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A natural extract as scale and corrosion inhibitor for steel surface in brine solution

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ABSTRACT

The hazardous effects of most synthetic corrosion inhibitors were the motivation for studying the possible use of eco-friendly extract; olive (Olea europaea L) leaf extract, as a scale and corrosion inhibitors for steel surface in brine solution. The antiscale properties of the natural extract were studied using electrochemical impedance spectroscopy (EIS), and chronoamperometry techniques in conjunction with a microscopic examination. The inhibitive characteristics were investigated using EIS and potentiodynamic polarization curve measurements. Mineral scales were deposited from the brine solution by cathodic polarization of the steel surface at −0.9 V (vs. SCE). The mechanism of scale inhibition was attributed to the formation of cytotoxically inactive complex of calcium caffeate which adsorb on the steel surface at an early stage and poisoned crystal nuclei around them. Potentiodynamic polarization curves indicated that the extract inhibits the corrosion of steel by controlling the cathodic oxygen reduction process. The results showed that olive leaf extract can inhibit corrosion of steel and scale build-up under the conditions tested.

1. Introduction

The use of chemical compounds in a variety of applications is conditioned by environmental and health concerns. Accordingly, during the last years, industrial requirements for chemical compounds refer not only to their efficacy but to safety as well. The requisites for these compounds should focus on non-mutagenic, non-carcinogenic products with characteristics more environmentally acceptable than systems currently in use [1,2].

A number of antiscalants are commercially available and new formulations are continuously being developed and tested for a variety of scaling species [3–16]. Moreover, many corrosion inhibitors have been used in cooling water systems [5]. Particularly, chromates and many other heavy metals were the standard corrosion inhibitors of choice, because of a long history of successful commercial usage and their excellent effectiveness over a wide range of conditions. However, the popularity of inhibitors containing heavy metals is diminishing, because of the concern over their toxic effects on aquatic, and possibly animal, life [17]. Therefore, the hazardous effects of most synthetic corrosion inhibitors are the motivation for the use of natural products. Recently, plant extracts have again become important as an environmentally acceptable, readily available and renewable source for a wide range of needed inhibitors. Plant extracts are viewed as an incredibly rich source of naturally synthesized chemical compounds that can be extracted by simple procedures with low cost. Various natural products were used as corrosion inhibitors in different applications [18–22]. The obtained data showed that plant extracts could serve as effective environmentally friendly 'green' corrosion inhibitors.

Olive is one of the most important trees cultivated in the Mediterranean coastal zone, which grows well under calcareous soil conditions, and provided huge economic and dietetic benefits. The major active components in olive leaves are known to be oleuropein and its derivatives such as hydroxytyrosol and tyrosol, as well as caffeic acid, p-coumaric acid, vanillic acid, vanillin, luteolin, diosmetin, rutin, luteolin-7-glucoside, apigenin-7-glucoside, and diosmetin-7-glucoside [23]. Oleuropein—the most abundant biophenols in olive leaves—prevents cardiac diseases by protecting membrane lipid oxidation [24], acting on coronary dilation and by antiarythmic action [25]; and presents antiviral properties [26,27]. Hydroxytyrosol, an oleuropein derivative, also can be used to protect against cardiac and tumoural disease with effect similar to those of oleuropein; in addition, it protects against atherosclerosis [28].

The aim of this study was to investigate the effect of olive leaf extract as a novel, environmentally friendly, antiscalant and corrosion inhibitors for steel in alkaline $CaCl_2$ brine solution using electrochemical impedance spectroscopy (EIS), potentiodynamic polarization, chronoamperometry techniques and microscopic examination.

2. Materials and methods

2.1. Materials

Double distilled water and analytical reagent-grade NaCl, $NaHCO_3$, Na_2SO_4 and $CaCl_2$ were used for preparing solutions. $CaCl_2$ brine solution was prepared to a concentration of 0.7 M NaCl, 0.0025M $NaHCO_3$, 0.028M Na_2SO_4 and 0.01M $CaCl_2$ [3,29]. Stock solutions of olive leaf

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(Olea europaea L.) extract was obtained by drying the leaves for 2 h in oven at 70 °C and grinding to powdery form. A 5 g sample of the powder was refluxed in 100 mL distilled water for 1 h. The refluxed solution was filtered to remove any contamination. The concentration of the stock solution was determined by evaporating 10 mL of the filtrate and weighting the residue. The concentration of the stock solution was expressed in term of grams per liter.

2.2. Electrochemical techniques

The electrochemical measurements were carried out in a cell with three-electrode mode; platinum sheet and saturated calomel electrode (SCE) were used as counter and reference electrodes. The material used for constructing the working electrode was steel that had the following chemical composition (wt.%): C, 0.21; S, 0.04; Mn, 2.5; P, 0.04; Si, 0.35; balance Fe. The steel was encapsulated in epoxy resin in such a way that only one surface was left uncovered. The exposed area (1 cm^2) was mechanically abraded with a series of emery papers of variable grades, starting with a coarse one and proceeding in steps to the finest (600) grade. The samples were then washed thoroughly with double distilled water, followed with analar grade (A.R.) ethanol and finally with distilled water, just before insertion in the cell. Chronoamperometry, electrochemical impedance and polarization curves measurements were performed using Gill AC instrument. Chronoamperometry curves were carried out by polarizing the steel electrode to -0.9 V (vs. SCE) in test solution for 20 h. Thus, the current passing through the steel electrode, during calcareous deposits, is recorded with respect to time. Polarization curves measurements were obtained at a scan rate of 20 mV/min starting from highly cathodic potential going to anodic direction. EIS measurements were done at -0.9 V (vs SCE) during scale deposition processes and at rest potential for inhibition studies. The frequency range for EIS measurements was 0.1 to 1×10^4 Hz with applied potential signal amplitude of 10 mV. All the measurements were done at 40.0 ± 0.1 °C in solutions open to the atmosphere under unstirred conditions. To test the reliability and reproducibility of the measurements, triplicate experiments were performed in each case at the same conditions.

