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Green Anti-scalent for Cooling Water Systems

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The effect of Punica granatum hull and Punica granatum leaf extracts as green inhibitors for the formation of calcium carbonate scale have been investigated using conductivity measurements, electrochemical impedance spectroscopy (EIS), and chronoamperometry techniques in conjunction with the scanning electron microscopy (SEM), energy- dispersive x-ray analysis (EDX) and optical microscopic examinations. Mineral scales were deposited from the brine solution by cathodic polarization of the steel surface. The results showed that the anti-scaling property of the extracts could be attributed to the presence of ellagic acid. In solution, ellagic acid retards calcium carbonate precipitation via formation of a complex with the calcium cations. Thin, smooth and non adherent film formed over the steel surface, under cathodic polarization, by the deposition of the calcium-ellagate complex. The hull extracts were found to exhibit better anti-scalant properties than Punica granatum leaf extract. The stability of the aqueous extracts with time was also investigated.

Keywords: anti-scalant; inhibitors; extract; alkaline.

1. INTRODUCTION

The formation of mineral scales is one of the persistent and expensive problems in many industrial operations such as distillation, cooling and heat exchange processes [1, 2]. Scales cause severe economic loss, since it limit heat exchange and can reduce tube diameter causing a significant decrease in water flow. In order to solve this problem many scale inhibitors have been used in cooling water systems [3, 4]. Currently plant extracts are employed as scale inhibitors in order to develop new cleaning chemicals for green environment [5-7]. Plant extracts are viewed as an incredibly rich source of naturally synthesized chemical compounds that can be extracted by simple extract procedures with low cost.

The aim of this study was to investigate Punica granatum leaf and Punica granatum hull extracts as a novel environmentally friendly anti-scalant for $CaCO_3$ calcareous deposits on steel in an alkaline $CaCl_2$ brine solution using electrochemical impedance spectroscopy (EIS), chronoamperometry techniques, conductivity measurements 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 $CaCl_2$ [8]. Stock solutions of Punica granatum extract was obtained by drying the leaf or hull for two hours 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 one hour. 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, and electrochemical impedance spectroscopy measurements were performed using Gill AC instrument (UK). Chronoamperometry curves were carried out by polarizing the steel electrode to –0.9 V (vs. SCE) in test solution for 20 hours. Thus, the current passing through the steel electrode, during calcareous deposits, is recorded with respect to time. EIS measurements were done at rest potential just after scale deposition processes. The frequency range for EIS measurements was 0.1 to $1x10^4$ Hz with applied potential signal amplitude of 10 mV. All the measurements were done at $40.0 \pm 0.1^{O}C$ 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. Conductivity test:

The test setup as described elsewhere [8].consists of a glass container, mechanical stirrer and conductivity sensor of TRACEABLE conductivity meter. The setup were carefully cleaned by 1M H_2SO_4 and double distilled water to remove all traces of deposits which could become a source of crystal nuclei. Prior each experiment, 5 mL of 0.1 M $CaCl_2$ solution is added to appropriate volume of the stock solution of the extract then the mixture is completed to 100 mL by doubly distilled water. The conductivity of stirred solution is measured during titration by 0.1M Na_2CO_3. The titrating solution was added in portions of 0.2 mL each. Measurements were done at 25.0 ± 0.1°C.

2.4. Optical microscopic examination:

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

2.5. Scanning Electron Microscopy and Energy- Dispersive X-Ray Analysis

A Joel GFM 5300 scanning electron microscope (SEM) connected to energy-dispersive x-ray (EDX) was used to study the morphology and analyze the film formed over the steel surface.

