Electrochemical chemical performance of green synthesis of NiO-Syzygium cumini complex as corrosion inhibitor on mild steel in low pH environment

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Abstract

The efficiency of novel synthesized NiO-Syzygium cumini complex as a corrosion inhibitor was evaluated on mild steel in 0.5 molar sulphuric acid by potentiodynamic polarization (PDP) and electrochemical impedance spectroscopy (EIS) measurements. It was noticeably confirmed that the inhibition efficiency increased with increasing concentration of inhibitor, due to a decrease in the corrosion currents and impeding of the active sites. Due to presence of organic molecules from the NiO on the carbon steel surface was confirmed by FT-IR spectroscopy. The adsorption of species on the alloy surface was modelled using the Langmuir isotherm. A decrease in the carbon steel acid corrosion in the presence of NiO-Syzygium cumini was also confirmed through contact angle measurements and scanning electron microscopy (SEM)

Keywords: *Corrosion Inhibitor; Mild steel; PDP:, EIS, SEM*

1. Introduction

Green synthesis methods in the field of chemistry are going to be superior alternatives over conservative synthesis methods. These recent methodologies are more effective, modest, low cost, eco-friendly and can be suitable for large scale manufacturing processes [1]. In environmental science, metal oxide nanoparticles play vital role for the adsorption based on removal of metals from the wastewater [2]. Nanomaterials are potential materials that are cost-effective, can be reused, and possess high stability [3, 4]. Employing corrosion inhibitors is one of the best practical methods for protection from corrosion environment, specifically in acidic medium to inhibit unexpected metal dissolution and acid ingestion [5, 6]. Acidic solutions are widely used for cleaning machinery parts that get affected by corrosion. Corrosion inhibitors are used to minimize material losses during the cleaning process [7]. In general, aromatic organic compounds that are commonly used are harmful to the human health and environment. Hence, eco-friendly materials like plant extracts containing particular organic molecules have been used as substitute to traditional corrosion inhibitors. In general, organic molecules are used as corrosion inhibitors and the activity is attributed to their adsorption on the metal surface. Due to the presence of heteroatoms like N, O, S, P and C=C bonds contain π electrons that interact with vacant metal d-orbitals [8-12]. Vegetal extracts usually act as mixed inhibitors [13]. Natural extracts show outstanding efficacy as environment-friendly corrosion inhibitors which offer simple and practical formulations and applied in low pH environment [14]. The naturally occurring corrosion inhibitor on mild steel such as caffeic acid [15], tannic acid and gallic acid [16]. Some other organic molecules are also examined as corrosion inhibitors that contain alkaloids [17], flavonoids [18] and phenolic acids [16]. Different nanoparticles and superficial modified nanoparticles were used to increase the protective

barrier properties of epoxy coating [19–27]. Nickel oxide (NiO) is a transition metal oxide with cubic structure and is drawing increasing attention due to its potential use for a variety of applications such as: catalysis [28], electrochromic films [29], battery cathodes [30, 31], gas sensors [32], and magnetic materials [33]. It exhibits anodic electrochromism, excellent durability and electrochemical stability, large spin optical density and various manufacturing possibilities. It can also be widely used in dye sensitized photocathodes [34]. The inhibitor is used mostly for protection against corrosion in acid environment. In most of the industries inhibitors are used to control metal dissolution, particularly in acidic, basic and neutral environments. In most of the industries, efficient corrosion inhibitors used are organic compounds that contains at least one functional group (Hetero atoms) which act as active centre for the adsorption on the surface metal and blocking the active sites on the metal [35]. Most of the industrial machine parts are made of mild steel and machinery parts are cleaned using descaling and acid pickling. To overcome the drawbacks, it has been envisaged to use nickel oxide to form a complex, due to less toxicity compared with other metal oxides and are also eco-friendly to our environment. Hence, in the present study, the novel NiO-syzygium cumini complex has been prepared by a novel green synthesis method and its corrosion inhibition, its characterization techniques followed by the electrochemical performance of the corrosion inhibitor complex in low pH environment

