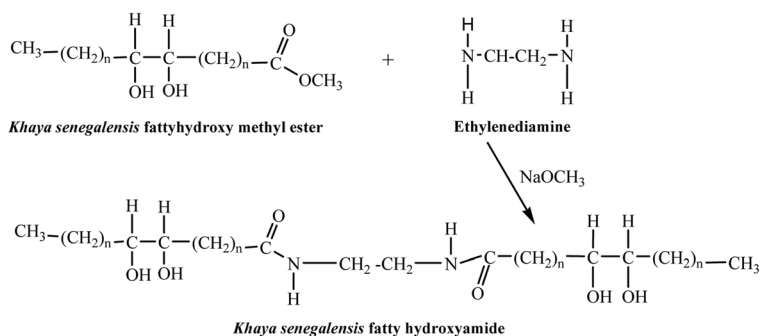
Reaction scheme

a Esterification of free fatty acid in *Khaya senegalensis* oil with 2% $\text{H}_2\text{SO}_4/\text{MeOH}$ **b** Conversion of *Khaya senegalensis* oil to methyl esters using 1% KOH/MeOH **c** Hydroxylation of *Khaya senegalensis* fatty acid methyl esters

First step: Formation of Performic acid



Second step: Hydroxylation reaction

**d** Synthesis of *Khaya senegalensis* fatty hydroxyamide

Scheme 1 Synthesis of KSFA. **a** Esterification of free fatty acid in *Khaya senegalensis* oil with 2% $\text{H}_2\text{SO}_4/\text{MeOH}$. **b** Conversion of *Khaya senegalensis* oil to methyl esters using 1% KOH/MeOH . **c** Hydroxylation of *Khaya senegalensis* fatty acid methyl esters. **d** Synthesis of *Khaya senegalensis* fatty hydroxyamide

100-mL capacity beakers containing 50 mL test solution. The Al sheets were pre-weighed, after which they were separately suspended in different beakers filled with the solution. The coupons were retrieved at 30-min intervals progressively for 72 h, washed thoroughly in deionized water, cleaned, dried in acetone, and re-weighed. The weight loss was considered as the difference in weight of the Al coupons before and after immersion in test

solutions. The tests were repeated at different temperatures (298–333 K) in order to determine the effect of temperature on rate of corrosion.

Results and discussion

Synthesis of KSFA

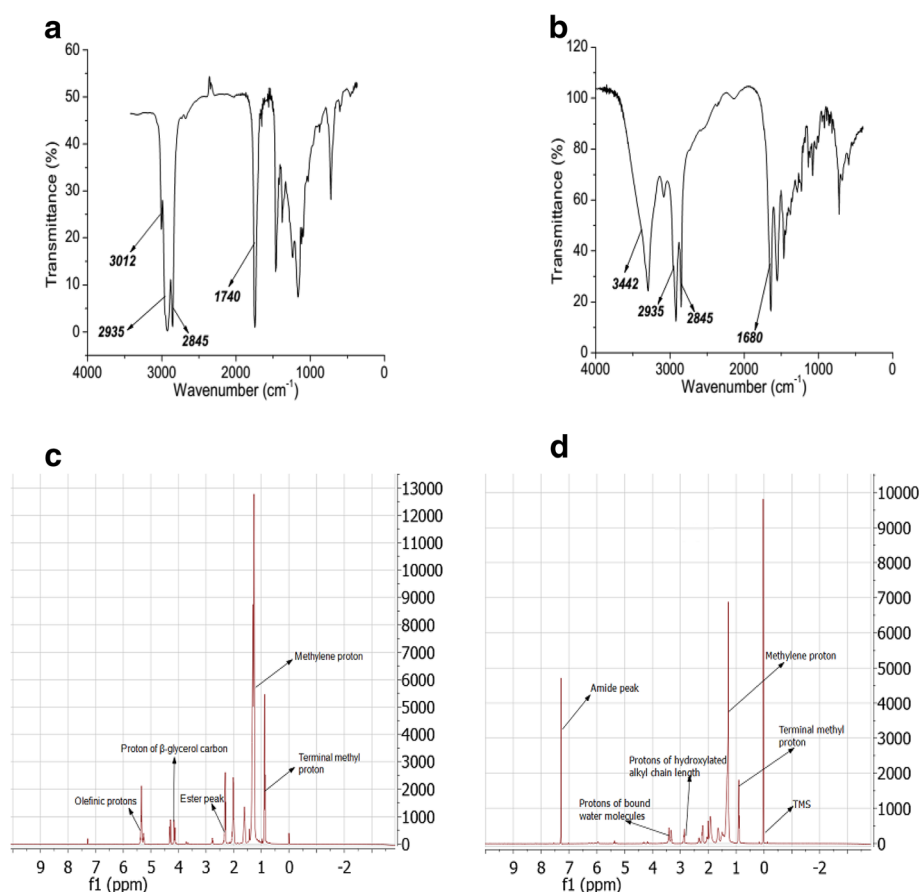
The oil yield from the seed of *K. senegalensis* was found to be 60.59%. The fatty acid composition is presented in