3. RESULTS AND DISCUSSION

3.1. Conductivity measurements

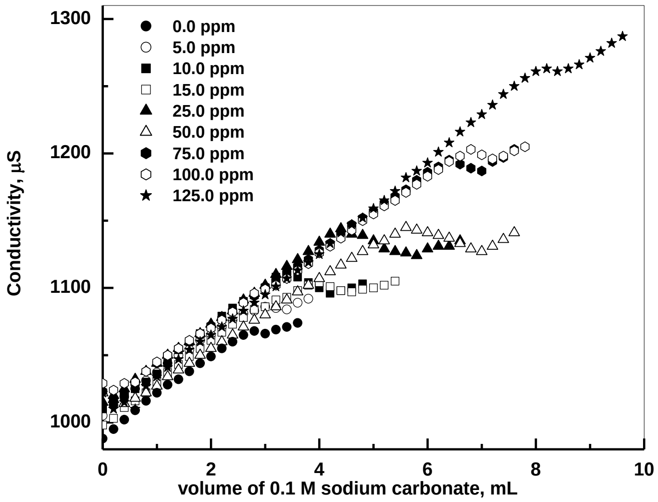


Figure 1. Variation of conductivity of 0.1 M $CaCl_2$ solution in the presence and absence of different concentrations of Punica granatum hull extracts with the volume of 0.1 M Na_2CO_3 at 25°C.

In order to test and evaluate the ability of a given substance to inhibit the scale formation Drela et al.[8] developed a rapid and simple chemical test based upon monitoring the solution conductivity while calcium carbonate is being precipitated from calcium chloride solution by addition of sodium carbonate. So, this method was used as the first step to test the efficiency of Punica granatum hull and Punica granatum leaf extracts as scale inhibitors.

Fig. 1 shows the variation of solution conductivity of $CaCl_2$ with the amount of sodium carbonate added in the presence and the absence of different Punica granatum hull extract concentrations**.**

As seen, the conductivity of the solution increases linearly with increasing the added amount of the sodium carbonate up to a certain point where the solution becomes supersaturated, where a rapid precipitation of $CaCO_3$ begins and a decrease of conductivity results. After complete precipitation, further addition of sodium carbonate produces more ions in the solution that increases the conductivity again. However, the figure reveals that increasing Punica granatum hull extract concentration shifts the maximum, after which precipitation occurs, to a higher amount of sodium carbonate. Similar observations were recorded for Punica granatum leaf extract indicating that the presence of Punica granatum hull or Punica granatum leaf extracts impedes the supersaturation. The anti-scaling property may be attributed to the presence of chelating agents. The chemical constituents of Punica granatum were thoroughly reviewed by Wang et al.[9]. They reported that ellagic acid, Fig. 2, is abundant in every part of pomegranate and its content can be as high as 0.2% in the pericarp (hull) and leaves.

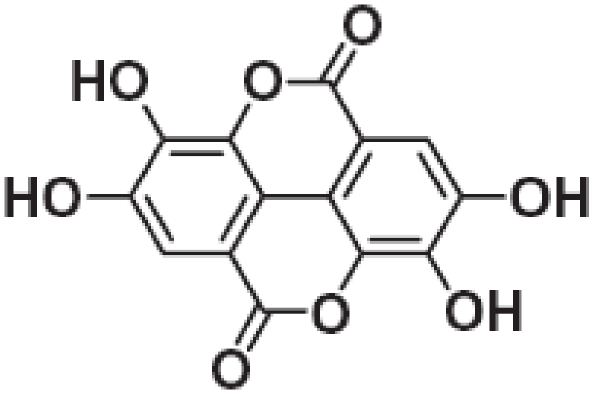


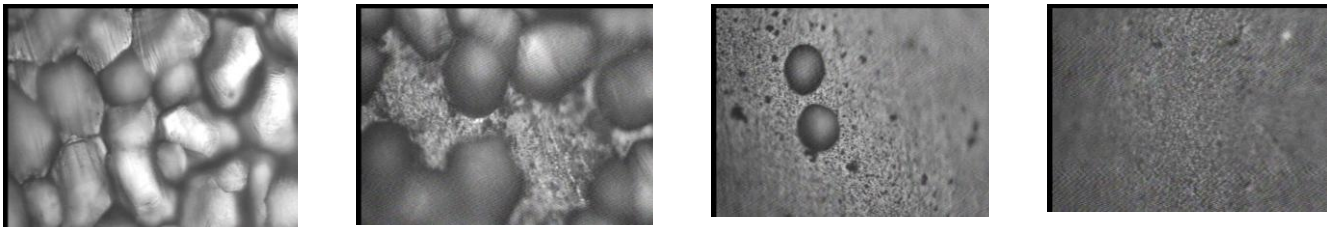
Figure 2. Chemical structure of ellagic acid

Przewloka et al. [10] reported that calcium-ellagate complexation occurred at basic pH, beginning between pH 7 and 8.5 and peaking at pH 10.5. Therefore, the mechanism of retarding calcium carbonate precipitation could be attributed to complex forming properties of the gallic acid together with the calcium cations.

