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Research article

Investigation of Agricultural Waste as Economical and Effective Bio-Inhibitors for Inhibiting Scaling in Natural Hard Water

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Abstract.
In this study, agricultural waste was utilized as new bio-inhibitors to prevent scale formation in hard waters. Aqueous extracts of strawberry and tomato leaves were utilized for reducing the scale deposits formed on metallic surfaces by Bounouara ground hard water, which supplies Constantine city in Algeria. Anti-scaling properties were evaluated by chronoamperometry and impedancemetry techniques. The effect of temperature and concentration on the efficiency of the bio-inhibitors was assessed. The results showed that the anti-scaling effect of strawberry leaf extracts started at the very low concentration of 1 ppm, with 31% efficiency, reaching complete scaling inhibition at 15 ppm (20°C), whereas the inhibitory effect of tomato leaf extracts was noticed at 2.5 ppm, with 36% efficiency, and total inhibition at 20 ppm (20°C). The efficiency of strawberry and tomato leaf extracts at 40°C was also confirmed, although total inhibition was attained at a higher concentration.

Keywords: hard water, agricultural waste, strawberry leaves, tomato leaves, bio-inhibitors, scaling inhibition

1. Introduction

In natural aquatic ecosystems, ground waters present high concentrations of calcium and magnesium, which leads to a natural, spontaneous formation of undesirable scaling deposits on surfaces. These scaling deposits are mainly due from the precipitation of calcium carbonate [1–3], which causes various undesirable effects, such as the formation of those insoluble mineral salts that almost totally block the water distribution pipelines or the cooling water tubes [4,5], reducing the flow rate. Moreover, the scale formation significantly reduces the water treatment technology's efficiency, and of the desalination and water softening systems [6–8].

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During decades, many researchers have investigated the scale deposits from natural, industrial, or synthetic waters [9–12], to hinder or control scaling process. The most common method that was investigated to avoid scale formation was the addition of chemical substances to the hard waters, that are known as chemical inhibitors [13–16]. Researchers proved that a small amount of these substances can highly reduce the scale precipitation and change the kinetics of the scale formation process. Despite the high efficiency of these inhibitors, they may be toxic to the environment and dangereous to the human health.

Recently, research to find new inhibitors compatible with the environment is underway, using the so-called green inhibitors, according to three criteria: Toxicity, bioaccumulation, and biodegradation [17-19]. To go further with this aim, this work focuses on new bio-inhibitors, for reducing the scaling deposits formed by Bounouara ground water, which supplies the entire southern region of the Constantine city in Algeria and is characterized by 60°f hardness. The bio-inhibitors utilized are aqueous extracts of strawberry and tomato waste, since a large amount of these waste accumulates annually, having a negative impact on the environment. To our knowledge, no study has so far being performed on the anti-scaling effect of strawberry and tomato leaves. Chronoamperometry combined with impedancemetry were used to investigate the efficiency of strawberry and tomato leaves aqueous extract on the inhibition of calcium carbonate deposition on metallic surface. The effect of water temperature and inhibitor concentration was studied in detail.

The chronoamperometry and impedancemetry methods have been widely used to study the scaling power of water and the inhibitors efficiency [9-11]. They are based on the controlled precipitation of calcium carbonate on a metal surface, by applying a negative cathodic potential (-1 V versus SCE) to reduce the oxygen, leading to the production of hydroxyl ions (Eq. 1). The hydroxyl ions increase the pH value near the electrode’s surface, which forces the calcium carbonate to precipitate on the surface of the working electrode (Eqs. 2 and 3).

$$\mathrm{O_2 + 2H_2}O\mathrm{ + 4e^- \leftrightarrows 4OH^-} \qquad (1)$$

$$\mathrm{HCO_3{}^- + OH^- \leftrightarrows CO_3{}^{2-} + H_2O} \qquad (2)$$

$$\mathrm{Ca^{2+} + CO_3{}^{2-} \leftrightarrows CaCO_3} \qquad (3)$$

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2. Material and methods

Preparation of extracts. Strawberry and tomato leaves were collected from a greenhouse in Jijel city, Algeria. After collection, they were washed, dried, and crushed, to be ready for use. The extraction was performed by adding 100 ml of boiling distilled water to 5 g of leaves and leaving them for 15-20 min, to infusion. After that, they were filtered, with a paper filter of 0.5 mm of porosity, thus obtaining an extract of 5% (mass/volume). The filtrate was evaporated, and the residue was weighed.

