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Study of Inhibiting Effect of Orange peel on Hard Growth Water

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Abstract

Scaling is one of undesirable problems of natural hard water, which causes enormous technical and economic consequences by the formation of compact and adherent deposit on pipes and industrial or domestic installations. The present work examines the effect of natural inhibitor (orange peel) on the $CaCO_3$ precipitation in Algerian ground water of Bounouara having a hardness of 58°F. The main objective was to reduce the scaling power and then to prevent the fouling phenomenon met in the equipments supplied by this water. Chronoamperometry tests show that Bounouara water is extremely scale-forming water by scaling time of (t_E = 9.17min) and an index scaling (I_E = 107 min^{-1}). The accelerated scaling curves registered at different temperatures of raw water of Bounouara showed that scaling time decreases by increasing the temperature, and Bounouara water become more scale-forming in high temperatures. The anti-scale treatment with orange peel is more efficient in low temperature, because the total inhibition of hardness of Bounouara water was realized at 20°C with an addition of 0.75g/L of orange peel but at 40°C, 1g/L of orange peel must be added to Bounouara water to totally block the precipitation of tartar. So orange peel is an effective inhibitor for the scaling treatment of drinking water and for the valorization of orange peel and protection of the environment from food industry waste that reject 60% of citrus fruits in the form of waste.

1. Introduction

The pumping of groundwater is necessary to cover most of the enormous water needs, but unfortunately, most of the groundwater has a high hardness. Hard ground 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. During the last twenty years, various methods have been developed in order to estimate the scaling propensity of natural waters [3], electrochemical methods [4], [5] and [6], thermal or chemical methods [7]. The sites of our study is drilling water of Bounouara, it is known as major water resource that supply a large part of east of Constantine of drinking water and also used for industrial and agricultural implantation. The major drawback of this water is that they have a very high hardness in the range of 58°F. The high hardness of this water (Bounouara water) involves consequences inevitable and undesirable by the formation of compact and adherent deposits on metallic or non-metallic surfaces and scale inhibitor treatment is very necessary. In this work, our study is consecrated to the treatment of hard water of Bounouara by natural inhibitor (orange peel) using the electrochemical method of chronoamperometry. The evaluation of the scaling power of Bounouara raw water and the inhibitory effect of orange peel was performed by using electrochemical method of the scaling accelerated method. Bounouara water is extremely scale-forming water by scaling time of (t_E = 9.17min) and an index scaling (I_E = 107 min^{-1}). The accelerated scaling curves registered at different temperatures of raw water of Bounouara showed that scaling time decreases by increasing the temperature, and Bounouara water become more scale-forming in high temperatures. The total inhibition of hardness of Bounouara water was realized at 20°C with an addition of 0.5g/L of orange peel but at 40°C, more than 0.75g/L of orange peel must be added to Bounouara water to totally block the precipitation of tartar.

All chemical inhibitors of scaling are phosphates, phosphonates or carboxylates. The use of these inhibitors has harmful consequences on health, that's why although their efficiency softening, chemical inhibitors are used only for boiler water or industrial water. In this work, we used extracts of orange peel as scale inhibitor containing organic compounds of an acidic attitude (carboxylate) and the use of these extracts is natural food and ecological inhibitor that present a better alternative for treating hard water used for consumption (drinking water). So orange peel is an effective inhibitor for the scaling treatment of drinking water and for the valorization of orange peel and protection of the environment from food industry waste that reject 60% of citrus fruits in the form of waste.

2. **Experimental procedure**

2.1. Preparation of orange peel extract

Lemon peel was collected in the winter season from frech 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 [8] .

2.2. Principle of the Chronoamperometric method

The electrochemical techniques are founded on the controlled formation of calcium carbonate deposit on a working electrode through the electrochemical reduction of the dissolved oxygen [9, 10] (R1). Potential is imposed to a negatively value (-1V/ECS). Hydroxyl groups, which are generated by this reaction, induce a strong increase of the pH in the immediate and involving the formation of CO_3^{-2} (R2) .The solubility product $(Ca^{2+})(CO_3^{2-})$ therefore increases there is precipitation of $CaCO_3$ (R3) on the electrode which becomes insulating.