It must be noted that the conductivity method is a screening test, similar to that provided by NACE standards [11], designed to measure the ability of inhibitors to prevent the precipitation of calcium carbonate from solution. These test methods describe the tendency of the extract to inhibit scale in the solution (complex forming, dispersion and liquefaction) and are not applicable to film forming inhibitors.

3.2. SEM, EDX and Optical microscopic examination

An important feature of cathodic protection in seawater is the formation of calcareous deposits. This part aims to study the ability of the used extracts to inhibit the scale deposition under real conditions for cathodically protected systems. The micrographic photo shown in Fig. 3 displays that for the cathodically polarized steel in $CaCl_2$ brine solution, in the absence the Punica granatum hull extracts, a complete surface coverage by extremely dense scale crystals takes place. The scale deposits decrease with increasing extract concentrations up to 100 ppm of the extract where a smooth film formed over the surface. Similar observations were recorded for Punica granatum leaf extract.



Blank 10 ppm 50 ppm 100 ppm

Figure 3. Optical micrograph photo (40X) for cathodically polarized steel in $CaCl_2$ brine solution in the absence and presence of different Punica granatum hull extract concentrations after 21 hours at 40^oC.

The mechanical scratch of the films formed in the presence of 100 ppm of Punica granatum hull or Punica granatum leaf extracts, Fig. 4, indicated the non adherence character of the formed films**.**

Punica granatum hull Punica granatum leaf

Figure 4. Optical micrograph photo (40X) for cathodically polarized steel in $CaCl_2$ brine solution in the presence of 100 ppm of extracts after 21 hours at 40^oC with film scratching.

The scanning electron microscope photo, Fig. 5, obtained for the film formed over the steel surface that was polarized at -0.9 V (vs. SCE) in brine solution containing 100 ppm punica grantum hull extracts for 21 hours shows smooth, thin and continuous film cover the electrode surface.

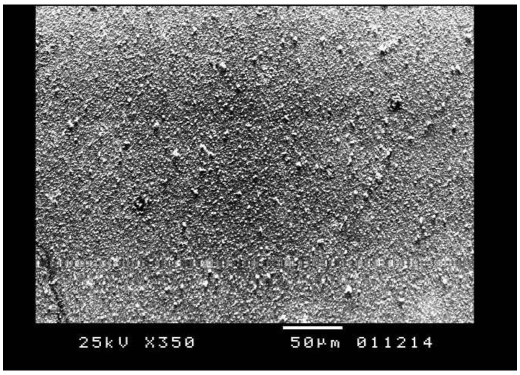


Figure 5. Scanning electron microscope photo for the film formed over steel surface that was polarized at -0.9 V (vs. SCE) in brine solution containing 100 ppm punica grantum hull extracts for 21 hours.

The elemental analysis data obtained from EDX analysis for the film are given in Table 1. Mirdehghan and et al [12] reported that Punica granatum is an important source of macronutrients (P, K, N, Mg, Ca and Na) and micronutrients (Zn, Cu, Mn, Fe and B) in arils and peel of Punica granatum**.**

Table 1. The elemental analysis data obtained from EDX analysis for the film formed.

Element	**Fe**	**Ca**	**Na**	**Si**	**Mn**	**P**
$K_\propto$	**56.0**	**19.3**	**11.2**	**6.7**	**4.2**	**2.6**

The high percent of calcium suggests that the antiscalent action of the extracts may take place via deposition of thin film of calcium-ellagate complex that is previously formed in solution, over the electrode surface, i.e., surface modification.