3. Electrochemical experiments

The electrochemical tests (chronoamperometry and impedancemetry) were carried out in a thermostated double-walled conventional three-electrode cell, in pyrex glass, with a capacity of 500 mL (Fig. 1). Before each experiment, the cell was cleaned with ethanol, rinsed with distilled water, and dried. A saturated calomel electrode (SCE), was used as the reference electrode, having a platinum wire as the auxiliary electrode. The working electrode was a stainless-steel electrode (SS) made of XC10, with 1 cm^2 active area, embedded in inert resin. The surface of SS electrode was polished before every assay with abrasive papers (first P#400, and then P#800), cleaned with acetone, and rinsed with distilled water.

For the chronoamperometric tests, the electrodes were centred in the electrochemical glass cell at a constant distance, connected to a Potentiostat-Galvanostat ZRA (Reference 3000), controlled by Gamery analysis software. The experiments were operated in batch mode, for 60 minutes, applying a potential of -1V vs SCE. Tests were run at 20 and 40°C, utilizing 400 mL of Bounouara raw water, in the absence or in the presence of strawberry or tomato leaves extract. Solutions were continuously stirred during the experiments, at 500 rpm.

The electrochemical impedance diagrams were recorded with the operating system utilized for chronoamperometry, at a scaling potential of -1V vs SCE, after 60 min polarisation. The measurements were carried out in the frequency range 100 kHz - 10 mHz, with 10 points per decade, and an amplitude of 10 mV. The disturbance amplitude parameter had already been optimized in a previous study.

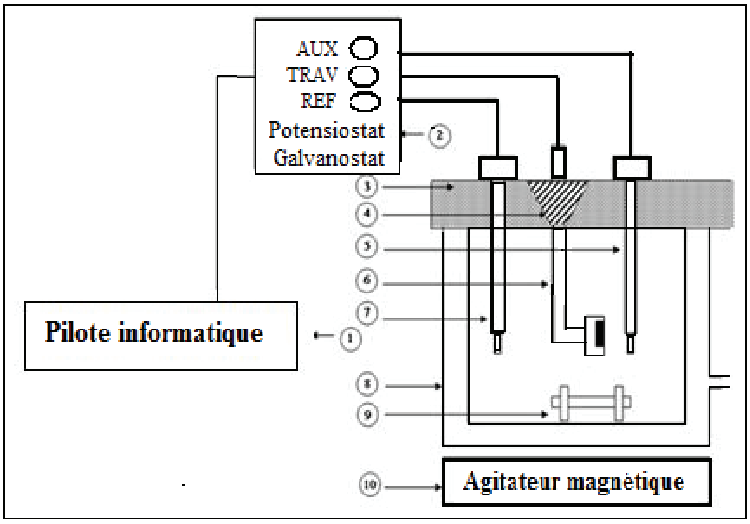

Figure 1: Experimental set-up.

4. Results and discussion

Chronoamperometric study. Figure 2 presents the chronoamperometric curves of Bounouara water in the absence of the inhibitors, at different temperatures. The curve represents the resulting current density as a function of time during scaling deposition. According to Ledion [20], the scaling power of water can be characterized by the scaling time and the scaling index values obtained from the chronoamperometric curve of this water: the scaling time, t_s, corresponds to the minimum time needed to obtain a residual current, which remains stable after that time; the scaling index, I_s, is calculated from the scaling time, according to Eq. 4.

