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## INHIBITION OF CALCIUM CARBONATE BY THREE MIXTURES: GALLIC ACID+QUERCETIN, QUERCETIN+ALGINATE AND GALLIC ACID+ALGINATE

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### Abstract

The Hamma groundwater provides water to Constantine, a city in eastern Algeria. The high concentration of calcium ions (136 mg/L) and hydrogen carbonate (442 mg/L) accounts for the strong scaling power of the water. This study is the first attempt to mix green inhibitors randomly to determine which is the most effective. The use of three new mixtures gallic acid+quercetin, quercetin+alginate, and gallic acid+alginate) to decrease or to prevent calcium carbonate formation is the main topic of this research. Due to their low environmental impact, these mixtures have proven to be effective green scale inhibitors. The inhibition efficiency occurs at extremely low concentrations: gallic acid+quercetin (6mg/L), quercetin+alginate (60mg/L), and gallic acid+alginate (3mg/L). The inhibition effects of these mixtures are evaluated using electrochemical techniques (chronoamperometry and impedancemetry). The results showed that the most efficient scaling inhibitor is gallic acid+alginate since it produced positive results at a lower dosage (3mg/L) than the other mixtures.

*Key words:* chronoamperometry, green inhibitor, impedancemetry, mixtures, scale inhibition

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### 1. Introduction

Constantine, a city located in Algeria, gets its drinking water from the Hamma subterranean water source. Due to the low thermal conductivity of the solid layer that results from the circulation of this water, scale formation leads to a substantial economic problem, for instance a decrease of the efficiency of heat exchangers, and may even results in failures in industrial installations (Zidoune, 1996). Chemical synthesis and addition also resulted in intolerable economic consumption.

The choice of a treatment using chemical inhibitors is based on different factors such as the total cost, the inhibition efficiency, the biodegradability, the use and their lack of toxicity. In fact, in recent

years, researchers have employed inhibitors of green chemistry (Lourteau et al., 2019; Karar et al., 2020; El housse et al., 2021a). Green chemistry aims to reduce or eliminate the use of hazardous materials and their production (Taj et al., 2006). Plant extracts used as scale inhibitors have attracted the attention of several studies (El housse et al., 2023, Souiad et al., 2023). They are an interesting alternative to conventional scale inhibitors thanks to their non-toxicity and biodegradability. In the study of El housse et al. (2021b), the performance of tannic acid towards scale formation was investigated because this organic molecule is a natural polyphenol synthesized by plants as a secondary metabolite.

Our primary objective in this work is to determine if the application of three green mixtures

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gallic acid-quercetin, quercetin-alginate, and gallic acid-alginate can change the scaling power of hard water (Hamma) using two electrochemical techniques:

- Chronoamperometry by following the variation of the current as a function of time.
- Impedancemetry, which allows for a good understanding of the characteristics and the adherence of the calcium carbonate deposit by measuring the scale that have precipitated at the interface metal-calcium carbonate deposit-electrolyte.

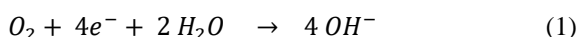
The use of green inhibitors is intended to reduce the possibility of environmental pollution.

## 2. Material and methods

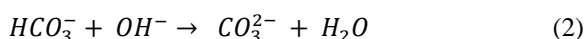
For both chronoamperometry and impedancemetry, data is collected and processed on a Gamry system, PC14 / 750 Potentiostat / Galvanostat / ZRA.

### 2.1. Chronoamperometry

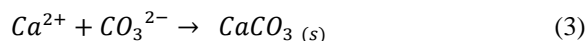
A classical three-electrodes cell was used for chronoamperometric tests. A platinum electrode and a saturated calomel electrode (SCE) were used as counter electrode and reference electrode respectively. They are provided from Tacussel. The working steel electrode is fixed at low enough potential (-1V/SCE) to induce dissolved oxygen reduction according to (Eq.1):



The formation of hydroxide ions causes a local increase in pH and promotes the reaction 2 (Eq. 2):



In turn, the increase of the  $CO_3^{2-}$  ions induces the precipitation of  $CaCO_3$  on the electrode surface according to Eq. 3:



The calcium carbonate deposits formed on the electrode surface causes an increase of electrical resistance, eventually isolating the metal from the water. As a result, the current intensity decreases over time for a given electrode potential. The recorded current intensity versus time provides information on the recovery of the electrode by a layer of calcium carbonate and the scaling rate. Finally, the scaling time ( $t_E = 12min$ ) is inversely proportional to the scaling power of water, and it decreases as the scaling power increases.

#### 2.1.1. Experimental setup

The experimental setup used to carry out our essays is illustrated in Fig. 1.

