Desalination and Water Treatment
www.deswater.com
doi: 10.1080/19443994.2014.987174

57 (2016) 2870–2876
February

Taylor & Francis
Taylor & Francis Group

Investigation of a novel environmentally friendly inhibitor for calcium carbonate scaling in cooling water

D.E. Abd-El-Khalek[a,*], B.A. Abd-El-Nabey[b], Mervat A. Abdel-kawi[c], S.R. Ramadan[c]

[a]*Marine Chemistry Department, National Institute of Oceanography and Fisheries, Elanfoshy, Alexandria, Egypt, Tel. +20 1003859412; Fax: +20 34801499; email: dalia1282002@yahoo.com*
[b]*Faculty of Science, Chemistry Department, Alexandria University, Ibrahimia, P.O. Box 426, Alexandria 21321, Egypt, Tel. +20 1223307408; email: profbesheir@gmail.com*
[c]*Environment Department, Institute of Graduate Studies and Research, El-Horrya Road, Alexandria, Egypt, Tel. +20 1224879931; email: mervat_kawi@yahoo.com (M.A. Abdel-kawi), Tel. +20 1064951889; email: sarah_ramadanchemist@yahoo.com (S.R. Ramadan)*

Received 9 April 2014; Accepted 24 October 2014

ABSTRACT

The antiscale properties of palm leaves extract (*Phoenix dactylifer* L) were studied using electrochemical impedance spectroscopy (EIS) and chronoamperometry techniques, in addition to microscopic examination. Calcium carbonate scales were deposited from the brine solution by cathodic polarization of the steel surface at −0.9 V (vs. SCE). Chronoamperometry curves and EIS measurements displayed that palm leaves extract increased the time of $CaCO_3$ nuclei formation and consequently, retarded the growth step. The optical micrographs of the steel electrode clarified that the surface area occupied by the scale particles decreased with increasing plant extract concentrations. The results showed that palm leaves extract could be considered as efficient inhibitor for $CaCO_3$ precipitation.

Keywords: Green antiscalant; Palm leaves; EIS; Chronoamperometry

1. Introduction

Cooling is the largest use of water in industry. Calcareous scaling on heat exchangers and petroleum production equipment surfaces is often the persistent problem in cooling water systems, boilers, secondary oil recovery, and desalination plants [1–3]. In order to solve this problem, many scale inhibitors have been used in cooling water systems [4–8].

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 [9,10]. Some green antiscalants were tested and evaluated [11,12]. Currently plant extracts are employed as scale inhibitors in order to develop new cleaning chemicals for green environment [13–15].

This work aims to examine the efficiency of palm leaves extract as antiscalant in cooling water using chemical and electrochemical techniques.

---

*Corresponding author.

2. Materials and methods

2.1. Materials

Double distilled water and analytical reagent grade $NaCO_3$, 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, 0.0025-M $NaHCO_3$, 0.028-MNa_2SO_4, and 0.01-M $CaCl_2$. The 0.7-M NaCl solution was chosen to produce the total ionic strength of natural seawater at 35 salinity [16]. Stock solutions of Palm leaves (*Phoenix dactylifer* L) extract was obtained by drying the leaves for two hours in oven at 70℃ 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 weighing the residue. The concentration of the stock solution was expressed in terms of grams per liter.

2.2. Conductivity test

The test setup as described elsewhere [17] consists of a glass container, mechanical stirrer, and conductivity sensor of HQ14d conductivity meter. The setup was carefully cleaned by 1-M 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 double distilled water. The conductivity of stirred solution is measured during titration by 0.1-M Na_2CO_3. The titrating solution was added in portions of 0.2-mL each. Measurements were done at 25.0 ± 0.1℃.

2.3. 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, respectively. 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; and balance Fe. The steel was encapsulated in an 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 Gamery instrument R600™ Potentiostat/Galvanostat/ZRA. 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. EIS measurements were done at rest potential just after scale deposition processes. The frequency range for EIS measurements was 0.1–1 × 104 Hz with applied potential signal amplitude of 10 mV. All the measurements were done at 40.0 ± 0.1℃ 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.