2. Materials and Methods

2.1 Instrumentation

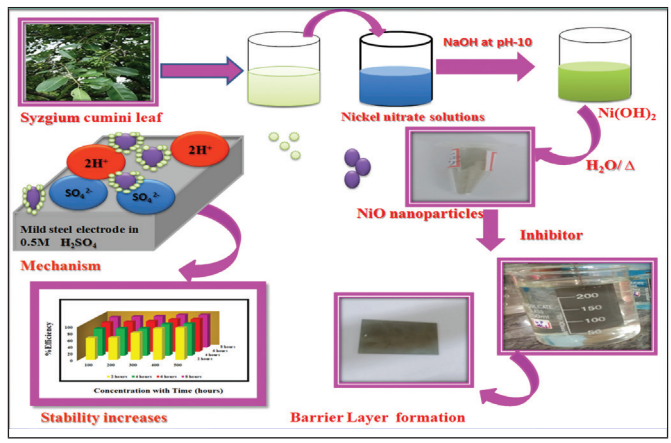
Pellets made from NiO-Syzygium cumini complex and KBr were subjected to FTIR investigation on a Perkin-Elmer 337 spectrometer in the frequency range between 4000-500 cm^{-1}. XRD spectrum was record using Rigaku Maniflex diffractometer (Japan) and JSM-6390 Scanning Electron Microscope was used to determine the structural morphology of the synthesized NiO-Syzygium cumini complex materials. EIS and Potentiodynamic polarization studies were registered in ECLAB 10.37 model instrument. Weight loss method (gravimetric) was used for the study of corrosion inhibition efficiency.

2.2 Preparation of aqueous leaf extract of syzygium cumini (java plum)

Syzygium cumini (Java plum) leaves were collected from Veltech University, Chennai, Tamil Nadu, India. The freshly prepared leaf extract was slightly modified as reported in literature [36]. The collected Syzygium cumini leaves were washed with double-distilled water repeatedly to remove the impurities. Then, 10 g of sample leaf was powdered and boiled in 200 ml of double distilled water for 30 min until the colour changes to dark solution. The leaf extract was filtered by Whatman filter paper grade No. 1 filter paper. The filtrate solution was used for further analysis.

2.3 Green synthesis of nickel oxide nanoparticles (NiO NPs)

20 ml of aqueous Syzygium cumini leaf extract was added into 200 ml of 0.1 M nickel nitrate aqueous solution at normal room temperature. The mixed solution was further heated to 60 °C with constant magnetic stirring for 1 h. The reaction mixture was adjusted at a pH of 10 using sodium hydroxide until acquiring greyish green powder [37]. The resultant product was allowed to cool and centrifuged for 15 min. The precipitate collected was dried at around 400 °C in hot air oven for 2 h. The dried powder samples were used for further characterization. The steps involved in the formation of nickel oxide nanoparticles using green synthesis approach are shown in scheme.1



Scheme.1. The mechanism of formation of green synthesized nickel oxide nanoparticles

3. Results and discussion

3.1 FTIR analysis NiO-Syzygium cumini complex

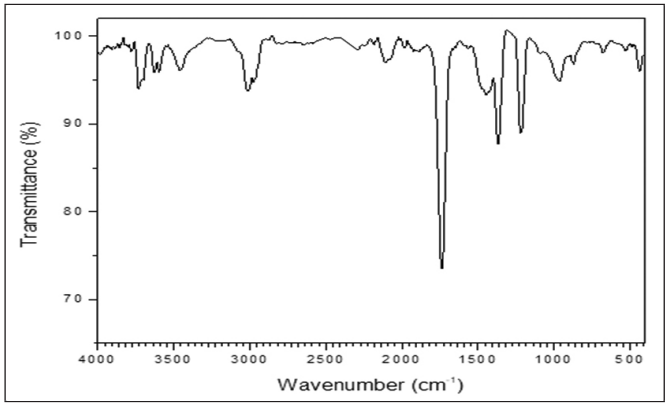


Fig. 1. FT-IR spectrum of NiO-Syzygium cumini complex

The FTIR spectrum of NiO-Syzygium cumini complex synthesized from the leaf extract in the range of 4000-500 cm^{-1} is shown in Fig.1. The FT-IR spectrum shows stretching vibrations at 3403 cm^{-1} due to hydroxyl ions presence, 3300 cm^{-1} due to stretching frequency of -NH, 1631 cm^{-1} due to carbonyl group, 1446 cm^{-1} and 1072 cm^{-1} due to stretching frequency of aromatic saturated and unsaturated carbon atom (Fig.1). These strong peaks indicate the presence of -OH, -NH, -C=O, C=C and C-C groups on the surface of nickel oxide nanoparticles. The IR band at 800 cm^{-1} is due to stretching band of nickel oxide [37, 38].

