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Inhibition of scale formation by electrochemical means in the presence of a green inhibitor: citric acid

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Abstract

The most industrial, natural waters or consumption contain calcium and carbonate ions, which may cause scaling phenomena in plants, which can lead to serious malfunctions (blockage of pipes, clogging of the membranes, loss of efficiency exchangers heat etc...). Various methods decarbonation as the precipitation with lime or sodium carbonate or the acid vaccination are commonly used.Some chemical inhibitors are sometimes added to block the germination of crystals of calcium carbonate (carboxylates, phosphates ...). As part of our study and to meet the growing water needs of the city of Constantine, these needs to pump into groundwater of high hardness such as Hamma with a hardness of 55.4°F. To reduce scaling, electrochemical techniques (chronoamperometry and impedancemetry) were applied to hard water in the presence of citric acid.The scaling power was assessed by time scaling of the raw water of Hamma (14 min) by chronoamperometry at 30°C.The tests carried out in the presence of increasing concentrations of citric acid considerably increase the time scaling. By against, the temperature increase causes a reduction of the time scaling values.The deposit obtained from the raw and treated water was evaluated using electrochemical impedance measurements and provided us to show that:

- Charge transfer resistance the obtained scale from the raw water of Hamma confirms its adherence.
- Charge transfer resistance decreases with increasing concentration of citric acid following the reduction of the deposit and the number of active sites increases and this is confirmed by the increase in the high frequency capability.

1. Introduction

Scaling caused by hard water and underground Hamma is characterized by the appearance on a metal surface or not a compact and adherent mineral deposit consists primarily of calcium carbonate as calcite [1]. These deposits lead to significant technical and economic problems [2]. Several chemical and electrochemical treatments exist to inhibit scale from hard water [3-9]. In addition, new green inhibitors should be considered because they are biodegradable and do not affect in the environment [10-13].

Our study focuses on the inhibition of hard water scaling power Hamma by citric acid as green inhibitor, none toxic and using two electrochemical techniques: chronoamperometry and impedancemetry. Since the origin of citric acid is a vegetable, it is economical and efficient. In addition, it offers several uses (taste enhancer, pH food regulator and chelator).It is recommended for descaling household appliances (washing machine, coffee machine, kettle ...) and softening drinking water.

2. Material and methods

2.1. Water studied:

The physicochemical results of the analysis of Hamma water are recapitulated in Table 1.

By considering these results, we see that water of Hamma has a significant relative content of organic matter (TOC: 2 mg/L).

In addition, it is strongly mineral-bearing with a significant hardness (TH 554 mg/L $CaCO_3$). Therefore it is a primarily bicarbonated calcic [14].

Table 1: Hamma water analysis

Parameter	Value
Temperature °C	32
pH	7.35
EC mS/cm	0.899
TOC mg/L	2.00
CO_2 mg/L	37.05
HCO_3^- mg/L	417
TH mg/L$CaCO_3$	554
Ca^{2+} mg/L	148
Mg^{2+} mg/L	45
Cl^- mg/L	145
SO_4^{2-} mg/L	190
NO_3^- mg/L	7.00
NO_2^- mg/L	-
PO_4^{3-} mg/L	0.03
NH_4^+ mg/L	-
Na^+ mg/L	84
K^+ mg/L	3.00

2.2. Tests of accelerated scaling

In order to measure the $CaCO_3$ formation kinetics, the electrodeposition technique was first developed by Ledion in 1985 [15] which was the subject of various developments and improvements. In addition, it is the basis of other methods, such as chronoelectrogravimetry and impedancemetry.

Its principle consists in covering with $CaCO_3$ a metal surface carried to a fixed negative potential of -1V compared to calomel reference electrode (Figure.1).

