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# Evaluation of the inhibitive effect of *Diospyros kaki* (Persimmon) leaves extract on St37 steel corrosion in acid medium

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ABSTRACT

A study was conducted to assess the inhibitive effect of *Diospyros kaki* leaves extract on St37 steel corrosion in 0.1 M HCl solution. Electrochemical (PDP, EIS, DEIS), chemical, and surface morphological screening (SEM, EDS, FTIR) techniques were used in the study. Results show that *D. kaki* leaves extract is an excellent inhibitor for St37 steel in HCl solution. Maximum inhibition efficiency of 91% was afforded by the highest studied concentration of the extract from PDP measurements. PDP results reveal that the extract components act principally as cathodic type inhibitor suppressing the reduction of hydrogen ions in the cathodic region of the metal. DEIS results show that the studied systems exhibit non-stationary character and the adsorbed extract components were stable particularly at long exposure time. SEM, EDAX, and FTIR results support experimental results that components of *D. kaki* leaves extract were adsorbed on St37 surface.

## 1. Introduction

Metals corrosion is a serious problem particularly in the oil and gas industries. Corrosion scientists have devised different approaches such as, the use of corrosion inhibitors (Umoren and Solomon, 2014), cathodic protection (Abreu et al., 1999), application of paint systems containing corrosion inhibitors (Mansfeld and Tsai, 1991), etc. in attempt to control corrosion. However, the use of corrosion inhibitor is simpler and less expensive than other techniques (Umoren and Solomon, 2014). Inorganic (mainly chromates, phosphates, and nitrates) and organic (those having heteroatoms and/or π-bonds) compounds are the commonly used metals corrosion inhibitors. The inorganic compounds have been observed to oxidize metal surface forming impervious film that deny aggressive agents in the environment access to the surface (Salasi et al., 2007). The organic inhibitors, in the other hand, inhibit through the mechanism of adsorption onto metal surface using their heteroatoms and/or π-electrons as adsorption center (Umoren and Solomon, 2014; Tansuğ et al., 2015). Unfortunately, these compounds have generated heated argument in recent times on their suitability as corrosion inhibitors. The inorganic compounds are believed to have toxicity that is unhealthy to human life and the natural environment (Congress, 1995; Toxicological profile for chromium, 1989) while the organic counterparts are said to be expensive (Umoren and Solomon, 2014) and undermine the primary aim of corrosion control which is economic maximization (Umoren et al., 2014a).

Research attention is at present focused on polymers (Abdallah et al., 2012; Awad et al., 2013; Zor et al., 2010; Umoren et al., 2014b) and substances that are of plant origin (Umoren et al., 2014a; Al-Otaibi et al., 2014; Gerengi et al., 2015). However, most reports on polymers portrayed them as moderate inhibitor (Rajeswari et al., 2013; Solomon et al., 2010) leaving corrosion scientists with the option of modification; an act which might not be cost effective. The use of plant parts extract therefore becomes an indispensable area that must be explored. Plants, apart from being environmentally friendly are readily available, cost effective, and renewable. Reports have shown that extracts from plant parts can effectively retard metals corrosion in various corrosive environments. Suleiman et al., (2016) investigated the influence of plant extract, Umbrella Thorn (*Acacia tortilis)* on mild steel exposed to 0.5 M $H_2SO_4$ using gravimetric and electrochemical corrosion techniques. The result gotten indicated that the extract behaved as mixed type corrosion inhibitor and have the ability to protect the metal surface up to 93.19%. Extracts of the leaves of *Acacia tortillus* (Suleiman et al., 2016), *Sansevieria trifasciata* (Oguzie, 2007), *Anacyclus pyrethrum* (Selles et al., 2012), bamboo (*Dendrocalmus sinicus* Chia *et* J.L. Sun) (Li et al., 2014), damsisa (*Ambrosia maritime* L.) (Abdel-Gaber et al., 2008), *Ipomoea invulcrata* (Obot et al., 2010), *Occimum viridis, Telferia occidentalis, Azadirachta indica,* and *Hisbiscus sabdariffa* (Oguzie, 2008) to mention but a few have been reported to be effective as metals corrosion inhibitors.

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*D. kaki* (of the genus *Diospyros* and family *Ebenaceae*) is a native China fruit tree which has long spread over Turkey. The leaves have been reported to possess some medicinal properties which could endear them to the treatment of diseases like haemorrhoids and diarrhea (Xie et al., 2015). The isolation of five triterpenoidal compounds namely, uvao, oleanolic acid, betulinic acid, 19 α-hydroxyursolic acid, and19 α, 24-dihydroxyursolic acid by Guang et al. (2000) from the leaves of *D. kaki* makes the plant part to fulfill in part, a requirement as a metal corrosion inhibitor. There are documentations in the literature on the use of extracts from the leaves of *D. kaki* as inhibitor for steel corrosion in HCl environment. For example, Chen et al. (2015) studied the corrosion inhibitive potentials of extracts of *D. kaki* leaves on Q235A steel in 1 M HCl medium using weight loss and potentiodynamic methods. The results obtained showed that the extracts significantly (maximum inhibition efficiency of 94.3% was gotten) prevented Q235A steel dissolution in the studied environment. Zhang et al. (2013) had earlier reported the effectiveness of the extracts of *D. kaki* leaves on the same metal and environment as that of Chen et al. (2015). The investigation by Zhang et al. (2013) was undertaken using the same techniques as that of Chen et al. (2015). It is obvious from these reports that the extracts of *D. kaki* leaves could be relied upon as metals corrosion inhibitor and thus becomes expedient for a comprehensive work that can provide clearer insight into the inhibitive ability and the mechanism of inhibition (a part which previous works did not take into consideration) by the extracts to be carried out.

