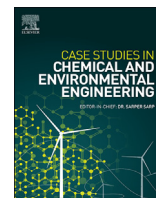


# TUTDoR

## Synthesis, corrosion and structural characterization of kenaf nanocellulose on Zn-ZnO-xCn electrolytic coatings of mild steel for advanced applications.

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# Synthesis, corrosion and structural characterization of kenaf nanocellulose on Zn-ZnO-C<sub>n</sub> electrolytic coatings of mild steel for advanced applications



## ARTICLE INFO

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## ABSTRACT

Combating the menace of corrosion attack in pipeline is a significant source of expenditure for most oil and gas industries. Mild steel is the most utilized steel employed in producing oil pipelines as a result of their availability, machinability, and cost. This research aimed to develop ternary zinc-zinc oxide-nanocellulose (Zn-ZnO-C<sub>n</sub>) coatings on mild steel substrates for improved structural and corrosion resistance in acidic media by electrodeposition method. Potentiodynamic polarization was used to determine the corrosion resistance properties of the coating. The surface morphologies were determined by scanning electron microscopy equipped with energy dispersive spectroscopy, and x-ray diffractometer. The results showed that all the developed composite coatings recorded lower corrosion rate values than that of the substrate (mild steel) sample, whose value was 5.3243 mm/yr. Sample C8 (Zn-20gZnO-20gC<sub>n</sub>) had the lowest corrosion rate value of 0.1682 mm/yr and this corresponded to a coating protection efficiency of 96% on the substrate. Also, sample B1 (Zn-20gZnO-0gC<sub>n</sub>), among the developed coatings, gave the highest corrosion rate value of 1.8435 mm/yr with a protection efficiency of 66%. The combined properties of the coating materials were able to form protective barriers on the substrate in the corrosive media.

## 1. Introduction

Globally, majority of the oil storage facilities and pipes used for petroleum product transportation, whether upstream or downstream, are made of mild steel [1–3]. These pipelines or storage facilities come in contact with petroleum products, which aids corrosion. However, mild steel still possess some challenges during service [4]. The degradation of mild steel in acidic, salty, and high alkaline environments has become a topic of interest among researchers in recent years. Given enough time, corrosion has the potential to degrade mild steel [5–7]. If unchecked, the effects can come rapidly, and the resulting consequences can be highly catastrophic and costly. Battling the menace of corrosion is a significant source of expenditure for most Oil and Gas Industries [8].

Mild steel, being the primary material employed in the fabrication of oil pipelines, thus, have limited ability to resist corrosion attack in some environment. Hence, the continuous search to improve its corrosion resistance properties becomes paramount [9–11]. Various methods have been developed and reported for corrosion control and prevention for mild steel in a different environment. Among the processes, the use of surface modifications in the form of composite coatings for reducing the corrosion rate has been reported to be effective [10–12].

Composite coatings provide chemical and mechanical stability, as well as corrosion resistance to mild steel substrates. They may also offer thermal protection depending on the materials employed for the coating. Plasma coating, hot dipping, sol-gel, electroless coating, and electrolytic deposition, etc. are part of the different methods by which these coatings can be deposited on a substrate [13–16]. But, coating by electrodeposition is economical, easy to use, effective and also has a good deposition rate.

This research focuses on the electrodeposition of zinc- (zinc oxide-cellulose) nanoparticle blends on mild steel substrates for improved corrosion protection in acidic media. The corrosion rates of the deposited coatings were determined via potentiodynamic polarization for comprehensive results. Scanning electron microscopy, equipped with energy dispersive spectroscopy (SEM/EDS), was used to reveal the grain refinements and morphologies of the deposited coats on the substrate as well as obtain the percentage elemental compositions. The phase evolution of the composite coatings was determined with the aid of an x-ray diffractometer.