The application of this negative potential involves the reduction on the surface of metal primarily, of oxygen, according to the equation:

$$\mathbf{O_2 + 2\,H_2O + 4\,e^- \rightarrow 4\,OH^-}$$

In the vicinity of this electrode, the presence of the ions hydroxides involves an increase in the pH locally and the ions hydrogenocarbonates can be transformed into ions carbonates according the reaction:

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

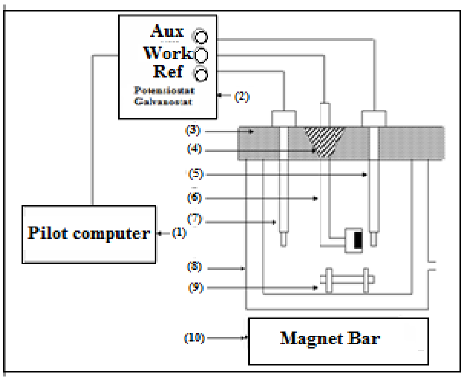
The increase in the content of CO_3^{2-} then involves the precipitation of calcium carbonate on the surface of the electrode according to the reaction:

$$\mathbf{Ca^{2+} + CO_3^{2-} \rightarrow CaCO_3\ (S)}$$

In this technique, water is characterized by a time scaling t_E. More t_E is little more of scaling water. An anti scale treatment will be effective when t_E treated water becomes higher than that of the raw water. In addition, over the residual current (I_{res}) is low more tartar is compact and adherent. If the inhibitory effect of a product is positive, there is increased residual current. There is more adhesion of scale on the electrode.

2.3. Origin of citric acid

Citric acid ($C_6H_8O_7$) an α-hydroxytricarboxylic acid is a natural component of animal and plant tissues. It appears as colorless crystals or white powder. The citric acid can be obtained from sources such as lemon or pineapple juice, by mycological fermentation using candida spp, and by a solvent extraction process from a fermentation liquor, Aspergillusniger.



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. Chronoamperometry raw water of Hamma

The tests were carried out on water Hamma at 30 ° C and a volume of 500mL.

The shape of the curve for raw water of Hamma is given by (Figure 2).

It is note that the scaling water with a time of 14min scaling and low residual current 9.74µA /cm^2, resulting in the formation of a firmly adhering precipitate calcium carbonate.

According to [15] the calculation of the index scaling allows us to place vis-à-vis scaling water.

The index scaling is given by the equation: $i = 1000 / t_E$ (min).

The classification of water is as follows:

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

The index for scaling Hamma is 71.42min^{-1}. Therefore, water Hamma is in the range of very scale-forming water.

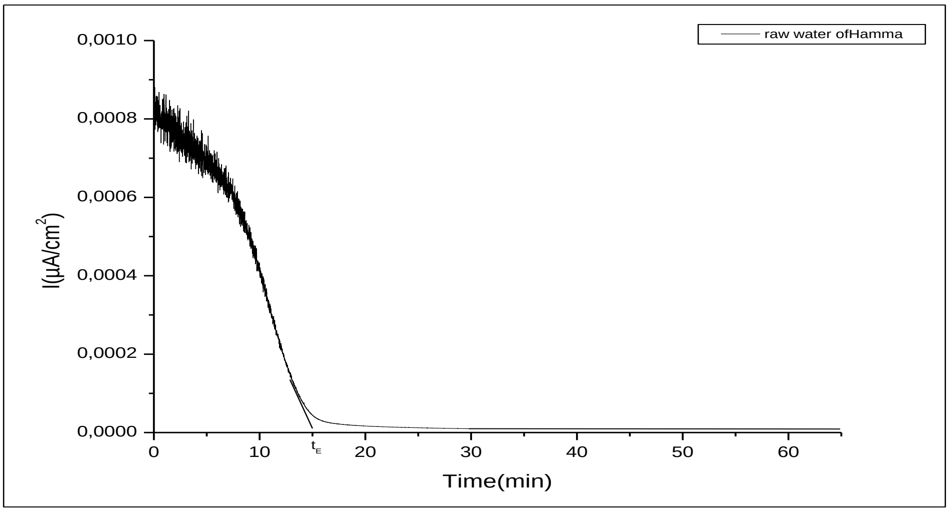


Figure 2: Curve chronoamperometry for raw water of Hamma.

