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A Green Approach to the Corrosion Inhibition Effect of Waste Extract on Copper in an Alkaline Environment

O. Sanni, S.A. Iwarere, M.O. Daramola*

Sustainable Energy & Environment Research Group (SEERG), Department of Chemical Engineering, Faculty of Engineering, Built Environment & Information Technology, University of Pretoria, Hatfield, 0028, Pretoria, South Africa.

*Corresponding author: michael.daramola@up.ac.za

Abstract. Waste extract was examined to inhibit copper corrosion in 0.5 M KOH (alkaline) solutions. The inhibitory action of the waste extract was investigated using potentiodynamic polarization and gravimetric methods. The result indicated that the extract prevented the copper corrosion in the tested environment, achieving 90.68% effectiveness. The polarization test indicates that the extract is a mixed-type corrosion inhibitor, capable of inhibiting both cathodic and anodic processes in the Cu/KOH system. The inhibitory effect was due to the waste extract sticking to the copper surface, which formed a barrier that prevented harmful ions from reaching the metal. The molecules extracted adsorb on the surface of the metal following Langmuir adsorption model, denoting the extract forms a monolayer protective film on the copper surface. Consequently, the waste extract can effectively prevent copper from corroding in an alkaline environment.

Keywords: Corrosion inhibitor, Plant extract, Copper, Adsorption, Tafel

1. Introduction

One of the most significant economic sectors in the world is agriculture. Each year, this sector spends billions of dollars. Numerous industries make use of agricultural waste. Anticorrosion properties of natural plant extract from agricultural wastes have been investigated [1-5]. This is due to the fact that the plant extract is cheap and has little to no impact on the ecosystems. Potassium hydroxide (KOH), a corrosive chemical utilized in some industrial processes, is to either manage the corrosion it generates or use its extremely alkaline nature for specialized metal treatment applications. In both acidic and alkaline solutions, copper can corrode, especially when oxidants like oxygen and chlorides are present. One of the most common methods of reducing the metallic substrates corrosion is the application of corrosion inhibitor [5]. The most common of the edible leaf class, known as "greens," which also includes turnip tops, mustard, dandelion, and beets, is spinach (Spinacia oleracea). In order to have growth during the coolest periods of the season, spinach is produced as a crop in both the early spring and late autumn. When spinach is cultivated in warm temperatures, it becomes rough and fibrous and loses its typical flavour, becoming harsh and unpleasant. The fact that spinach is highly perishable and frequently discarded as waste is unfortunate, even though it has substantial nutritional and economic value. The potential for utilizing spinach as a valuable resource remains largely unexplored, which calls for more research.

Researchers have recently investigated the biological and physical characteristics of spinach, including its antibacterial, antioxidant, and anti-obesity [6] qualities as well as its capacity for ion adsorption. Furthermore, a number of research have looked into their uses in different sectors [7]. Despite these developments, not much research has been published on spinach's potential applications in corrosion prevention, materials protection, and industrial water treatment. Corrosion inhibitors made from natural plants are more economical, eco-friendly, and green than chemically synthesized corrosion inhibitors. Remarkably, plant extract served as the basis for the first corrosion inhibitor patent [8]. The leaves, roots, stems, and wastes of different plants have been used to make a number of natural corrosion inhibitors that have been researched thus far. Eddy et al. [9] reviewed plant wastes as an alternative source of environmentally friendly and sustainable corrosion inhibitors. The author also noted that plant extracts are effective corrosion inhibitors because they contain phytochemicals with atoms having potential adsorption tendencies, such as P, O, N, and S atoms, as well as conjugated, aromatic, and π-electron systems. The choice of spinach leaf is justified by its anti-oxidant properties. Spinach leaf belongs to the amaranth family. One vegetable that is incredibly nutrient-rich is spinach. In addition to having high levels of carotenoids, vitamin C, vitamin K, folic acid, iron, and calcium, it also has potassium, magnesium, and the vitamins B6, B9, and E. Spinach may lower blood pressure, prevent cancer, improve eye health, and lessen oxidative stress. Having been successfully used for different purpose, considering spinach leaf extract for corrosion control as anti-corrosion agent is important. Motivated by these findings, we carried out a preliminary investigation into the preparation of spinach aqueous extract and assessed its ability to suppress the corrosion of copper in a 0.5 M KOH solution. The novelty lies in the first-time use of spinach leaf extracts for copper as a green corrosion inhibitor in 0.5 M KOH (alkaline) media, supported by experimental approach to confirm its efficiency and adsorption mechanism. The use of spinach extract is both sustainable and economically feasible because the main raw material for preparation is just the spinach leaf that is discarded as waste.

