Novel Green Corrosion Inhibitor for Mild Steel Protection in an Alkaline Environment

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Abstract
This paper investigated *Corchorus olitorius* leaves extract efficiency in preventing MS corrosion, when immersed in a KOH solution. This will be the first report on the application of this plant extract in an alkaline medium of any kind, for mitigating metals corrosion. Pc analysis was employed along with PDP and FITR spectroscopy. Pc compounds, such as steroids, saponins, flavonoids, tannins, alkaloids and phenols, were found in the extract, which produced maximum IE(%) of 99.93%. Highest CR of $5.644e^{+003}$ mm/year was obtained, while theoretical fittings of various adsorption models for the extract found that it obeyed Langmuir's isotherm. K_{ads} was 0.9729 g/L, with R^2 of 0.9616. ΔG°_{ads} calculated at room temperature was -9.882 kJ/mol. As a result, COLE adsorption onto the MS surface was found to follow physical adsorption mechanism.

***Keywords*:** COLE; inhibition; isotherm model; MS; Pcs; PDP.

Introduction•

MS selection for diverse industrial applications is due to its excellent mechanical properties, affordability and high availability [1-2]. Steel containers can be used to handle acid, salted and alkali solutions. KOH, Na_2CO_3, NaCl, NaOH and $Ca(OH)_2$, are some of the corrosive chemicals utilized in industries. Corrosion is a natural phenomenon that is primarily observed in industrial settings, due to its effect on metallic structures and chemical components. Industry risks equipment failure if corrosion-contaminated products are not handled [3]. In terms of product leakage, rehabilitation, replacement and environmental contamination, corrosion has financial repercussions [4]. Therefore, controlling corrosion is essential in terms of ecology, economy and practice [5]. Prior to plating, painting or storing, chemicals are typically sprayed to metal surfaces, as part of the final finishing steps [6]. Scales, dirt and minor rust can be removed from metal surfaces using chemicals [7]. Inhibitors are frequently added to process fluids in many industrial activities to

• The abbreviations and symbols definition lists are in page 19.

reduce metal CR. CI are chemicals that, when applied to corrosive media, at very low concentrations, reduce metals reactivity with their surroundings. By adhering to the metal surface, an inhibitor can lower CR. CI have been the subject of numerous scientific studies [10]. Nevertheless, most of what is understood has been found through trial and error research in labs and on the field. There are insufficient principles, formulas or hypotheses to direct the creation or application of CI [11].
Although most inorganic inhibitors have good corrosion-inhibiting properties, they are dangerous, as they can permanently harm human's organs such as kidneys or liver, or can interfere with the body's enzyme system. Therefore, plants are increasingly viewed as sources of green CI, due to environmental considerations. They replace hazardous chemicals in shielding metals and alloys from hostile conditions [8-9]. The effective use of plant extracts as corrosion protection for metals in a variety of acidic environments has received some academic attention [12]. They have been studied with the aim to modify corrosive conditions where metals are in service. Existing green CI contains Pc such as flavonoids, saponins and tannins. These organic compounds are designed to reduce and prevent corrosion by adhering to the steel surface. Additionally, plants are unquestionably accessible, affordable, and constitute renewable resources [13-14]. The main outcomes obtained with the use of plant extracts as inhibitors for MS protection in different alkaline environments are summarized in Table 1.

Table 1: List of plant sources used in investigations of CI on MS in non-acidic media.

Extract	Corrosive medium	Maximum IE(%)	Adsorption isotherm	Ref.
Allium sativum	NaCl	92	-	[11]
Pentaclethra macrophylla bentham	KOH	84.02	Langmuir´s	[15]
Psidium guajava	NaOH	89.0	Langmuir´s	[16]
Beta vulgaris	Simul. oil well water	94	-	[17]
Agri-food wastes	NaCl	98.0	-	[18]
Thymus vulgar	NaCl	80.49	Temkin	[19]
Arecanut husk	NaOH/HCl	94. 347	Langmuir´s	[20]
Pterocarpus soyauxii taub	Na_2CO_3	70.05	Langmuir´s	[21]
Azadirachta indica	$Ca(OH)_2$ + NaCl	86	-	[22]
Olea europaea	NaOH + NaCl	91.9	-	[23]
Seaweed	Saline form. water	93.64	Temkin's	[24]

