Measurement 78 (2016) 90–103

Contents lists available at ScienceDirect

Measurement

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

The capability of ultrafiltrated alkaline and organosolv oil palm (*Elaeis guineensis*) fronds lignin as green corrosion inhibitor for mild steel in 0.5 M HCl solution

M. Hazwan Hussin [a,b,*], Afidah Abdul Rahim [a], Mohamad Nasir Mohamad Ibrahim [a], Nicolas Brosse [b]

[a] Lignocellulosic Research Group, School of Chemical Sciences, Universiti Sains Malaysia, 11800 Minden, Penang, Malaysia
[b] Laboratoire d'Etude et de Recherche sur le MAteriau Bois (LERMAB), Faculte des Sciences et Techniques, Universite de Lorraine, Bld des Aiguillettes, F-54500 Vandoeuvre-les-Nancy, France

ARTICLE INFO

Article history:
Received 17 April 2015
Received in revised form 21 June 2015
Accepted 4 October 2015
Available online 22 October 2015

Keywords:
Oil palm fronds
Lignin
Ultrafiltration
Acid corrosion
Corrosion inhibition

ABSTRACT

The inhibitive effect of ultrafiltrated oil palm fronds (OPF) lignins on the corrosion of mild steel in 0.5 M HCl solution has been investigated by electrochemical impedance spectroscopy (EIS), potentiodynamic polarization (PP) and weight loss measurement. The presence of smaller lignin fractions reduces remarkably the corrosion rate of mild steel. The highest corrosion inhibition efficiency for all ultrafiltrated lignins were attained at maximum concentration of 500 ppm ($IE_{P.Soda}$: 87% > $IE_{P.Organosolv}$: 83% > $IE_{P.Kraft}$: 81%). The results from this corrosion test clearly reveal that all ultrafiltrated lignins behaved as a mixed-type inhibitor with predominant anodic (organosolv lignin) or cathodic (alkaline lignin) effectiveness. It was deduced that the inhibition process was spontaneous and the inhibitors were mainly physically adsorbed onto the mild steel surface.

1. Introduction

The corrosion of mild steel in acidic media has been extensively studied in recent years due to its industrial relevance. Acid solutions have been widely used in cleaning, descaling, pickling, and oil well acidizing, requiring the use of corrosion inhibitors to reduce their corrosion attack on metallic structures or materials [1,2]. In general, most of the potential synthetic/natural corrosion inhibitors posses an active functional group such as nitro ($-NO_2$), hydroxyl ($-OH$), heterocyclic compounds and π electrons leading to an adsorption (physisorption or chemisorption) process between the inhibitor and the steel surface [3–6]. Nevertheless, most synthetic inhibitors are highly toxic [7,8] and this has drawn new attention to the use of naturally occurring corrosion inhibitors [9–11] which are low cost and non-hazardous to both human and the environment. More recently, the use of natural polymers (e.g. natural honey, saccharides and tannins) as alternative corrosion inhibitors is of great interest for the corrosion scientists because of their inherent stability and cost effectiveness [12–14]. These polymers form complexes with metal ions on the metal surface which later protect the metal surface from corroding.

Lignin is one of the most abundant naturally occurring polymers and is a by-product of pulping processes which are normally discarded in large quantities. It is built up by the oxidative coupling of three major C6–C3 (phenylpropanoid) units; trans-p-coumaryl alcohol, trans-coniferyl alcohol and trans-sinapyl alcohol. Due to the high content of diverse functional groups (phenolic and

* Corresponding author at: Lignocellulosic Research Group, School of Chemical Sciences, Universiti Sains Malaysia, 11800 Minden, Penang, Malaysia. Tel.: +60 4 653 6378; fax: +60 4 657 4854.
E-mail addresses: mhh@usm.my, mhh.usm@gmail.com (M.H. Hussin).

http://dx.doi.org/10.1016/j.measurement.2015.10.007
0263-2241/

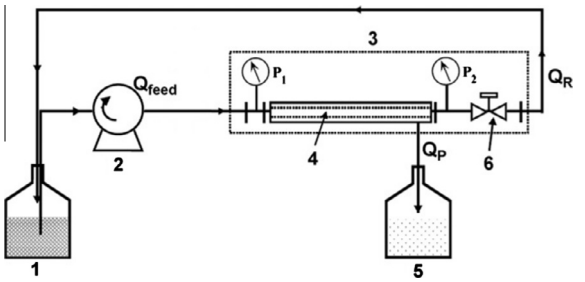

Fig. 1. Scheme of the experimental set-up for batch ultrafiltration: (1) tank with feed mixture, (2) peristaltic pump, (3) membrane cassette, (4) PES membrane, (5) tank with permeate solution and (6) circulating valve. P_1 is the pressure gauge inlet, P_2 is the pressure gauge outlet, Q_{feed} is the feed flow, Q_P is the permeate flow and Q_R is the retentate flow.