3.2 XRD analysis of NiO-Syzygium cumini complex

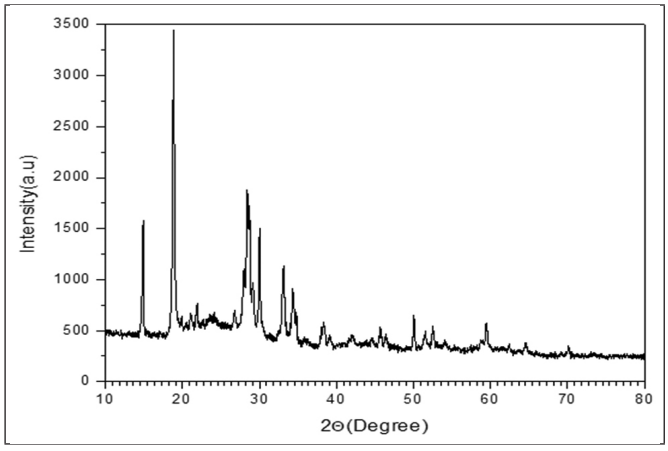


Fig. 2. XRD pattern of NiO-Syzygium cumini complex

The broader peaks (Fig.2) in the XRD pattern of nickel oxide- Syzygium cumini complex confirmed that the formation of NiO nano particles [24]. The characteristic peaks of NiO nanoparticles were observed at 23.8º (012), 36.02º (110), 38.73º (320) 49.80º (024), 62.70º (214) and 61.17º (300) in the XRD pattern [37, 38].

3.3 SEM/EDX analysis of NiO-Syzygium cumini complex

The scanning electron microscope (SEM) image of NiO-Syzygium cumini complex is shown in Fig.3. **Fig. 3(A)** shows that the granular like structure having diameter 61.69 nm to 84.70 nm. Some slight modification in synthesis process results in the modification of spherical shape to irregular shape [22,36,37]. The EDX analysis (**Fig. 3(B)**), showed the presence of Ni, O, C and N in the NiO-Syzygium complex that acts as protective layer in aggressive environment [39].

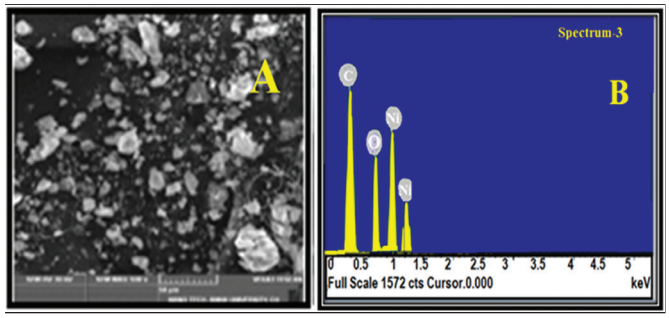


Fig. 3 SEM image and EDX of NiO-Syzygium cumini complex

3.4 Preparation of electrode materials

Plates of mild steel, having dimension of 4 cm x 2 cm x 0.2 cm with the composition corresponding to C: 0.21%, Si: 0.035%, Mn: 0.25%, P: 0.082% and Fe: 99.28% were abraded with various grades of emery papers. The abraded specimens were cleaned by distilled water, ethanol, acetone and desiccated. Gravimetric studies were accomplished with freshly polished coupons [26].

3.5 Preparation of hostile solutions

0.5 M aggressive solution used for dwindling of metal pieces were obtained by diluting the AR. grade sulphuric acid. Solutions employed for inhibition measurements were prepared by adding different amounts of NiO-Syzygium cumini complex (100-500 ppm) to hostile solutions.