2. Experimental section

2.1. Metal specimen and spinach leave extract preparation

For the gravimetric and surface inspection investigations, a copper electrode measuring 2 x 2 x 0.2 cm and composed of 99% pure copper was utilized. As recommended by ASTM G1-03 (Standard Practice for Preparing, Cleaning, and Evaluating Corrosion Test Specimens), the metal specimen was polished, cleaned with distilled water, degreased with acetone, and allowed to air dry before each experiment. After being diluted with distilled water, the electrolyte 0.5 M KOH was prepared and standardized. The copper electrode surfaces were carefully polished using clean sandpaper with a mesh size of 400, 800, 1200, and 2000 before conducting electrochemical testing. After cleaning the copper electrodes' surface with demonized water, they were ultrasonically cleaned with anhydrous ethanol to get rid of any remaining copper chips and sandpaper particles, and they were then allowed to air dry. This will improve the spinach molecules' ability to be adsorbed on the electrodes. Epoxy glue was used to encapsulate the remaining region, leaving a 1 cm^2 contact area exposed to the aggressive media. It was then stored for further research in a desiccator. The spinach leaves was collected from Gauteng, South Africa, cleaned, dried, and extracted following [10]. Separately, the extract was diluted in KOH solution to concentrations of 100, 200, 300, 400, and 500 ppm.

2.2. Weight loss measurements

250 mL of the aggressive solutions, 0.5 M KOH, without and with varying SLE concentration, was used to suspend the pre-weighed mirror-polished copper rods. The inhibition efficiency and corrosion rate was computed from the weight loss as follows [5]. The same gravimetric method was used for 500 ppm of SLE at temperatures of 303, 313, and 323 ± 1 K to examine the temperature effect on SLE effectiveness.

2.3. Electrochemical measurement

The conventional three-electrode method was employed in the electrochemical test. A saturated silver/silver chloride electrode was chosen as the reference electrode, while a platinum rod served as the auxiliary electrode. With 1 mV/s potential sweep rate, the OCP (open circuit potential) polarization range of the electrochemical Tafel curve spans the potential range of -250 mV to +250 mV. Additionally, the copper electrodes are allowed to reach the steady-state potential prior to conducting any tests. In order to ensure reproducibility, every experiment was conducted at least twice. The anodic and cathodic Tafel curves' slopes, βa and βc, respectively, as well as the corrosion potentials, Ecorr, and corrosion currents, Icorr were recorded.

2.4. Surface investigation studies

To investigate the nature of the developed films on the surface of the electrode, the exposed sample to blank electrolytes 0.5 M KOH and electrolyte containing optimal concentration of SLE were studied. Scanning electron microscopy (SEM) was used to examine the surface morphologies of the metal coupons that were unprotected and those that were protected by SLE. The SEM images were captured at a 10 kV accelerating voltage.

3. Results and discussion

3.1. Mechanism of metal weight loss

The weight loss method was used to investigate the spontaneous copper dissolution exposed to 0.5 M KOH with 0, 100, 200, 300, 400, and 500 ppm SLE at 303 ± 1 K. Table 1 displays the rates of corrosion and the associated inhibition efficiencies. Analyzing the results showed that as the concentration of SLE increased, the rate of metal corrosion steadily decreased and efficiency increased. The transfer of SLE component from the bulk electrolytes to the surface of the copper, where it was adsorbed as thin layer that protected the metal surface from the harsh environments, was the reason for the corrosion reduction. A higher amount of SLE components covering a bigger portion of the metal surface was responsible for the increased efficiency at 500 ppm.