3.2. Inhibition of scale formation by citric acid:

In order to reduce the scaling power of the waters of Hamma, increasing concentrations (0.25, 0.5, 0.75 and 1 mg/L) of citric acid was applied to these hard water. For each applied concentration, evaluation is carried out by trying to accelerate scaling (chronoamperometry). The study showed that the curves for the raw water, the time scaling is 14min and the delay scaling occurs from 0.25 mg/L added. And when the citric acid concentration increases, the delay in precipitation of calcium carbonate becomes important (Figure 3). In addition, it is observed that the residual current increases as a function of the concentration of citric acid as the deposit becomes more porous and less compact (Table 2). At an addition of 1 mg/L, the curve becomes a straight line, indicating the complete inhibition of calcification (Figure 3). The time scaling has become almost infinite and $CaCO_3$floc formation is manifested on the curve by oscillations. There is more adhesion of calcium carbonate to the electrode because the residual current is important.

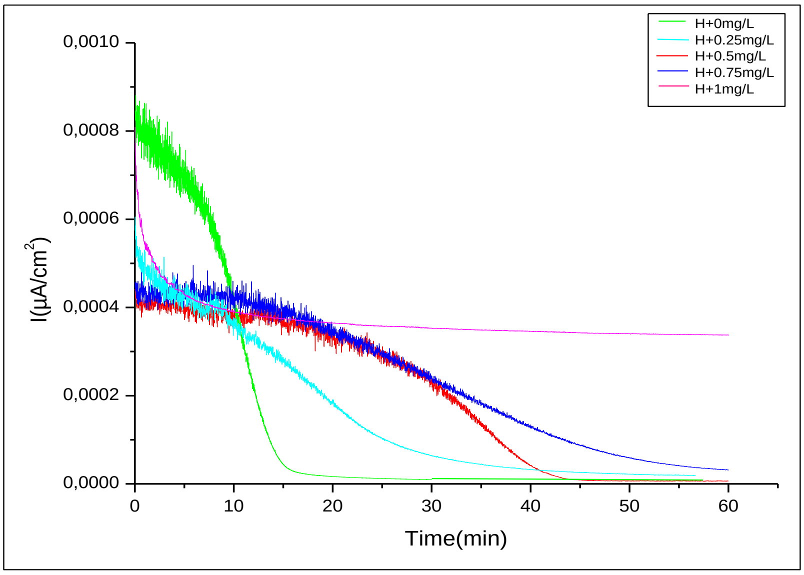


Figure 3: Curves chronoamperometry for water treated with citric acid.

Table 2: Values of the remaining time and current scaling for water treated with citric acid

Concentration(mg/L) of citric acid	Time scaling (min)	Residual current (µA / cm^2)
00	14.01	9.74
0.25	28.30	13.65
0.5	40.87	26.38
0.75	52.31	37.35
1	∞	337.9

3.3. The effect of temperature on the chronoamperometric curves for the treated water 0.75mg/L citric acid.
Citric acid concentration of 0.75mg / L was introduced at the Hamma water at different temperatures (20, 30, 40 and 50°C). For each applied concentration is carried out by assessing the accelerated scaling test. The study of curves revealed that the time scaling decreased with increasing temperature view (Figure 4) and (Table 3).

