Journal of Environmental Chemical Engineering 2 (2014) 1048–1060

Contents lists available at ScienceDirect

Journal of Environmental Chemical Engineering

journal homepage: www.elsevier.com/locate/jece

Inhibition of mild steel corrosion in H_2SO_4 solution by coconut coir dust extract obtained from different solvent systems and synergistic effect of iodide ions: Ethanol and acetone extracts

Saviour A. Umoren*, Moses M. Solomon, Ubong M. Eduok, Ime B. Obot, Aniekemeabasi U. Israel

Materials and Corrosion Protection Research Laboratory, Department of Chemistry, Faculty of Science, University of Uyo, Uyo, Nigeria

ARTICLE INFO

Article history:
Received 10 February 2014
Accepted 30 March 2014

Keywords:
Acid corrosion
Mild steel
Corrosion inhibition
Coconut coir dust
Synergistic effect

ABSTRACT

Weight loss and electrochemical (open circuit potential, potentiodynamic polarization, and electrochemical impedance spectroscopy) techniques were used to assess the effectiveness of ethanol and acetone extracts of coconut coir dust as corrosion inhibitor for mild steel in 0.5 M H_2SO_4 solution at 30–60 °C. It was found that both ethanol and acetone extracts of coconut coir dust retard the dissolution of mild steel in 0.5 M H_2SO_4 solution, but a pronounced effect was noted with ethanol extract. The inhibition efficiency increased with increase in extract concentration but decreased with rise in temperature, which is suggestive of physical adsorption mechanism. Addition of KI was found to synergistically enhance the protective ability of coconut coir dust extracts obtained from both solvent systems investigated. The synergistic effect was confirmed from the synergism parameter (S_0) which was found to be greater than unity. Potentiodynamic polarization result suggests that coconut coir extracts functioned as mixed-type inhibitor. The adsorption of coconut coir dust extracts onto the mild steel surface followed Freundlich adsorption isotherm model. The mechanism of physisorption of the extracts onto the steel surface is proposed from the trend of inhibition efficiency with temperature which is corroborated by the values of activation parameters obtained from the experimental data.

Introduction

One of the practical and cost effective methods of controlling metallic corrosion is the use of corrosion inhibitors. They may be inorganic or organic substances. Inorganic substances suitable as metal corrosion inhibitor must easily oxidize the metal to form an impervious layer which prevent direct ions–metal interaction and hence retard the rate of metal dissolution in the medium. The organic counterpart, on the other hand, must possess features including presence of heteroatoms and /or double bonds, large surface area, active center, etc. which upon adsorption on the metal surface will blanket a large area of the metal and thus isolate it from the aggressive ions present in the environment. The use of inorganic (silicates, nitrates, nitrites, molybates, phosphates, and borates) and organic (predominantly, those with O, N, S, and P heteroatoms) compounds have been reported in the literature as metal corrosion inhibitors in different corrosive environments [1–5]. However, the toxic nature of most inorganic metal corrosion inhibitors and the exorbitant prices of the organic counterparts are the major setbacks for their continuous use.

The search for an efficient inhibitor for metal corrosion in different aggressive media has, in recent times, taken a new dimension owing to the clarion call for green chemistry. More so, since the whole idea of metal protection is anchored on economic gain and environmental sustainability, the substance to be used as metal corrosion inhibitor must be cheap, readily available, and friendly to the environment. Hence research activities are geared towards finding a replacement for inorganic and organic metal corrosion inhibitors. Plant is one of the sources of low cost green metal corrosion inhibitors. Plant products are organic in nature, and contain certain phytochemicals including tannins, flavonoids, organic and amino acids, alkaloids, and pigments which could be extracted by simple less expensive procedures. Extracts from different parts of plant have been widely reported as effective metal corrosion inhibitors in various corrosive environments [6–11]. To enhance the efficiency of metal corrosion inhibitors, extensive studies have been undertaken to identify the synergistic effect of other additives. Li et al. [12] noted that synergism provides a way of improving the inhibitive force of inhibitor, decreasing the quantity of inhibitor usage, and diversifying the application of the inhibitor in an aggressive environment. Reports on the synergistic influence of cations (Ba^{2+}, Sr^{2+}, Ca^{2+}, and Zn^{2+}) [13,14] and anions on metal corrosion inhibitors can be found in corrosion inhibition literatures. For the anions, the halides are the most studied. It is believed that the halide ions are preferentially adsorbed on the metal surface and improve the efficiency of the inhibitor by forming intermediate bridges between the metal surface and the positive end

---

* Corresponding author.
E-mail address: saviourumoren@yahoo.com (S.A. Umoren).

2213-3437/$ - see front matter © 2014 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.jece.2014.03.024

of the inhibitor [15,16]. The synergistic influence by halide ions has been established to follow the trend: $I^- > Br^- > Cl^-$. According to Jeyaprabha et al. [17], the greater influence of iodide ion in comparison to other halide ions could be attributed to its large ionic radius, high hydrophobicity, and low electronegativity. Corrosion inhibition effect of some plant extracts and synergistic influence of iodide addition has been reported by some researchers [18–21].

Coconut coir is a brown, spongy particle which usually falls out when fiber is shredded from the coconut husk. It is usually produced in large quantity as bye-product when coconut husks are processed for the extraction of long fibers from the husk. According to Tejano [22], the coir dust account for about 70% of the weight of the husk. It is a rich source of lignins and tannins. Cellulose, pentosan, and furfural have also been reported as constituents of coir dust [23,24]. Surprisingly, coir dust has, up to now, little commercial or industrial use and is still considered waste and nuisance to the environment; they are normally incinerated or disposed indiscriminately [25,26]. Reported uses of coir dust include in the tropics as a locally available material for preparing soilless growing media for containerized crop production [27,28], as an environmentally sound peat substitute for container-grown ornamental plants [29,30], as a biological filter for odor control and casing layer in mushroom production [31].