[25-26] have successfully used CO plant stems as CI on MS in H_2SO_4, and the results demonstrated their feasibility and efficacy in inhibiting corrosion in selected environments, with high IE(%) of 93 and 94.34%, respectively. However, despite the impressive IE(%) of CO stems, there has been no investigation on their leaves for the same purpose, in an alkaline environment. Therefore, this paper examines COLE effectiveness in mitigating MS corrosion in KOH. This will be the first report on the application of this plant extract in an alkaline medium. Pc study and techniques, such as PDP and FTIR, were used to characterize MS, and to test IE(%) of COLE.

Experimental work

Materials

MS composition was 0.15% C, 0.36% P, 0.03% Si, 0.6% Mn, and the remainder Fe. MS coupons were cut into dimensions of 2 × 2 × 0.2 cm, with a 0.05 cm hole drilled in the center. They were degreased and polished with emery paper, to expose them for corrosion attacks.

COLE procurement and preparation

Fresh CO leaves were bought from Abakaliki international market, Nigeria. They were dried for six days, under hot sun, to remove moisture content. Thereafter, they were ground to fine powder and filtered, to obtained fine particles. The obtained raw fine powder was then stored in a container. The resulting filtrate was utilized as CI in its purest form. Ct of 1, 1.5, 2, 2.5 and 3 g/L COLE were used in 1.5 M KOH test solutions.

Qualitative analysis of Pc

By looking for secondary metabolites, such as steroids, saponins, alkaloids, flavonoids, tannins, phenols and terpenes, qualitative analysis was done to determine the presence of these Pc on the powdered CO leaves, according to the method of [27].

PDP test

PDP method was also carried out in accordance with instructions given in [28], where a 3-electrode cell was employed for the analysis, with SCE, graphite and MS coupon as reference, counter and working electrodes, respectively. Table 3 shows the results.

FTIR analysis

FTIR spectrophotometer was employed to perform analyses on MS coupons immersed in KOH without and with COLE, to observe its residue absorbed onto the alloy surfaces.

Results and discussion

Pc analysis of COLE

Results for Pc analysis of COLE are shown in Table 2.

Table 2: Pc analysis of COLE.

Pc	Results
Steroids	++
Saponins	++
Flavonoids	++
Tannins	++
Alkaloids	+
Phenols	+
Terpenes	++

Fairly present +, heavily present ++

CI calculation using PDP method

I_{corr}(%) determination was done by PDP (Fig. 1).