The electrode surface active sites unblocked at the electrode/KOH interface are where corrosion happens; these sites might be inhibited by the adsorption of SLE components; SLE showed 90.68% efficiency for copper in KOH solution, this could be attributed to the active components such as alpha-lipoic acid, phenolic compounds, and carotenoids present in the spinach leaf. These findings demonstrated that the nature of the KOH anions and the degree of protonation had an impact on the metal corrosion process. Since the maximum corrosion inhibition efficiency was recorded at 303 ± 1 K, weight loss test was performed at 303–323 ± 1 K to examine temperature impact on the corrosion inhibition effectiveness with 500 ppm SLE, Figure 1 presents the findings. The data unequivocally shows that SLE had corrosion-mitigating impact across the whole temperature range, albeit its effectiveness declined as the temperature rose. These findings demonstrate the temperature-dependent corrosion protection capability of SLE as well as the increased reactivity of the aggressive corrosion medium's active components. Desorption of the deposited SLE from the electrode surface may also contribute to the efficiency drop, indicating physical adsorption mechanisms. The current SLE exhibits superior/comparable inhibition performance to numerous other inhibitors, such as the following: Myrrh (82.8%) [11], Strychnos nux-vomica seed extract (98.2%), Mucuna pruriens seed extract (69.2%), Piper longum seed extract (80.4%) [12], Thymus satureioides (87%) [13], and Santolina chamaecyparissus extracts (86.9%) [14].

Table 1: Corrosion rates and inhibition efficiency at different SLE concentrations for copper in 0.5 M KOH media.

Inhibitor concentration (ppm)	**Corrosion rate (mm/year)**	**Degree of surface coverage (θ)**	**Inhibition efficiency (IE%)**
Blank	70.89	-	-
100	26.44	0.6271	62.71
200	11.92	0.8319	83.19
300	10.29	0.8549	85.49
400	9.51	0.8659	86.59
500	6.61	0.9068	90.68

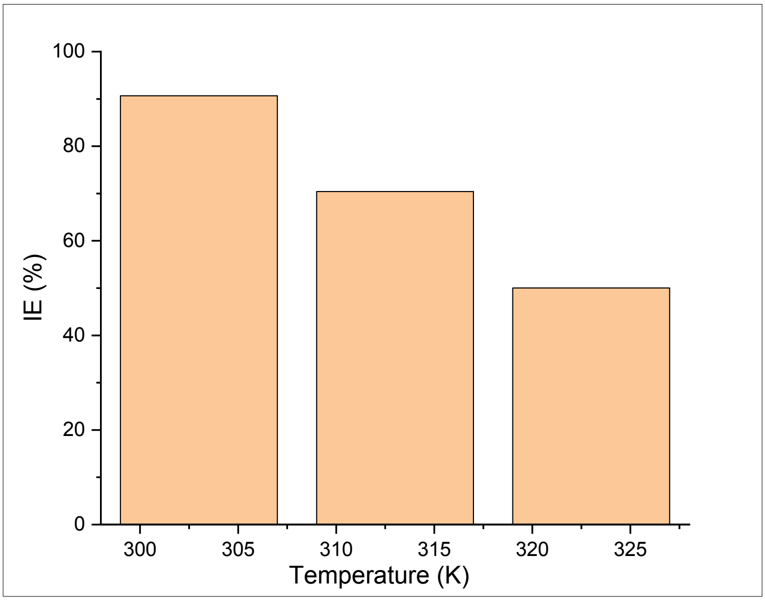


Fig. 1. Temperature effect on the corrosion inhibition efficiency in 0.5 M KOH solutions.

3.2. Activation and thermodynamic parameter

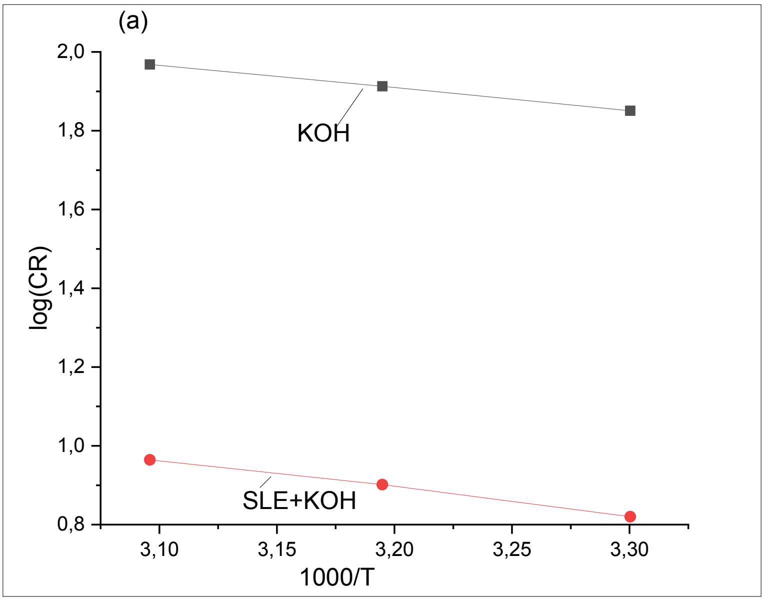
The Arrhenius and Eyring transition state equations, equations 1 and 2 [15], was applied in order to obtain a better understanding of the metal dissolution thermodynamics in SLE-containing KOH and inhibitor-free electrolytes:

$$Cr = Ae^{\left(\frac{-Ea}{RT}\right)} \tag{1}$$

$$Cr = \frac{RT}{Nh}\exp\left(\frac{\Delta S^*}{R}\right)\exp\left(\frac{-\Delta H^*}{RT}\right) \tag{2}$$

where h is Planck's constant, A is a pre-exponential factor, R is the gas constant, Ea is the apparent activation energy of the corrosion process, N is the Avogadro number, ΔH* and ΔS* stand for the apparent enthalpy of activation, and apparent entropy of activation respectively.

The slopes of the linear plots of log (Cr) vs 1/T were used to determine the value of Ea for the corrosion process (Figure 2a). For copper, the Ea values for the 0.5 M KOH containing SLE were greater than those for the inhibitor-free electrolytes. The SLE adsorption on the surface of the electrode causes a rise in the energy barrier, which indicates a shift in the corrosion process. The intercept (log (R/Nh) + (ΔS*/2.303R)) and slope (-ΔH*/2.303R) of the linear plot transition states of log (Cr/T) vs 1/T (Figure 2b) were used to calculate ΔH* and ΔS*. The increased dissolution metal rate at hig temperature is the reason why ΔH* value is positive for SLE-containing and blank 0.5 M KOH solutions. The SLE-inhibited solutions had more positive ΔH* values. This confirms the barrier film formation from the inhibitor molecule and shows that additional heat energy was needed for the metals dissolving process. In SLE-free electrolytes, negative ΔS* value indicate that water molecule was adsorbed uniformly onto the surface of the metal; in contrast to their SLE-free counterparts, the solutions inhibited exhibit less negative ΔS* value, reflecting the disorder caused by the presence of distinct bonding interaction modes between the SLE molecules and the metal surface.



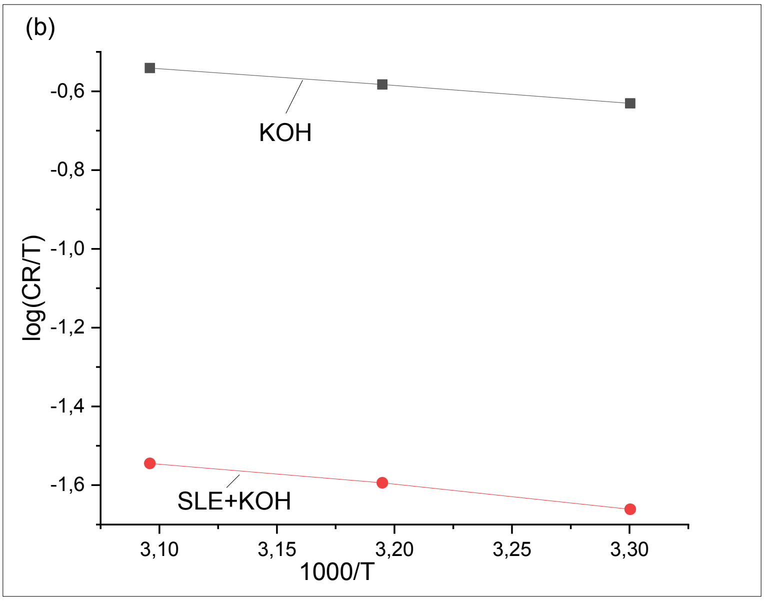


Fig. 2. (a) Arrhenius plot (b) transition state plot for copper corrosion in 0.5 M KOH solution in the absence and presence of SLE.