Table 1 Fatty acid composition of *Khaya senegalensis*

Fatty acid	Composition (%)
C16:0	8.23
C18:0	12.54
C18:1	68.46
C18:2	8.33
C18:3	0.80
C20:0	0.91
Others	0.73

Table 1. C18:1 (68.46%) was the most abundant fatty acid in the oil followed by C18:0 (12.54%). The unsaturation of the oil was 77.59%; this high unsaturation of the oil was what led to the modification and synthesis since the unsaturated bonds in the oil is one of the possible areas of carrying our modification on seed oils. The FTIR spectra of the oil of *K. senegalensis* and KSFA are shown in Fig. 1a, b. The carbonyl of ester functional group appeared at 1740 cm^{-1} in the spectrum of the oil. This ester peak disappeared in the KSFA with the appearance of a peak at around 1680 cm^{-1} which was

accounted for as being the C=O vibrational frequency of amide. The disappearance of the ester peak is an indication that amidation reaction had taken place which led to the conversion of ester functional group to amide. The peak corresponding to the C–H stretching of $\text{C}=\text{C}-\text{H}$ was found in the oil at 3012 cm^{-1} which suggests the presence of unsaturation in the oil; this unsaturation peak was not found in KSFA which may be due to the conversion of the unsaturated bonds to hydroxyl functional group with the appearance of peak at 3442 cm^{-1} which was accounted for as being the vibrational frequency of the OH functional groups in KSFA. The band at 2935 cm^{-1} and 2845 cm^{-1} were attributed to the C–H stretching of $-\text{CH}_3$ and $-\text{CH}_2$ respectively; both peaks were found in the spectra of the oil and that of KSFA. The result of the ^1H NMR is presented in Fig. 1c, d. The ^1H NMR revealed the presence of the olefinic protons in the oil at 5.3 ppm, which confirms the presence of unsaturation, which was seen in the FTIR spectrum of the oil at 3012 cm^{-1} . This peak was not found in KSFA confirming that the double bonds (unsaturation) had been hydroxylized. The proton of the C–H backbone of the β -glycerol carbon of the oil was

**Fig. 1** a FTIR of the oil of *Khaya senegalensis*. b FTIR of KSFA. c ^1H NMR of the oil of *Khaya senegalensis*. d ^1H NMR of KSFA

observed at 4.4 ppm while the ester peak appeared at 2.4 ppm. The signal at 3.3 ppm in KSFA was attributed to internally bound water molecules present in KSFA. Saturated methylene groups were found in the range 1.2–1.5 ppm while terminal methyl groups appeared at 0.8 ppm in both oil and KSFA. The peak at 2.8 ppm was assigned to the OH group of the hydroxylated alkyl chain length in KSFA while the amide peak was seen at 7.3 ppm.

The CHN analysis of the KSFA revealed carbon content to be 73.34%, hydrogen to be 14.63%, and nitrogen to be 9.04%. The particle size distribution was found to be 0.0644 μm , which was also bimodal as shown in Fig. 2a. The zeta potential is presented in Fig. 2b; the value tends to be unstable between pH 2 and 6 but increased steadily as pH value increased above 6. Figure 2c reveals the TG analysis of KSFA. The graph showed a loss in weight at around 80–190 $^{\circ}\text{C}$ which may be due to the loss of volatile molecules formed as KSFA, disintegrate on heating. This loss in weight within 80–190 $^{\circ}\text{C}$ may also be attributed to loss in internally bound water molecules in KSFA. A sharp loss in mass was also noticed within the range 200–450 $^{\circ}\text{C}$,

which may be considered as degradation of amide while loss found at above 450 $^{\circ}\text{C}$ can be attributed to loss of compounds resulting from the hydroxylated alkyl chain length (Siyanbola TO et al. 2015). The result of the TG-MS is presented in Fig. 2d, which showed the loss of five different masses with m/z values 16, 17, 18, 28, and 44. The m/z values may likely be due to the loss of oxygen ($m/z = 16$), ammonia ($m/z = 17$), water ($m/z = 18$), carbon dioxide ($m/z = 28$), and acetaldehyde ($m/z = 44$). The loss of mass of m/z 18 further corroborate the loss in mass observed at around 80–90 $^{\circ}\text{C}$ in Fig. 2c which was attributed to loss of water molecules. The XRD of KSFA is shown in Fig. 2e with a diffraction pattern similar to those of amorphous molecules. The SEM image of KSFA is also shown in Fig. 2f. The surface is homogeneous. The surface looks compact with agglomeration, which suggests an interaction among the hydroxyl group of the hydroxylated alkyl chain length, which may have resulted in inter-particle interactions causing the observed agglomeration.