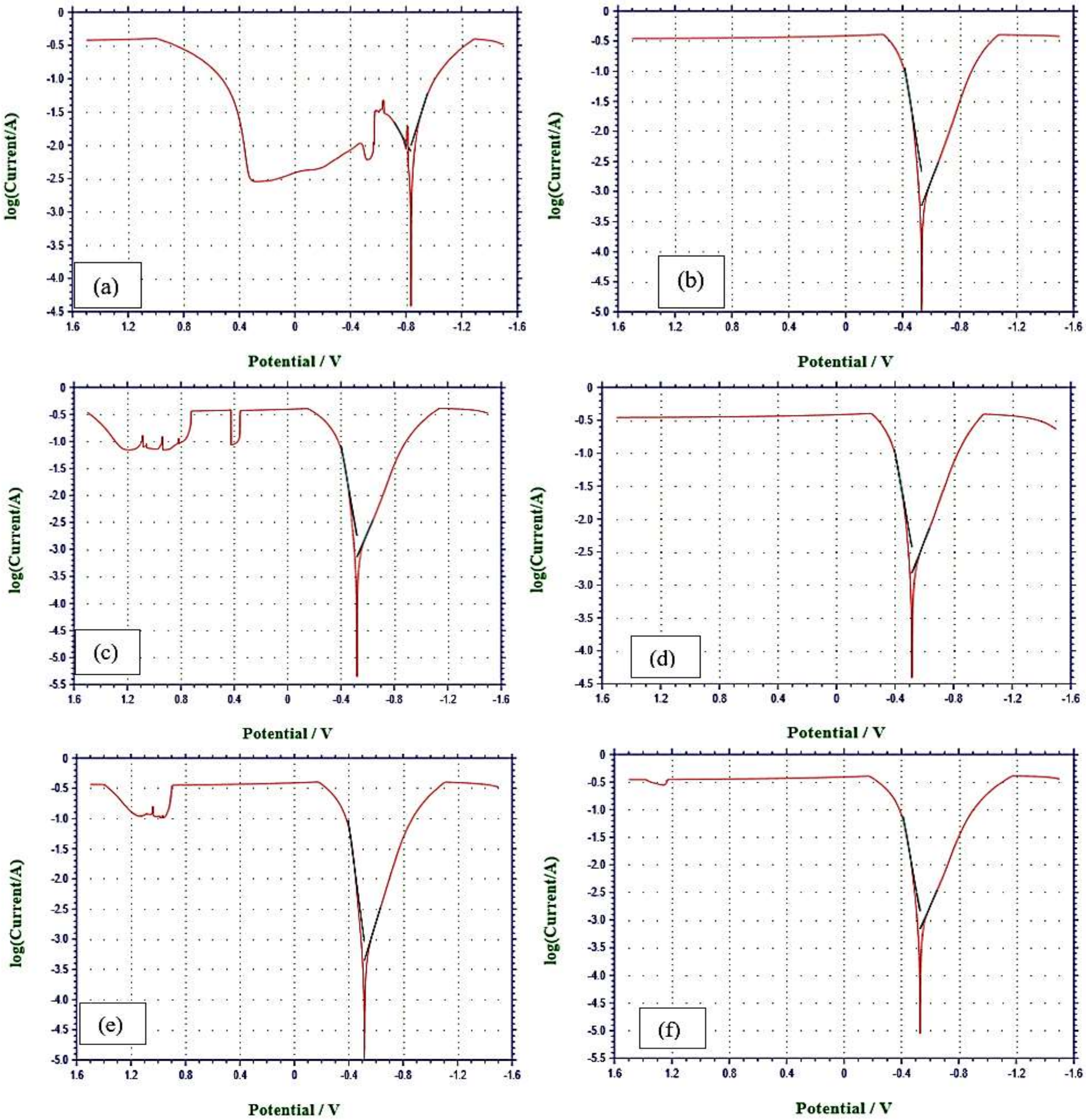

Figure 1: PDP behavior of MS in- **(a)** blank 1.5 M KOH; and with COLE in the Ct of - **(b)** 1; **(c)** 1.5; **(d)** 2; **(e)** 2.5; and **(f)** 3 g/L.

Calculations were carried out using eq.(1) [29].

$$\%I_{corr} = = \left[\frac{I_{corr(0)} - I_{corr(1)}}{I_{corr}}\right] \times 100 \qquad (1)$$

where $I_{corr(0)}$ and $I_{corr(1)}$ are I_{corr} without and with inhibitor, respectively. Corrosion parameters collected from PDP, as listed on Table 3, were plotted (Figs. 2 and 3).

Table 3: PDP corrosion parameters obtained in 1.5 M KOH without and with COLE, at 298 K.

Ct of COLE (g/L)	E_{corr} (V)	I_{corr} (A)	CR (mm/year)	IE(%)	SC (θ)
0	-0.834	$1.227e^{-002}$	$5.644e^{+003}$		
1	-0.532	$7.665e^{-004}$	$6.162e^{+002}$	93.75	0.9375
1.5	-0.519	$8.171e^{-004}$	$6.568e^{+002}$	93.34	0.9334
2	-0.515	$2.060e^{-003}$	$1.656e^{+003}$	83.21	0.8321
2.5	-0.514	$4.725e^{-004}$	$3.799e^{+002}$	96.14	0.9614
3	-0.529	$8.321e^{-004}$	$6.689e^{+002}$	99.93	0.9993

Fig. 2 shows that, generally, CR decreased with higher Ct of COLE. This decrease in CR can be linked to the physical adsorption process, which took place as COLE molecules were absorbed onto the MS surface [30]. CR was stable with 1 and 1.5 g/L COLE, but increased with 2 g/L, and decreased with 2.5 g/L. Lowest CR was obtained with 2.5 g/L COLE.

