Moroccan Journal of Chemistry
ISSN: 2351-812X
http://revues.imist.ma/?journal=morjchem&page=login
Y. Bendaoud-Boulahlib / Mor. J. Chem. 5 N°1 (2017) 72-80

# Study of Inhibiting Effect of natural products on Hard Growth Water, Valorization of lemon peel in the treatment of hard water

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## Abstract

Hard water forms compact and adherent deposit to the walls of pipes and industrial or domestic installations. Several studies have been done in order to reduce the adverse scaling consequences and to achieve effective softening, but most of inhibitors used are chemical compounds that have damaging effects on health and the environment. There for we have used in this work an under natural alimentary product as scaling inhibitor. Our study focuses on softening hard water of Bounouara- having a hardness of 58°F in the presence of lemon peel extracts as scaling inhibitor. The evaluation of scaling power of Bounouara water and inhibitory effect of lemon peel was performed by using two techniques: - scaling accelerated method to evaluate the scaling power of raw Bounouara water electrochemically in the presence of natural inhibitors (lemon peel) - Impedancemetric method to appreciate globally, using the high frequency resistance, the importance and adherence of calcium carbonate deposit. Chronoamperometric study shows that scaling time decreases by increasing of temperature. So hard water become more scale-forming in high temperatures. Application of the treatment on Bounouara water showed that total hardness inhibition requires addition of lemon peel of 0.5 g/L at 20°C and 1 g/L at 40°C.

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*Received 31 Aug 2016, Revised 24Dec 2016, Accepted 11 Feb 2017*

***Keywords:*** *Scaling, natural inhibitor, chronoamperometry, impedancemetry.*

# 1. Introduction

The increasing of demand of water, due to the increase in population and the rise in the standard of living and the will of a sustainable development, a pumping of the underground water to be elaborate in order to cover most of the enormous requirements out of water, but unfortunately most of these ground waters are of important hardness. Hard water form compact and adherent deposits to the walls of pipes and industrial or domestic installations [1] causing enormous technical and economic problems, such as total or partial obstruction of pipes, leading to a decrease in flow rate, reduced heat transfer, seizure of valves and clogging of filters. In nuclear power plants, the scaling phenomena can reduce efficiency and limit the power production [2]. Therefore, it is very important to establish a treatment of hard ground waters in order to reduce their hardness and exploit them. Treating hard water has been interest from several works in order to reduce the adverse consequences of tartar. Several studies have been done in order to achieve effective softening, but most of the inhibitors used are chemical compounds that have damaging effects on health and the environment. In this work our study focuses on softening hard water of Bounouara having a hardness of 58°F in the presence of lemon peel extract as scaling inhibitor. Scaling tests were performed using the chronoampero-metric method [3] and confirmed with impedance metric method. Scaling accelerated method is used to evaluate the scaling power of Bounouara raw water, effect of temperature on scling power of hard raw Bounouara water and the inhibitory effect of under natural products (lemon peel) at source temperature 20°C and at temperature of 40°C. The measurement of electrochemical impedance deposits precipitated metal deposit of calcium carbonate-electrolyte interface was used to appreciate globally, using the high frequency resistance, the importance and adherence of calcium carbonate deposit [4]. The electrochemical method of measurement of the impedance of the electrode interface - deposit and electrolyte, is a powerful method of electrochemical characterization of surface films deposits of calcium carbonate [5] formed in water Bounouara raw or treated with lemons peel. According to the chronoamperometry study, Bounouara raw water is characterized by scaling time ($t_E$) of 9.17min and an index scaling ($I_E$ = 107 $min^{-1}$). Thus, we can classify Bounouara water as extremely scale-forming and the scaling time decreases by increasing the temperature. So hard water of Bounouara become more scale-forming in high temperatures. In the presence of natural inhibitor, the risk of scaling is reduced. The time scaling and the residual current increase with the addition of inhibitors and the effective concentration for the inhibition of calcification of Bounouara water is 0.5g/L of lemon peel at source temperature of 20°C and 1 g/L at 40°C [6]. This has been confirmed by the increase in high frequency power and the decrease in charge transfer resistance of the deposits depending on the inhibitor concentration.