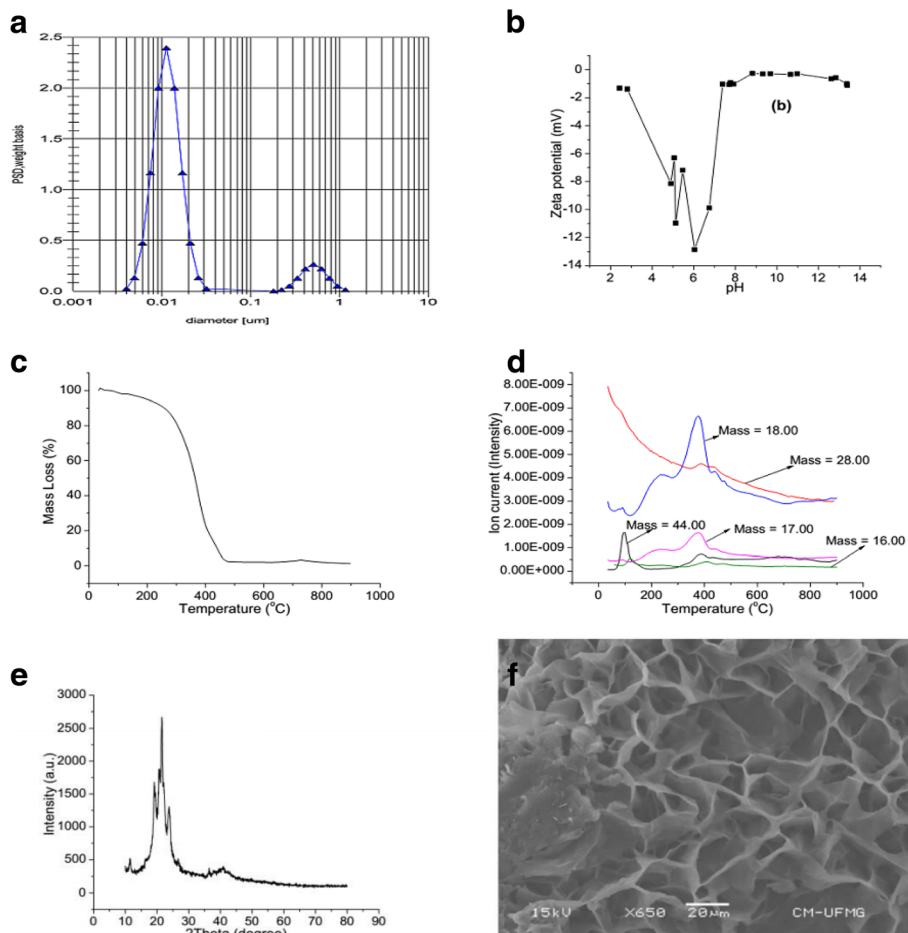


Fig. 2 a Particle size distribution of KSFA. b Zeta potential of KSFA. c TG of KSFA. d TG-MS of KSFA. e XRD of KSFA. f SEM image of KSFA

Corrosion study

Organic compounds having high basicity and electron density due to presence of heteroatoms such as oxygen, sulfur, and/or oxygen have been reported to have the tendency to resist corrosion (Dasami et al. 2015). KSFA contains both oxygen and nitrogen (Scheme 1) which are active centers for the process of adsorption on the surface of Al. The corrosion inhibition was studied by weight loss and the surface was monitored using SEM. The surface morphology of Al before and during corrosion is presented in Fig. 3. The surface of Al before the process of corrosion was seen smoother than what the surface looks like during corrosion. The surface of the pure Al sheet is presented in Fig. 3a while b and c show its corroded surface with and without the inhibitor (KSFA) respectively. The surface of the Al sheet looks homogeneous but degraded on dipping it in 0.5 M HCl with appearance of precipitates at the surface as shown in Fig. 3b, c. The introduction of KSFA in the system inhibited the corrosion process with the possibility of forming a protective inhibition layer on the surface of the Al sheet. A closer observation of the surface also showed a more dense precipitate at the uninhibited surface (Fig. 3c) than the surface inhibited with KSFA (Fig. 3b). KSFA might have probably covered the surface of Al and as a result minimizing the attack from HCl. The EDS peaks are shown in Fig. 4. This provided information on the types of elements

present at the surface of Al. The surface of the cleaned and degreased Al sheet before corrosion reveals the presence of only Al as seen in Fig. 4a while the surface of the KSFA treated and untreated Al sheet (b and c) reveals the presence of Al, oxygen, and chlorine. The oxygen peak suggests the formation of aluminum oxide/hydroxide while the chlorine peak may be due to the formation of aluminum chloride during the corrosion process because of the attack of the 0.5 M HCl that is the corrosion initiator. Carbon was found at the surface of Al treated with KSFA which suggested that this surface was covered by KSFA. From the weight loss measurement, it was observed that KSFA inhibited corrosion at the surface of Al.