2.4. Optical microscopic examination

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

3. Results and discussion

3.1. Conductivity measurements

In order to test and evaluate the efficiency of a given substance as scale inhibitor, Drela et al. [17] 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 palm leaves extract as scale inhibitors.

Fig. 1 shows the variation in conductivity of 0.1-M $CaCl_2$ solution in absence and presence of different concentrations of palm leaves extract with volume of 0.1-M Na_2CO_3 added. It is clear that the conductivity of the solution increases linearly with increasing the added amount of the sodium carbonate up to certain point, at which the solution becomes supersaturated, where a rapid precipitation of calcium carbonate 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. Moreover, the figure reveals that increasing palm leaves extract concentration shifts the maximum, after which precipitation occur to a higher amount of sodium carbonate. This indicates that the presence of plant extract impedes

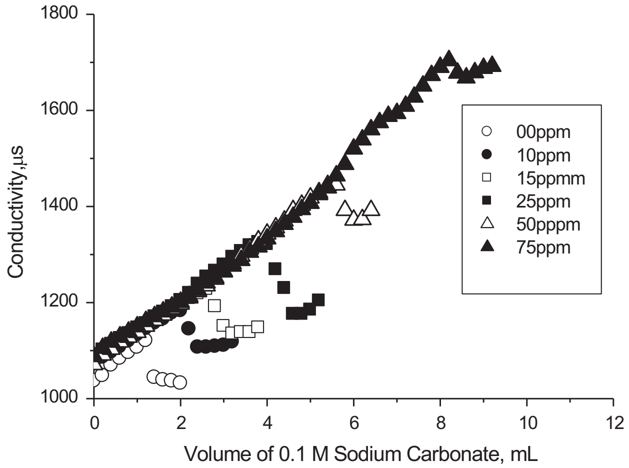

Fig. 1. Variation of conductivity of 0.1-M $CaCl_2$ solution in the absence and presence of different concentrations of palm leaves extract with volume of 0.1-M Na_2CO_3.

the supersaturation that may be attributed to complex forming of the extract together with the cations present and in this way reduces the rate of nucleation and crystal growth. In addition, the presence of the extract may cause suspended solid to disperse and liquify through adsorption, which changes the structure and properties of scale [13]. 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 of the above. These cases of adsorption can arise since the phytochemical screening of palm leaves extract demonstrated the presence of alkaloids, flavonoids, phenols, phytosterols, tannins, amino acids, terpenoids, carbohydrates [18], and saponin glycoside [19] which are shown in Fig. 2. These compounds contain lone pairs of electrons, and conjugated π- type bond system which may be responsible for the adsorption.

Chemistry behavior of the extract of the plants is complex as a result of the complex chemistry involved. This chemistry is made even more complex by the fact that we do not know exactly the extracted compounds in the plants that might be preventing scale formation.

3.2. Chronoamperometry measurements

Several investigators [20–22] have used the chronoamperometry technique to investigate scaling processes. The current passing through the electrode is recorded with respect to time, while the electrode is polarized at the diffusion limiting current of oxygen (−0.9 V vs. SCE). It is well documented that the scales can be formed on metal surfaces under cathodic polarization. These scales cover the active surface area available for the electrochemical reactions and consequently reduce the current density [23].

Fig. 3 shows the chronoamperometry curves for polarized steel electrode in the $CaCl_2$ brine solution in the absence and presence of different concentrations of palm leaves extract at 40˚C. As seen, in the absence of plant extract, the initial current decrease is attributed to some decrease in the oxygen reduction rate