## 2. Experimental methods

### 2.1. Materials preparation and procedures

A pure zinc bar (99.9%) measuring 30 mm x 20 mm x 4 mm and about 220g of zinc oxide (ZnO) nanoparticles were sourced from one of the significant chemical vendors at Ibadan, South-west, Nigeria. Also, about 150g of nano-cellulose fibers extracted from kenaf (*hibiscus cannabinus* L) bast and prepared by a 2-stage alkali digestion and acetylation processes following suggestions by Ref. [6]. The substrate was then prepared following recommendations outlined in Refs. [1–3]. Samples measuring 50 mm x 20 mm x 2 mm were polished with emery papers to 600 grits to erase existing impurities. They were then degreased in trichloroethylene and immediately rinsed in water to eliminate any organic contaminant from them. This was followed by substrate activation by dipping in 10% HCl solution for 10 seconds and then rinsed in distilled water. The bath contents were of analytical grade chemicals and distilled water. It contains zinc chloride, ZnCl (100 g/lit.), glycine (10g/lit.), thiourea

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**Table 1**  
Experimental design of the coating matrix.

Runs	Nanoparticles mix	Voltage (V)	Sample ID
1	20gZnO-5gC <sub>n</sub>	0.3	C1
2	20gZnO-10gC <sub>n</sub>	0.3	C2
3	20gZnO-15gC <sub>n</sub>	0.3	C3
4	20gZnO-20gC <sub>n</sub>	0.3	C4
	20gZnO-0gC <sub>n</sub> (Control 2)	0.3	B1
	As received substrate (Control 1)	–	A
5	20gZnO-5gC <sub>n</sub>	0.5	C5
6	20gZnO-10gC <sub>n</sub>	0.5	C6
7	20gZnO-15gC <sub>n</sub>	0.5	C7
8	20gZnO-20gC <sub>n</sub>	0.5	C8
	20gZnO-0gC <sub>n</sub> (Control 3)	0.5	B2
	As received substrate (Control 1)	–	A

(10g/lit.), zinc oxide nanoparticles, ZnO (20g/lit.) and crystallized nano-cellulose (5–20g/lit.). The relevant theme in this study was to admix zinc with various quantities of nano-particulates of zinc oxide-nano-cellulose (Zn–20ZnO-xC<sub>n</sub>) so as to form an in-situ thin composite coating on the substrates. Table 1 shows the experimental design adopted from Taguchi L8 orthogonal array.

The positive end of the rectifier was connected to the anodes made of the 99.9% zinc bar. The immersion depth and distance between the anodes and cathode were kept constant. The bath contents were heated and maintained at 40 °C to ensure the mixing and dissolution of any particles. The solution was continuously agitated by the aid of a mechanical stirrer up to 1000 rpm to achieve homogeneity of the electrolytes. The deposition was carried out at two different potentials (0.3 & 0.5 V), varying

concentration of additives, and a constant current density of 2.0 A/cm<sup>2</sup> for 20 mins. Shown in Fig. 1, are the pictures of the developed composite coatings.

## 2.2. Corrosion rate analysis of the developed composite coatings and substrate

AUTO LAB Potentiostat/Galvanostat was used to study the corrosion behavior of the as-received sample and that of the deposited composite coatings in 1 M HCl media. The procedures followed recommendations from Ref. [5–10]. The solutions were prepared at ambient temperature. A saturated calomel electrode was used as the reference electrode, while graphite served as the counter electrode. The samples were made in the working electrode. One side of the sample, measuring 1 cm<sup>2</sup> was exposed to the corrosive medium, while the other side was isolated. The samples were scanned from a potential of -2.7 V with respect to a stabilized open circuit potential at a rate of 0.01 V/s. Finally, Nova 2.1 software was used to extrapolate the progression of the corrosion activity obtained from the Tafel plots.

## 2.3. Characterization of the samples

The surface morphologies of the samples were examined via a TESCAN scanning electron microscope equipped with energy dispersive spectroscopy, at a magnification of 1000X. The phase evolution and crystallographic parameters of the samples were done with an X-ray diffractometer. Phase presence and quantification of the samples were determined by matching them via an X'PERT High-Score Software