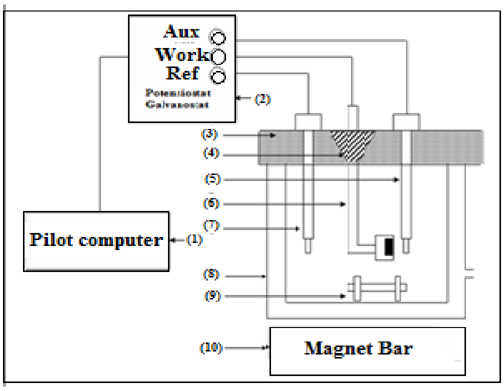
$$O_2 + 2H_2O + 4e \rightarrow 4OH^- \qquad R1$$

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

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

2. 3. Equipment used

Accelerated scaling is an electrochemical technical which determines the power scaling of water by controlled precipitation of calcium carbonate [9, 11]. The chronoamperometric experiments 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 [12].



1-Pilot computer equipped with software
2-Potentiostat-galvanostat
3-Cover electrode holder
4-Door plug-sample
5-Platinum electrode
6- Working electrode
7- Reference electrode
8- Thermostatted cell
9- Magnet bar
10-Magnetic stirrer

Figure 1: Chronoamperometry experimental device.

3. **Results and discussion**

3. 1. Water quality of Bounouara

The composition of the water of Bounouara is given in the Table 1. It shows that the considered water of Bounouara is mineral-bearing and present important hardness.

3. 2. Chronoamperometric Study of raw water of Bounouara

To determine the scaling power of raw water of Bounouara, we used the electrochemical method of accelerated scaling to a negative potential imposed at -1V relative to a calomel reference electrode saturated KCl. The progressive occupancy of the metal surface by the insulating layer reduces the current intensity down to zero for a fully compact layer or to a small value for a porous layer.

Table 1 Qualities of raw water of Bounouara

Paramètre	Water of Bounouar
T, °C	20
pH	7.2
CE, mS/cm	1.787
O_2 dissolved mg/L	8
Oxygen consumed by the organic matter (mg/L)	1.53
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

Therefore, the time variations of the current intensity (chronoamperometric method) can be used empirically as an indicator of the scaling rate [9, 10, 11, 13]. Fig (2) shows the shape of the Chronoamperometric curve of raw water of Bounouara. From this curve, we can determine: * The scaling time (t_E) of raw water of Bounouara which is 9.17min * The residual current (I_R) of raw water of Bounouara which is 16.64µA.

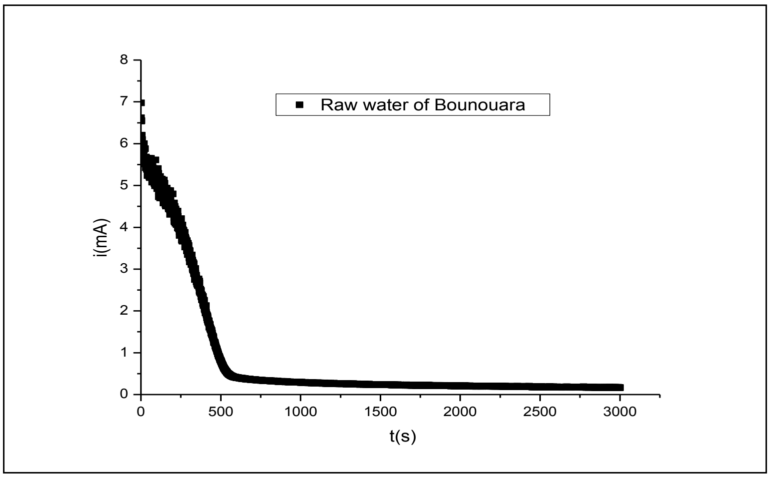


Figure 2: Chronoamperometric curve of Bounouara raw water at 20°C.