#### 2.1.2. Procedure

Before starting any essay, the cell was cleaned with 50% hydrochloric acid, then rinsed with distilled water. To guarantee good sensitivity and reproducibility with a fixed electrode, we followed the steps below:

- 1- The working electrode was polished with a400 grit abrasive paper, then a 600 grit paper.
- 2- The working electrode was manually brushed with a mild steel brush.
- 3- Particular care was taken to position the working electrode close to the platinum electrode and the saturated calomel electrode (SCE) used as counter electrode and reference electrode respectively, keeping a constant spacing between them.
- 4- The cell was filled with 500 mL of raw water, provided from the Hamma groundwater. Throughout the essay, the temperature was held at 30 °C and the stirring rate was kept at 400 tr/min.
- 5- Using the observed  $I = f(t)$  curve, we calculate the traditional scaling time ( $t_E$ ) and residual current ( $I_{res}$ ).
- 6- Between each essay, a thorough cleaning was done via brushing.

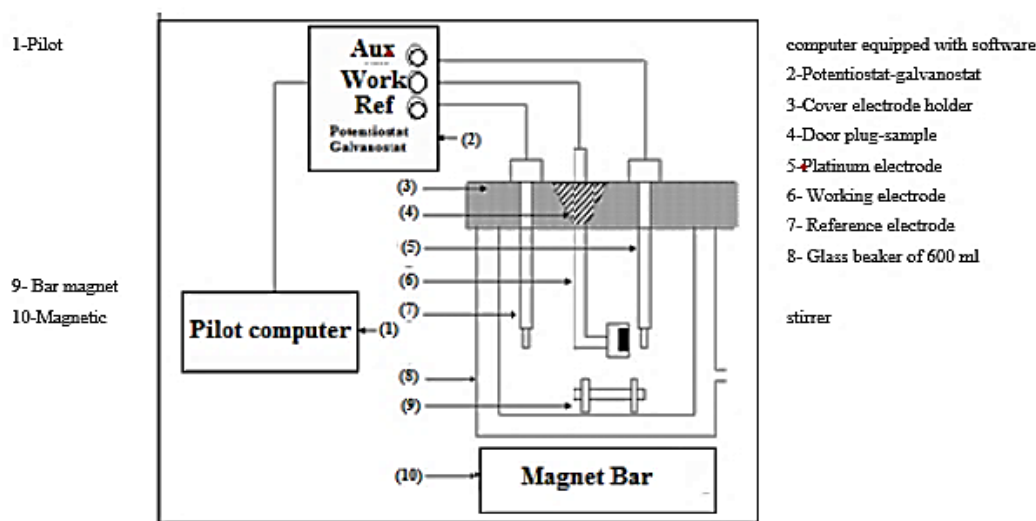


Fig. 1. Experimental setup (Ghizellaoui et al., 2017)

## 2.2. Impedanceometry

The accumulated deposit was measured at the interface (metal-calcium carbonate-electrolyte), which enables global appreciation of the importance and adhesion of the calcium carbonate deposit via high frequency resistance. Impedance measurements have been used successfully to assess the adherence of scale deposit on the metallic electrode.

### 2.2.1. Experimental setup

The same setup is used for data acquisition and processing as for chronoamperometry. A stainless steel working electrode, a reference electrode, and a counter-electrode are included in the three-electrode cell. Impedance measurements are performed at a potential corresponding to dissolved oxygen reduction (-1V/SCE), with a disturbance amplitude of 20 mV, over a frequency range from 100 kHz to 100 mHz. To obtain the Nyquist diagrams, the variation of the imaginary impedance ( $Z_i$ ) with respect to the real resistances ( $Z_r$ ) was recorded.

### 2.3. The originality of the used inhibitors

Quercetin is a flavonoid found as a secondary metabolite in plants. It can be extracted from plants, for example, from dry onion scales (Horbowicz, 2002), making the pure molecule readily available. Quercetin, an aqueous extract of olive leaves, contains phenolic groups that can complex with calcium (II) via the lone pairs of electrons on the oxygen atoms (Aidoud et al., 2017; Erdogan and Karadag, 2005; Goldin et al., 2005).

Alginic acid, also known as algin or alginate, is a natural anionic carbohydrate. Actually, alginate is a linear polysaccharide. It is derived from marine brown algae, as well as some microorganisms. The properties of alginate, including biocompatibility, low toxicity, relative low cost and ease of gelation, make it an ideal biomaterial for various applications, related to the food, chemical, medical, and agricultural industries (Lagopati and Pavlatou, 2020).

Gallic acid is a natural molecule found in many plants and is the primary structural component of

many polyphenols found in tea, nuts, grapes, and other foods (Shahrzad et al., 2001). This molecule is used in a variety of applications, including pharmaceutical products (Parveen et al., 2019). These three inhibitors were purchased from Sigma Aldrich. Stock solutions were prepared in distilled water.

## 3. Results and discussion

### 3.1. Hamma water quality

Table 1 summarizes the results of the physicochemical analysis performed on Hamma water. It is worth noting that Hamma waters are mineral-rich and extremely hard.