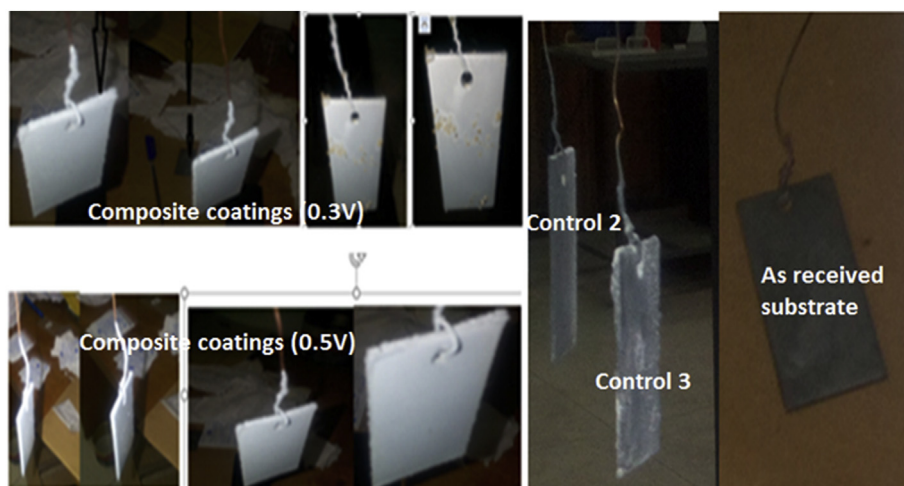


Fig. 1. Section of the developed composite coatings.

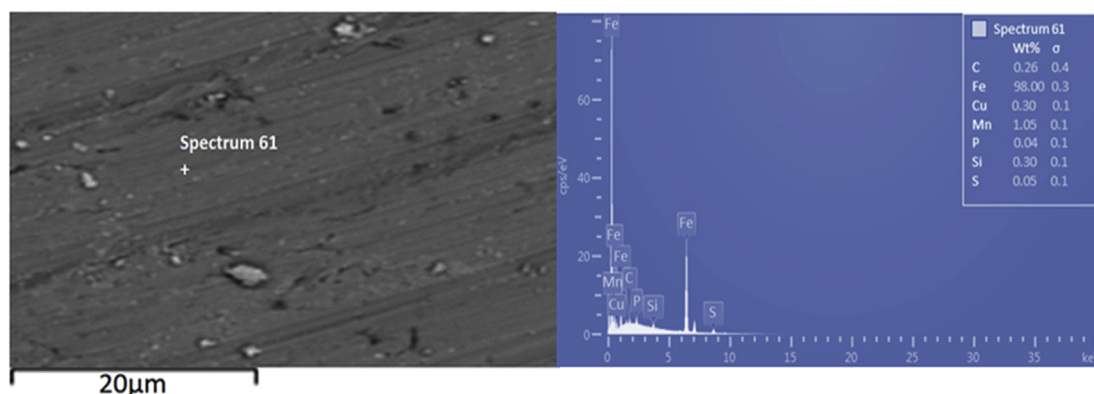


Fig. 2. SEM/EDS spectra of the substrate.

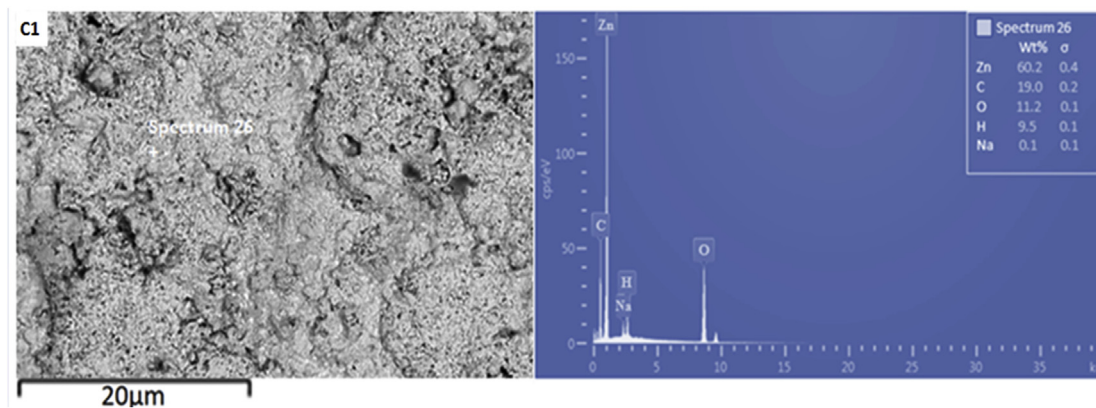


Fig. 3. SEM/EDS spectra of the developed composite coatings at 0.3V.