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

$I_E\ min^{-1}$ =1000/(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 Bounouara water as extremely scale-forming water.

3. 3. Effect of temperature on the raw water of Bounouara

The accelerated scaling tests using the water of Bounouara at various temperatures (10°C, 20°C, 30°C, 40°C and 60°C), gave the chronoamperometric curves of the (Fig 3). From the slope of the linear part of the curves and according to the work of Boulahlib-Bendaoud [12], it can be concluded that the scaling rate increases with temperature; it results of both the increase of the oxygen reduction rate [13] 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°C to 60°C (Table 2).

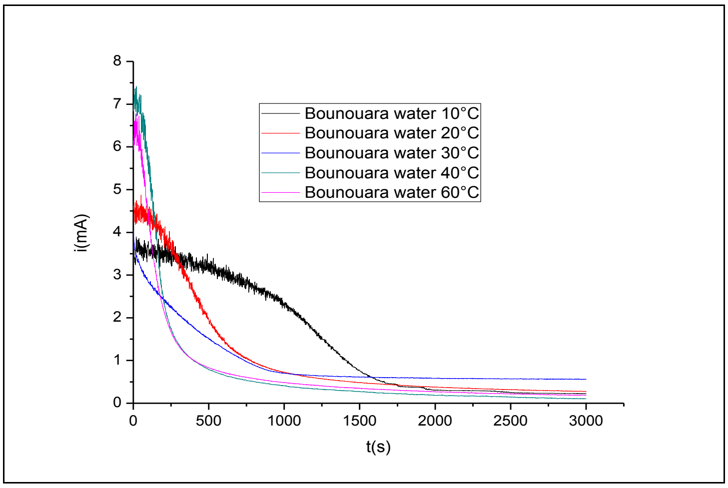


Figure 3: Chronoamperometric curve of Bounouara raw water at different

According to the pace of accelerated scaling curves registered at different temperatures of the raw water of Bounouara, time scaling decreased by increasing of the temperature (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 9.17 min and increase of the scaling index from 34.29 to 109.17 min^{-1} were founded (Table 2). Raising the temperature increases the speed of oxygen reduction reaction and the chemical precipitation of tartar.

Table 2: Time scaling, residual current and the index scaling of the chronoamperometric curves of Bounouara water at different temperatures.

	Temperature	t_E (min)	$I_R.10^6$ (A)	I_E (min^{-1}) = 1000/t_E (min)
Raw water of Bounouara	10°C	29.16	22.69	34.29
	20°C	17.5	19.27	57.14
	30°C	9.17	16.64	109.17
	40°C	5	15.27	200
	60°C	4	10	250

3. 4. Treatment of Water of Bounouara

In order to treat water Bounouara and to reduce its power scaling, water of Bounouara was treated with natural product: peel of orange at increasing concentrations and we operate a chronoamperometric study to evaluate the inhibitory effect of treatment at two temperatures 20°C and 40°C (Figures 4 and 5). The choice of the temperature of 20 ° C and 40 ° C is to determine the effective concentration of the treatment to the temperature of the source, and even when the temperature increases during the summer season and the scaling power of water becomes more pronounced.. The study of these chronoamperometric curves shows that the addition of 0.15 g/L of orange 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 orange 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 0.3 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 orange peel inhibitor at two differente temperatures 20°C and 40°C are summarized in (Table 3).

From the values of the scaling time and the residual current deducted from accelerated scaling curves performed on the treated water of Bounouara with orange 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 orange peel inhibitor increases the scaling time from the addition of concentration of 0.15 g/L at source temperature. As against, orange peel treatment influences the scaling power by increasing the time scaling of Bounouara water at 40°C from the addition of concentration of 0.3 g/L. The mode of action of natural inhibitor on the inhibition of $CaCO_3$ is: the citrate molecule existing in the orange peel and in all citrus react with calcium ions to form calcium citrate as a cyclic and bi-molecular structure (Fig 6);