We have earlier reported on the corrosion inhibition of aluminum in HCl solution by coconut coir dust extract obtained from acetone as the extractive solvent [32] and mild steel in H_2SO_4 using coconut coir dust extract obtained from water and methanol as solvents of extraction [33]. The present work reports on the inhibitive effect of coconut coir dust extract obtained from ethanol and acetone as extractive solvents and the synergistic effect existing between the extracts and iodide ions for mild steel in sulfuric acid solution using chemical and electrochemical techniques in furtherance of our continuous quest to explore green corrosion inhibitors and ways of utilization of coconut coir dust.

Experimental

Materials preparation

A flat sheet of mild steel 0.09 cm in thickness with the following composition: C = 0.13%; Si = 0.18%; Mn = 0.39%; P = 0.40%; S = 0.04%; Cu = 0.025%; and the balance Fe was used in the study. The mild steel was mechanically press-cut into coupons of 5 cm × 4 cm (area = 20 cm^2) dimensions, for weight loss measurements and 1 cm × 1 cm for electrochemical measurements. The coupons were ground with different grades (# 400, 600, 800 and 1000) silicon carbide paper, degreased in absolute ethanol, dried in warm air and stored in moisture-free desiccators prior to use. The aggressive medium was 0.5 M H_2SO_4 prepared from 98% analytical grade supplied by Sigma–Aldrich. Deionized water was used for the preparation of all reagents. Acetone (boiling point = 56 °C; polarity index = 5.1 and density = 0.791 g/mL at 20 °C) and ethanol (boiling point = 78 °C; polarity index = 5.2 and density = 0.789 g/mL at 20 °C) were used as extractive solvents.

The coconut coir dust was obtained from local farmers and transported to the laboratory. One kgs of the coconut coir dust was extracted in Soxhlet apparatus using the extractive solvents for 48 h. The extracts were concentrated initially using vacuum evaporator and finally by evaporation to dryness on a steam bath to obtain a solid residues devoid of the extractive solvents.

Weight loss measurements

Weight loss measurements were performed using 250 mL capacity beakers containing 200 mL test solution under total immersion in stagnant aerated condition at 30–60 °C maintained in a thermostated water bath. The pre-cleaned and weighed mild steel coupons were suspended in the beakers with the help of rods and hooks. The coupons were withdrawn at 2 h interval progressively for 10 h, cleaned as previously reported 33 and reweighed. The weight loss, in grams, was taken as the difference in the weight of the mild steel coupons before and after immersion in different test solutions. Tests were performed for the blank solution (0.5 M H_2SO_4), solutions of 0.1–0.5 g/L ethanol and acetone extracts of coconut coir dust at different temperatures. The experiments were done in triplicate to ensure good reproducibility. The standard deviation values among parallel triplicate experiments were found to be smaller than 5%, indicating good reproducibility. From the weight loss values, corrosion rates were computed using the expression:

$$C_R = \frac{m_1 - m_2}{At} \quad (1)$$

where m_1 and m_2 are weight loss (mg) of mild steel coupons before and after immersion respectively in test solutions, A is the area of specimen (cm^2) and t is the exposure time (h).

The inhibition efficiency (η%) was computed using Eq. (2)

$$\eta\% = \frac{C_{R(\text{blank})} - C_{R(\text{inh})}}{C_{R(\text{blank})}} \times 100 \quad (2)$$

where $C_{R(\text{blank})}$ and $C_{R(\text{inh})}$ are the corrosion rate in the absence and presence of the inhibitors respectively in 0.5 M H_2SO_4 at the same temperature.

Electrochemical measurements

The electrochemical experiments were performed using a VERSASTAT 400 complete dc voltammetry and corrosion system, with V3 Studio software. A conventional three-electrode Pyrex glass cell was used for the experiments. Test coupons with 1 cm^2 exposed areas were used as working electrode and a graphite rod as counter electrode. The reference electrode was a saturated calomel electrode (SCE), which was connected via a Luggin's capillary. The test electrolyte was 0.5 M solution of H_2SO_4. All experiments were undertaken in stagnant aerated solutions at 30 ± 1 °C. The working electrode was immersed in a test solution for one h until a stable open circuit potential was attained.

Electrochemical impedance spectroscopy (EIS) tests were made at corrosion potential (E_{corr}) over a frequency range of 100 kHz to 100 mHz, with a signal amplitude perturbation of 5 mV. The data were interpreted with Zsimpwin software also supplied by PARC. The potentiodynamic polarization study was from cathodic potential of −250 mV to anodic potential of +250 mV with respect to the corrosion potential at a sweep rate of 1 mV/s. The linear Tafel segments of the anodic and cathodic curves were extrapolated to corrosion potential to obtain the corrosion current densities (i_{corr}). Each experiment was carried out three times to estimate reproducibility and average values of the electrochemical parameters are reported.

AFM surface morphology

The analysis of the morphology of the mild steel surface was carried out using atomic force microscopy (AFM), operated in the contact mode under ambient conditions using 5420 Atomic Force Microscope (AFM) (N9498S) (Agilent Technologies, UK). Images of the specimens were recorded after 6 h exposure time in 0.5 M H_2SO_4 without and with 0.5 g/L EtOH and ACE extracts of coconut coir dust and this concentration of both extracts in combination with 5 mM KI at 25 ± 1 °C.

Results and discussion

Preliminary phytochemical screening

The preliminary phytochemical screening of the coconut coir dust obtained from ethanol and acetone as the extractive solvents was