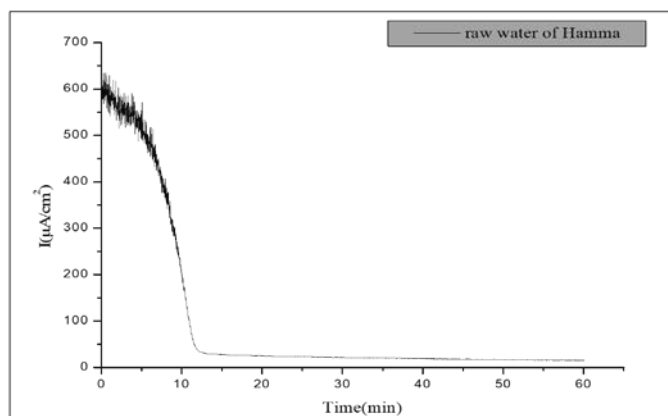
**Table 1.** Physicochemical properties of the Hamma water

Parameter	Measured Value
Temperature (°C)	30
pH	7.23
Conductivity (mS/cm)	0.961
Dissolved O <sub>2</sub> (mg/L)	7.55
HCO <sub>3</sub> <sup>-</sup> (mg/L)	442
TH (mg/L CaCO <sub>3</sub> )	575
Ca <sup>2+</sup> (mg/L)	136
Mg <sup>2+</sup> (mg/L)	56.4
Cl <sup>-</sup> (mg/L)	136
SO <sub>4</sub> <sup>2-</sup> (mg/L)	138
NO <sub>3</sub> <sup>-</sup> (mg/L)	7
Dry residue at 105 °C (mg/L)	700

### 3.2. Scaling power evaluation of the Hamma raw water

We assessed the scaling power of the Hamma raw water, in the absence of inhibitor, using chronoamperometry at a potential of -1V/SCE. The experiments were performed with 500 mL of water and at 30°C. For the Hamma raw water without treatment, the scaling time ( $t_E$ ) is 12 minutes and the residual current density is 13.2 A/cm<sup>2</sup> (Fig. 2). The scaling index ( $I_e$ ) is defined by the formula (Eq. 4) (Lédion et al., 1985):

$$I_e = 1000 / t_E \quad (4)$$



**Fig. 2.** Chronoamperometric curve of the Hamma raw water at 30 °C

Depending on the value of  $I_e$ , water can be classified as follows:

- Water that forms scale extremely quickly:  $100 < I_e < 1000$
- Water that forms scale very easily:  $15 < I_e < 100$
- Water with medium scale formation:  $5 < I_e < 15$
- Slightly forms water scale:  $0.5 < I_e < 5$ .

For the Hamma water,  $I_e$  is  $83 \text{ min}^{-1}$  and is therefore considered as a scaling water.

### 3.3. Inhibition of scale formation

At  $30^\circ\text{C}$ , the Hamma water with an increasing concentration of inhibitors was subjected to the same experiment as raw water with no additive (Tables 2-4). We have previously studied the effectiveness of two inhibitors separately (quercetin and gallic acid) to eliminate scale formation in water, where we have found that they have a high efficiency. In this context, these two inhibitors were combined in order to determine the effectiveness of the mixture on removing calcium carbonate from water.

**Table 2.** Scaling time ( $t_E$ ), residual current ( $I_{res}$ ) and percentage of scale inhibition of the Hamma water treated with Quercetin at  $30^\circ\text{C}$

Quercetin concentration (mg/L)	$t_E$ (min)	$I_{res}$ ( $\mu\text{A}/\text{cm}^2$ )	Inhibition of scaling (%)
0.0	12	13.2	-
0.2	19	10.7	25.7
0.5	20	13.1	29.9
0.8	22	17.9	34.2
1.0	25	18.2	43.8
1.5	42	19.7	65.9
2.0	$\infty$	199.5	100

**Table 3.** Scaling time ( $t_E$ ), residual current ( $I_{res}$ ) and percentage of scale inhibition of the Hamma water treated with gallic acid at  $30^\circ\text{C}$

Gallic acid concentration (mg/L)	$t_E$ (min)	$I_{res}$ ( $\mu\text{A}/\text{cm}^2$ )	Inhibition of scaling (%)
0	12	13.2	-
1	20	15.2	38.4
2	27	18.8	54.6
3	39	24.0	68.8
4	$\infty$	140.8	100

Ghizellaoui et al. (2019) discovered that the inhibition efficiency is 25.72% for an addition of 0.2 mg/L of quercetin, while an addition of 2 mg/L of quercetin is effective to block completely scale deposition (Table 2). According to Boumagoura et al. (2021), the inhibition of scaling becomes total with a gallic acid addition of 4 mg/L (Table 3).

Table 4 presents the parameters obtained from chronoamperometric tests in the presence of sodium alginate. The scaling time increases with inhibitor concentration. The inhibition efficiency is 32.4% with an addition of 10 mg/L of sodium alginate

whereas  $t_E$  was 12 min with the untreated water. It can be observed that with 70 mg/L of alginate, the scaling time is indefinite (Table 4), which means that the inhibition is total.