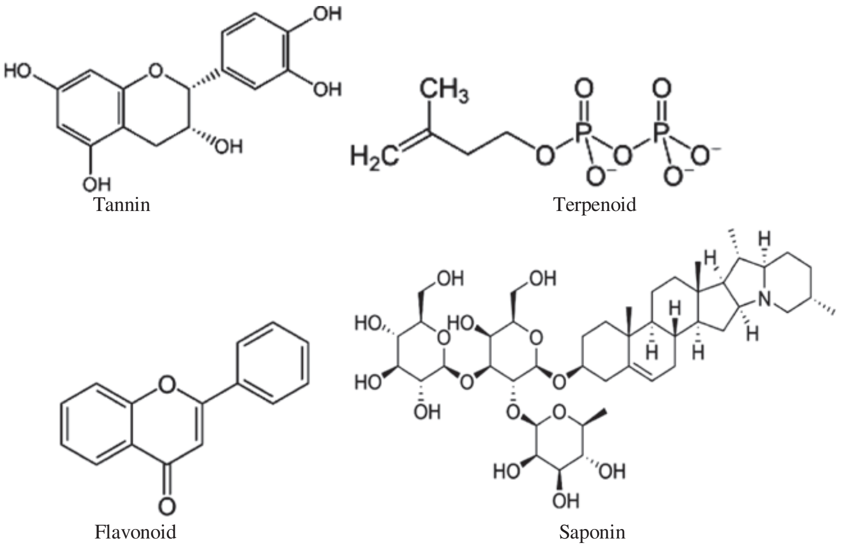

Fig. 2. Structure of some of main chemical ingredients of palm leaves extract.

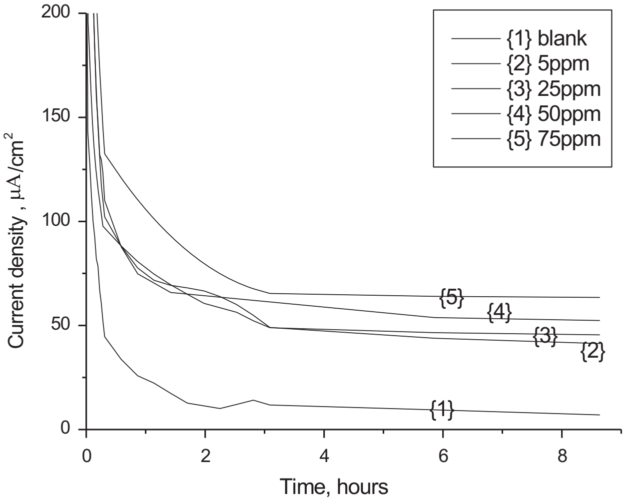

Fig. 3. Chronoamperometry curves for polarized steel electrode in $CaCl_2$ brine solution in the absence and presence of different concentrations of palm leaves extract at 40°C.

that is strongly dependent on the electrode pretreatment. The scaling process is initialized by increasing the local pH near the electrode surface by means of the reduction of the dissolved oxygen in brine solution according to chemical equation [13]:

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

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

$$Ca^{2+} + \ HCO^{3-} + OH^- \rightarrow CaCO_3(s) + H_2O$$

Further linear decrease of the current indicates that the nuclei already born were growing and occupied the surface leaving some parts free. After 6 h, the current reach a limiting value of 9 μA, which define 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 was completely blocked, the current would be zero.

On the other hand, in the presence of palm leaves extract, 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 (5 ppm) indicating that this extract impedes the crystal growth stage by retarding the nucleation step. Increasing the concentration of palm leaves extract from 5 to 75 ppm increases the residual current density from 55 to 75 μA indicating the effectiveness of palm leaves extract as antiscalant.

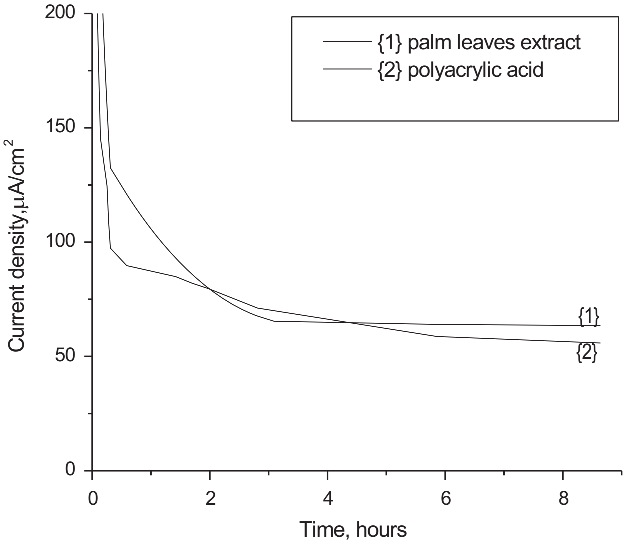

Fig. 4. Chronoamperometry curves for polarized steel electrode in $CaCl_2$ brine solution in the presence of 75 ppm of palm leaves extract and polyacrylic acid at 40°C.