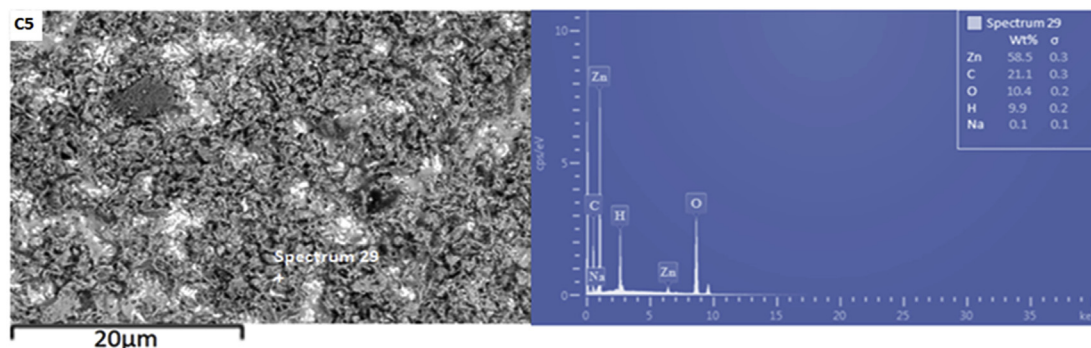


Fig. 4. SEM/EDS spectra of the developed composite coatings at 0.5V.

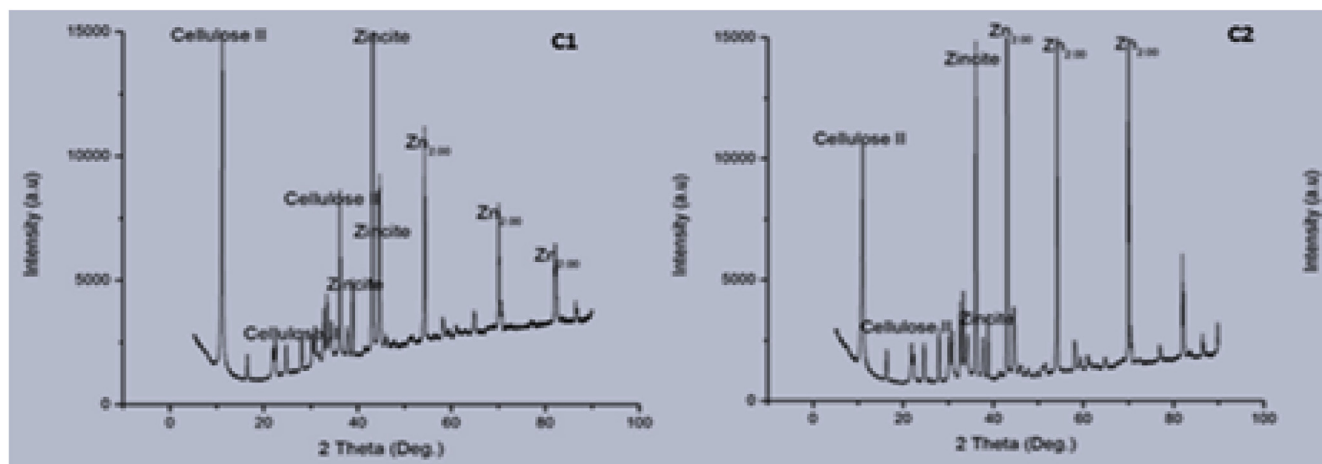


Fig. 5. XRD spectra of the developed composite coatings at 0.3V.

equipped with PDF4/ICDD Database.

### 3. Results and discussions

#### 3.1. Structural characterization

The surface morphology and percentage elemental compositions of the substrate are shown in Fig. 2. The substrate contains 98% of iron and 0.26% of carbon. This value falls within the range of carbon contents specified for mild steel. In addition, the substrate presents through the EDS shows closeness to the ASTM mild steel series of acceptable values.