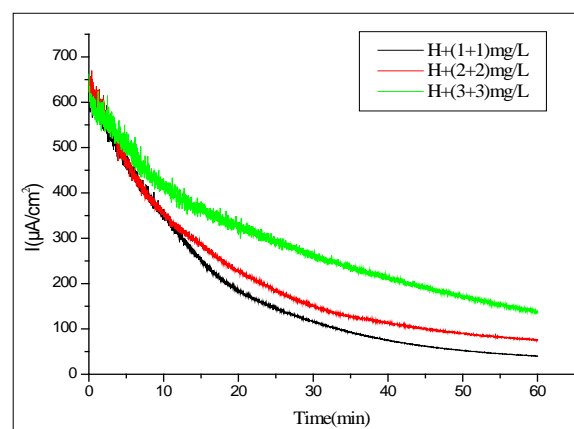
**Table 4.** Scaling time ( $t_E$ ), residual current ( $I_{res}$ ) and percentage of scale inhibition of the Hamma water treated with sodium alginate at  $30^\circ\text{C}$

Sodium alginate concentration (mg/L)	$t_E$ (min)	$I_{res}$ ( $\mu\text{A}/\text{cm}^2$ )	Inhibition of scaling (%)
0	12.0	13.2	-
10	17.5	11.0	32.4
30	26.6	55.3	54.9
50	36.3	168.3	66.9
70	$\infty$	240.3	100

These results show that separately, the three scale inhibitors are efficient to inhibit scale formation on the electrode surface.

#### 3.3.1. Scale inhibition by the mixture quercetin+ gallic acid

The obtained chronoamperometric curves are shown in Fig. 3 and Table 5.



**Fig. 3.** Chronoamperometric curves of the Hamma water in the presence of different concentrations of quercetin+ gallic acid

**Table 5.** Scaling time ( $t_E$ ), residual current ( $I_{res}$ ) and percentage of scale inhibition of the Hamma water treated with quercetin+gallic acid at  $30^\circ\text{C}$

(Quercetin + Gallic acid) concentration (mg/L)	$t_E$ (min)	$I_{res}$ ( $\mu\text{A}/\text{cm}^2$ )	Inhibition efficiency (%)
0	12	13.2	-
(1+1)	26	40.1	53.0
(2+2)	40	75.8	70.0
(3+3)	$\infty$	137.2	100

The lowest curve on the Fig. 3 reveals that the scaling time increases from 12 min for the Hamma raw water to 26min in the presence of 2 mg/L of the mixture quercetin+gallic acid, and  $t_E$  doubled by

adding 2 mg/L of the mixture. This result indicates that the CaCO<sub>3</sub> formed more slowly on the electrode surface in the presence of the mixture. Accordingly, these curves show that an increase in the concentration of quercetin+gallic acid from 2 to 6 mg/L leads to a rise in the scaling time, tending to an infinite time at 6 mg/L, as reported in Table 5.

Translated in terms of limescale deposition inhibition, the addition of 2, 4 then 6 mg/L of quercetin+gallic acid prompts an inhibition efficiency of 53.70 and 100% respectively. Quercetin+gallic acid inhibits scale formation, probably by blocking the germination-growth sites on CaCO<sub>3</sub> crystals.

3.3.2. Inhibition of scaling by quercetin+alginate)

Figure 4 presents the obtained chronoamperometric curves. The scaling time increases from 12 to 31 min in the presence of the

mixture of 10mg/L quercetin and 10mg/L alginate. These curves show that an increase in the concentration of quercetin+alginate from 0 to 60 mg/L leads to a rise in the scaling time, tending to an infinite time at 60 mg/L, as reported in Table 6.

In the presence of 60 mg/L, no scale was detected on the electrode surface. In conclusion, 60mg/L of quercetin+alginate is the most effective amount and this inhibitor can be used as a good antiscalant.

3.3.3. Inhibition of scaling by gallic acid+alginate

Figure 5 illustrates the obtained chronoamperometric curves. These curves show that an increase in the concentration of gallic acid+alginate from 0 to 3 mg/L leads to a rise in the scaling time, tending to an infinite time at 3 mg/L, as reported in Table 7.

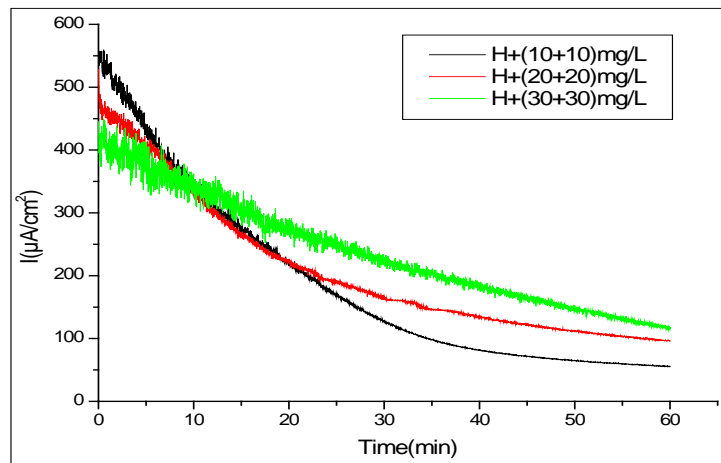


Fig. 4. Chronoamperometric curves of Hamma water added with different concentrations of quercetin+alginate

Table 6. Scaling time (*t<sub>E</sub>*), residual current (*I<sub>res</sub>*) and percentage of scale inhibition of the Hamma water treated with quercetin+alginate at 30 °C.