Al and its alloys have the potential of forming a protective oxide film of amorphous alumina, which dissolves in acidic medium leading to corrosion of its surface. In acid solution, the cathodic reaction is the reduction of hydrogen ions to hydrogen atoms, which forms hydrogen molecules:



Under this condition the mechanism of dissolution of aluminum can be described as (Prabhu and Rao 2013):

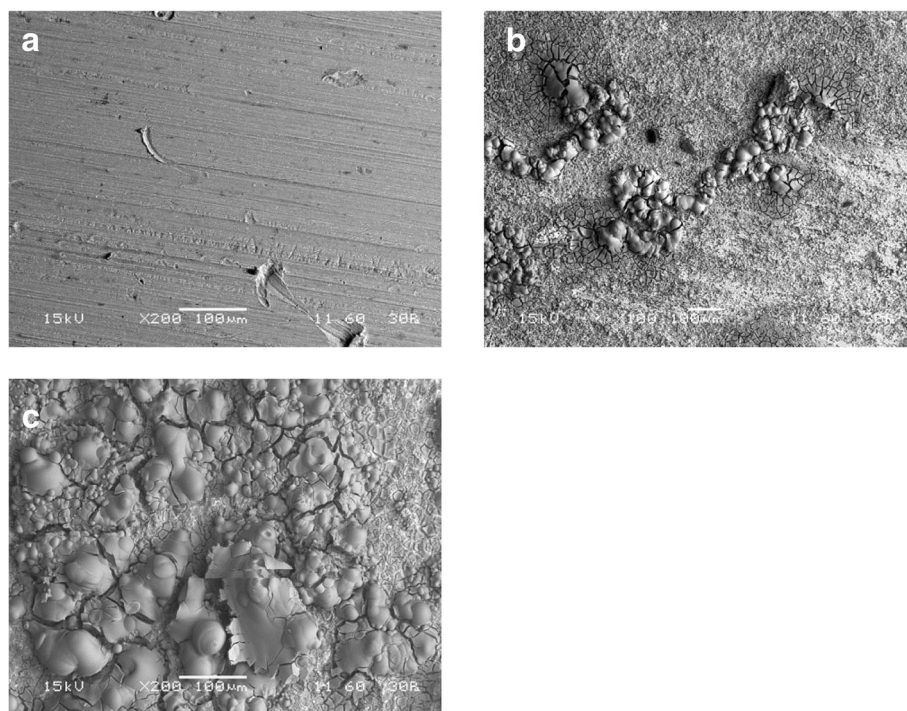


Fig. 3 SEM images of the surface of **a** Al sheet before corrosion, **b** corroded Al sheet in the presence of KSFA, and **c** corroded Al sheet in the absence of KSFA

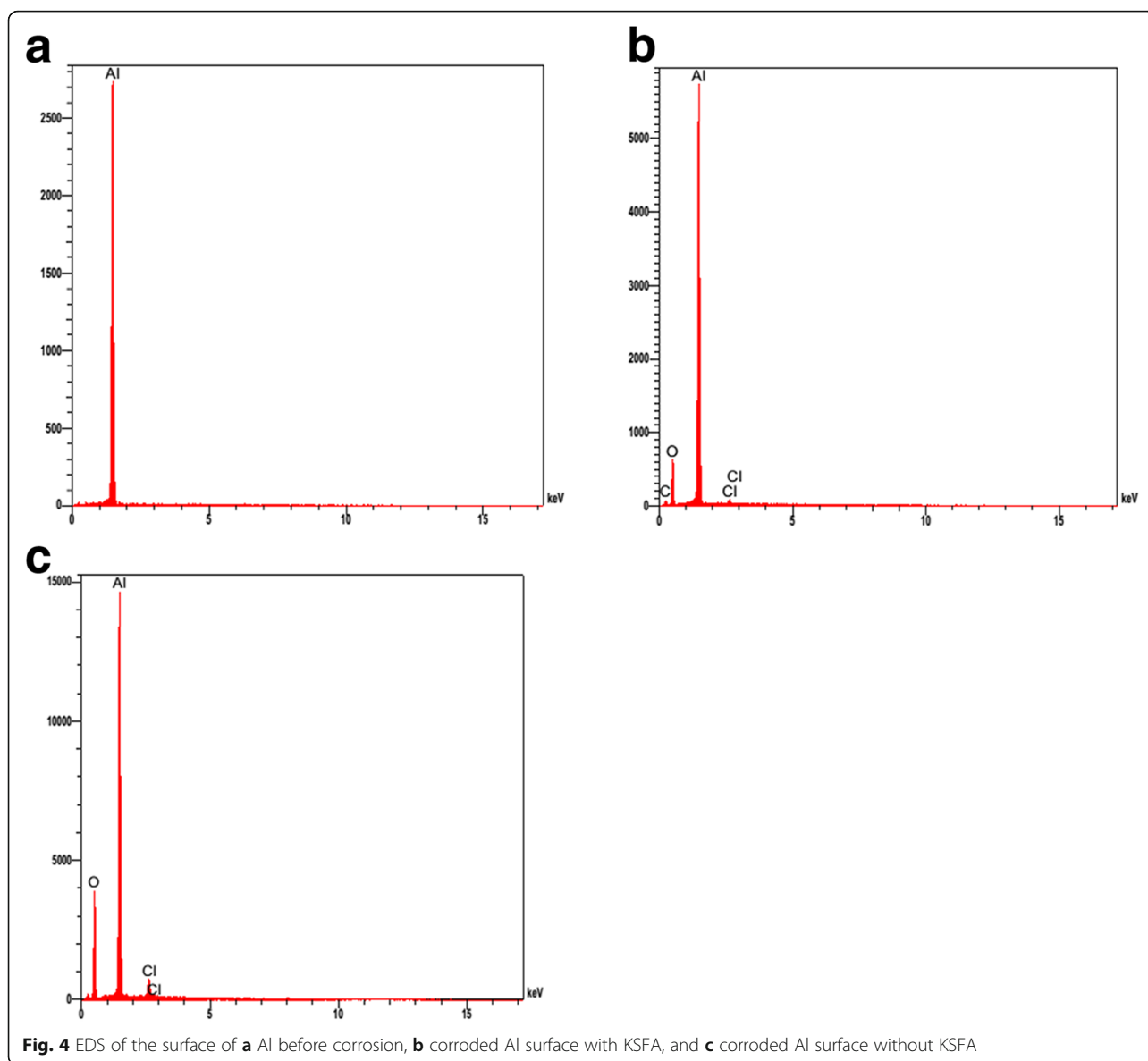
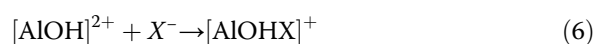
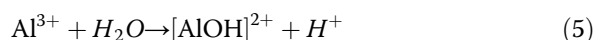
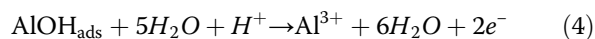
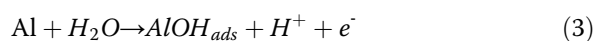
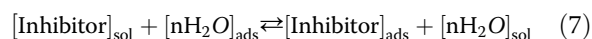