The tracing of the impedances diagrams obtained from the scale formed in the Bouanouara raw water compared to treated water shows a decrease in the quantity of calcium carbonate scale and its adhesion. This has been confirmed by the increase in high frequency power and the decrease in charge transfer resistance of the deposits depending on the inhibitor concentration. So lemon peel is an effective inhibitor for the scaling treatment of drinking water and for the protection of the environment.

# 2. Materials and methods

## *2.1. Preparation of plant extract*

Lemon peels were collected in the winter season from fresh peel of Citrus Mitidja plains area, a region in the north of Algeria. The lemon peel fruits are peeled, dried and ground into powder. The extraction was performed by adding 100 ml of boiling distilled water to 5g bark and leaving them for 15 min to infusion extracted with a paper filter is a filter of 0.5mm of porosity, thus obtaining an extract of 5% (mass / volume) and passed to electrochemical tests [7].

### *2.2. Electrochemical measurements*

Electrochemical methods essentially consist to forced precipitation of calcium carbonate on metal surface of electrode at cathodic potential (-1V/ECS) to produce the electrochemical reduction of dissolved oxygen to protect of hydroxide ions (R1) which causes a local rise in pH resulting in the precipitation of calcium carbonate on the working electrode according to the reactions (R2, R3):

$O_2 + 2H_2O + 4e \rightarrow 4OH^-$ *R1*

$OH^- + HCO_3^- \rightarrow CO_3^{2-} + H_2O$ *R2*

$Ca^{2+} + CO_3^{2-} \rightarrow CaCO_{3(s)}$ *R3*

The electrochemical impedance spectroscopy has been used to control the deposit and adherence of scale of calcium carbonate by electrochemical methods.

### *2. 3. Equipment used*

As has already given in the article of Boulahlib-Bendaoud [8], accelerated scaling is an electrochemical technical which determines the power scaling of water by controlled precipitation of calcium carbonate. The chronoamperometric experiments and impedances tests were performed in the natural water of Bounouara using a classical three-electrode cell. The working electrode is made of Steel XC10 with 1.00 $cm^2$ area. The electrode surface was polished with silicon carbide paper (P #400), rinsed thoroughly with pure water and carefully dried. Potential was measured versus the reference saturated calomel electrode (SCE). A platinum electrode was used as counter electrode and a potentiostat was connected to the three electrodes. Work temperature was maintained using a double glass wall recipient. Its large volume (500 ml) allowed avoiding a significant variation of species concentration during the formation of the deposit. The plot of impedance diagrams of the deposit formed by chronoamperometry was performed on the same setup used in the accelerated scaling tests. We applied high frequency varying from 100kHz to 100MHz and has been recorded variation imaginary resistors (Zi) compared to the real resistors (Zr).

## 3. Results and Discussions

### *3.1. Water quality of Bounouara*

The results of the physicochemical analyze of Bounouara water are given in Table 1:

**Table 1.** Physicochemical analyze of water of Bounouara.

| Parameter | Water of Bounouara |
|---|---|
| T, °C | 20 |
| pH | 7.2 |
| CE, mS/cm | 1.787 |
| $O_2$ dissolved mg/L | 8 |
| $HCO_3^-$, mg/L | 396 |
| TH, mg/L $CaCO_3$ | 580 |
| $Ca^{2+}$, mg/L | 192 |
| $Mg^{2+}$, mg/L | 38.4 |
| $Cl^-$, mg/L | 189 |
| $SO_4^{2-}$ mg/L | 29.41 |

It should be noted that the water of Bounouara is quite mineral-bearing (EC = 1.78 mS/cm) and very charged in anion hydrogen carbonate and the content calcium is very high. The title hydrotimetric (TH) is 580 mg/L (TH = 58°F) what corresponds to very hard water.

### *3.2. Tests of accelerated scaling*

#### *3.2. 1. Raw waters of Bounouara*

Chronoamperometry curves referring Bounouara water is presented in Figure (1) at source temperature 20°C. One plots the curve I= f (t). This curves exploited in order characterize the scaling power and the index of scaling of Bounouara water.

