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Electrochemical and surface characterizations of morus alba pendula leaves extract (MAPLE) as a green corrosion inhibitor for steel in 1 M HCl

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ABSTRACT

Recently the researchers' attention has been directed toward using environmentally friendly corrosion inhibitors extracted from plant leaves for corrosion protection of steel structures against acidic environments. The objective of this study is using morus alba pendula leaves extract (MAPLE) as a new green corrosion inhibitor for carbon steel in 1 M HCl solution at different concentrations(0.1–0.4 g/L) and temperatures (25–60 °C). In addition, the effect of addition of potassium iodide (KI) to the MAPLE was studied. Electrochemical investigations were performed by electrochemical impedance spectroscopy (EIS) and polarization test. Also, surface characterizations were done on the steel panels exposed to 1 M HCl solutions containing MAPLE by atomic force microscope (AFM) and Fourier transform infrared spectroscopy (FT-IR). The inhibitor adsorption/desorption behaviors in the 1 M solution was studied by UV–visible analysis. Results obtained from electrochemical measurements revealed that a high inhibition efficiency value of 93% was achieved in the presence of 0.4 g/L MAPLE at room temperature (25 °C). A synergistic effect was observed between KI and MAPLE with optimum concentration of 0.4 g/L MAPLE+ 10 mM KI. Adsorption of extract on the steel surface in the presence of KI resulted in an inhibition efficiency of 96%. The presence of flavonoids such as morusin, kuwanonC and kuwanonG, phenolic acids and pyrrole alkaloids in the MAPLE is responsible for its high inhibition efficiency in 1 M HCl solution on the steel surface. It was found that MAPLE acted as a mixed type corrosion inhibitor and the inhibition efficiency was increased by increasing the inhibitor concentration obeying a Langmuir adsorption isotherm.

1. Introduction

Metals and their alloys are temporary in exposure with acids in industrial processes, *i.e.* oil well acidizing, acid pickling and acid descaling [1]. Corrosion inhibitors are usually added to the acid solutions to prevent or slow down the metal loss and acid consumption rate [2–4]. However, some of these corrosion inhibitors are toxic to the environment and this has prompted the search for finding eco-friendly corrosion inhibitors for metals in acid solution [5]. Different organic and inorganic compounds have been introduced as efficient inhibitors to protect metals from corrosion attack. Usually, organic compounds, that exert a significant influence on the extent of adsorption on the metal surface, can be used as effective corrosion inhibitor. The inhibition effect of most of the organic corrosion inhibitors is related to the presence of heteroatoms *i.e.* S, O or N, and heterocyclic compounds and π-electrons in their structures. The polar function is usually regarded as the reaction center for the establishment of the adsorption process [6–8]. Adsorption of the organic molecules on the metal surface takes place by four mechanisms: (a) electrostatic attraction between the charged molecules and charged metal, (b) interaction of uncharged electron pairs in the molecule with metal, (c) interaction of π-electrons with metal and (d) combination of (a) and (c) [8].

In the last 10 years the researchers attention have been directed toward exploring green and eco-friendly corrosion inhibitors based on the plant origin. These compounds are inexpensive, readily available and renewable sources of materials [5]. It has been shown that the extracts from leaves, barks, seeds, fruits and roots of plants contains mixtures of organic compounds with N, S, and O atoms that are effective compounds of metal corrosion inhibition in aggressive electrolytes [4,7,9–12].

The inhibition effect of green products extracted from the plant leaves have been reported by several authors [2,3,6,10,12,13].

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Odewunmi et al. studied water melon rind extract (WMRE) as an effective corrosion inhibitor for mild steel protection in HCl solution. They found that WMRE can be physically adsorbed on the mild steel surface in acidic media following a Temkin adsorption isotherm [4]. Satapathy et al. studied the corrosion inhibition of justicia gendarussa plant extract (JGPE) in hydrochloric acid solution. The polarization studies showed that JGPE acts as mixed-type inhibitor and the inhibition efficiency of 93% was achieved using 150 ppm of JGPE at 25 °C [12]. Deng et al. investigated the corrosion inhibition properties of Ginkgo leaves extract (GLE) for steel in hydrochloric and sulfuric acid solutions. They showed that GLE is an efficient corrosion inhibitor, with better performance in 1.0 M HCl than 0.5 M H_2SO_4. The adsorption of GLE on carbon steel surface obeyed a Langmuir adsorption isotherm. GLE acted as a mixed-type inhibitor in 1.0 M HCl solution, but with dominant effect on the cathodic reaction in 0.5 M H_2SO_4 [2]. Bonknana et al. studied olive pomace extract as a corrosion inhibitor for steel in HCl medium. An inhibition efficiency of 92.1% was obtained using 1.4×10^{-5} g/L olive pomace [13]. Ji et al. studied musa paradisia peel extract (MPPE) as green corrosion inhibitor for mild steel in HCl solution. Results manifested that the highest corrosion inhibition was achieved using raw banana peel extracts, while ripe banana peel extract showed minimum inhibition potential among the studied extracts. HPLC study revealed that the extracts, *i.e.*, RMMPE, RIMPPE, and ORIMPPE, were abundant in gallocatechin and catechin, which was responsible for the inhibition effect of the inhibitors. Results show that musa paradisiac peel extract obeyed a Langmuir adsorption isotherm [3]