Fig. 4 EDS of the surface of **a** Al before corrosion, **b** corroded Al surface with KSFA, and **c** corroded Al surface without KSFA



The final complex ion formed leads to the dissolution of the Al metal. The dissolution process was inhibited in this study using KSFA. This inhibition can be considered to be via adsorption which may have taken place due to the electrostatic forces between the electric charges on the Al metal surface and the ionic charges or dipoles on KSFA molecules. This is often described as a displacement reaction involving the removal of adsorbed water

molecules from the metal surface (in this case Al) and replacing them with the inhibitor's molecules (Bhat and Alva 2011) as shown below:



where n is the amount of water molecules displaced by one inhibitor molecule. The charge on inhibitors depends on the presence of loosely bound electrons, lone pairs of electrons, π -electron clouds, aromatic ring systems, and functional groups containing elements of group V or VI of the periodic table (Sastri 1998). The strength of adsorption or displacement of the water molecules depends on the charge on the heteroatoms present in the inhibitor. In the case of KSFA, oxygen

and nitrogen are present in its molecule, which may have played active role in this regard.

The effect of concentration of KSFA on weight loss over a period is presented in Fig. 5a. The blank (without KSFA) had the highest weight loss over the period studied. The weight loss was also found to reduce with increase in concentration of KSFA which might be attributed to the availability of more molecules of KSFA to interact with the corroding surface of Al as concentration of KSFA increased.

Corrosion rates and inhibition

Different electrochemical and non-electrochemical techniques can be used to determine corrosion rate. Presently, we have used the gravimetric technique of weight loss to monitor the corrosion rate of Al because of the simplicity and reliability of this method (Popova et al. 2003; Obot and Obi-Egbedi 2010). Weight loss technique has been reported by several authors to compare favorably with other known techniques such polarization measurement, hydrogen evolution, thermometric technique, and electrochemical impedance spectroscopy for monitoring corrosion (El-Naggar 2007; Krishnaveni and Ravichandran 2014; Tawfik 2015; Lebrini et al. 2016). The value of the corrosion rate was determined from the equation:

$$R = \frac{\Delta W}{At} \quad (8)$$

where R ($\text{mg cm}^{-2} \text{h}^{-1}$) is the corrosion rate, ΔW is the average weight loss after immersion, A is the surface area of the Al sheet (cm^2), and t is the time (h) of immersion. The inhibition efficiency ($\%IE_w$) was calculated from the corrosion rate using equation:

$$\%IE_w = \left(R_o - \frac{R_t}{R_o} \right) \times 100 \quad (9)$$

where R_t and R_o are corrosion rates of Al sheet with and without KSFA, respectively. The corrosion rate and inhibition efficiency were calculated at different concentrations and temperatures as presented in Table 2. The inhibition efficiency increased with increase in concentration of KSFA whereas the corrosion rate reduced with increase in concentration of KSFA. Figure 5b presents the plot of corrosion rate and inhibition efficiency against temperature at concentration of 0.001 mg/L of KSFA. It was observed that the inhibition efficiency of KSFA reduced with increase in temperature while the corrosion rate increases. Similar observation has been reported in our previous study (Adewuyi et al. 2014). Variation in inhibition efficiency with change in temperature has been presented as an important parameter in determining the mechanism of adsorption of inhibitors; if the