3.3. Impedance Measurements

Figure 6 shows the Bode impedance plots, for steel that was cathodically polarized at -0.9 V (vs. SCE) for 21 hours in the brine solution free from and containing different concentrations of Punica granatum hull extract. The Figure shows that the maximum of Bode theta plots shifts to the higher frequency region with decreasing extract concentration. This shift is most likely attributed to the formation of surface deposits because its appearance correlates with the surface dielectric film that is normally having a small time constant and so has a phase shift in the high frequency range [13, 14]. Moreover, it is also observed that the modulus impedance at minimum frequency, R_{min}, values increase with decreasing Punica granatum hull extract concentration. These observations indicate that increasing the extract concentration inhibits the formation of surface deposits. Similar observations were recorded for Punica granatum leaf extract.

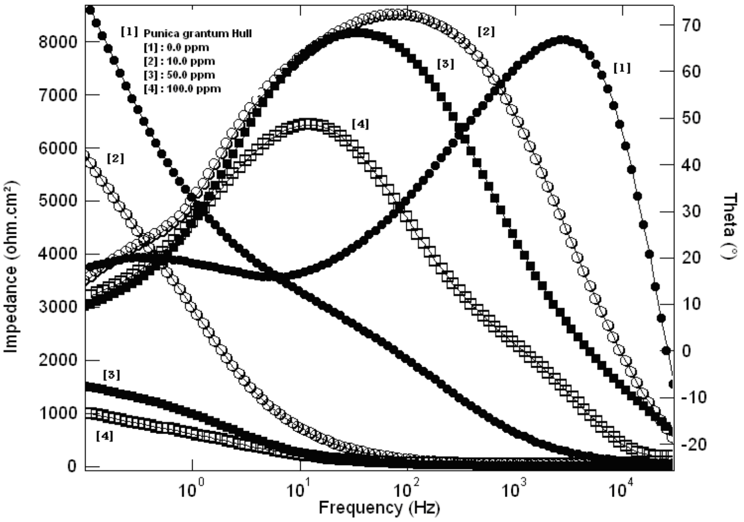


Figure 6. Bode impedance plots, for steel that was cathodically polarized for 21 hours at -0.9 V in the brine solution free from and containing different concentrations of Punica granatum hull extract.

3.4. Chronoamperometry measurements

Figure 7 shows the chronoamperometry curve for polarized steel electrode in the $CaCl_2$ brine solution in the absence and presence of different concentrations of Punica granatum hull extract.

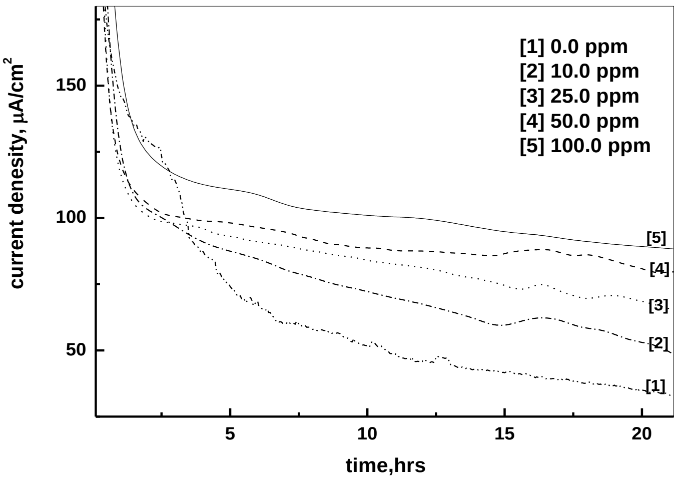


Figure 7. Chronoamperometry curves for cathodically polarized steel electrode at -0.9 V (vs. SCE) in the $CaCl_2$ brine solution in the absence and the presence of different concentrations of Punica granatum hull extract at 40^oC.