3.3 Adsorption Isotherms

It is assumed generally that adsorption of inhibitor on the surface of metals is crucial in the inhibition mechanisms. To estimate the surface coverage, it was assumed that inhibitor efficiency is primarily due to the blocking effects of the adsorbed species, the surface coverage value from weight loss tests was theoretically fitted into different adsorption isotherm, to gain insight into the extract adsorption mode on the surface of the copper. Weight loss data was utilized to estimate surface coverage value (θ) for the adsorption of varying SLE concentration on the surface of the copper. When the SLE is added, the corrosion inhibitor molecules give the cuprous ions a single pair of electrons and create an adsorption film with them. This prevents copper from corroding further, and the adsorption mechanism follows equation 3:

$$Cu^{+}{}_{ads} + ninh \rightarrow \left[Cuinhn\right]_{ads}^{+} \tag{3}$$

To determine the most appropriate adsorption isotherm on the copper surface for SLE adsorption, a variety of adsorption isotherms were graphically examined. The Langmuir model (R^2 = 0.9972), which assumes perfect monolayer adsorption without intermolecular interactions, was determined to be the closest fit. As observed from this study, the deviation of the slope from unity could be ascribed to the interaction between adsorbate species on the surface of the copper and adsorption heat changes with increase in surface coverage. It also corresponds with experimental evidence. It was discovered that a monolayer on the copper electrode absorbed the SLE. The Langmuir isotherm (Equation 4) gave the best linear fit (Figure 3) for copper in the electrolyte (KOH) solution among the several adsorption isotherms evaluated.

$$\frac{C}{\theta}=\frac{1}{K}+C \tag{4}$$

Where C denotes SLE concentrations and K is the adsorption equilibrium constant. The graph of C/θ vs C, which yields straight lines with almost unit slope for SLE with 1/K intercept, is shown in Figure 4. Equation 5 describes the link between standard adsorption free energy (G°ads) and the adsorption equilibrium constants (K):

$$K=\frac{1}{1000}e^{\left\langle -\frac{\Delta G^{0}{}_{ads}}{RT}\right\rangle} \tag{5}$$

Where T is the absolute temperature, R is the gas constant, and the H_2O concentration is 1000 g/L. For SLE adsorption on the surface of copper in 0.5 M KOH solution, the equilibrium constant is 24.18 and the free energy of adsorption is -25.467 $kJ.mol^{-1}$. The extract adsorbs on the copper surface spontaneously, as indicated by the negative value of ΔG°ads. ΔG°ads at -20 kJ mol^{-1} or greater is typically used to describe the electrostatic interaction (physisorption) between the charged metal and the charged particles. In negative ones larger than 40 kJ mol^{-1}, inhibitor molecules share or transfer their charges to the surface of the metal to form coordinate bonds (chemisorption). The ΔG°ads values calculated is close to -20 kJ mol^{-1}, suggesting that physisorption may represent the SLE adsorption mechanisms on copper in 0.5M KOH solutions. Since the numerical value of ΔGads is more than -20 kJ/mol, the active molecules are adsorbed on the metal substrate by electrostatic adsorption. When ΔGads is smaller than -40 kJ/mol, chemical adsorption via chemical bonding is taken into consideration. Furthermore, it is thought to have a hybrid effect of chemical and physical adsorption if the ΔGads value falls in the middle. Furthermore, it was found that the adsorption behaviour of the SLE was accomplished by a complementary strategy of physisorption and chemisorption; the values of ΔGads vary from -20 to -40 kJ/mol at different temperatures.

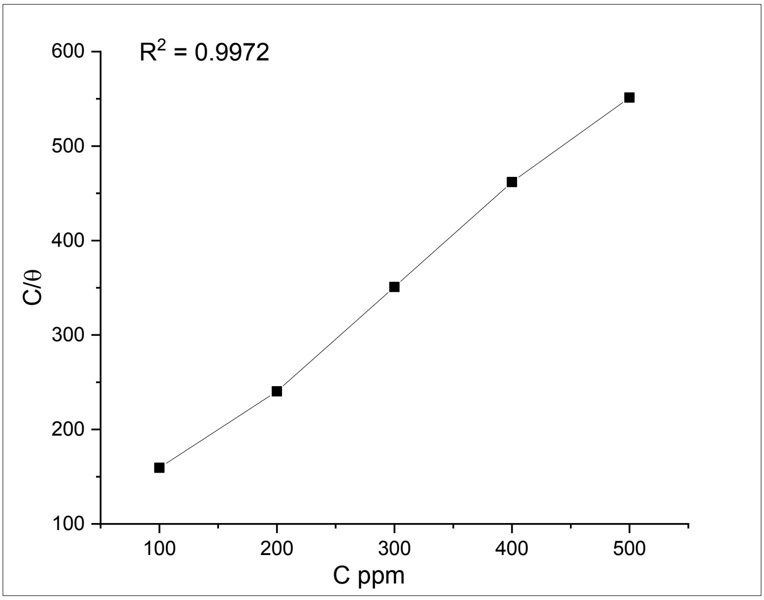


Fig. 3. Langmuir adsorption isotherms for dissolution of copper in KOH solution with different SLE concentration