The present communication was designed to fill the missing gap in previous reports by carrying out holistic corrosion and corrosion inhibition study on St37 steel in 0.1 M HCl without and with extracts of *D. kaki* leaves. The study was done using weight loss, electrochemical (Potentiodynamic Polarization (PDP), Electrochemical Impedance Spectroscopy (EIS), and Dynamic Electrochemical Impedance Spectroscopy (DEIS)) methods complemented by surface morphological screening (Scanning Electron Microscopy (SEM), Energy Dispersive Spectroscopy (EDS), and Fourier Transform Infrared Spectroscopy (FTIR)).

## 2. Experimental

### 2.1. Materials

Tests were conducted on St37 steel of the following chemical composition (wt%): C 0.217, Cr 0.064, Mn 0.426, Mg 0.0001, Si 0.001, P 0.026, Ni 0.001, Mo 0.001, Cu 0.001, V 0.001, W 0.03 and the balance Fe.

### 2.2. Inhibitor

Fresh leaves of *D. kaki* (Persimmon) were obtained from Duzce University garden, Turkey. They were washed with clean water and dried at 60 °C. Then the dried leaves were ground into powders. 5 g of the powdered *D. kaki* leaves was extracted via soxhlet extractor using ethanol as the extracting solvent for 3 h at 80 ⁰C. The mixture was then cool to room temperature, filtered, and solvent removed by using a rotary evaporator.

### 2.3. Solutions

The corrosive solution of 0.1 M HCl was prepared by dilution of AR grade 37% HCl. The concentration range of *D. kaki* leaves extract was 90, 135, 180, and 225 ppm.

### 2.4. Electrochemical measurements

#### 2.4.1. Electrochemical Impedance Spectroscopy (EIS) and Potentiodynamic Polarization (PDP)

Electrochemical experiments were carried out in a three-electrode-type cell with different compartments for the reference electrode (Ag/AgCl). The counter electrode was a platinum plate, while the working electrode was St37 steel of 0.75 $cm^2$ surface area. Prior to the experiments, the St37 steel specimens were abraded with abrasive paper of 400–1800 grade to obtain flat and clean surfaces. Following this procedure, the abraded St37 coupons were rinsed with distilled water and degreased with acetone. Before each experiment, the working electrode was immersed in test solution for 2 h at 25 °C to attain a stable open circuit potential (OCP) (Gerengi et al., 2015). All electrochemical measurements were performed using a Gamry Reference 600 potentiostat/galvanostat/ZRA instrument, which was controlled by Global software provided by Gamry Instruments Company.

The potentiodynamic polarization study was done at a constant sweep rate of 1 mV/s at −250 to +250 mV interval with respect to corrosion potential ($E_{corr}$). Corrosion current density ($I_{corr}$) values were calculated using Tafel extrapolation method and by taking an extrapolation interval of 100 mV around $E_{corr}$ value once stable. EIS measurements were carried out at $E_{corr}$ using an amplitude signal of 10 mV peak-to-peak, using AC signal at $E_{corr}$ in a frequency range of 10 mHz to 100 kHz. The analyses of EIS data were done using the ZSimpwin 3.21 program.

#### 2.4.2. Dynamic Electrochemical Impedance Spectroscopy (DEIS)

This technique which had been used in previous reports for corrosion studies (Ryl et al., 2011; Gerengi et al., 2009, 2010) was adopted primarily to track the changes taking place on St37 steel surface in HCl solution without and with inhibitor. This method is especially useful because it enables the time of the best inhibition activity by inhibitor molecules to be determined (Gerengi et al., 2014). Fig. 1 shows the DEIS set up. The generation of the multi-sinusoidal perturbation was done with a National Instruments Ltd. PCI-4461 digital-analogue card. The same card was used for the measurement of the current perturbation and voltage response signals with a sampling frequency of 12.8 kHz (Gerengi et al., 2013). Easily assembled, home-made galvanostat equipment, and a current–voltage converter were employed to supply galvanostatic conditions. The perturbation signal was a package which contained current sinusoids of the frequency range from 4.5 to 0.5 Hz. The minimum frequency of the perturbation signal must be higher than the rate of the investigated process; that is, the low frequency limit is a function of the time scale of the analysis performed (Mendoza and Corvo, 2000).

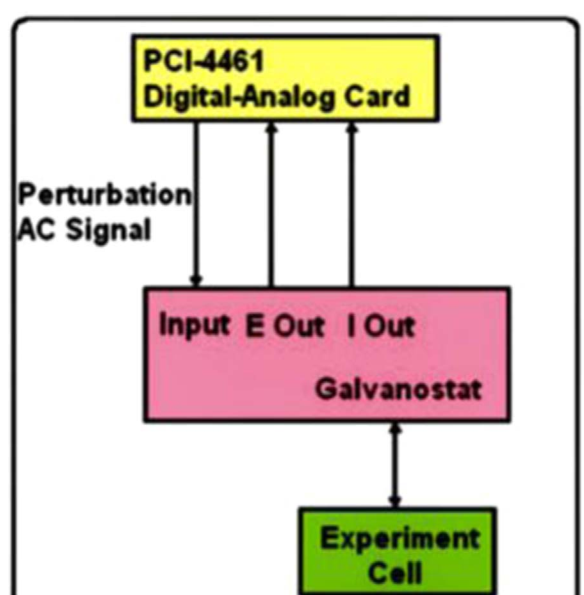


**Fig. 1.** DEIS set up.