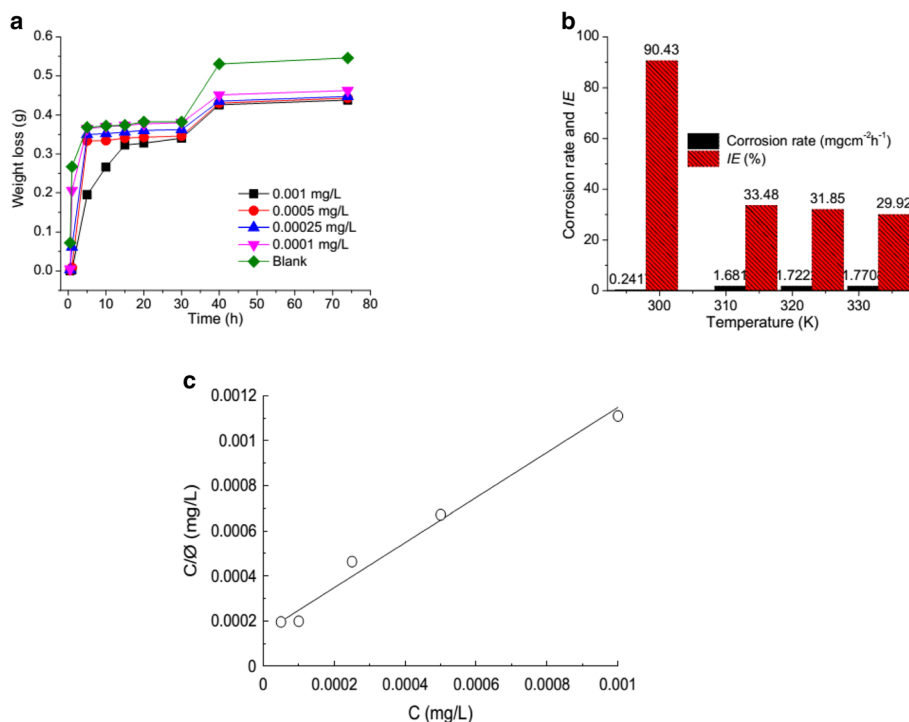


Fig. 5 **a** Plot of weight loss against time under different concentration of KSFA at 298 K, **b** plot of corrosion rate and IE against temperature at 0.001 mg/L of KSFA, and **c** Langmuir adsorption plot for Al in 0.5 M HCl containing KSFA

Table 2 Values of corrosion rate, inhibition efficiency, and surface covering at 298 K

Con (mg/L)	Corrosion rate (mg cm ⁻² h ⁻¹)	Inhibition efficiency (%/E _w)	Degree of surface covering (θ)
0.001	0.2417	90.43	0.9043
0.0005	0.6458	74.44	0.7444
0.00025	1.1657	53.87	0.5387
0.0001	1.2556	50.31	0.5031
0.00005	1.8829	25.49	0.2549
Blank	2.5269	–	–

adsorption mechanism is chemisorption, the inhibition efficiency increases with increase in temperature, but if the mechanism is physisorption, the inhibition efficiency decreases with increase in temperature (Talati and Daraji 1991; Obot and Obi-Egbedi 2010). This observation suggests the inhibition by KSFA to be through physisorption.

Adsorption isotherm

The interaction between the surface of Al and KSFA may be studied using adsorption isotherm. To achieve this, the surface coverage was derived from the expression:

$$\theta = \left(R_o - \frac{R_t}{R_o} \right) \quad (10)$$

where R_t and R_o are corrosion rates of Al with and without KSFA, respectively. The correlation between surface coverage (θ) and the amount of KSFA in the corroding medium was subjected to isotherm models in order to determine the isotherm that best describes the process. Langmuir isotherm best described the adsorption of KSFA on Al. The Langmuir adsorption isotherm was plotted using the expression:

$$\frac{C}{\theta} = \frac{1}{K_{\text{ads}}} + C \quad (11)$$

where C is KSFA concentration, θ is the surface coverage, and K_{ads} is the equilibrium constant of KSFA adsorption process. The Langmuir isotherm was based on the assumption that adsorption will only take place at specific homogenous sites within the adsorbate surface and that the adsorption process is monolayer in nature (Kaewprasit et al. 1998). The average plot of C/θ versus C gave a straight line with an r^2 value of 0.9924 as shown in Fig. 5c which suggested a monolayer adsorption of KSFA at the surface of Al. The essential characteristic of Langmuir isotherm was calculated from the equation:

$$K_R = \frac{1}{1 + K_{\text{ads}}C} \quad (12)$$

K_R is the equilibrium parameter, K_{ads} is the Langmuir constant, and C is the KSFA concentration. The parameter

K_R is a parameter, which is capable of suggesting the shape of the isotherm. This can be interpreted as presented in Table 3. The value of K_R obtained is 0.1667 ($0 < K_R < 1$) which suggested that Langmuir isotherm was favored.