As seen, in the absence the Punica granatum hull extracts the plot can be separated into three regions: a nucleation region, a growth region and complete surface coverage of the electrode surface region. During the nucleation period, up to three hours, the scaling process is initialized by increasing the local pH near the electrode surface by the reduction of the dissolved oxygen in brine solution according to chemical equation:

$$O_2 + 2H_2O + 4e \rightarrow 4OH^-$$

The resulting hydroxide ions force few nuclei of $CaCO_3$ to be born on the electrode surface according to the chemical reaction.

$$Ca^{2+} + HCO_3^- + OH^- \rightarrow CaCO_3(s) + H_2O$$

In the growth period, 3-8 hours in 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 eight hours, the current reach a limiting value which defines practically the scaling time at which total coverage of the electrode surface was obtained. The low limiting current value suggests that the surface coverage is porous, since if it were completely blocked, the current would be zero.

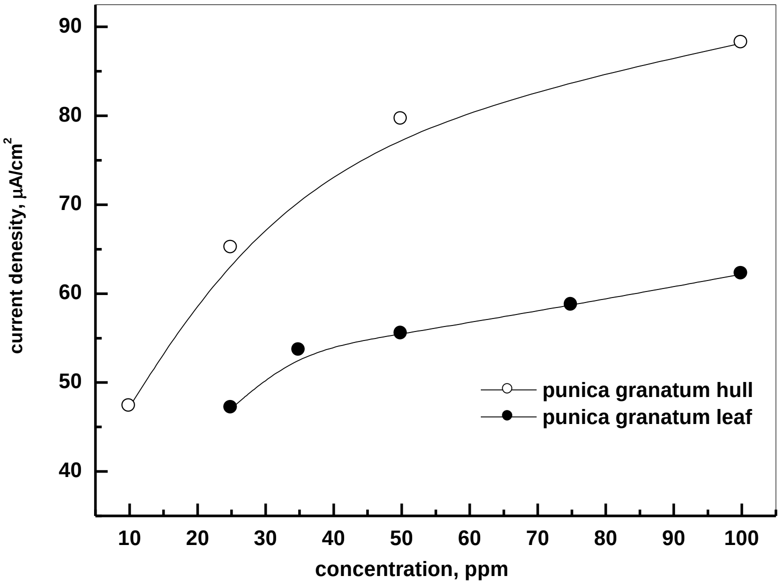
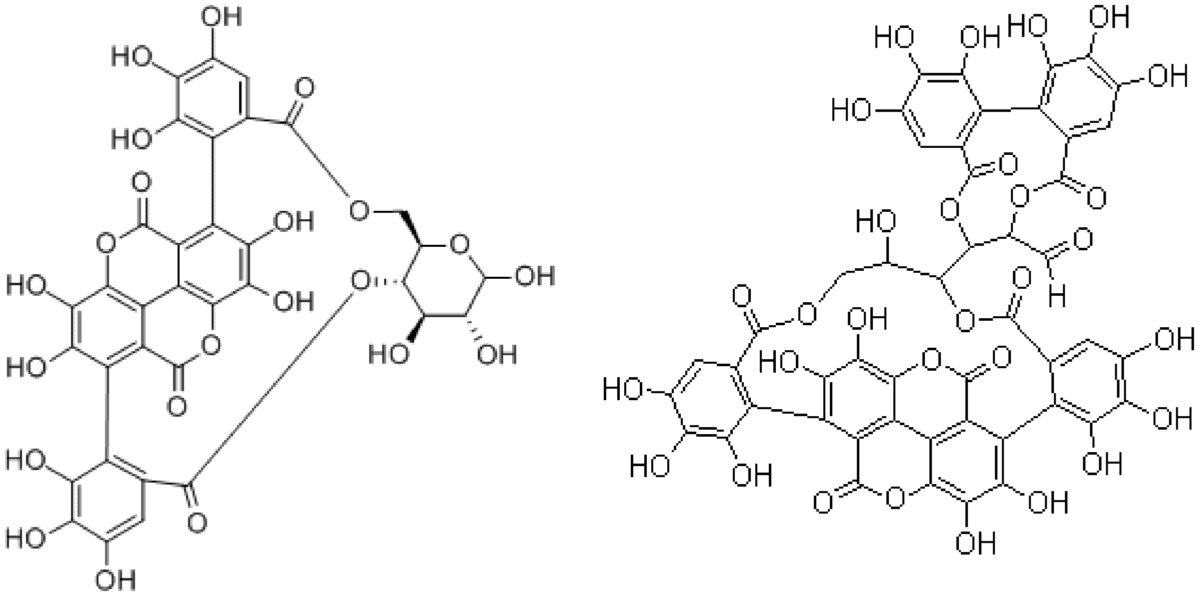


Figure 8. Variation of current density after polarizing the steel electrode for 21 hours in brine $CaCl_2$ solution in the absence and the presence of different concentrations of plant extracts.

