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Natural products for materials protection: Corrosion protection of aluminium in hydrochloric acid by *Kola nitida* extract

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ABSTRACT

The ethanol extract of *Kola nitida* seed (KN extract) was investigated for its ability to mitigate the corrosion of aluminium alloy AA3003 in acidic environment using joint experimental and computational approach. The obtained results revealed that KN extract hindered the corrosion reaction. The effectiveness of protection became more pronounced with increasing extract concentration but decreased with prolonged exposure time. Electrochemical data showed that organic constituents of the extract adsorbed on the Al surface, in agreement with the Langmuir equation and reduced the anodic and cathodic current densities. Computational simulations were adopted to visualize the adsorption of various constituents of KN extract on Al (110) slab.

1. Introduction

Although aluminium has the ability to form a stable oxide film that can induce corrosion protection in varied environments, it is still susceptible to corrosion in low and high pH environments. An effective approach to corrosion protection in fluid media is the use of corrosion protection additives; and a wide variety of additives ranging from inorganic, synthetic organic molecules have been shown to inhibit aluminium corrosion in varied media [1–10].

Economic and environmental considerations have, in recent times, stimulated the study of extracts from plants and natural products for corrosion preventing efficacy [10–30]. The use of such natural products advances several advantages; they are biodegradable, renewable and inexpensive are composed of vast number of organic compounds (such as tannins, alkaloids, carbohydrate, vitamins, amino acids, protein, saponins, pigments, resins, etc.), which are similar in electronic structure and function to conventional organic corrosion inhibitors [31–34]. Again, the multicomponent composition means that the limitation posed by the specificity of action associated with the use of a single-compound corrosion inhibitors will be overcome [12]. In other words, natural product corrosion inhibitors will be more versatile in application influencing the corrosion process in many different ways. Conversely, this complex composition also places considerable limitations to precise mechanistic interpretation of the inhibition process; which means it would be difficult to account for the individual inhibiting contributions of the vast organic constituents. We are currently developing a methodology to overcome this constraint; which involves identifying the surface active organic compounds present in the extracts and subsequently subjecting them to molecular dynamics simulation to model their electronic and adsorption structures [12,20,35]. This would afford some insights on the individual inhibiting potentials of the constituents and how they contribute to the corrosion inhibition effect of the studied extract.

The current study presents the experimental and theoretical assessment of the adsorption and corrosion inhibiting efficacy of ethanol extracts of *Kola nitida* seeds (KN) on the acid corrosion of aluminium alloy AA3003. The interest on the selected biomass lies on the fact that it has been reported to contain many organic constituents which render good corrosion protection on mild steel in acidic media [36].

2. Experimental section

2.1. Materials preparation

Experiments were conducted on aluminium alloy (AA3003) collected from an aluminium company (First Aluminium Company Ltd., Port Harcourt, Nigeria) with nominal elemental composition similar to the one presented elsewhere [1]. The metal sheets were press cut into coupons of dimensions 30 mm × 30 mm × 1.4 mm, degreased with ethanol, rinsed with double distilled water, dried in acetone and warm air and stored in desiccators prior to use. The acid solution employed was

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0.1 M HCl solution. The stock solution of biomass extract were prepared by soaking weighed amounts of the dried and ground seeds of *K. nitida* (KN) in ethanol for 48 h. The resulting solution was triple filtered and the amount of plant material extracted into the ethanol solution was quantified by comparing the weight of the dried residue with the initial weight of the dried plant material before extraction. Inhibitor test solutions were prepared in the desired concentrations by serial diluting the stock extract with the corrodent solution (HCl). The chemicals and reagents used in this study were of analytical grade and were used as sourced without further treatment.

2.2. Gravimetric experiments

The pre-cleaned coupons were weighed to ascertain their initial weight and suspended under total immersion conditions in 250 mL beakers containing aerated and unstirred test solutions, using glass hooks and rods. The total duration for the immersion experiment was 360 h while the coupons were retrieved every 72 h intervals. To determine the weight loss with respect to time (h), the coupons (when retrieved) were appropriately cleaned with soft brush and distilled water, dried in warm air and reweighed. Then, the weight loss was calculated from the difference between the weight of the retrieved coupons at a given time and the initial weight before immersion. All tests were run in triplicate to verify the reproducibility of the results and the average data with standard deviation ranging from 0 to 0.013 were reported. The weight loss experiment was achieved using a FAJA digital weighing balance of the range 0.0001 to 200 g.