$$I_s = \frac{1000}{t_s} \tag{4}$$

From the slope of the linear part of Bounouara water curve at 20°C (Fig. 2), it can be seen that Bounouara water has a scaling time of around 16 minutes, with a scaling index of approximately 64 min^{-1}. According to this I_s, Ledion [20] classifies Bounouara water as very hard scaling forming water. Comparing the curves shape of Bounouara water at 20 and 40°C, it can be observed that temperature has a favourable role upon scaling deposition, as expected. The scaling rate increases when the temperature was raised from 20 to 40°C, the scaling time decreases from 16 min to 8 min, the residual current also decreases, and Bounouara water becomes more scale-forming at high temperature. The explanation for this fact is described in the literature [21,22], since the temperature decreases the solubility of dissolved oxygen and increases the diffusion coefficient [22], which leads to an increase of cathodic current of oxygen reduction (Eq.

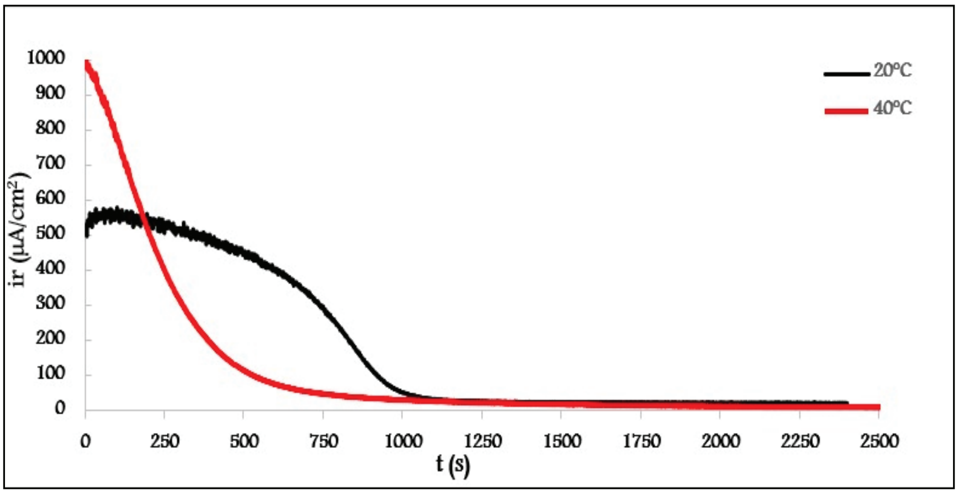

Figure 2: Chronoamperometric curves of Bounouara raw water at 20°C and 40°C on a SS electrode at -1 V (vs SCE), Ω= 500 rpm .

1) [23]. As observed in Fig.2, the initial current increases when temperature raises from 20 to 40°C.

To study the effectiveness of tomato and strawberry leaves in inhibiting the formation of calcium carbonate, the chronoamperometric assays were carried out for Bounouara water in presence of various concentration of inhibitors extracts, at 20°C and 40°C (Figs. 3 to 6). Figures 3 and 4 present the chronoamperometric experiments realized at different concentration of strawberry leaves extracts for inhibition calcium carbonate formation. The efficiency of the inhibitors, I_{eff}, is calculated according to Eq.5 [9]. The scaling time and residual current increases with inhibitors concentration, and 1 ppm of strawberry extract was sufficient to change the shape of Bounouara raw water curve (Fig. 3a). The scaling time increased from 16 min to 24 min with efficiency of 31%, and the residual current increases from 20 to 31 µA. The scaling time and residual current keep increasing with the strawberry leaves extract concentration. For 15 ppm, at 20 °C, and 30 ppm, at 40 °C, no current reduction was observed, and the scaling time became undetermined (Fig. 4).

$$I_{eff}\,(\%) = 200\ x\ \frac{t_s\,(treated\ water) - t_s\,(raw\ water)}{t_s\,(treated\ water) + t_s(raw\ water)} \tag{5}$$

Tomato leaves extract has a similar effect on the scaling time and residual current as showing in (Fig 5). However, its efficient in calcium carbonate inhibition is lower, since it reacts with higher concentrations when compared to strawberry leaves extract, and the total inhibition (almost no reduction in current during the assay) was obtained at 20 ppm (Fig. 6a). At 40°C, similar behaviour is observed, i.e., the residual current increases with the inhibitors extract concentration, until reaching a constant value of