On the other hand, in the presence the Punica granatum hull extracts the crystal growth and total blocking of the electrode surface stages were not observed within the exposure period even in the presence of low concentration of the extract (10 ppm) indicating that this extract impedes the crystal growth stage by retarding the nucleation step. The residual current density increase from 47 to 88 μA with increasing the concentration of the Punica granatum hull extract from 10 to 100 ppm indicating the effectiveness of Punica granatum hull extract as anti-scalant.

Figure 8 shows the variation of current density obtained from chronoamperometry curves for polarized steel electrode in the $CaCl_2$ brine solution after 21 hours with the concentrations of Punica granatum hull and leaf extracts. The figure focuses on the concentration range that totally impedes the crystal growth step. Since, the current density is inversely proportional to the area covered by the calcareous scale. Therefore, the observed high current density obtained in the presence of Punica granatum hull extract indicates that the hull extracts exhibit better anti-scalant properties than Punica granatum leaf extract. This may be explained on the basis that: among the different constituents of Punica granatum extract, punicalin and punicalagin, Fig. 9 (a and b), are the major constituents of hull; however, they are practically undetected in the leaves [9].



punicalin punicalagin

Figure 9. The chemical structure of (a) punicalin, and (b) punicalagin

Therefore, punicalin and punicalagin may causes suspended solid to disperse and liquefy through adsorption, which changes the structure and properties of scale. The adsorption could take place via (i) electrostatic attraction between the charged particles and the charged chemical constituents of the extract (ii) dipole–type interaction between unshared electron pairs in the extracted molecules and growing particles (iii)π- interaction with particles surfaces, and (iv) a combination of all the above [7]. These cases of adsorption can arise since the chemical constituents of punicalin and punicalagin, contain lone pairs of electrons, and conjugated π- type bond system. The high efficiency of Punica granatum hull extracts may be attributed to its ability to inhibit scale in the solution (complex forming, dispersion and liquefaction) and to acts as film forming inhibitors.

3.4.1. Effect of shelf storage time on the anti-scale efficiency:

Most of the aqueous extracts are unstable; therefore, it is worth studying the shelf storage time of the extract on anti-scale efficiency. Figure 10 shows the chronoamperometry curves for the cathodically polarized steel electrode at -0.9 V vs. SCE in the brine solution containing 50 ppm of Punica granatum hull extract at different shelf storage time. The aqueous extract was stored at 5 °C during the test period.