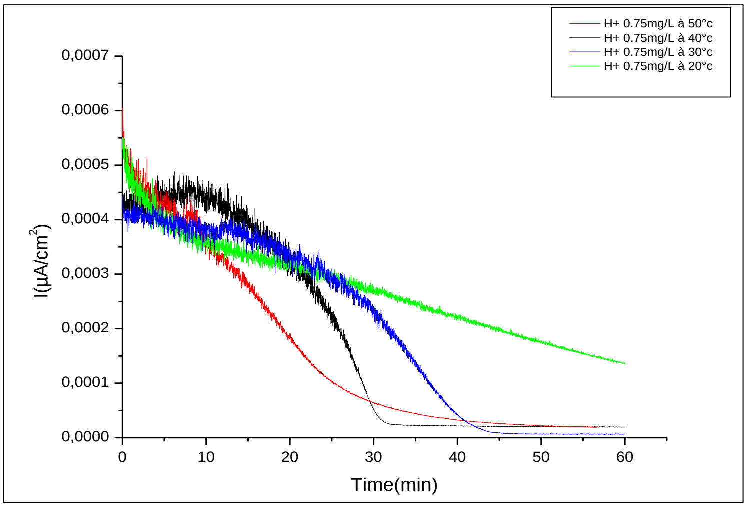


Figure 4: The effect of temperature on the chronoamperometric curves for the treated water 0.75mg /L citric acid

The scale-forming water becomes more important at 50 ° C than at 30 °C and the residual current has dropped, indicating the formation of a more compact and adherent scale.

3.4. Impedance of raw water of Hamma

The formation of calcium carbonate deposit was performed at a potential (-1 V/SCE)and a time of longer than 60min the time scaling to ensure the formation of tartar on the working electrode. The deposits impedance measurements obtained from the raw water and the treated water of Hamma with citric acid were carried out in the frequency domain (100 KHz to 100 mHz). The electrochemical assembly used (cell electrodes) is identical to that used for the chronoamperometry. The Nyquist plot obtained from the deposit of the raw water is given by (Figure 5). Note the appearance of two loops impedance due to the recovery of the metal surface of the electrode by depositing a compact and adherent. The first loop observed at high frequencies translated charge transfer of the oxygen reduction reaction and the second obtained at low frequencies corresponds to the diffusion of oxygen. So there is a mass transfer which occurs at the second loop.

Table 3: The effect of temperature on the time scaling and the residual current for treated water 0.75mg /L citric acid

Temperature (° C)	Time scaling (min)	Residual current (µA / cm^2)
20	∞	136.53
30	40.87	70.00
40	30.02	49.00
50	25.04	37.35

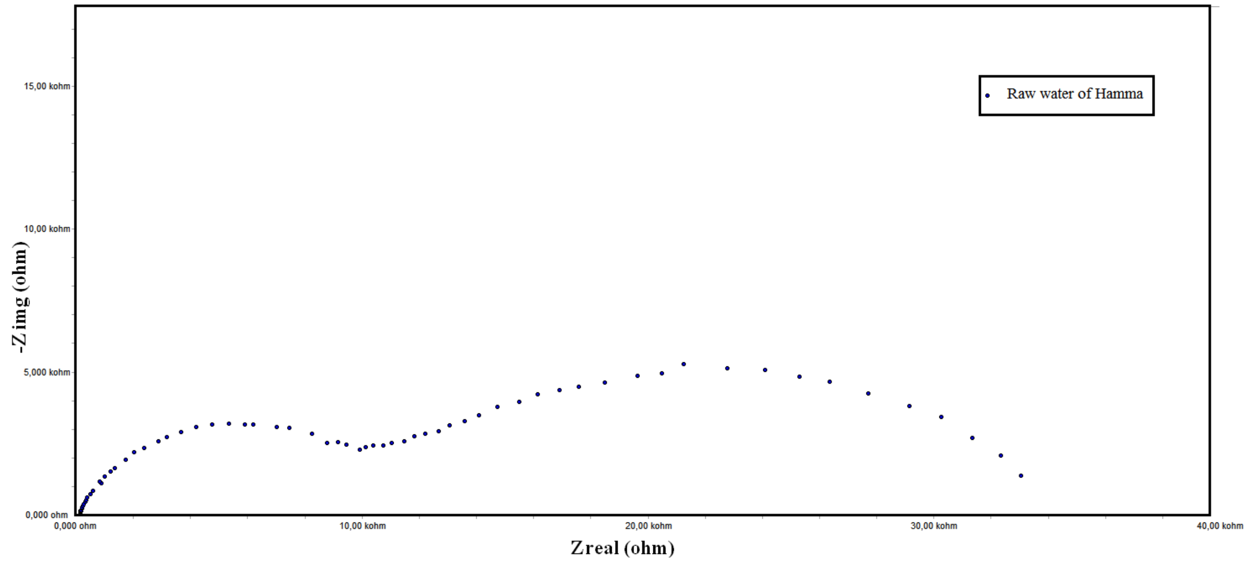


Figure 5: Diagram of impedance obtained for the Hamma raw water.