Quercetin+alginate concentration (mg/L)	<i>t<sub>E</sub></i> (min)	<i>I<sub>res</sub></i> (µA/cm <sup>2</sup> )	Inhibition of scaling (%)
0	12	13.2	-
(10+10)	31	55.3	60.9
(20+20)	35	96.4	65.7
(30+30)	∞	116.4	100

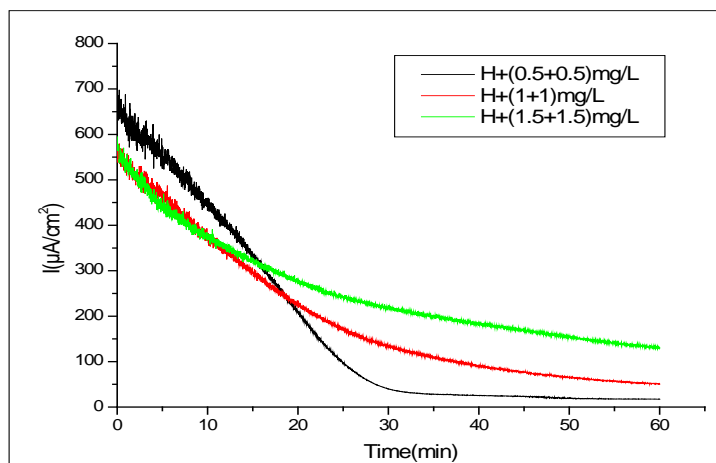


Fig. 5. Chronoamperometric curves of Hamma water added with different concentrations of gallic acid+alginate

The scaling time has become almost infinite and  $\text{CaCO}_3$  formation is manifested on the curve by oscillations. There is more adhesion of calcium carbonate to the electrode because the residual current is important. Gallic acid has a carboxylic group and three alcohol groups in its structure. Alginate is a polysaccharide that contains several carboxylic groups. Quercetin molecule is a polyphenol. It is well known that molecules which contain carboxylic groups can inhibit calcium carbonate formation by chelation between carboxylic groups and  $\text{Ca}^{2+}$  ions (El housse, 2021).

**Table 7.** Scaling time ( $t_E$ ), residual current ( $I_{res}$ ) and percentage of scale inhibition of the Hamma water treated with gallic acid+alginate at different concentrations at 30 °C

gallic acid+alginate concentration (mg/L)	$t_E$ (min)	$I_{res}$ ( $\mu\text{A}/\text{cm}^2$ )	Inhibition of scaling (%)
0	12	13.2	-
(0.5+0.5)	29	17.4	59.1
(1+1)	33	50.5	63.3
(1.5+1.5)	$\infty$	130.0	100

Recent study was done by Chhim et al. (2020) using mixture of green additives avoid or delay scale formation proved that the result obtained is a combination of both effects: PESA (polyepoxysuccinic acid) addition increases the delay time of crystallization whereas HA (homopolymer of acrylic acid) addition decreases the crystal growth rate. The experiment performed with  $0.5 \text{ mgL}^{-1}$  of PESA (corresponding to a total concentration of additives of  $1 \text{ mgL}^{-1}$ ) in the mixture have a much lower delay time for crystallization than the one obtained for PESA alone. In addition, under the same conditions as for the PESA + PASP (polyaspartic acid) mixture, apparent delay time was much shorter with PESA+HA. The inhibition rate of crystal growth is slightly increased (from 92% to 97%) by the presence of PESA when compared to the experiment performed with HA alone. Recent studies on the same water (Hamma) were conducted using the same strategy (chronoamperometry) but different green inhibitors to inhibit scale formation. Ghizellaoui et al. (2017) showed that the curves for the raw water, the time scaling is 14min and the delay scaling occurs for  $0.25 \text{ mg/L}$  of citric acid. When the citric acid concentration increases, the delay of the  $\text{CaCO}_3$  precipitation becomes important. 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. At an addition of  $1 \text{ mg/L}$ , the curve becomes a straight line.

In another study, Menzri et al. (2019) demonstrated that the effect of a mixture of two vitamins: thiamine (50%) and pyridoxine (50%) began at  $2 \text{ mg/L}$ , with a scaling time of 13.3 min, corresponding to a 10% inhibition. The total limescale inhibition, on the other hand, is achieved at 1500

$\text{mg/L}$ . Therefore, (gallic acid+quercetin), quercetin+alginate, and gallic acid+alginate reveal to be very effective green inhibitors in hard water.