3.4 Tafel Polarization Curves

The copper Tafel polarization curves working electrodes in a 0.5 M KOH solutions with diverse SLE concentration are displayed in Figure 4. The corrosion potential (Ecorr) of copper swings from -0.220V to -0.195V when the SLE concentration in the corrosive solution increases, however the corrosion current density (icorr) in the Tafel zone noticeably drops in comparison to the blank solution. Table 2 illustrates, the polarization resistance (Rp) rises and the corrosion potential (Ecorr) turns favorably when the SLE concentration in 0.5 M KOH increases. The corrosion inhibition efficiency continuously improves as a result of the significant fall in the corrosion current density (icorr) that occurs concurrently. These findings show that the corrosion inhibition efficiency improves with increasing SLE dosage. Icorr drops to 683μA/cm^2 with a 500 ppm SLE dosage, compared to 69μA/cm^2 for the blank, yielding 89.89% corrosion inhibition efficiency. The chemical composition of SLE, which may include organic acids, phenols, and flavonoids, is responsible for this behavior. The oxygen atoms in these components' carboxyl (−COOH) and hydroxyl (−OH) groups have lone pairs of electrons and strong electronegativity. By forming coordination connections with the metal surface's unoccupied d-orbitals, these lone pairs can prevent corrosion by creating a protective layer.

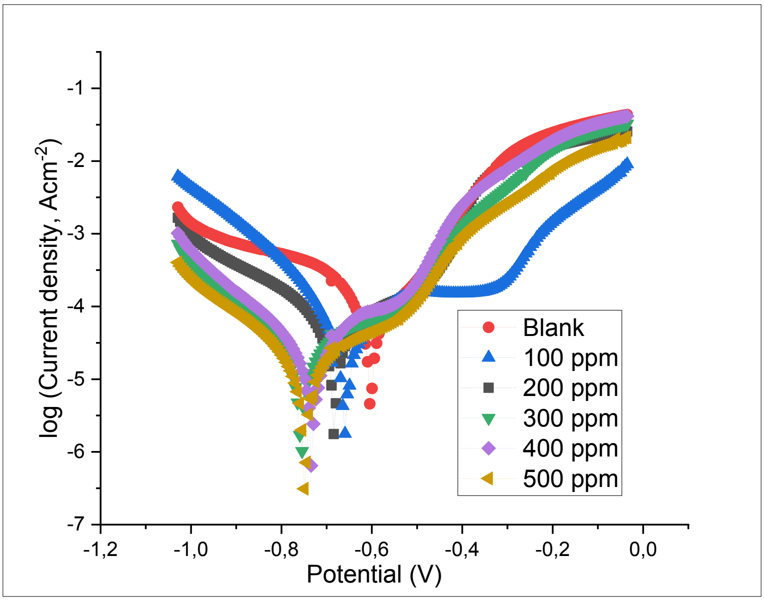


Fig. 4. Copper Tafel plots in 1 M KOH solutions with the absence and presence of SLE

Table 2. Potentiodynamic polarization data for copper at various SLE concentrations at 303 ± 1 K.

SLE Concentration (ppm)	βc (V/dec)	βa (V/dec)	Ecorr (V)	Rp (Ω)	Icorr ($\mu A/cm^2$)
Blank	0,251	0,124	-0.220	99	683
100	0,257	0,118	-0.192	171	299
200	0,232	0,108	-0.195	235	217
300	0,163	0,083	-0.191	278	168
400	0,181	0,103	-0.195	314	131
500	0,222	0,089	-0.195	350	69

3.5 Morphology Studies

The surface morphologies provide a reliable indicator of the degree of corrosion attack. Figure 5 shows the copper SEM result in both free and 500 ppm SLE after inundation in the aggressive solutions. According to SEM result, the morphology of copper in the aggressive solution only showed that the surface of the sample was severely distorted and that copper oxides and corrosion products covered the majority of the specimen surface (Figure 5a). The surface of the copper specimen appears smooth and less damaged in the absence of KOH solution-containing SLE. After polishing, some scratches are visible, indicating obstructions in the electric charge transfer by creating the SLE's adsorption film, which prevents the copper from corroding. These results demonstrate that SLE molecules attach to copper surface and creates protective layer that blocks harmful ions effectively from destructing the surface.