Figs. 3 and 4 shows the representative figures of the SEM/EDS Spectra of the developed composite coatings at 0.3V and 0.5V applied potentials, respectively. All the developed coatings had good surface adherence and stable film. The uniformity of the coatings differs from one sample to another as a result of differences in additive (nano-particles) concentration and applied potential [13]. From the EDS scan attached with the SEM morphologies, it can be seen that all the developed composite coating had a combination of Zn, C, and small quantities of O, and H in their composition. It is pertinent to state also that the morphology of the coated samples show more dominant zinc oxide nanoparticle layer. From Figs. 5 and 6, interfacial phase change was seen from the XRD Spectra for

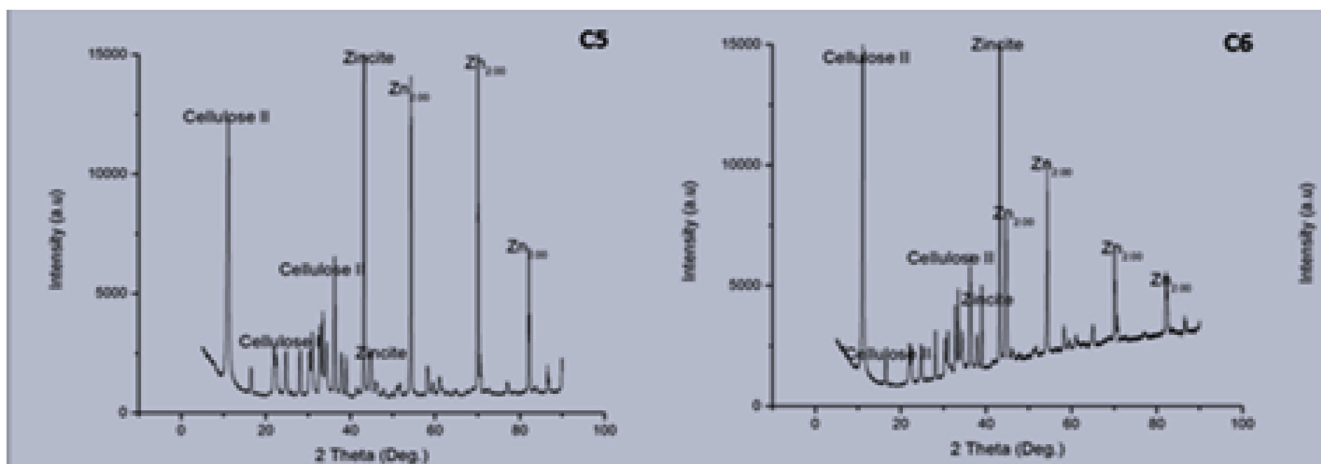


Fig. 6. XRD spectra of the developed composite coatings at 0.5V.

Table 2

Potentiodynamic polarization data for the substrate and coatings at 0.3V

Sample	Polarization resistance ( $\Omega$ )	E <sub>corr</sub> (V)	i <sub>corr</sub> (A)	Corrosion rate (mm/yr)
C1	22.3351	-0.7281	0.000086260	1.5617
C2	37.9192	-0.7103	0.000044044	1.1452
C3	107.7212	-0.7093	0.000011810	0.2258
C4	66.6841	-0.7101	0.000021130	0.6342
B1	15.7297	-0.9872	0.000091077	1.8435
A	8.0897	-1.5089	0.000986764	5.3243

Table 3

Potentiodynamic polarization data for the substrate and coatings at 0.5V

Sample	Polarization resistance ( $\Omega$ )	E <sub>corr</sub> (V)	i <sub>corr</sub> (A)	Corrosion rate (mm/yr)
C5	83.1692	-0.7904	0.000063100	1.0817
C6	97.1947	-0.7887	0.000057901	0.6731
C7	136.8966	-0.7372	0.000017900	0.2076
C8	154.9823	-0.7176	0.000014500	0.1682
B2	53.9371	-1.0905	0.000074857	1.4264
A	8.0897	-1.5089	0.000986764	5.3243

all the developed composite coatings at 0.3V and 0.5V with intermetallic phase identification. The spectra showed evidence crystallize cellulose II, and zincite phase evolutions, with zinc been the most intense peak. The zinc phase was more because it was the major coating component of the

deposited composite coatings employed in the study.