2.3. Electrochemical experiments

The aluminium alloy sheets were mechanically machined into coupons of dimensions 1.5 × 1.5 cm^2 and employed for the electrochemical experiments. Each coupon was appropriately sealed with epoxy resin in such a way that only a square surface of the area (1.0 cm^2) was left uncovered. The exposed surface area was degreased in ethanol and acetone respectively, rinsed with double distilled water and dried in warm air. Electrochemical experiments were conducted in a three-electrode corrosion cell using VERSASTAT 400 complete DC voltammetry corrosion system with V3 studio software (Princeton Applied Research), for electrochemical impedance spectroscopy (EIS) measurements, and Potentiostat/Galvanostat PAR Model 263 corrosion system, with Powersuite software (Princeton Applied Research) for potentiodynamic polarization (PDP) measurements. A graphite rod and a saturated calomel electrode (connected to the system via a Luggin capillary) were used as counter and reference electrodes respectively. Measurements performed in aerated and unstirred solutions at the end of 1 h of immersion at 303 K. The impedance measurements were taken at corrosion potentials (E_{corr}) over a frequency range of 100 kHz–0.1 mHz, with applied potential signal amplitude perturbation of 10 mV. While the potentiodynamic polarization studies were carried out after 1 h of immersions at a potential range ± 250 mV versus open circuit potential (OCP) with the scan rate of 0.5 mV/s. Each experiment was run in triplicate to verify the reproducibility of the systems.

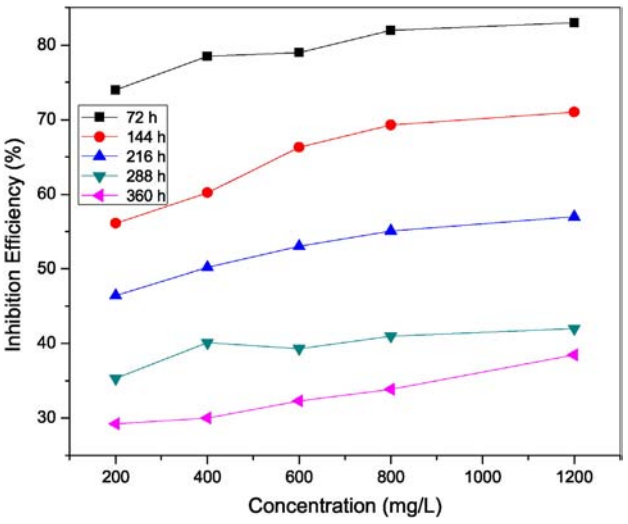

Fig. 2. Variations of the inhibition efficiency with KN extract concentration in 0.1 M HCl for different exposure times.

2.4. Computational studies

Computational modelling of the electronic structures and adsorption properties of selected active constituents identified in KN extract previously [36] were performed using Forcite and DMol3 codes in the Material Studio software (BIOVIA, Inc.).

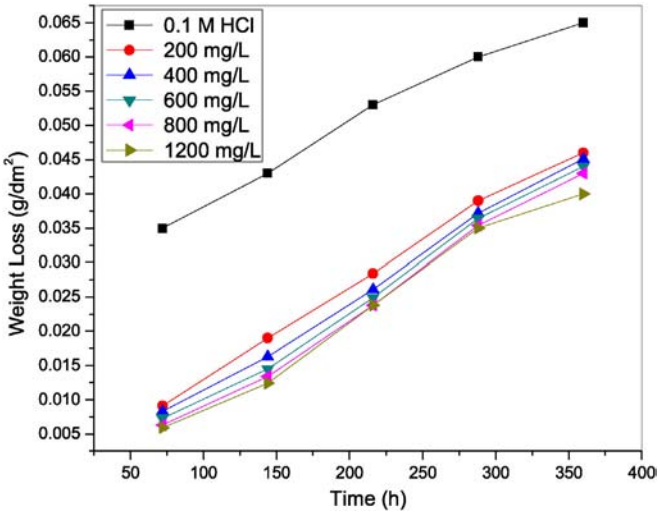

Fig. 1. Weight loss of AA3003 in 0.1 M HCl as a function of KN extract concentration and immersion time.

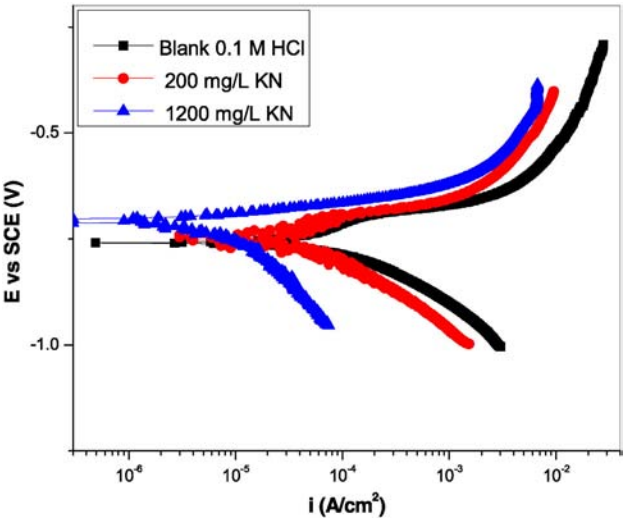

Fig. 3. Potentiodynamic polarization curves for AA3003 in 0.1 M HCl in the absence and presence of KN extract.