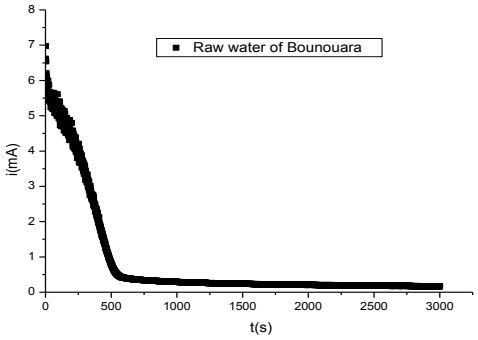


**Figure 1.** Chronoamperometry curve of Bounouara raw water at 20°C.

According Ledion [9], recognizing that the hardness of the Bounouara water is 58°F. We can classify the scaling power of water of Bounouara by scaling time and the scaling index of raw water of this source. The index of scaling is defined by:

$$i_E(min^{-1}) = \frac{1000}{t_E\,(\mathrm{min})}$$

- $100 < i_E < 1000$: extremely scale-forming water.
- $15 < i_E < 100$: very scale-forming water.
- $5 < i_E < 15$: medium scale-forming water.
- $0.5 < i_E < 5$: slightly scale-forming water.

As water of Bounouara present time scaling $t_E$ of 9.17min, calculating of the scaling index gave a value of 109 $min^{-1}$. So we can classify water of Bounouara as extremely scale-forming water.

#### *3.2.2. Effect of temperature on the scaling power*

The accelerated scaling tests using the water of Bounouara at various temperatures (10°C, 20°C, 40°C and 60°C), gave the chronoamperometry curves of the (Fig. 2). From the slope of the linear part of the curves, it can be concluded that the scaling rate increases with temperature; it results of both the increase of the oxygen reduction rate [10] and the decrease of the $CaCO_3$ solubility. For this, the scaling time decreases from 29.16 to 4 min when the work temperature increases from 10 to 60°C (Table 2). Here, it could be noted that the more significant effect of temperature was registered between 10°C and 20°C. Indeed, a sharply decrease of the scaling time from 29.16 to 9.16 min and increase of the scaling index from 34.3 to 109.19 $min^{-1}$ were founded (Table 2). However, some differences can be evoking:

• Firstly, the effect of temperature is less important on the scaling time and index for the high temperature; $t_E$ and $i_E$ varied by about 80 and 54% for the variation of temperature from 10°C to 20°C whereas they were about 7 and 14% in the case when temperature varied from 20 to 30°C [8].

• Secondly, the temperature affects the compactness of the formed scale layer on the metallic surface. When the temperature is increased, the residual current and the scaling index increase that the formed layer is more porous than the temperature increases.

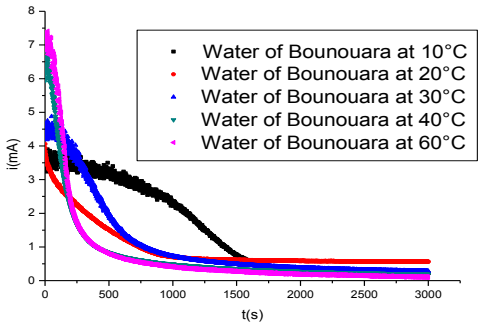


**Figure 2.** Chronoamperometry curves plotted for different temperatures in the water of Bounouara.

**Table 2**: Effect of temperature on the scaling time, residual current and the scaling index of Bounouara water.

| Work temperature | $t_E$ (min) | $I_R$ (µA) | $i_E$ ($min^{-1}$) |
|---|---|---|---|
| 10°C | 29.16 | 10 | 34.29 |
| 20°C | 9.16 | 15.27 | 109.17 |
| 30°C | 7.40 | 16.64 | 135.13 |
| 40°C | 5 | 19.69 | 200 |
| 60°C | 4 | 22.55 | 250 |

### *3.3. Scale inhibition by Lemon Peel*

In order to treat water Bounouara to reduce their power scaling, water of Bounouara was treated with natural product: peel of lemon at increasing concentrations. With the aim to reduce the scaling tendency of the studied water, by the increasing of the scaling time, lemon peel extract was added at very low amounts to the raw water of Bounouara. All experiments were performed at two temperatures 20°C and 40°C.