aliphatic-OH, carbonyls, carboxyls, etc.) and its phenylpropanoid structure, lignin can act as a neutralizer or inhibitor in the oxidation processes, via the stabilizing reactions induced by oxygen radicals and their respective species. The applicability of lignins from different sources as potential antioxidants has also been successfully tested [15–17]. Moreover, it was revealed that the extraction processes of lignin may give major effect on its antioxidant capacity [18]. The antioxidant properties exhibited by lignin can lead to broader applications as anti-microbial, anti-aging agent and corrosion inhibitor. Although not many studies have been done on the capability of lignin as corrosion inhibitors, most of the findings have agreed that lignin and its derivatives possess inhibitive properties toward the corrosion of metals in corrosive media [19–25].

Unfortunately, the high non-homogeneity complex structure of lignin with high molecular weight distributions has affected its usage in the industrial sectors. In addition, high hydrophobicity of lignin can limit its capability to be employed in other possible applications. Therefore, the modulation of suitable lignin structures (by considering its solubility, molecular weight, phenolic-OH content) is important so that it can overcome such implications. Obviously, the properties of lignin can be improved by modifying the structure into a more suitable structure type. Fractionation of lignin has become a promising method to obtain a more specific molecular weight fraction with different chemical compositions and functionalities. Membrane technology via ultrafiltration was said to be a better method than differential precipitation method to obtain different fractions of lignin with specific molecular weights and low contamination [26]. The effectiveness of the ultrafiltration technology to separate the macromolecular solution is indeed beneficial for the purification and fractionation of lignin, making it suitable for any potential applications.

The oil palm (*Elaeis guineensis*) fronds, OPF have been identified as the major contributor of biomass waste in Malaysia. Recently, we have demonstrated that the ultrafiltration process allows the production of lignins with different chemical structures and antioxidant capacity, enhanced solubility and subsequently making it more adequate for commercial applications [27]. Therefore, the aim of the present work is to test the capability of these ultrafiltrated alkaline and organosolv lignins as green mild steel corrosion inhibitor in acidic solution. The corrosion behavior was evaluated using the electrochemical impedance spectroscopy (EIS), while the potentiodynamic polarization, weight loss measurement and the inhibited mild steel surface were analyzed via the scanning electron microscopy/energy dispersive X-ray spectroscopy (SEM/EDX), X-ray diffraction (XRD) and potential zero charge (PZC). The inhibition pattern was later fitted to various isotherms to determine the adsorptive nature of the ultrafiltrated lignin.

2. Experimental

2.1. Materials

The oil palm fronds (OPF) were obtained from the Valdor Palm Oil Mill near Sungai Bakap plantation (Seberang Prai, Malaysia) in mid 2013. The composition (% w/w) of the OPF according to TAPPI T203 cm-09 and laboratory analytical procedure (LAP) method is cellulose 35.73 ± 1.34%, hemicelluloses 28.39 ± 1.34% and Klason lignin 24.62 ± 1.17% on a dry weight basis. It also contains sugars such as glucans 56.30 ± 3.20%, xylans 16.80 ± 0.60%, arabinans 0.90 ± 0.10%, mannans 0.90 ± 0.00% and galactans 0.40 ± 0.00%. The OPF leaves were removed and the strands were chipped into small pieces. After sun dried for 3 days, the chips were then ground to a 1–3 mm size using Wiley mill and the fiber was further dried in an oven at 50 °C for 24 h. The OPF biomass was first subjected to Soxhlet extraction with ethanol/toluene (2:1, v/v) for 6 h before use. All chemical reagents used in this study were purchased from Sigma Aldrich, Merck, QRec (Malaysia) and VWR (France) and used as received. Dried matter contents were determined using a moisture balance, KERN MRS 120-3 Infra-red moisture analyzer (drying at 105 °C to constant weight). The effective dry matter content of raw OPF biomass was ~89%.

Mild steel coupons having chemical composition (wt%) of 0.08 C, 0.01 Si, 1.26 Mn, 0.02 P and remaining Fe were used. The specimens were polished successively using 400, 600 and 800 gritted emery papers. Next, the specimens were degreased with methanol and washed with distilled water before and after each experiment. The solutions were prepared using AR grade hydrochloric acid. Appropriate concentrations of acids were prepared by using distilled water.

2.2. Alkaline lignin extraction

Both Kraft and soda pulping processes were carried out in a 4 L rotary digester. All pulping conditions followed the method outlined by Hussin et al. [27,28], with slight modifications. For Kraft pulping, a 20% of active alkali and 30% of sulfidity with water to fiber ratio of 8 was used. The time of maximum cooking temperature (170 °C) was set for 3 h. For soda pulping, 30% of active alkali alone was applied at the same condition as described above. The pressure of both Kraft and soda pulping was around 12–15 bar. The