3.5. Impedance of treated water of Hamma

The impedance diagrams recorded when obtaining deposits from water treated with citric acid show that the addition of 0.25mg/L of citric acid causes the disappearance of the second oxygen diffusion loop. In addition, the diameter of the loop which corresponds to the high frequency charge transfer resistance decreases with increasing concentration of citric acid. The scale deposited by the treated water is less electrically insulating, so less compact than that deposited from a scale-forming raw water (Figure 6) and (Table 4). Even finding was made by [16]. The high frequency capability (C_{hf}) measures the number of available active sites on the metal surface. The latter is changing with remaining active surface. So, we can highlight the evolution of the recovery rate of the working electrode over the calculus inhibition assays with increasing concentration of citric acid.

The maximum recovery rate of the working electrode corresponds to one of C_{hf} 0.069µF/cm^2, ie it is the deposit obtained from the Hamma raw water. By against the surface of the electrode becomes active (no deposit) to a maximum concentration of inhibitor introduced in 1 mg/L. In addition, the effectiveness of scale inhibition increases with increasing concentration of citric acid and the formed scale becomes porous, and therefore less compact (Table 4).

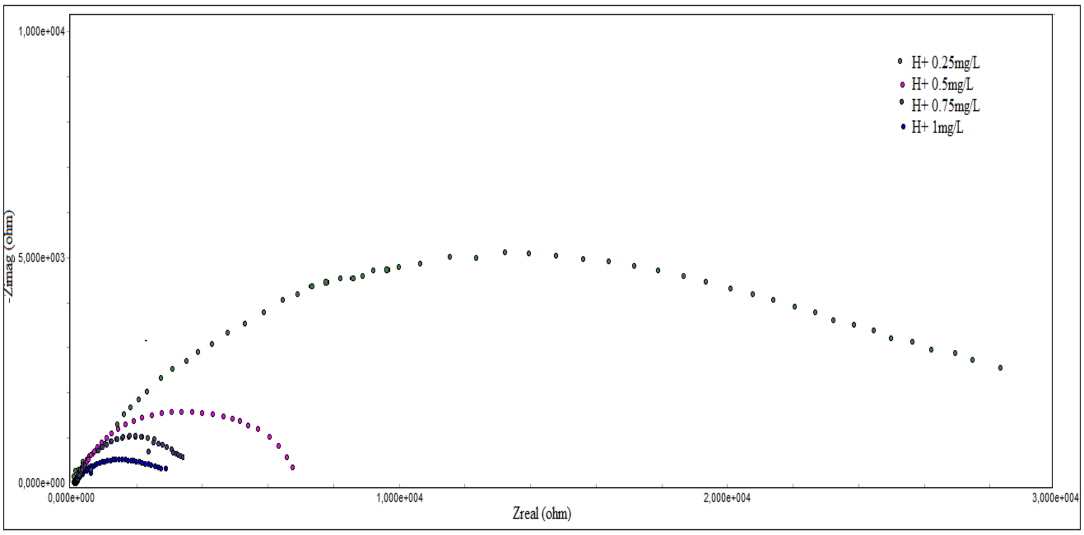


Figure 6: Impedance diagrams obtained for the treated water of Hamma.

Table 4: high capacity and high frequency resistance of treated water of Hamma.

Concentration of citric ac (mg/L)	C_{hf}(μF/cm^2)	R_{hf}(kohm.cm^2)	Efficiency
00	0.069	14.62	-
0.25	0.132	10.24	29.95
0.5	1.465	3.42	76.60
0.75	3.86	2.36	83.85
1	8.68	1.47	89.90

3.6. The temperature effect on the impedance diagrams for treated water 0.75mg / L citric acid.

To study the effect of temperature on concentration of 0.75 mg / L of citric acid added in Hamma water. We choose a temperature range between 20 ° C and 50 ° C.