Fig. 4 shows comparative study between chronoamperometry curves for polarized steel electrode in $CaCl_2$ brine solution in the presence of palm leaves extract and poly acrylic acid. It is clear that the current

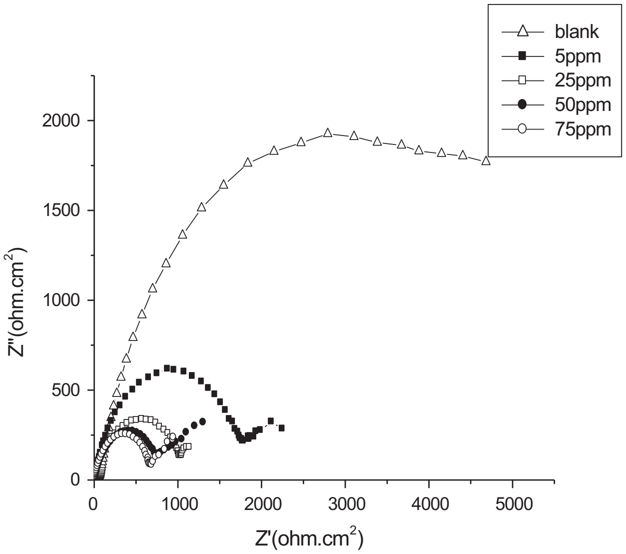

Fig. 5. Impedance spectra of steel in brine solution in the absence and presence of different concentrations of palm leaves extract after polarizing steel electrode for 8 h at −0.9 V (vs. SCE).

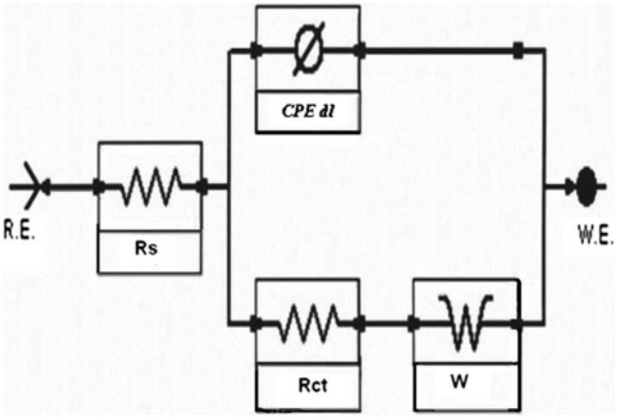

Fig. 6. Schematic for the equivalent circuit model used to determine the impedance parameters for scale process in the $CaCl_2$ brine solution in the absence and presence of palm leaves extract.

value in presence of palm leaves extract is higher than that in presence of PAA. The data proved the efficiency of palm leaves extract as $CaCO_3$ scale inhibitor.

3.3. Impedance (EIS) measurements

Several problems arise for interpreting chronoamperometry curves. First, the dc current gives only partial information on the screening effect of the insulating scale deposit on the electrode surface [24]. Second, no information is obtained about the thickness and porosity of the scale layer [25]. The use of impedance technique can improve the understanding of the electrochemical scaling process.

Fig. 5 shows Nyquist plots for steel that was cathodically polarized at −0.9 V for 8 h in brine solution in the absence and presence of different concentrations of palm leaves extract. As seen, the figure shows distorted semicircles whose size decreases with increasing plant extract concentration. These observations indicate that increasing the concentration of the antiscalant decreases the insulation resulting from scale layer.