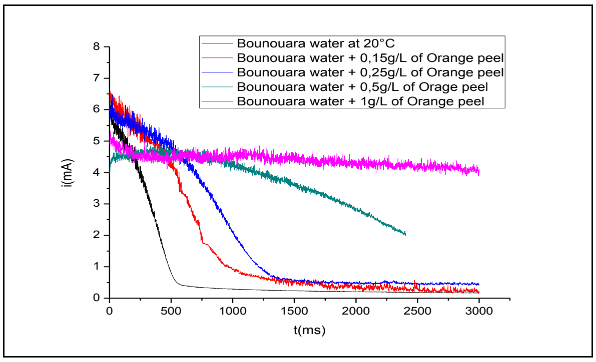


Figure 4: Chronoamperometric curves of Bounouara water treated with different concentrations of orange peel at temperature of 20°C.

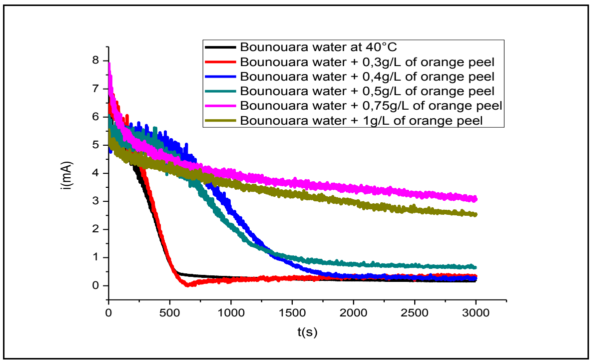


Figure 5: Chronoamperometric curves of Bounouara water treated with different concentrations of orange peel at temperature of 40°C.

treated

Bounouara water + orange peel at 20°C.	Concentration of orange peel (g/L)	t_E (min)	I_R (mA)	$I_E = 1000/t_E$ (min)
	00	9.16	16.64	109.17
	0.15	16.66	20.30	60.02
	0.25	23	43	43.47
	0.5	∞	-	-
	1	∞	-	-
Bounouara water + orange peel at 40°C.	00	5	19.27	200
	0.3	11.66	31	85.76
	0.4	25.33	35	39.47
	0.5	29.16	63	34.29
	0.75	∞	-	-
	1	∞	-	-

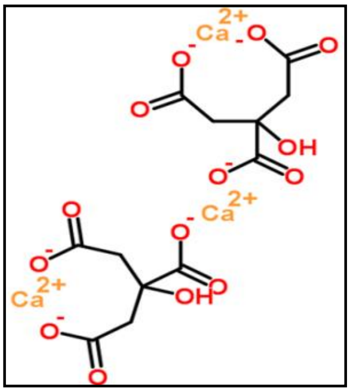


Figure 6: Structural forme of calcium citrate complex [14]

This one was too proved by Fredric Ceo [14] 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 medium to form a cyclic bi-molecular complex. Tlili [15] and most of the work subsequent, 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 [15]. In the case of hight temperature (40°C), the solubility of all salts increases and the treatment of hard water needs of the higher concentration of inhibitors.

Conclusion

From the results obtained in this study:
-The use of the chronoamperometric method may characterize the scaling power of Bounouara water at different temperatures, raw or treated with natural orange peel as inhibitor of scaling. -The chronoamperometric 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 109.17min^{-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 [15] and the decrease of the $CaCO_3$ solubility. -The treatment of scaling of Bounouara water by natural inhibitor orange 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 orange peel increase in water of Bounouara, the scaling power is reduced to total inhibition. -The inhibitory effect of orange peel on water of Bounouara at a temperature of 20°C starting from the concentration of 0.15 g/L, and total inhibition is reached at a concentration of o.5 g/L. -The treatment of Bounouara water at a temperature of 40°C by the same inhibitor shows that the use of concentrations of 0.5 g/L of orange peel can not 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 orange 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. So the orange peel recovery and valorisation in the treatment of hard water is a better solution to reduce the risk of tartar and for environmental protection protection of citrus peel.

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