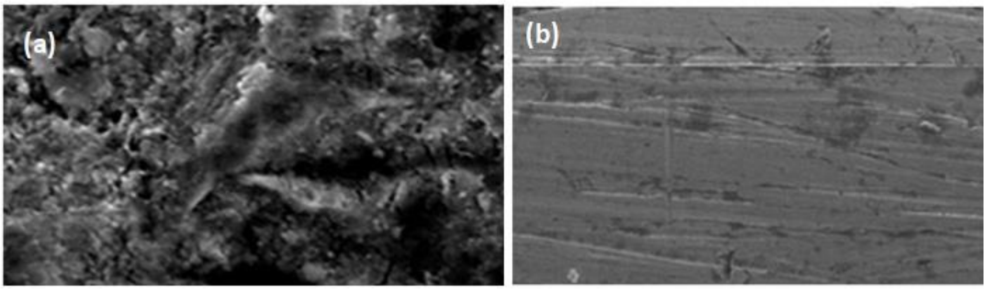


Fig. 5. SEM of copper in 0.5 M KOH solution without (a) with 500 ppm SLE (b)

3.6. Proposed mechanism of inhibition

The inhibitor's adsorption mechanism onto the surface of the metal, which is dependent on a number of variable such as; the metal, the corrosive medium's nature, the inhibitor's molecular size, its electronic structure, the adsorption centres, and more, is typically what determines the process of corrosion inhibition. Analyzing the results showed that as the concentration of SLE increased, the rate of metal corrosion steadily decreased and efficiency increased. The transfer of SLE component from the bulk electrolytes onto the surface of the copper, where it was adsorbed as thin films that protected the surface of the metal from the corrosive solution, was the cause of the corrosion reduction. A higher amount of SLE components covering a bigger portion of the metal surface was responsible for the increased efficiency at 500 ppm. The unobstructed active sits on the electrodes surface at the electrodes/KOH interface are where corrosion happens; these sites may be inhibited by the SLE components' adsorption.

It can be inferred from the electrochemical and weight loss investigations that SLE's ability to mitigate corrosion resulted from its adsorption at the electrolyte/electrode interface. According to earlier studies, there are three possible mechanisms for inhibitor adsorption on electrode surfaces: chemical adsorption, physisorption, or complex mix of the two. The active components of SLE in the current investigation were either cationic species (protonated SLE) or neutral molecules in KOH solution. The adsorption of SLE cationic component took place through electrostatic interaction between SLE cationic specie and anion adsorbed on the surface of the metal, whereas the neutral SLE component was adsorbed through donor-acceptor interaction amid the heteroatoms' free electron pair and the π electron. Particularly, low-hydration ions were adsorbed onto the electrode surface in KOH. Because of the net negative charges this produced at the electrolyte-electrode interface, cationic inhibitor components were strongly adsorbed, increasing efficiency. The polarization data clearly show mixed mode inhibition of SLE.

4. Conclusion

- SLE's corrosion efficiency decreased with temperature but rose with concentration. By blocking the active site through SLE adsorption on the copper surface, hence, copper corrosion was reduced. With 500 ppm of SLE at 303K, the results of weight loss show inhibition efficiency of 90.68%.
- The inhibitory behaviour is based on the adsorption of spinach extract on the surface of copper, which creates a charge and mass transfer barrier that shields the surface of the copper from harmful ion. Additionally, the fitting of the isothermal adsorption model demonstrated that the SLE's adsorption behaviour was spontaneous and consistent with Langmuir's monolayer adsorption theory.
- The polarization approach demonstrated the extract's mixed-mode inhibitory behaviour; thermodynamic and activation data verified that the corrosion protection effectiveness of SLE is dependent on temperature. There was good concordance between the electrochemical analysis and weight loss results.

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