### 3.2. Corrosion study of the composite coatings

The results of the potentiodynamic polarization data for the substrate and developed composite coatings at 0.3V and 0.5V applied potentials are shown in Tables 2 and 3, respectively. It can be seen that all the developed composite coatings had lower corrosion rate values than that of the substrate. The value reduces magnificently as the nano-particles increases. Sample C8 (Zn-20gZnO-20gC<sub>n</sub>) had the lowest corrosion rate with a value of 0.1682mm/yr. This was followed closely by sample C7(Zn-20gZnO-15gC<sub>n</sub>), offering a corrosion rate value of 0.2076mm/yr. Now, among the coatings developed, sample B1(Zn-20gZnO-0gC<sub>n</sub>), gave the highest corrosion rate value of 1.8435mm/yr. The substrate (control 1) had a corrosion rate value of 5.3243 mm/yr. With these values, the coatings on sample C8, C7, and B1 gave degrees of surface protection of 0.96, 0.95, and 0.66 respectively to the substrate. More so, the results from the potentiodynamic data elucidate that the developed coatings offered high values of polarization resistances ( $\Omega$ ) and corrosion potentials (E<sub>corr</sub>) compared to the ‘as received’ sample (substrate). This is also confirmed in the potentiodynamic polarization curve for all samples at 0.3V & 0.5V (Fig. 7). The corrosion potential values for all developed coatings are higher than that of the substrate. Also, the corrosion current (i<sub>corr</sub>) values of the developed coatings are more negative than that of the substrate.

### 4. Conclusion

Component failure due to corrosion is a global challenge and

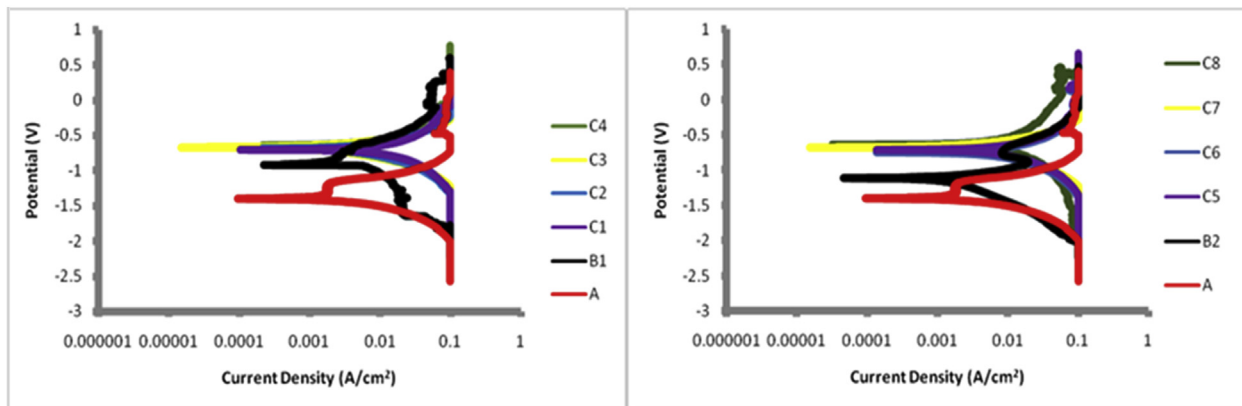


Fig. 7. Potentiodynamic polarization curve for all samples at 0.3V & 0.5V.

successful deposition of kenaf nanocellulose on Zn–ZnO–C<sub>n</sub> was achieved to address this catastrophe. The result shows that all the developed composite coatings recorded lower corrosion rates against the substrate, whose value was 5.3243 mm/yr. Sample C8 (Zn-20gZnO-20gC<sub>n</sub>) had the lowest corrosion rate of 0.1682 mm/yr. The effect of nanocellulose particulates on the electrolytic deposition bath was seen to provide strengthening characteristics for the mild steel developed surface, thereby retarding the rate of corrosion attack.

### Conflict of interest

The researchers declare that there is no conflict of interest during and after the study.

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