Fig. 6 shows the equivalent circuit that was earlier proposed by Wanga et al. [26] to fit the experimental data of impedance plots for the scale formation processes. In the circuit R_s represents the solution resistance; R_{ct} corresponds to the charge transfer resistance; CPE_{dl} is associated to the double-layer capacitance. The CPE is used in this model to compensate for nonhomogeneity in the system and is defined by two values, Q and n. If n equals one, the impedance of CPE is identical to that of a capacitor and in this case Q gives a pure capacitance (C). For non-homogeneous system, n values range 0.9–1. W is the Finite-Length Warburg (FLW) element that is defined by three values, W_R, W_T, and W_P. To use the FLW equation, set $W_P = 0.5$ and set its freedom to "fixed". In the diffusion interpretation, $W_T = L^2/D$. (L is the effective diffusion thickness, and D is the effective diffusion coefficient of the particle). This version of the Warburg element terminates in a finite resistance [27]. The fit results of the impedance spectra measured after polarizing steel electrode in brine $CaCl_2$ solution to −0.9 V (vs. SCE) after 8 h are given in Table 1. The data clarify that increasing palm leaves extract concentration decreases the charge transfer resistance and film resistance, while increases the non-ideal film capacitance confirming the inhibitive effect of this substance towards the scales formation process.

The percentage of scale inhibition could be determined from the following equation [4,13].

$$\% \text{ scale inhibition} = \left[(R_{ct})_0 - (R_{ct})_i\right] / (R_{ct})_0 \times 100$$

where $(R_{ct})_0$ and $(R_{ct})_i$ are the obtained charge transfer resistances after polarizing the steel electrode at −0.9 V (vs. SCE) in scaling environment for 8 h in the absence or the presence of the palm leaves extract. The data displays that the maximum percent of scale inhibition was 89.7% in presence of 75 ppm of palm leaves extract.

Table 1
Computer fit results of the impedance spectra obtained for the steel electrode that was cathodically polarized in the $CaCl_2$ brine solution containing different concentrations of palm leaves extract for 8 h

Conc. (ppm)	Time (h)	R_s (Ω cm^2)	Q (μF)	n	R_{Ct} (Ω cm^2)	W	% Inhibition
0	8	37.83	501.7	0.7	6,579	0.032	–
5	8	6.285	47.81	0.78	1,712	0.0067	73.9
25	8	5.702	161	0.72	1,029	0.015	84.3
50	8	5.345	269	0.77	718.2	0.0109	89.1
75	8	3.832	285.7	0.81	672.6	0.035	89.7

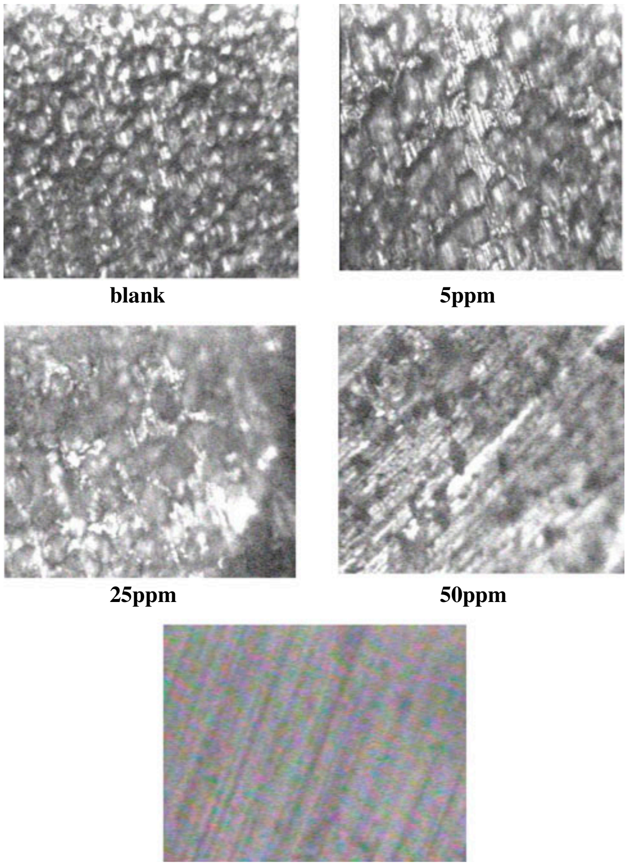

Fig. 7. Optical micrograph photo (40X) for cathodically polarized steel in $CaCl_2$ brine solution in the absence and presence of different palm leaves extract concentrations after 8 h.