Other studies on different waters were conducted using chronoamperometry with different green inhibitors. Kamali and Arefinia (2020) have studied the inhibition effect of poly (acrylic acid:2-acrylamido-2-methylpropanesulfonic acid:tert-butyl acrylamide) (PAAT) as an environmentally friendly terpolymer on the calcium carbonate scaling in artificial seawater by chronoamperometry at 25 °C. They supposed that the optimal inhibitory effect of 71.2% is obtained in the presence of PAAT at a concentration of 2 ppm.

Zhang et al. (2020) have studied the inhibition effect of an environment-friendly scaling inhibitor composed of 10-methylacridinium iodide (MAI) and sodium citrate (SC). The experimental results showed that MAI-SC mixture presented an excellent scale inhibition performance up to 98.3%. The electrochemical stability of the inhibitor film was investigated by chronoamperometry (CA).

According to Khamis et al. (2018), chronoamperometry was used in another attempt to study the effect of a novel environmental antiscalant inhibitor, also known as arghel leaf extract on the precipitation of  $\text{CaCO}_3$ . They supposed that the optimal inhibitory effect of 87.1 % is obtained in the presence of arghel leaf extract at a concentration of 50ppm.

Khamis et al. (2021) used two natural polymers, chitosan and sodium alginate as scale inhibitors. Overall results show that chitosan is more efficient for the inhibition of calcium carbonate formation (400 ppm). However, the addition of sodium alginate to chitosan (50ppm of alginate+400 ppm of chitosan), as a package has a dual effect on carbonate scale inhibition with good efficiency up to 88%. This new phosphorus-free package represents an effective antiscalant and could be used as green inhibitor.

In another study, El housse et al. (2021) evaluated the effectiveness of two extracts of Crocus Sativus L (CSL) wastes towards the formation of calcareous scale, namely the Aqueous Extract of Leaf (ALE) and the Aqueous Extract of Petal and Stamen (AEPS). Total inhibition occurs after the addition of  $60 \text{ mg/L}$  of AEPS to the calco-carbonic solution with a hardness of  $40^\circ\text{F}$ , whereas an amount of  $82 \text{ mg/L}$  of ALE was the optimal concentration to completely inhibit  $\text{CaCO}_3$  formation.

Abd-El-Khalek et al. (2021) showed that sulfonated polyaniline (SPANI) is an efficient new inhibitor in controlling the precipitation of calcium carbonate scale. They found that the inhibition efficiency increased proportionally with polymer concentration up to 100 ppm. However, the total limescale inhibition is achieved only with 500 ppm where the maximum inhibition efficiency was 90%.

Karar et al. (2020) found that at  $32^\circ\text{C}$ , a complete scale inhibition was obtained using a



concentration of 150 mg/L of *Paronychia arabica* (PA).

Lourteau et al. (2019) found that a concentration of *Hylocereus undatus* solution at 180 mg.L<sup>-1</sup> was required to totally prevent the precipitation of CaCO<sub>3</sub>. Hassan et al. (2022) showed that the copolymer exerted good CaCO<sub>3</sub> inhibition with increasing inhibitor concentration despite the observed anomalous behavior. Thus, the abovementioned features achieved by polymerization of (5-nitro-2-orthanilic acid) make the obtained polymer highly promising for applications as a new multifunctional scaling inhibitor of CaCO<sub>3</sub> precipitation.

### 3.4. Electrochemical impedance spectroscopy (EIS) of Hamma raw water

Before recording the Nyquist diagram on Hamma raw water, it was electrolyzed for 60 minutes at -1 V/SCE, 30 °C, and 400 rotations/mn. This period is significantly longer than the scaling time and ensures the formation of limescale on the electrode surface via dissolved oxygen reduction. A large frequencies interval, including high frequencies, varying from 100 KHz to 100 mHz, was applied for EIS measurements.

Figure 6 depicts the Nyquist impedance diagram, which shows variations of the imaginary resistance (-Z<sub>i</sub>) versus the real resistance (Z<sub>r</sub>) obtained on Hamma raw-water. There are two loops in the diagram. The first loop, observed at high frequencies,

represents charge transfer, while the second loop, obtained at low frequencies, represents the oxygen diffusion process. A high frequency resistance ( $R_{hf}$ ) of 18.1 KΩ is measured. This high value is due to the formation of a layer made of a compact limescale deposit, which is non-conductive and highly resistant to diffusion. The low value of  $C_{hf}$  (1.09.10<sup>-6</sup>μF /cm<sup>2</sup>) confirms the presence of a thick and compact layer of limescale on the steel electrode surface (Gabielli et al., 1997). Studies on the same water (Hamma water) were conducted using impedancemetry with quercetin, gallic acid and alginate separately to inhibit scale formation.