Note that R_{hf} increased with temperature and calculus becomes more compact and adherent. Even finding was made by chronoamperometry. This reflects a decrease of C_{hF} and the achieved value is very low 0.26 uF/cm^2. (Figure 7) (Table 5).

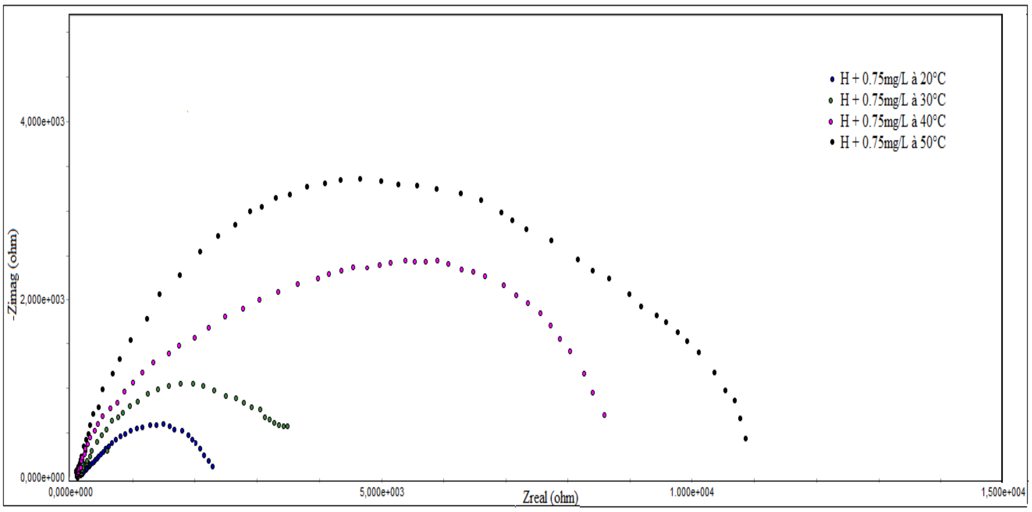


Figure 7: The effect of temperature on the impedance diagrams obtained for the treated water from Hamma to 0.75mg / L citric acid.

Table 5: The effect of temperature on the high frequency capability and the high frequency resistance for the treated water 0.75mg / L citric acid.

Temperature (°C)	C_{hf} (µF/cm^2)	R_{hf} (kohm.cm^2)
20	12.38	1.38
30	4.23	2.36
40	3.86	5.09
50	0.26	9.06

Conclusion

Scaling from Hamma groundwater consists mainly of calcium carbonate.

In our study, electrochemical methods (chronoamperometry, impedancemetry) inhibiting calcification were performed at the laboratory scale.

These methods have been applied to evaluate and inhibit the scaling power of waters.

The results of chemical analysis revealed that Hamma ground water has a hardness of 55.4°F.

In addition, these waters are very scale-forming because the index scaling of these waters is 71.42 min^{-1}.

The role of the citric acid has been highlighted and it is possible to determine the appropriate concentration of inhibitor to reduce hardness.

For chronoamperometrytests showed that 0.25 mg/L is the lowest dose of citric acid resulting in a delay precipitation.Same remark was made by [13] where in the field used (0.01 - 0.1mg / L) of citric acid, no reduction in scale is observed.

Against by an addition of 1 mg/L leads to a time scaling (t_E) infinite and calcium carbonate no longer adheres to the working electrode.

Another electrochemical method (impedancemetry) which was applied to the deposits obtained by the raw water and treated water of Hamma shows that:

Charge transfer resistance decreases as the concentration of citric acid increases.

In addition, the high frequency capacitance increases with increasing concentration of inhibitor. The obtained deposit becomes increasingly porous.

The results obtained in impedancemetry are in agreement with those obtained by chronoamperometry.

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