3.4. Optical microscopic examination

The optical micrographs of the steel electrode that was polarized at −0.9 V vs. SCE for 8 h in the $CaCl_2$ brine solution in the absence and presence of different palm leaves extract concentrations are shown in Fig. 7. These micrographs display that, in the absence of plant 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 retardation of the nucleation time and the accompanied decrease in the growth rate in presence of palm leaves extract lead to 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 plant extract concentrations and in presence of 75 ppm palm leaves extract, the surface of the steel is completely free from $CaCO_3$ deposit. These data are in good agreement with those obtained using chronoamperometric and impedance spectroscopy techniques.

4. Conclusion

This work has mainly explored the possibility for using natural products as antiscalant in cooling systems used in desalination plants, pharmaceuticals, and food industries.

Palm leaves extract decreases the rate of scale formation by bonding off the active chemical ingredients to the cations from the neutral extract, thus forming a soluble complex or by dispersion of the suspended solids through an adsorption process.

Addition of 75 ppm of palm leaves extract in brine solution prevents complete coverage of the electrode surface with 89.7% scale inhibition, indicating that these compounds can be used with good results as antiscalants.

No reference to the use of such a scale inhibitor has been found in literature: it is thus believed to represent a potentially new greener approach to the chemical treatment of cooling water system.

References

[1] A.P. Morizot, A. Neville, Insights into electrodeposition of an inhibitor film and its inhibitive effects on calcium carbonate deposition, J. Colloid Interface Sci. 245 (2002) 40–49.

[2] A. Martinod, A. Neville, M. Euvrad, K. Sorbie, Electrodeposition of a calcareous layer: Effects of green inhibitors, Chem. Eng. Sci. 64 (2009) 2413–2421.

[3] D.J. Choi, S.J. You, J.G. Kim, Development of an environmentally safe corrosion, scale, and microorganism inhibitor for open recirculating cooling systems, Mater. Sci. Eng. Ser. A 335 (2002) 228–235.

[4] D.E. Abd-El-Khalek, B.A. Abd-El-Nabey, Evaluation of sodium hexametaphosphate as scale and corrosion inhibitor in cooling water using electrochemical techniques, Desalination 311 (2013) 227–233.

[5] A.L. Kavitha, T. Vasudevan, H.G. Prabu, Evaluation of synthesized antiscalants for cooling water system application, Desalination 268 (2011) 38–45.

[6] B.R. Zhang, L. Zhang, F.T. Li, W. Hu, P.M. Hannam, Testing the formation of Ca–phosphonate precipitates and evaluating the anionic polymers as Ca–phosphonate precipitates and $CaCO_3$ scale inhibitor in simulated cooling water, Corros. Sci. 52 (2010) 3883–3890.

[7] R. Ketrane, B. Saidani, O. Gil, L. Leleyter, F. Baraud, Efficiency of five scale inhibitors on calcium carbonate precipitation from hard water: Effect of temperature and concentration, Desalination 249 (2009) 1397–1404.

[8] T.Y. Soror, Scale and corrosion prevention in cooling water systems Part I: Calcium carbonate, Open Corros. J. 2 (2009) 45–50.

[9] V.V. Paustovskaya, Some results of a research in the problem inhibitors of metal corrosion. Toxicology and industrial hygiene, Prot. Met 36 (2000) 89–93.

[10] C.A. Grillo, M.V. Mirífico, M.L. Morales, M.A. Reigosa, M. Fernández Lorenzo de Mele, Assessment of cytotoxic and cytogenetic effects of a 1,2,5-thiadiazole derivative on CHO-K1 cells: Its application as corrosion inhibitor, J. Hazard. Mater 170 (2009) 1173–1178.