K_{ads} is related to the standard free energy of adsorption, ΔG_{ads}^o with the following equation:

$$\Delta G_{\text{ads}} = -2.303RT \log(55.5K_{\text{ads}}) \quad (13)$$

where K_{ads} is the equilibrium constant of adsorption, R the gas constant, T is the absolute temperature, and the value 55.5 is the molar concentration of water solution in mol L⁻¹. The calculated ΔG_{ads}^o was -31.06 kJ mol⁻¹ at 298 K, -30.04 kJ mol⁻¹ at 313 K, -30.86 kJ mol⁻¹ at 323 K, and -31.64 kJ mol⁻¹ at 333 K. The negative value of ΔG_{ads}^o is an indication that the adsorption of KSFA on Al was spontaneous. Previously, the absolute magnitude of change in free energy for physisorption has been reported to range between -20 and 0 kJ/mol while chemisorption has a range of value more negative than -40 kJ/mol (Behpour et al. 2008). In this study, the value lies in a range between -20 kJ/mol and -40 kJ/mol; hence, there may be the possibility of both physisorption and chemisorption taking place at the same time. Ansari et al. (2015) have reported similar observation in their study on Isatin derivatives as corrosion inhibitors. Yadav et al. (2015) also gave similar accounting indicating the possibility of both physisorption and chemisorption taking place at the same time from their research on acetohydrazide derivatives in acidic medium. However, sorption type may not be solely established based on the value of ΔG_{ads}^o other parameters needed to be considered (Tourabi et al. 2013); this includes the fact that physisorption has been established to precede chemisorption (Wang et al. 2008).

The enthalpy (ΔH_{ads}^o) and entropy (ΔS_{ads}^o) were obtained using equation:

$$\Delta G_{\text{ads}}^o = \Delta H_{\text{ads}}^o - T\Delta S_{\text{ads}}^o \quad (14)$$

From the above equation, ΔG_{ads}^o is the standard free energy of adsorption, T is the temperature for the adsorption process, ΔH_{ads}^o is the enthalpy of the process, and ΔS_{ads}^o is the entropy of adsorption process. The values of ΔH_{ads}^o and ΔS_{ads}^o were calculated from the slope ($\Delta H_{\text{ads}}^o/R$) and intercept ($\Delta S_{\text{ads}}^o/R - \ln 55.5$) of van't Hoff plots by plotting the values of $\ln K$ against $1/T$.

Table 3 Interpretation of K_R parameter

Values of K_R	Type of isotherm
$K_R > 1$	Unfavorable
$K_R = 1$	Linear
$0 < K_R < 1$	Favorable
$K_R = 0$	Irreversible

The $\Delta H_{\text{ads}}^{\circ}$ was calculated to be $25.853 \text{ kJ mol}^{-1}$, which is an indication that the adsorption process was endothermic. Previous studies have shown that $\Delta H_{\text{ads}}^{\circ}$ lower than $41.86 \text{ kJ mol}^{-1}$ indicates physisorption while $\Delta H_{\text{ads}}^{\circ}$ approaching 100 kJ mol^{-1} indicates chemisorption (Popova et al. 2003; Tareq et al. 2013). The present value of $\Delta H_{\text{ads}}^{\circ}$ suggests the adsorption of KSFA on Al to be through physisorption. ΔS° was found to be $969.135 \text{ J mol}^{-1} \text{ K}^{-1}$; this positive value of ΔS° is an indication of the degree of randomness at the Al/KSFA interface during the adsorption process.

Kinetic parameters

The presence of organic inhibitors can affect corrosion rate either by decreasing available reaction sites or by modifying the activation energy of the anodic or cathodic reactions occurring at the surface of the metal (Eddy et al. 2015). The mechanism of corrosion inhibitors can be explained using thermodynamic parameter and kinetic model. This mechanism is reported to depend on type of inhibitor, composition of metal and corrodent, structure of inhibitor, concentration, and temperature of inhibitor (Oguzie 2008). In order to calculate the activation parameters for the adsorption of KSFA on Al, the Arrhenius equation was used:

$$\log \frac{\rho_2}{\rho_1} = \frac{E_a}{2.303R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right) \quad (15)$$

where ρ_2 and ρ_1 are the corrosion rates at temperature T_1 (298 K) and T_2 (333 K), E_a is the activation energy, and R is the molar gas constant. The heat of adsorption (Q_{ads}) was also calculated as follows [26]:

$$Q_{\text{ads}} = 2.303R \left[\log \left(\frac{\theta_2}{1-\theta_2} \right) - \log \left(\frac{\theta_1}{1-\theta_1} \right) \right] \left(\frac{T_1 \times T_2}{T_2 - T_1} \right) \quad (16)$$

where θ_1 and θ_2 represents degree of surface coverage at 298 K (T_1) and 333 K (T_2) respectively.