Ghizellaoui et al. (2019) found that the efficiency increases as the inhibitor concentration increases. The addition of 2 mg/L of quercetin is efficient to inhibit totally scale deposition (96.47%) (Table8). Boumagoura et al. (2021) showed that increasing gallic acid concentration beyond 1 mg/L induces a continuous rise of the efficiency, though more slowly, reaching an inhibition efficiency of 86.5% at 4 mg/L (Table 9).

Moreover, the  $R_t$  value for raw water is 18.1 kΩ.cm<sup>2</sup>, and for 10mg/L of sodium alginate the  $R_t$  value is drastically decreased to 10.5 kΩ.cm<sup>2</sup>. However, for the addition of 50 mg/L and 70 mg/L of sodium alginate, the charge transfer resistance slowly decreased to 2.3 kΩ.cm<sup>2</sup>. Conversely, the double layer capacitance values are increased from 1.09.10<sup>-6</sup> μF/cm<sup>2</sup> to 91.4μF/cm<sup>2</sup> due to the inhibition of the scale by this inhibitor. The inhibition efficiency is around 87% (Table 10).

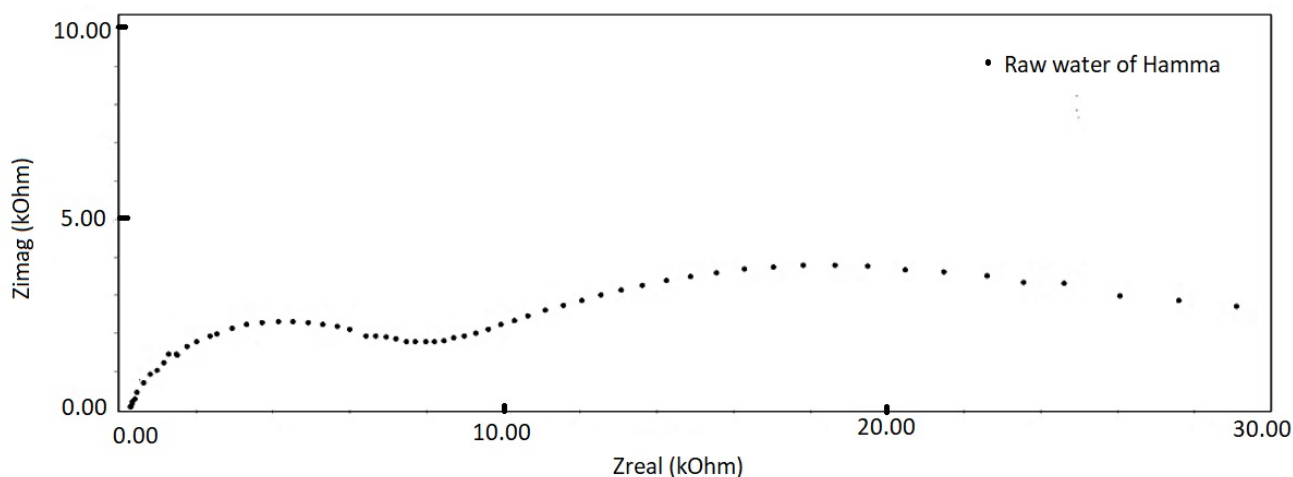


Fig. 6. Impedance diagram of the Hamma raw water

Table 8. Charge transfer resistance ( $R_{ct}$ ), double-layer capacity ( $C_d$ ) and efficiency for treated water at different concentrations of Quercetin

Quercetin concentration (mg/L)	$R_{ct}$ (kΩ.cm <sup>2</sup> )	$C_d$ (nF/cm <sup>2</sup> )	Efficiency (%)
0.0	29.43	48.74	-
0.2	28.66	49.51	2.6
0.5	21.38	52.50	27.4
0.8	12.60	55.50	57.2
1.0	11.76	61.36	60.0
1.5	9.55	94.60	67.6
2	1.03	110.30	96.5

**Table 9.** Evolutions of the high-frequency capacity ( $C_{hf}$ ), high frequency resistance ( $R_{hf}$ ) and limescale inhibition efficiency with gallic acid at different concentrations

Gallic acid concentration (mg/L)	$R_{hf}$ ( $k\Omega.cm^2$ )	$C_{hf}$ ( $\mu F/cm^2$ )	Inhibition efficiency (%)
0.0	18.10	$1.09.10^{-6}$	-
1	8.11	1.32	55.2
2	3.90	2.14	78.5
3	3.60	8.03	80.1
4	2.44	80.3	86.5

**Table 10.** Evolutions of the high-frequency capacity ( $C_{hf}$ ), high frequency resistance ( $R_{hf}$ ) and limescale inhibition efficiency with sodium alginate at different concentrations