3.6. Exploration of inhibition property

3.6.1 Deterioration measurements

NiO-Syzygium cumini complex was synthesized using various proportions of NiO and plant leaf extract. Among them, the composition containing 10 g leaf extract and 0.1M of nickel nitrate gave good inhibition properties on mild steel in aggressive environments. Effect of aggressive environment on mild steel surfaces was estimated by evaluating the loss in weight on keeping the pre weighed mild steel in 250 ml of blank and test solutions. The corroded mild steel coupons were removed from the low pH environment at regular two hour time intervals up to 8 h and cleaned with bristle brush in distilled water repeatedly, absolute ethanol and acetone. They were reweighed to determine inhibition efficacy (IE %) and surface coverage (θ) after drying. The formulae reported earlier [35] were adopted to calculate the above said parameters and are presented in Table 1

$$\%Efficiency = \frac{Wo-Wi}{Wo} X100\ g \text{ ----------(1)}$$

Where W_i and W_0 are weight loss values (g) on mild steel in 0.5 M H_2SO_4 with and without NiO-Syzygium cumini complex, respectively.

Table 1: Values of IE and θ deliberated from the weight loss measurements in 0.5 M blank and test solutions.

Conc. Of Composite (ppm)	2 hrs			4hrs			6hrs			8hrs		
	Weight	I.E (%)	ϴ	Weight	I.E (%)	ϴ	Weight	I.E (%)	ϴ	Weight	I.E (%)	ϴ
Blank	0.3495	-		0.3727	-		0.5836	-		0.8190	-	
100	0.1217	65	0.6517	0.0737	80	0.8022	0.0803	86	0.8624	0.0808	90	0.9013
200	0.1183	66	0.6615	0.0701	81	0.81	0.0649	88	0.887	0.0627	92	0.9234
300	0.0666	80	0.8094	0.0671	81	0.8199	0.0555	90	0.9049	0.0555	93	0.9322
400	0.0231	93	0.9339	0.0221	94	0.9407	0.0287	95	0.9508	0.0171	97	0.97912
500	0.0169	95	0.9516	0.0161	95	0.9546	0.0224	96	0.9616	0.0235	97	0.9724

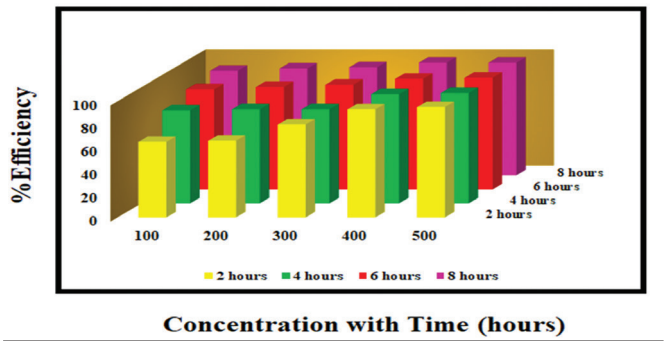


Fig. 4. Inhibition efficiency portrayal by bar chart for 0.5 M test solution

Data provided in the above table reveals that the NiO-Syzygium cumini complex is competent of giving protection against 0.5 M acidic solution with 97% efficacy for 500 ppm concentration of inhibitor solution at 8 h. Above results indicate that NiO-Syzygium cumini complex can be added with cleaning agents having acidic concentration less than or equal to 0.5 M [40].

3.6.2 Potentiodynamic polarization studies

The potentiodynamic polarization was conducted as per ASTM 415 to study the mild steel specimen response in 0.5 M sulphuric acid with the addition of different concentrations of NiO-Syzygium cumini complex. Fig. 5 shows the Tafel polarization curves of the working electrode submerged in the NiO-Syzygium cumini complex inhibitor at concentrations of 100, 200, 300, 400, and 500 ppm, including the blank solution measured at normal room temperature. The electrochemical parameters such as corrosion current density (I_{corr}), corrosion potential (E_{corr}), anodic (βa) and cathodic (βc) Tafel slopes, and inhibition efficiency (η). Fig. 5 shows that the anodic and cathodic Tafel curves shift to a lower current density (I_{corr}) after the addition of NiO-Syzygium cumini complex inhibitors. In the