E_a is very important during chemical reactions; it is the energy barrier that must be overcome during chemical reaction. For corrosion to be successful, Al is expected to have an appreciable amount of molecules with energy equal to or greater than the E_a . The E_a for the corrosion process was calculated and presented in Table 4. It was obvious that the E_a required for the process increased as the concentration of KSFA increased. This observation may be due to the ability of KSFA to have raised the E_a as its concentration increased and as a result slowing down corrosion process since a high-energy barrier is required for the process to be successful. The observed increase in E_a may also be accounted for as being due to a decrease in the active surface area on Al available for corrosion since KSFA may have been adsorbed on the surface; hence, high energy barrier will have to be overcome for

Table 4 E_a and Q_{ads} for corrosion of Al in 0.5 M HCl in the presence and absence of KSFA

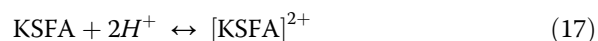
Con (mg/L)	E_a (kJ mol ⁻¹)	Q_{ads} (kJ mol ⁻¹)
	298–333 K	298–333 K
0.001	46.952	-73.018
0.0005	28.628	-51.559
0.00025	19.757	-39.664
0.0001	18.779	-37.664
0.00005	14.016	-30.917
Blank	5.352	-

corrosion to take place. Chami et al. (2015) recently reported a similar increase in E_a with increase in concentration in their work on ester-quarts surfactant. The heat of adsorption was also found to reduce with increase in concentration. The reduction in Q_{ads} with increase in concentration of KSFA is an indication of a good interaction between KSFA and surface of Al. With reduction in Q_{ads} , adsorption of KSFA is favored and with an increase in E_a , corrosion process is inhibited or slowed down.

Mechanism of KSFA as a corrosion inhibitor

The ability of KSFA to act as a corrosion inhibitor may be attributed to the presence of hydroxyl and amide functional groups in its molecule. This inhibition process can be considered as being physisorption. This process requires an electrically charged Al surface and charged species of KSFA in solution. In this system, Al may be present with vacant low-energy electron orbital while KSFA may exist in solution with relatively loosely bound electrons which can be described as hydroxyl group (oxygen as heteroatom)/amide group (nitrogen and oxygen as heteroatoms) lone pair electrons. These functional groups may adsorb at the surface of Al with three different possibilities: (a) Both the hydroxyl and amide group may be adsorbed on the Al surface site, (b) either the hydroxyl or amide group may be adsorbed on the Al surface site, while the other group is free in solution phase, and (c) both (a) and (b) may co-exist.

Nitrogen is a good donor of electron, which is easily protonated. So, in acidic medium (HCl), KSFA may be protonated which predominantly affects the nitrogen atom. In such case, KSFA might exist as a cation in equilibrium state (Yadav et al. 2015):



In Eq. 6 above, the X^- may be considered the chloride ions (Cl^-) from the corrosion initiator (HCl); this was also found on the surface of Al being corroded as shown in Fig. 4b, c. In this medium, KSFA cations ($[\text{KSFA}]^{2+}$) are driven towards the Cl^- ions by electrostatic interactions

and as a result reducing the attack of Cl^{-1} ions on Al which further reduces the dissolution of Al and hence corrosion is inhibited. Since the Al is capable of existing in the + 3 state in the medium, there is the possibility of electron transfer from the heteroatoms in KSFA molecules. As a result, there can be an electronic interaction between the surface of Al and the highest occupied molecular orbital of KSFA leading to the adsorption of KSFA on Al; similar observation has been reported in previous works (Quraishi and Sardar 2004; Obot and Obi-Egbedi 2010). In addition to this, the hydroxyl group in KSFA can readily form complex with trivalent aluminum in order for KSFA to adsorb at the surface of Al. In all, KSFA restricted the diffusion of ions to and/or from the surface of Al and thus inhibited the overall corrosion process.

Conclusion

KSFA has been synthesized from underutilized seed oil of *K. senegalensis* using simple reaction route. KSFA inhibited corrosion process on Al in 0.5 M HCl with an inhibition efficiency of 90.43% at 0.001 mg/L concentration. The corrosion inhibition of KSFA was by surface adsorption, which is spontaneous, and physisorption and described by Langmuir isotherm. The presence of heteroatoms in the molecules of KSFA was considered as the important features that determine the adsorption capacity exhibited by KSFA on Al.

Acknowledgements

The research work was supported by TWAS/CNPq. The authors are most grateful to TWAS/CNPq for awarding a postdoctoral fellowship at Universidade Federal de Minas Gerais, Minas Gerais, Brazil. Authors are grateful to the Department of Chemistry, Universidade Federal de Minas Gerais, Minas Gerais, Brazil, for research space and chemicals.

Funding

The present work was funded by TWAS-CNPq.

Availability of data and materials

Data sharing is not applicable to this article as no datasets were generated or analyzed during the current study.

Authors' contributions

Authors have done a team work to carry out this study. AA and RAO carried out experimental studies. AA and RAO wrote the manuscript. All authors read and approved the final manuscript.

Competing interests

The authors declare that they have no competing interests.

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Author details

¹Department of Chemical Sciences, College of Natural Sciences, Redeemer's University, Mowe, Osun state, Nigeria. ²Industrial Unit, Department of Chemistry, University of Ibadan, Ibadan, Nigeria.

Received: 28 August 2018 Accepted: 6 November 2018

Published online: 16 November 2018

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