[11] A. Ketsetzi, A. Stathoulopoulou, K.D. Demadis, Being "green" in chemical water treatment technologies: Issues, challenges and developments, Desalination 223 (2008) 487–493.

[12] E. Mavredaki, A. Stathoulopoulou, E. Neofotistou, K.D. Demadis, Environmentally benign chemical additives in the treatment and chemical cleaning of process water systems: Implications for green chemical technology, Desalination 210 (2007) 257–265.

[13] A.M. Abdel-Gaber, B.A. Abd-El-Nabey, E. Khamis, D.E. Abd-El-Khalek, Investigation of fig leaf extract as a novel environmentally friendly antiscalent for $CaCO_3$ calcareous deposits, Desalination 230 (2008) 314–328.

[14] A.M. Abdel-Gaber, B.A. Abd-El-Nabey, E. Khamis, D.E. Abd-El-Khalek, A natural extract as scale and corrosion inhibitor for steel surface in brine solution, Desalination 278 (2011) 337–342.

[15] A.M. Abdel-Gaber, B.A. Abd-El-Nabey, E. Khamis, H. Abd El-Rhmann, Green anti-scalent for cooling water systems, Int. J. Electrochem. Sci. 7 (2012) 11930–11940.

[16] S.H. Lin, S.C. Dexter, Effects of temperature and magnesium ions on calcareous deposition, Corrosion 44 (1988) 615–622.

[17] I. Drela, P. Falewicz, S. Kuczkowska, New rapid test for evaluation of scale inhibitors, Water Res. 32 (1998) 3188–3191.

[18] N.K.J. Al-Dawah, S.L. Ibrahim, Phytochemical characteristics of date palm (*Phoenix dactylifera* L.) leaves, Kufa J. Veter. Med. Sci. 4 (2013) 90–95.

[19] A.K. Gangwar, A.K. Ghosh, V. Saxena, Standardization and antiulcer activity of *Phoenix dactylifera* Linn. leaves, World J. Pharm. Pharm. Sci. 3 (2014) 1164–1172.

[20] W. Leroy, J. Lin, A. Ledion, J. Khalil, Characterization of scale-forming power of water to the test using electrodeposition comparative study of several methods, Water SRT-Aqua 42 (1993) 23–29.

[21] C. Deslouis, C. Gabrielli, M. Keddam, A. Khalil, R. Rosset, B. Tribollet, M. Zidoune, Impedance techniques at partially blocked electrodes by scale deposition, Electrochim. Acta 42 (1997) 1219–1233.

[22] C. Gabrielli, M. Keddam, A. Khalil, G. Mourin, H. Perrot, R. Rosset, M. Zidoune, Quartz crystal microbalance investigation of electrochemical calcium carbonate scaling, J. Electrochem. Soc. 145 (1998) 2386–2396.

[23] J.F. Yan, R.E. White, R.B. Griffin, Parametric studies of the formation of calcareous deposits on cathodically protected steel in seawater, J. Electrochem. Soc. 140 (1993) 1275–1280.

[24] C. Gabrielli, M. Keddam, A. Khalil, R. Rosset, M. Zidoune, Study of calcium carbonate scale by electrochemical impedance spectroscopy, Electrochim. Acta 42 (1997) 1207–1218.

[25] M. Sfaira, A. Srhiri, M. Keddam, H. Takenouti, Corrosion of a mild steel in agricultural irrigation waters in relation to partially blocked surface, Electrochim. Acta 44 (1999) 4395–4402.

[26] S. Wang, L. Yang, R. Niu, Z. liu, Scaling on stainless steel electrodes in simulated cyanidation leaching processes, Electrochim. Acta 97 (2013) 341–348.

[27] L. Bousselmi, C. Fiaud, B. Tribollet, E. Triki, The characterisation of the coated layer at the interface carbon steel-natural salt water by impedance spectroscopy, Corros. Sci. 39 (1997) 1711.