#### *3.3.1. Chronoamperometry study*

we operate a chronoamperometry study to evaluate the inhibitory effect of treatment at two temperatures 20°C and 40°C (Figure 3 and 4). The study of these chronoamperometry curves shows that the addition of 0.1 g/L of lemon peel in Bounouara water at 20°C, the scaling time increases to the value of 16.66 min with respect to time scaling of the raw water at 20°C ($t_E$ = 9.17 min). As against, adding of lemon peel to water of Bounouara at 40°C shows that this inhibitor begins to retard scale formation by increasing the time scaling to the value of 11.66 min with respect to time scaling of the raw water at 40°C ($t_E$ = 5 min) from an addition 0.2 g/L. The values of the time scaling, the residual current and scaling index of each scaling accelerated test of the water of Bounouara treated by lemon peel inhibitor at two different temperatures 20°C and 40°C are summarized in (Table 3).The found precipitation curves are given in (Figs. 3 and 4).

From the values of the scaling time and the residual current deducted from accelerated scaling curves performed on the treated water of Bounouara with lemon peel at the two temperatures (20°C and 40°C) we find that: the scaling time increases with increasing concentration of the inhibitor at each temperature up to complete inhibition (calcium carbonate does not adhere to the electrode steel); the residual current varies with the increase time scaling and this variation depends on the quantity of scale deposited on the working electrode. We can say that the addition of natural inhibitor reduce the scaling power of water of Bounouara at very low concentrations of additions even in low temperatures. The application of treatment of Bounouara water with the lemon peel inhibitor increases the scaling time from the addition of concentration of 0.1 g/L at the temperature source. As against, lemon peel treatment influences the scaling power by increasing the time scaling of Bounouara water at 40°C from the addition of concentration of 0.25 g/L.

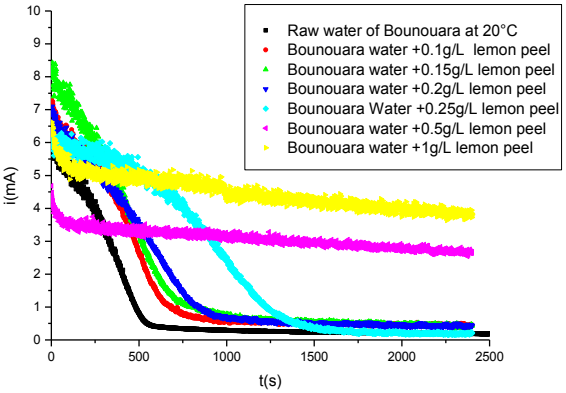


**Figure 3.** Chronoamperometric curves of Bounouara water treated with different concentrations of lemon peel at temperature of 20°C.

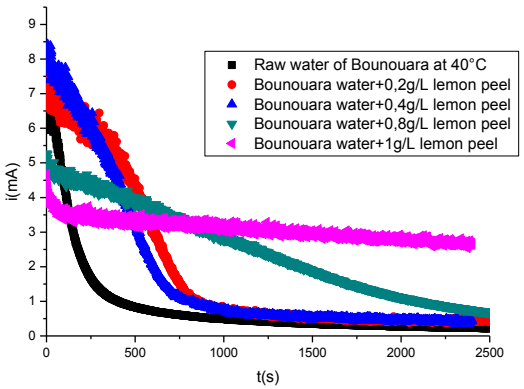


**Figure 4.** Chronoamperometric curves of Bounouara water treated with different concentrations of lemon peel at temperature of 40°C.