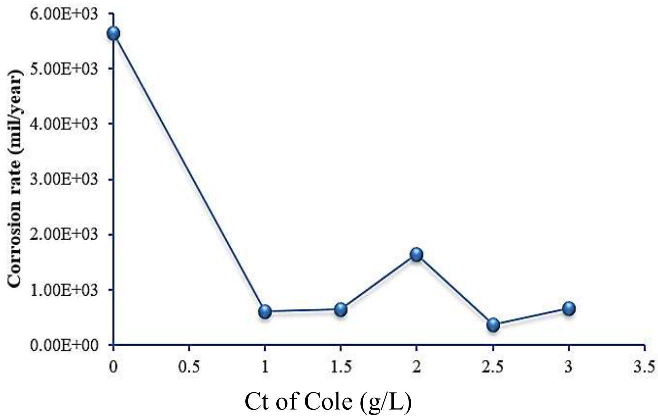

Figure 2: Plot of CR *vs.* COLE several Ct in 1.5 M KOH.

Fig. 3 displays IE(%) of COLE, which decreased with Ct from 1 to 2 g/L, and increased with 3 g/L, to reach its highest value of 99.93%.

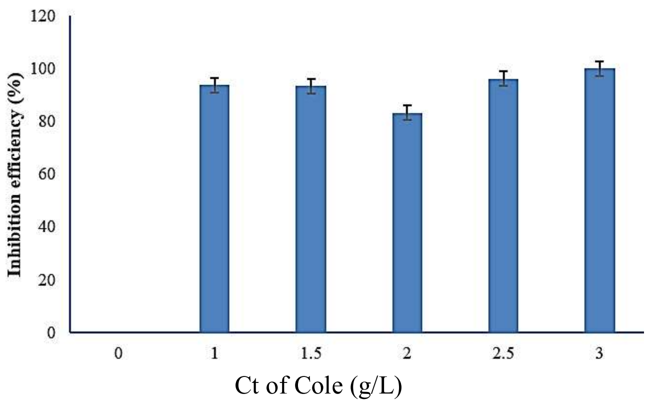

Figure 3: Plot of IE(%) of COLE *vs.* its several Ct in 1.5 M KOH.

FTIR

Fig. 4 shows FTIR remarkable broad peaks at stretching vibrations of 3859.7, 3833.6, 3814.9 and 3844.7 cm^{-1}, for coupons A to D, respectively, with COLE.