Morus alba pendula leaves (MAPL) belong to the Moraceae family that mainly growths in east Asia [14–16]. MAPL consists of (poly)phenolic substances *i.e.* phenolic acids and flavonoids such as caffeic acid, caffeoylquinic acids, kaempferol-3-*O*-(6-malonyl)–glucoside, quercetin-3-*O*-(6-malonyl)–glucoside, quercetin-3-*O*-glucoside, cinnamic acid derivatives as chlorogenic acid and flavonols as rutin [14,17–19]. It seems that most of these compounds are effective corrosion inhibitors for metals in aggressive environments. However, it has never been tested as corrosion inhibitor for steel in 1 M acidic solution. Thus the aim of this study is to investigate the effect of morus alba pendula leaves extract (MAPLE) as a new green corrosion inhibitor for steel in 1 M HCl solution. The inhibition role of the inhibitor used was investigated at different concentrations and temperatures in 1 M HCl solution by electrochemical techniques. Surface characterizations were done on the steel samples via AFM and FT-IR analyses. UV–visible analysis was conducted in order to determine the inhibitor consumption rate in the solution in the presence and absence of KI.

2. Experimental

2.1. Materials and sample preparation

Morus alba pendula grows in India, south America, north Europe and Asia. The MAPLE used in this study was prepared from the west of Iran and dried before use. The dry fresh MAPLE was washed with tap water, dried in shade, powdered into small pieces and extracted successively by distilled water. For this purpose, 6.250 g of powdered leaves were mixed with 500 ml distilled water on a magnetic stirrer at 70 °C for 3 h. After that the solution filtered by a filter paper and then stirred at same temperature for 2 days to get a concentrated solution. Finally, a dried high viscous dark brown gel was obtained and powdered after drying. The residue obtained was used as corrosion inhibitor in the experiments without further purification.

Carbon steel 1010 (Fe:99.18–9.62 %, Mn: 0.30–0.60 %, S:≤ 0.050%, P:≤0.040% and C:0.080-0.13%) specimens with $2 \times 5 \times 0.1$ cm and $1 \times 1.5 \times 0.1$ cm dimensions were prepared for electrochemical and surface characterization studies. The steel sheets were prepared from Foolad Mobarakeh Co. Before the experiments all of the specimens were abraded by 180 to 1200 emery papers and then degreased with acetone and washed thoroughly with distilled water followed by drying. An appropriate concentration of HCl 37% (mojallali) acid (1 M) was prepared in distilled water. The concentration range of MAPLE was varied from 0.1 to 0.4 g/L.

2.2. Methods

2.2.1. UV–visible and FT-IR analysis

UV/Visible analysis (Optizen 3220) was performed on the solutions without and with MAPLE in the presence and absence of KI to characterize the adsorption/desorption behavior of the inhibitor at different immersion times. The chemical composition of MAPLE was studied by FT-IR (Perkin Elmer, Fron pier model) analysis. Infrared spectra were recorded using KBr powder in the wavenumber range of 400–4000 cm^{-1}.

2.2.2. Electrochemical measurements

The inhibition effects of the MAPLE in 1 M HCl solution on the steel surface was studied by electrochemical impedance spectroscopy (EIS) and polarization techniques (Autolab potentiostat/galvanostat). Both experiments were conducted in a conventional three electrode cell containing carbon steel sheets of size 1×1 cm as working electrode (WE), a Platinum mesh with a large area as counter electrode (CE) and a saturated calomel electrode as reference electrode (RE). The experiments were conducted in 250 ml of 1 M HCl solutions without and with 0.1, 0.2, 0.3 and 0.4 g/L of MAPLE at various temperatures *i.e.* 25, 40, 50 and 60 °C. The measurements were performed at open circuit potential (OCP) after 2 h immersion where the electrode is in its steady-state condition. Potentiodynamic measurements were started from cathodic to the anodic direction at ± 250 mV around OCP with 1.0 mV/s scan rate. Also, the EIS experiments were carried out at frequencies ranged from 100 kHz to 10 mHz and peak to zero amplitude of ± 10 mV. Data analysis was performed via Nova (ver 1.7) software.

2.2.3. Surface analysis

The surface morphology of carbon steel specimens after exposure with 1 M HCl in the absence and presence of MAPLE was studied by an atomic force microscope (AFM) model Ara 1010/A. In addition, the MAPLE adsorption on the steel surface in the presence and absence of KI was investigated by FT-IR analysis with the similar condition mentioned previously.

3. Results and discussion

3.1. Characterization of MAPLE

The chemical structure of the MAPLE was studied by FT-IR and UV–visible analyses. The presence of different chemical bonds and absorption groups in MAPLE can be studied in this way. FT-IR spectrum and UV–visible plot of MAPLE are displayed in Fig. 1.

It can be seen from Fig. 1a that the absorption band at 3628 cm^{-1} (associated with hydroxyl groups) was overlapped by the strong stretching mode of N–H band. The N–H deformation mode can be seen at 1606 cm^{-1}. The peaks at wavenumber region 2929 cm^{-1} are assigned to the stretching mode of aliphatic and aromatic C–H groups, respectively [10]. The peak at 1606 cm^{-1}corresponds to the stretching modes of carbonyl groups in the forms of ester (R–CO–O–R) or aldehyde (R–CO–H) and ketones (R–CO–R) or organic acids (RCOOH). The peak at 1418 cm^{-1}

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