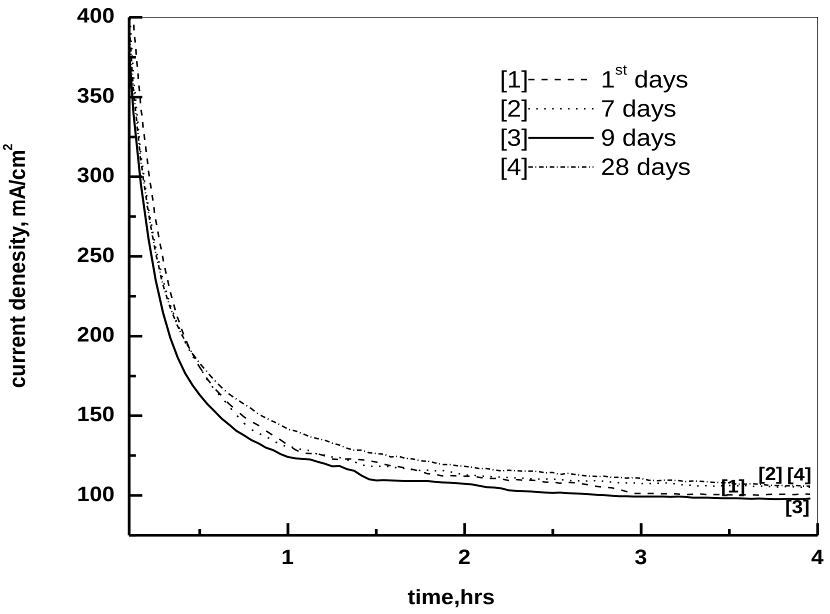


Figure 10. Chronoamperometry curves for cathodically polarized steel electrode at - 0.9 V (vs. SCE) in brine solution in presence of 50 ppm of Punica granatum hull extract at different shelf storage time

It is observed that increasing shelf storage time up to 28 days has a slight effect on the current density and did not affect the shape of the chronoamperometry curve within the storage time indicating the stability of the aqueous extract as anti-scalant inhibitor under the condition described. This conclusion was supported by micrographic photos obtained after polarizing the steel electrode in brine solution at -0.9 V (vs.SCE) for 4 hours containing 50 ppm Punica granatum hull at 1st day and after 28 days of storage, Fig. 11.

4. CONCLUSIONS

The results reported in this paper can be summarized as follows:

- Conductivity measurements showed the tendency of the Punica granatum hull or leaf extracts to inhibit scale in the solution.

- Microscopic examination for the film formed over the steel surface clarified that the anti-scalant action of the extracts may take place via surface modification.
- EIS measurements indicated that decreasing extract concentration shifts the maximum of Bode theta plots to the higher frequency region and increase the values of modulus impedance at the minimum frequency, R_{min}.
- Chronoamperometry measurements explained that the hull extracts exhibit better anti-scalant properties than Punica granatum leaf extract.
- Measurements of the effect of shelf storage time indicated the stability of the aqueous extracts as anti-scalant inhibitors under the condition described.

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References

1. K.D. Demadis, E. Mavredaki, A. Stathoulopoulou, E. Neofotistou, C. Mantzaridis, *Desalination* 213 (2007) 38–46.
2. Y. Tang, W. Yang, X. Yin, Y. Liu, Y.P. Yin, J. Wang, *Desalination* 228 (2008) 55–60.
3. A.L. Kavitha, T. Vasudevan, H. Gurumallesh Prabu, *Desalination* 268 (2011) 38–45
4. R. Ketrane, B. Saidani, O. Gil, L. Leleyter, F. Baraud, *Desalination* 249 (2009) 1397–1404.
5. A.M. Abdel-Gaber, B.A. Abd-El-Nabey, E. Khamis, and D.E. Abd-El-Khalek, *Desalination* 278(2011)337-342
6. Suharso, Buhani, Syaiful Bahri, Teguh Endaryanto, *Desalination* 265 (2011) 102–106.
7. A.M. Abdel-Gaber, B.A. Abd-El-Nabey, E. Khamis, D.E. Abd-El-Khalek, *Desalination* 230 (2008) 314–328
8. I. Drela, P. Falewicz and S. Kuczkowska, *Wat. Res.*, 32 (1998) 3188.
9. R. Wang, Y. Ding, R. Liu, L. Xiang, L.Du, *Veg. Cereal Sci. Biotech.*, 4(Special Issue 2) (2010) 77-87.
10. S.R. Przewloka, B.J. Shearer, *Holzforschung*, 56(2002) 13–19.
11. NACE Standard TM0374-95: laboratory screening tests to determine the ability of scale inhibitors to prevent the precipitation of calcium sulfate and and calcium carbonate from solution (for oil and gas production systems) Published 1995 by NACE in Houston.
12. S. H. Mirdehghan, M. Rahemi, *Sci. Hortic.*, 111 (2007) 120–127
13. S. Feliu, J.C. Galvan and M. Morcillo, *Corros. Sci*, 30 (1990) 989.
14. C.H. Tsai and F. Mansfeld, Corrosion, 49 (1993)727.