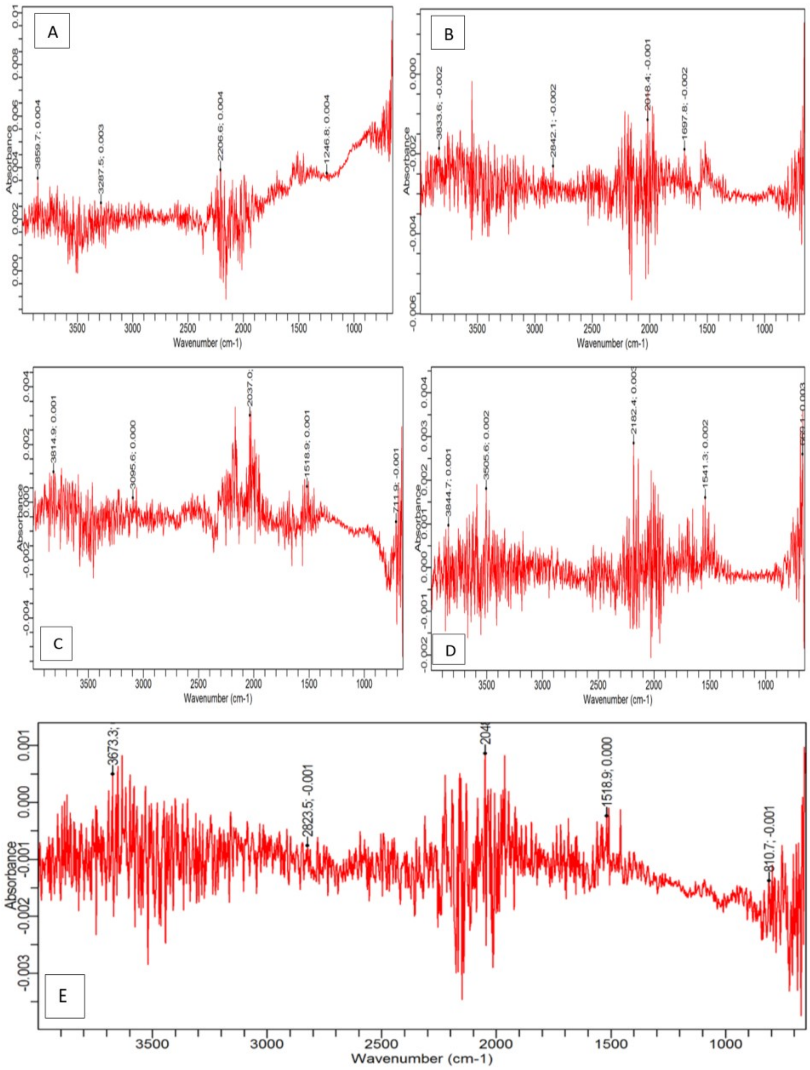

Figure 4: FTIR spectra for MS in 1.5 M KOH with COLE at Ct of- **(A)** 1; **(B)** 1.5; **(C)** 2; **(D)** 2.5; and **(E)** 0 g/L (control).

A lesser broad peak of 3673.3 cm^{-1} was found on the control (E). This stretching vibration could be due to the presence of N-H and/or O-H bonds. 2206.6, 2842.1, 2037.0, 2182.4 and 2823.5 cm^{-1} peaks were stretching vibrations caused by C-H and C=C bond groups. 1246.8, 1697.8, 1518.9, 1541.3 and 1518.9 cm^{-1} peaks were recognized as stretching vibrations linked to C-H vibration of CH_3 group [31]. Any other stretching vibrations below 1000 cm^{-1} were due to C-H vibration of the aromatic and/or aliphatic group, all in agreement with literature [31].

Adsorption isotherm

Generally, adsorption isotherms are crucial and helpful in determining and/or understanding the nature of CI mechanism, and the interaction between extract molecules and the MS surface [32]. The most consistently utilized isotherms are Frumkin's, Freundlich's, Langmuir's, Temkin's and Flory-Huggins', of which mechanisms are explained by the general formula shown in eq. (2) [24]:

$$f(\theta, x) \exp(2a\theta) = K_{ads} C \quad (2)$$

where f (θ, x) is the configurational factor that solely depends upon the physical adsorption model and the assumptions underlying the isotherm derivation, a is the interaction factor, θ is SC (IE/100) and C is Ct of COLE in 1.5 M KOH.

The results of this polarization investigation were found to fit Langmuir's adsorption isotherm, according to eq. (3) [33]:

$$\frac{C}{\theta} = \frac{I}{K_{ads}} + C \quad (3)$$

The plot of C/θ against C, at 298 K, gave a straight line, as seen in Fig. 5.

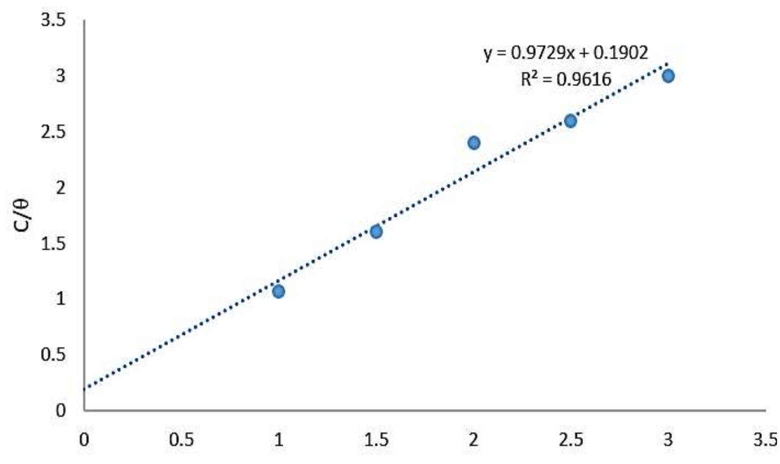

Figure 5: Langmuir's adsorption model plot of MS in various Ct of COLE, at 298 K.