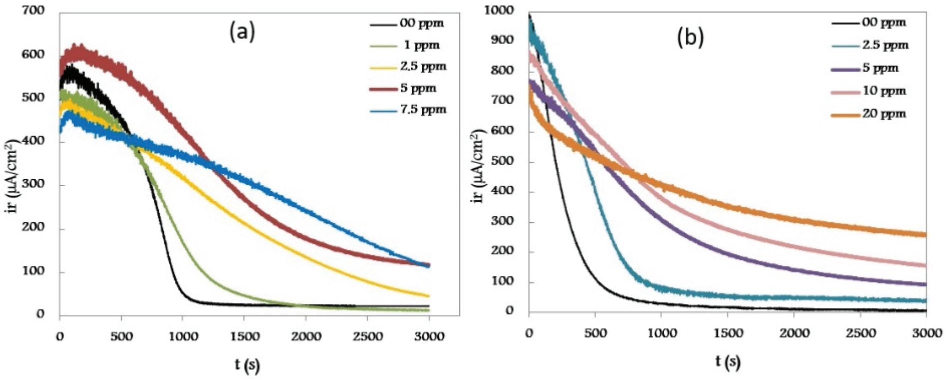

Figure 3: Chronoamperometric curves of Bounouara water in presence of different concentrations of strawberry leaves aqueous extract at 20°C (a) and 40°C (b) on a SS electrode at -1 V (vs SCE), Ω= 500 rpm.

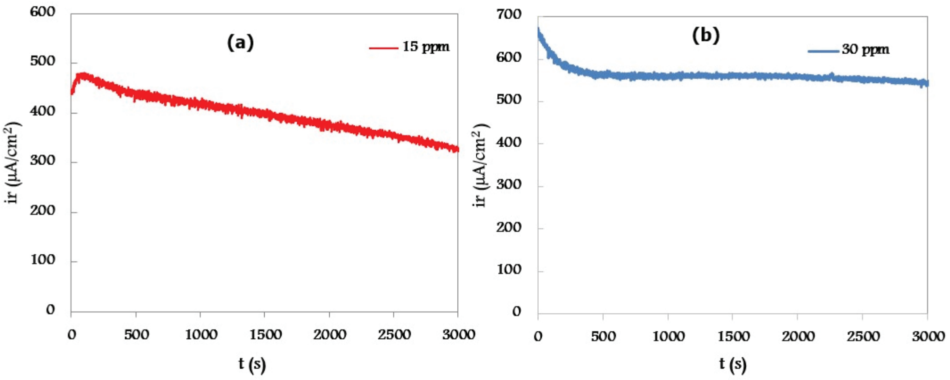

Figure 4: Chronoamperometric curves of optimum concentration of strawberry leaves aqueous extracts, at 20°C (a) and 40°C (b) on a SS electrode at -1 V (vs SCE), Ω= 500 rpm.

optimum concentrations. Since Bounouara becomes more scale-forming at 40°C, the extract seems to be less efficient at higher temperature, where higher concentrations were necessary to attain the same rate of inhibition obtained at 20°C (Fig. 6b).

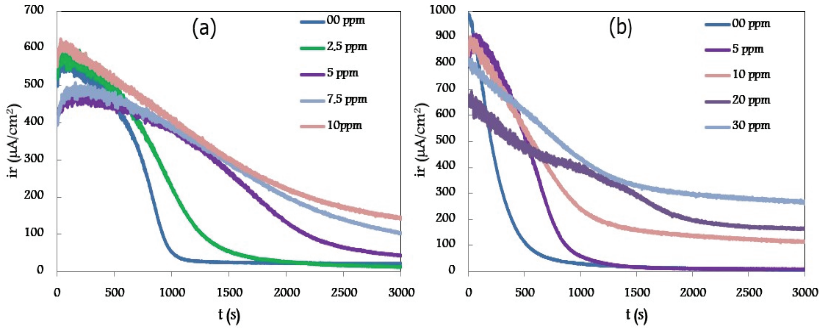

Figure 5: Chronoamperometric curves of Bounouara water in presence of different concentrations of aqueous extract of Tomato leaves at 20°C (a) and 40°C (b) on a SS electrode at -1 V (vs SCE), Ω= 500 rpm.