**Table 3:** Time scaling, the residual current and index scaling of chronoamperometry curves of Bounouara water treated with different concentrations of lemon peel at the source temperature20°C and at 40°C.

| | Concentration (g/L) | $t_E$ (min) | $I_R.10^6$ (A) | $i_E$ (min$^{-1}$) = 1000/$t_E$ |
|---|---|---|---|---|
| Bounouara water + lemon peel at 20°C | 00 | 9.16 | 16.64 | 109.17 |
| | 0.1 | 11.66 | 17.42 | 85.76 |
| | 0.15 | 12.5 | 39 | 80 |
| | 0.2 | 15.33 | 42 | 65.23 |
| | 0.25 | 22.5 | 44 | 44.78 |
| | 0.5 | ∞ | - | - |
| | 1 | ∞ | - | - |
| Bounouara water + lemon peel at 40°C | 00 | 5 | 19.69 | 200 |
| | 0.25 | 12.5 | 23.5 | 80 |
| | 0.4 | 15 | 41 | 24.39 |
| | 0.8 | 41.66 | 44.5 | 24 |
| | 1 | ∞ | - | - |

### 3.3.2. Tests of impedancemetry

Before the determination of impedances and in the aim to cover totally the working electrode by the precipitation of calcium carbonate in the absence and in presence of the natural inhibitor (lemon peel), the applied potential was maintained at (*-1 V/SCE*) during 50 minutes [11]. The impedances curves registered of calcium carbonate deposits of Bounouara water treated with increasing concentrations of lemon peel are given in Figures (5 and 6). According to those figures (Figs 5 and 6), the treatment of hard water of Bounouara by the lemon peel confirmed that the delay in the formation of tartar begins at an addition of 0.1 g/L at the temperature of the source 20°C and an addition of 0.25 g/L at the temperature of 40 ° C. The results corresponding to these tests are summarized in Figures (5, 6). Treated water of Bounouara water with different concentration of lemon peel at 40°C give impedance curves without a relative part corresponding to the diffusion observed in the case of treated water of Bounouara at source temperature 20°C. The augmentation of the lemon peel concentration decreases the diameter of the first circular half loop of impedance diagrams which shows that the electrode surface was not totally covered when the addition of lemon peel was accomplished even after 50 minutes of application of accelerated scaling.

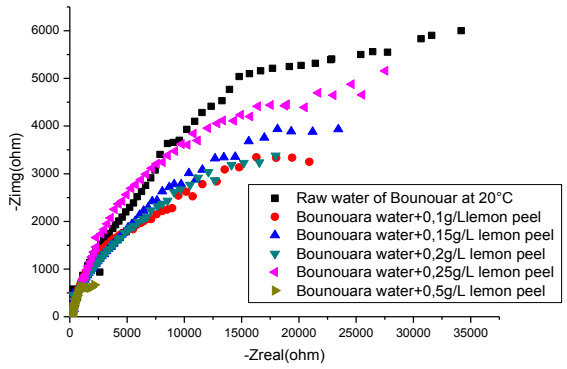


**Figure 5.** Impedance diagrams obtained in Bounouara water treated with different concentrations of lemon peel at 20°C.

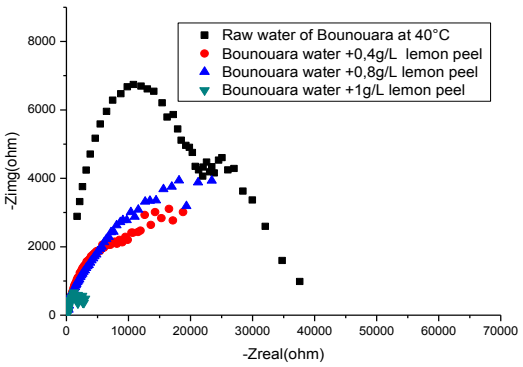


**Figure 6.** Impedance diagrams obtained in Bounouara water treated with different concentrations of lemon peel at 40°C.

**Table 4.** Capacity high frequencies and resistances of charge transfer obtained from the impedance curves of Bounouara water raw and treated with lemon peel at 20°C and 40°C.

| | Concentration of inhibitor (g/L) | $C_{hf}$ (µF/cm$^2$) | Rtc (Kohm.cm$^2$) |
|---|---|---|---|
| Bounouara water + lemon peel at 20°C | 00 | 0.218 | 5.571 |
| | 0.1 | 1.969 | 5.541 |
| | 0.2 | 3.744 | 4.534 |
| | 0.25 | 94.57 | 3.895 |
| | 0.5 | 99.25 | 1.270 |
| | Concentration of inhibitor (g/L) | $C_{hf}$ (µF/cm$^2$) | Rtc (Kohm.cm$^2$) |
| Bounouara water + lemon peel at 40°C | 00 | 1.76 | 21.060 |
| | 0.25 | 12.67 | 6.020 |
| | 0.4 | 28.2 | 4.017 |
| | 1.00 | 87.37 | 1.462 |