K_{ads} was determined to be 0.9729 g/L, and R^2 was found to be 0.9616, which is very close to unity. It was said that K_{ads} value could be associated with the strength of adsorption forces between inhibitor molecules and metal surface [33]. As the linear plot had high R^2, this could show that inhibition was due to COLE active organic compounds adsorbion onto the MS surface, which obeyed Langmuir's isotherm. Also, the determined positive value (0.1902) of the molecular interaction parameter known as "a" shows that there were attraction forces in the adsorption layer on the MS surface. This is in agreement with [24].

K_{ads} was related to ΔG°_{ads} , by eq. (4) [14]:

$$\Delta G^{\circ}_{ads} = \text{-RT In } (55.5\ K_{ads}) \qquad (4)$$

where 55.5 is molar Ct of water in the bulk solution, R is gas constant and T is temperature.

ΔG°_{ads} value calculated at 298 K was -9.882 kJ/mol. Its negative value indicates the possibility of the inhibitor spontaneous nature adsorption process. ΔG°_{ads} value of -20 kJ/mol or any other less negative values confirm physisorption, while those lower than -40 kJ/mol are taken to be chemical adsorption. Therefore, COLE adsorption onto the MS surface followed physical adsorption mechanism, in agreement with [34].

Conclusion and future outlook

This research successfully investigated COLE as a good CI. It was concluded that COLE proved to be a good eco-freiendly organic inhibitor capable of controlling and preventing CR of MS. COLE had very high IE(%) values of 96.14 and 99.93%, with Ct of 2.5 and 3 g/L, respectively.

E_{corr} decreased from -0.824 to -0.529 V, while I_{corr} reduced from 1.227e$^{-\ 002}$ to 8.321e^{-004} A, and there was a maximum SC of 0.9993. These results proved that COLE was able to control MS corrosion in a KOH solution.

Thermodynamic and other adsorption parameters revealed that COLE interaction with the MS surface was through physical adsorption, obeyeing Langmuir's isotherm.

This research contributed to understand MS corrosion in an alkaline solution, which was inhibited by COLE.

Further studies employing COLE as CI for MS and other metals, in various alkaline environments, are suggested, so as to compare them with the high IE(%) values recorded in this work.

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Conflict of interest

There are no conflicts of interest among the authors.

Authors' contributions

Chukwuka Ikechukwu Nwoye: offered intellectual assistance with data collection, analysis and interpretation; proofread the work, made the required modifications and approvrf the final version to be published; primarily contributed to the design and technical direction. **Uzoma Samuel Nwigwe**: conducted the study; analyzed the data and interpreted the results; wrote the article as the primary author, and read it; made a moderate contribution to the analysis, conceptualization and design.

Abbreviations

$Ca(OH)_2$: calcium hydroxide
CI: corrosion inhibitor/inhibition
COLE: *Corchorus olitorius* leaves extract
CR: corrosion rate
Ct: concentration
E_{corr}: corrosion potential
FTIR: Fourier-transform infrared spectroscopy
H_2SO_4: sulphuric acid
HCl: hydrochloric acid
I_{corr}: corrosion current
IE(%): percentage inhibition efficiency
KOH: potassium hydroxide
MS: mild steel
Na_2CO_3: sodium carbonate
Na_2SO_3: sodium sulfite
NaCl: sodium chloride
NaOH: sodium hydroxide
Pc: phytochemical
PDP: potentiodynamic polarization test
R^2: coefficient of determination
SC: surface coverage
SCE: saturated calomel electrode

Symbols definition

ΔG°_{ads}**:** Gibb's energy of adsorption
K_{ads} : adsorption-desorption equilibrium constant
θ: degree of surface coverage

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