repressed working electrode, the corrosion potential (E_{corr}), shifted towards the negative region. On the other hand, the corrosion current density (I_{corr}) shows desperation when the inhibitor is mixed to the test solution. The results of calculated E_{corr} and I_{corr} similarly indicate the corrosion protection of the inhibitor. **Table. 2** shows the recorded data of some electrochemical parameters E_{corr}, I_{corr}, βa, βc and η efficiency to obtain from the corrosion process, including the calculation of inhibition efficiency, η, using as shown below equation (2):

$$\%\,\eta\, Efficiency = \frac{I^0\text{corr} - Icorr}{I^0\text{corr}} X100 \quad \text{---------- (2)}$$

In the above equation, I^0_{corr} and I_{corr} are corrosion current densities in the absence and presence of inhibitors [41]. From the potentiodynamic polarization curve, we observed, that when increasing the inhibitor concentration 100 ppm to 500 ppm, the corrosion current density (I_{corr}) value decreases from (750 µA cm^{-2} to 201µA cm^{-2}) the inhibition efficiency observed was 62% for 100 ppm and 90% for 500 ppm. Since at lower concentration itself higher efficiency was noticed and with further addition there were no major changes.

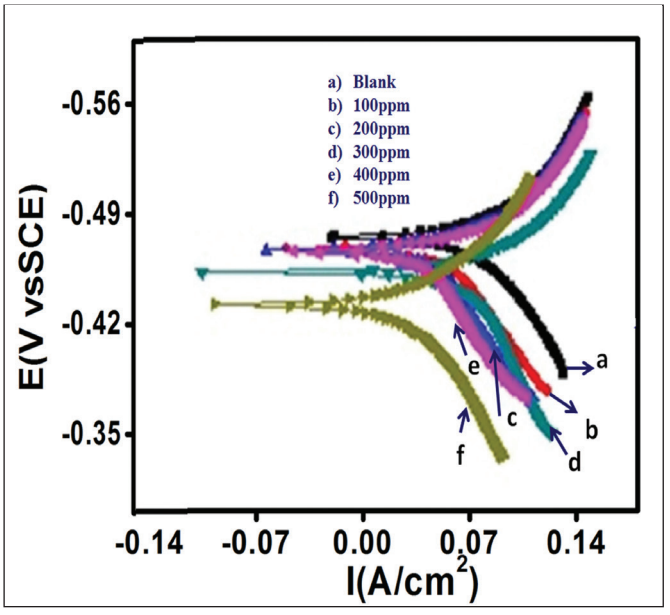


Fig 5: Potentiodynamic polarization curve of mild steel in 0.5 M blank and test solutions

Table 2: Corrosion resistive parameters in 0.5 M H_2SO_4 and test solution

Conc. of Inhibitor (ppm)	E_{Corr} (mV vs. SCE)	βa (mV dec^{-1})	β_c (mV dec^{-1})	I_{corr} (µA cm^{-2})	Inhibition Efficiency (η %)	Surface coverage (θ)
Blank	-452	63	66	1972	--	--
100	-497	29	38	750	62	0.6196
200	-479	37	39	680	65	0.6551
300	-497	25	20	501	75	0.7456
400	-474	26	40	350	82	0.8225
500	-487	22	23	201	90	0.8980

3.6.3. Electrochemical Impedance Spectroscopy (EIS) Measurements

The Impedance spectral data of mild steel in 0.5 M H_2SO_4 in the absence of inhibitor and presence of various concentration of NiO-Syzygium cumini complex are shown in the impedance plot **Fig. 6**. It clearly indicates that inhibition property on the mild steel has drastically changed after the addition of inhibitor to aggressive solution. By careful observation of the plot, the diameter of the semicircles increases in the inhibitor solution compared to without the inhibitor. The increase in size of capacitive loop with increase in inhibitor concentration indicates that, the NiO-Syzygium cumini complex inhibitor gets adsorbed over the metal surface and inhibits the flow of corrosion current and thereby act as a very efficient inhibitor in very low pH environment. According to the impedance results in **Table 3**, the charge transfer resistance (R_{ct}) value rises as the NiO-Syzygium cumini complex inhibitor concentration increases and the value of the double-layer capacitance (C_{dl}) decreases. The results of EIS parameters such as charge transfer resistance (R_{ct}) and double layer capactiance (C_{dl}) were determined and the electrical equivalent circuit diagram as depicted in **Fig. 7.** [22,41] was evolved. The percentage efficiency (η) was calculated using the below equation (3).