Impedancemetry study. The effect of strawberry and tomato leaves using impedancemetry was characterized by charge transfer resistance (R_{ct}) values, which

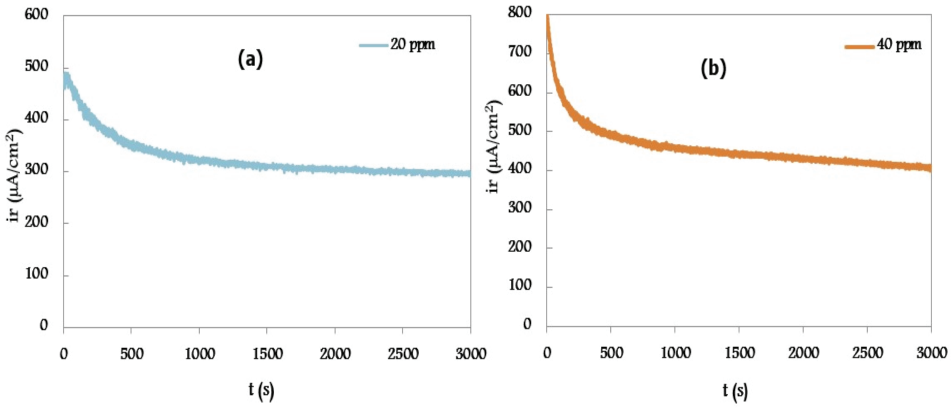

Figure 6: Chronoamperometric curves of optimum concentration of aqueous extract of Tomato leaves at 20°C (a) and 40°C (b) on a SS electrode at -1 V (vs SCE), Ω= 500 rpm.

were obtained after polarization of the SS electrode in the absence and in the presence of the bio-inhibitors strawberry or tomato leaves extracts (Figs. 7 and 8, respectively). A higher transfer resistance indicates that the formed scale is more compact, and the surface of SS electrode is highly covered by the calcium carbonate crystals. The rate efficiency (E) is calculated from (Eq.6), where R$_{ct(0)}$ and R$_{ct(inh)}$ refer to the charge transfer resistance for the solutions without and with plant leaves extract, respectively.

$$E(\%) = \frac{R_{ct(0)} - R_{ct(inh)}}{R_{ct(0)}} \times 100(6) \tag{6}$$

In the absence of the inhibitors, the impedance diagram consists of two loops with real impedances ranging from 0 to 2000 Ω/cm^2 and from 2000 to 8980 Ω/cm^2 at 20°C, from 0 to 4000 Ω/cm^2 and from 4000 to 13850 Ω/cm^2 at 40°C, compared with curves obtained in the presence of strawberry and tomato leaves extracts, where the first loop completely disappears. According Gabrielli et al. [10], the existence of two capacitive loops indicates the presence of the calcite crystals on surface of the electrode. It can also be clearly observed that the diameter of the diagrams loop is decreasing as extracts concentration increases, due to charge transfer resistance decreasing. In fact, R$_{ct}$ of Bounouara raw water is 8980 Ω/cm^2, and this value decreases more than 58% in the presence of 5 ppm of strawberry leaves extract, to become 3815 Ω/cm^2. The addition of similar concentration of tomato leaves extract (Fig. 8) decreases the R$_{ct}$ value to 4175 Ω/cm^2, with an inhibition of 52%. The minimum values of charge transfer resistance were obtained in the presence of 15 ppm at 20°C in the case of strawberry leaves extract and at 20 ppm for tomato leaves extract. These concentrations were also the optimum concentration in chronoamperometry curves. So, the results of impedancemetry are in agreement with those from chronoamperometry. The effect of temperature is noticed on the impedance diagrams, being the R_{ct}decrease, at 40°C, observed for higher concentrations.