The measurement of impedances of water Bounouara treated with the lemon peel confirms that the deposition of calcium carbonate decreases with the concentration of inhibitor, it is verified by the increase in the high frequency

capability ($C_{hf}$) and the decrease in charge transfer resistance ($R_{tc}$) versus increasing concentration of lemon peel added as shown in the values of Table 4. According Hui and Ledion [12], the more the transfer resistance fillers, the higher the scale deposition is compact and adherent and lowering the charge transfer resistance is related to the diffusion of oxygen in the solution. The mode of action of natural inhibitor (lemon peel) on the inhibition of $CaCO_3$ is: the citrate molecule existing in the lemon peel and in all citrus reacts with calcium ions existing in hard water to form calcium citrate as a cyclic and bi-molecular structure (Fig, 7);

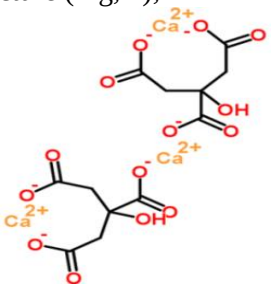


**Figure 7.** Structural of calcium citrate complex [13].

This one was to proved by Fredric Ceo [13] who used the of origin citrus citrate molecules to protect against the formation of calcium carbonate in the renal system of the human body. According to the work of Fredric Ceo, citrate citrus react with the calcium that is in the supersaturated waters to form a cyclic bi-molecular complex. Tlili [14] and most of the work subsequent poved, the citrus ions are selectively adsorbed on the growth sites of calcium carbonate crystals therefore; they slow down or block the precipitation of calcium carbonate [14]. In the case of high temperature (40°C), the solubility of all salts increases and the treatment of hard water needs of the higher concentration of inhibitors.

## 4. Conclusion

The results obtained from the calculations agree well with experimental values. From the results obtained in this study:

- The use of the chronoamperometry method may characterize the scaling power of Bounouara water at different temperatures, raw or treated with natural lemon peel as scaling inhibitor.
- The chronoamperometry study of the raw water of Bounouara at the source temperature 20°C shows that this water has a scaling time $t_E$ of 9.17min and a index scaling $i_E$ of 109.17$min^{-1}$ and by consequent Bounouara water is classified as extremely scale-forming water.
- The increase in the temperature supports the precipitation of calcium carbonate, the time of scaling becomes shorter and water becomes harder. This results of both the increase of the oxygen reduction rate and the decrease of the $CaCO_3$ solubility.
- The treatment of scaling of Bounouara water by natural inhibitor lemon peel at the source temperature 20°C and at 40°C increases considerably the time scaling relative to the time scaling of the raw water. This is the delay of the formation of scaling by the effect of inhibitor. The concentrations of lemon peel increase in water of Bounouara, the scaling power is reduced to total inhibition. -The inhibitory effect of lemon peel on water of Bounouara at a temperature of 20°C starting from the concentration of 0.1 g/L, and total inhibition is reached at a concentration of o.5 g/L.
- The treatment of Bounouara water at temperature of 40°C by the same inhibitor shows that the use of concentrations of 0.5 g/L of lemon peel cannot completely inhibit the formation of calcium carbonate; scaling inhibition can be achieved at an addition of 1 g/L. So the treatment of the scale of hard water of Bounouara with natural lemon peel is more effective at low temperatures with a low concentration, against at higher temperatures, the scale inhibition of hard water is applicable that 'at very high concentrations of inhibitor.

- The impedancemetry makes it possible to appreciate the importance and the texture of the carbonate of calcium deposits. In general, more the deposit is compact and adherent and more the high frequency resistance is great. This same measure shows that the control by mass transfer is observed only in the case of raw water and the tartar deposit and consequently the resistance decrease when the natural inhibitor concentration increases. The lemon peel inhibitor effect is more pronounced in the case of low temperatures. So the lemon peel recovery in treating hard water is a better solution to reduce the risk of tartar and for environmental protection.

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