2.3. Optical microscopic examination

Optical micrographs were taken by using Euromex Optical Microscope with colour video camera that is connected to a personal computer.

3. Results and discussion

3.1. Antiscalant behavior of olive leaf extracts

For proper evaluation of the antiscalants, the tests must be conducted as closely as possible to the actual system operating conditions. An approach using electrochemical techniques to accelerate the formation of scale on an electrode working as a cathode has been developed. It was reported that, even if the scale generated by applying a potential is known to be of a different nature to that formed by immersing in a supersaturated solution. This method is valid and allows a faster evaluation of the scaling power of various industrial, natural and chemically or physically treated waters [30].

3.1.1. Chronoamperometry measurements

Fig. 1 shows the chronoamperometry curves for polarized steel electrode in CaCl$_2$ brine solution in the absence and presence of different olive leaf extract concentrations at 40 °C. The curve obtained in the absence of the extract could be separated into three regions: nucleation, growth, and total coverage of the electrode surface. During the nucleation period, up to 3 h, the scaling process is initialized by increasing the local pH near the electrode surface by the reduction of the dissolved oxygen in brine solution. The resulting hydroxide ions force few nuclei of CaCO$_3$ to be born on the electrode. In the growth period, 3–8 h in the scaling environment, the current decreased linearly indicating that the nuclei already born were growing and occupied the surface leaving some parts free. In the total coverage period, more than 8 h, the current reached a limiting value, signifying the scaling time at which total coverage of the electrode surface was obtained.

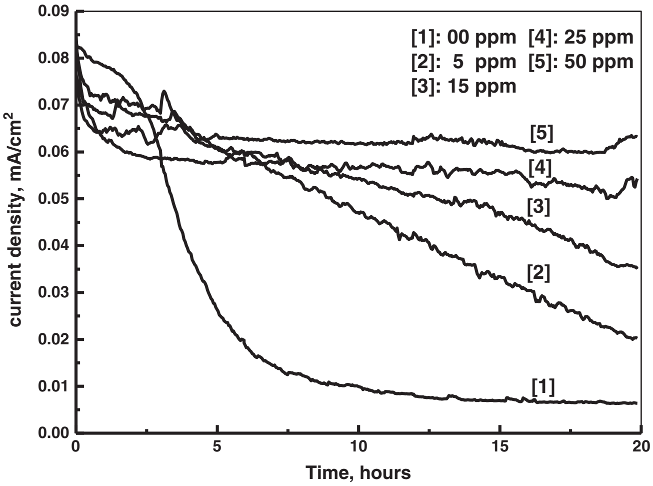

Fig. 1. Chronoamperometry curves for polarized steel electrode in the brine solution in the absence and the presence of different concentrations of olive leaf extract at 40 °C.

The curves obtained in the presence of 5–50 ppm of olive leaf extract show that these concentrations prevent total coverage of the electrode surface within the test period. Increasing extract concentration from 5 to 15 ppm decreases the growth rate that is described by the slope of the line representing the growth step. Higher concentrations (25 and 50 ppm) prevent both scale growth and total surface coverage. The increase of current density values with the extract concentration could be attributed to decrease of scale build-up over the electrode surface. Therefore, it can be concluded that the function of olive leaf extracts is to increase the nucleation time and consequently, retard the scale formation.

3.1.2. Optical micrographic photo

Fig. 2 shows the optical micrographic photo for the steel surface that was cathodically polarized at -0.9 V (vs SCE) for 20 h in brine solution in the presence of different concentrations of olive leaf extract. These micrographs display that, in the absence of olive leaf extract, a complete surface coverage by extremely dense scale crystals takes place that is mainly due to the fast growth rate and lower scale time. The resultant increase in the nucleation time and the accompanied decrease in the growth rate in the presence of the extract lead to a decrease in the amount of the scale deposited over the entire area compared to the uninhibited brine solution. The surface area occupied by the scale particles decreases with increasing olive leaf extract concentrations. The critical extract concentration required to inhibit completely the scale formation is found to be 50 ppm of olive leaf extract.

3.1.3. Impedance measurements

Fig. 3 shows Nyquist plots for steel that was cathodically polarized at -0.9 V for 20 h in brine solution in the presence of different concentrations of olive leaf extract. As seen, the figure shows different types of a distorted semicircle whose size decrease with increasing olive leaf extract. The shape of the obtained spectra was correlated to scale built up stages over the electrode surface [3]. In the absence of the extract, the impedance spectrum was related to complete surface