$$\%\,\eta\, Efficiency = \frac{Rct - R^0ct}{Rct} X100 \quad \text{----------(3)}$$

In the above equation, R^0_{ct} and R_{ct} are the charge transfer resistance of the blank and the inhibitor solution.

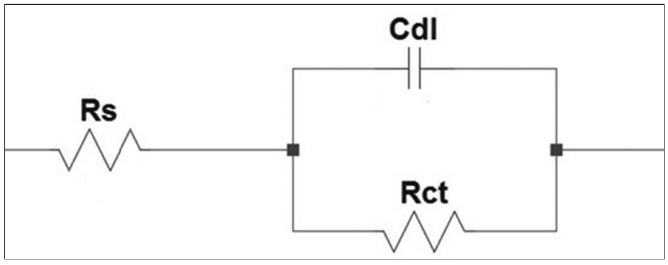


Fig. 7: Electrical equivalent circuit diagram

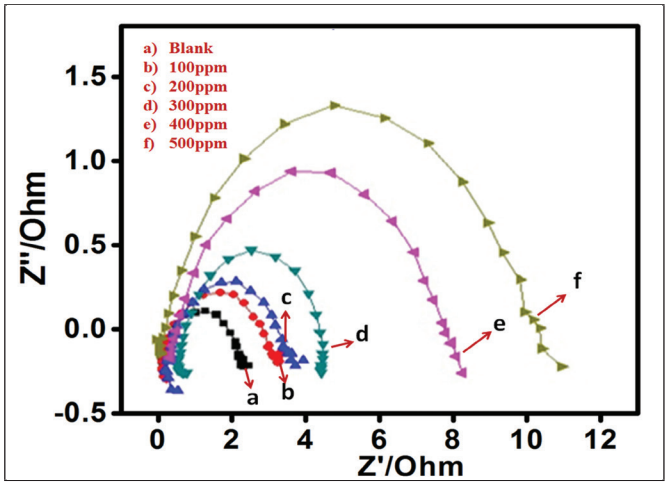


Fig 6: Impedance plot for mild steel in 0.5 M blank and test solution.

Table 3: Impedance parameters derived for 0.5 M blank and test solution

Conc. of Inhibitor (ppm)	R_s (Ω)	C_{dl} (μ F cm^{-2})	R_{ct} (Ω cm^2)	Inhibition efficiency (%)	Surface Coverage (θ)
Blank	0.9997	542	0.7685	--	--
100	1.0490	552	2.164	64	0.6455
200	1.0940	501	2.525	69	0.6956
300	1.1540	552	2.901	73	0.7351
400	1.0450	383	3.846	80	0.8001
500	0.9898	320	6.821	88	0.8874

4. Conclusions

The anti-corrosive electrochemical performance of NiO-Syzygium cumini complex synthesized from green synthesis was evaluated as a corrosion inhibitor on mild steel in low pH environment. IE of 97% was observed even with an immersion time up to eight hours by weight loss method. IE was also found to increase with surface coverage area. Potentiodynamic polarization study presented 90% efficacy and the NiO-Syzygium cumini complex system functioned mostly as a mixed type of inhibitor. The electrochemical impedance indicates that, owing to enlarged thickness of the surface layer on the mild steel surface an increase in Rct value and decrease in Cdl and Icorr values due to charge transfer. Therefore the result revealed that the inhibitor substance forms a protective barrier film on the mild steel surface. The increasing trend of protection efficiency with respect to increase in the concentration of inhibitor observed in weight loss, PDP and EIS studies implies that the water soluble substance can act as good safeguarding agent during the industrial cleaning process.

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