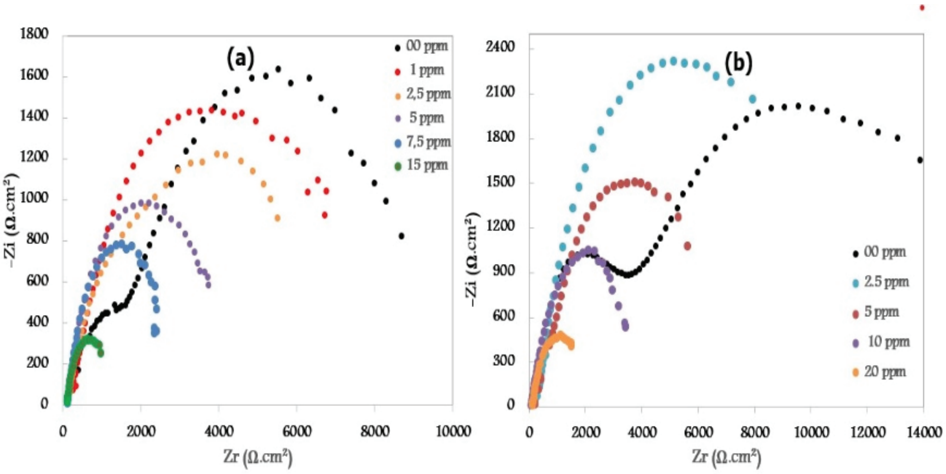

Figure 7: Impedance diagrams of Bounouara water in presence of various concentrations of strawberry leaves aqueous extract at 20°C (a) and 40°C (b), 500 rpm, on: SS at -1VvsSCE.

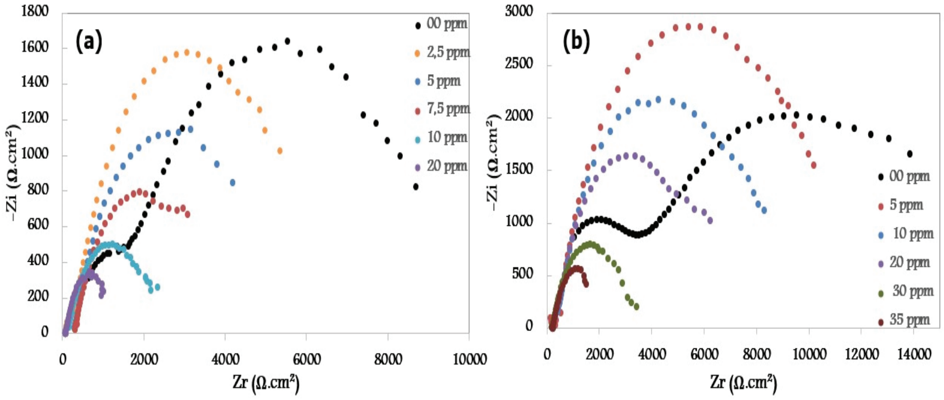

Figure 8: Impedance diagrams of Bounouara water in presence of various concentrations of Tomato leaves aqueous extract at 20°C (a) and 40°C (b), 500 rpm, on SS at -1VvsSCE.

5. Conclusions

The inhibition of scaling formation on a stainless-steel electrode from Bounouara water using agricultural waste was accomplished with success. The electrode's surface is uncovered with the scale particles in the presence of strawberry or tomato leaves extracts at an appropriate concentration. The results obtained show that the aqueous extract of strawberry leaves is more effective than the aqueous extract of tomato leaves because it acts at lower concentrations. The anti-scale capacity of tomato or leaves extracts are higher at lower temperature. Thus, the temperature and the inhibitor concentration influence the kinetics of the scale deposition. The inhibitory effect of natural products, which differs from one product to another, depends on its composition and therefore of its mode of action. Recovery and valorization of agricultural waste in the treatment of hard water is a good solution to clean and protect the environment.

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