Sodium alginate concentration (mg/L)	$R_{hf}$ ( $k\Omega.cm^2$ )	$C_{hf}$ ( $\mu F/cm^2$ )	Inhibition efficiency (%)
0	18.1	$1.09.10^{-6}$	-
10	10.5	$620.8.09.10^{-3}$	42
30	5.3	29.6	71
50	3.6	48.9	80
70	2.3	91.4	87

3.4.1. Effect of quercetin+gallic acid concentration on impedance diagrams

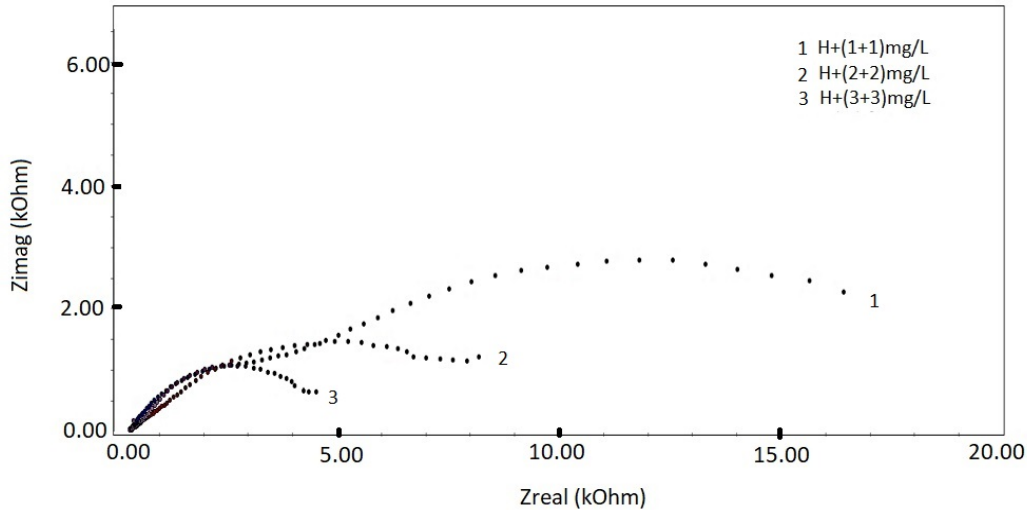
The impedance diagrams obtained by the calcium carbonate deposits of the Hamma water treated with increasing concentrations of (Quercetin+Gallic acid) are shown in Fig. 7.

When 2 mg/L of quercetin+gallic acid is added to Hamma water, the diffusion loop observed for the raw Hamma water disappears. Table 11 presents the high-frequency capacity ( $C_{hf}$ ) and high frequency resistance ( $R_{hf}$ ) values extracted from the impedance diagrams. With an increase in quercetin+ gallic acid concentration,  $C_{hf}$  value increases and  $R_{hf}$  value decreases.

From  $R_{ct}$ , we can deduce the scaling inhibition efficiency using Eq (.4) (Abd-El-Gaber et al., 2008):

$$\text{inhibition efficiency (\%)} = \frac{(R_{tc})_0 - (R_{tc})_i}{(R_{tc})_0} \cdot 100 \quad (4)$$

According to Table 11, a strong inhibition is achieved by the addition of as little as 2 mg/L of quercetin+gallic acid to Hamma water, the efficiency reaching a remarkable value of 78.23%. Figure 7 shows that increasing quercetin+gallic acid concentration beyond 2 mg/L induces a continuous rise of the efficiency, though more slowly, reaching 84.78 % at 6 mg/L.



**Fig. 7.** Impedance diagrams obtained for the Hamma water containing quercetin+gallic acid) at different concentrations

**Table 11.** Evolutions of the high frequency capacity ( $C_{hf}$ ), high frequency resistance ( $R_{hf}$ ) and limescale inhibition efficiency with quercetin+gallic acid concentration.

(Quercetin + Gallic acid) concentration (mg/L)	$R_{hf}$ ( $k\Omega.cm^2$ )	$C_{hf}$ ( $\mu F/cm^2$ )	Inhibition efficiency (%)
0	18.1	$1.1.10^{-6}$	-
(1+1)	3.9	1.3	78.2
(2+2)	3.7	18.8	79.4
(3+3)	2.8	74.0	84.8



3.4.2. Effect of quercetin+alginate concentration on impedance diagrams

We find an increase in  $C_{hf}$  and a reduction in  $R_{hf}$  when the concentrations of quercetin+alginate raise from 20 to 60 mg/L (Table 12). Table 12 shows that a strong inhibition is achieved by the addition of (10+10) mg/L of quercetin+alginate to Hamma water, the efficiency reaching a remarkable value of 80.31%. Table 12 shows that increasing quercetin+alginate

concentration beyond 20 mg/L induces a continuous rise of the inhibition efficiency, though more slowly, reaching 86.1 % at 60 mg/L.

3.4.3. Effect of gallic acid+alginate concentration on impedance diagrams

We see an increase in  $C_{hf}$  and a decrease in  $R_{hf}$  when the concentration of gallic acid+alginate increases from 1mg/L to 3mg/L (Table 13).

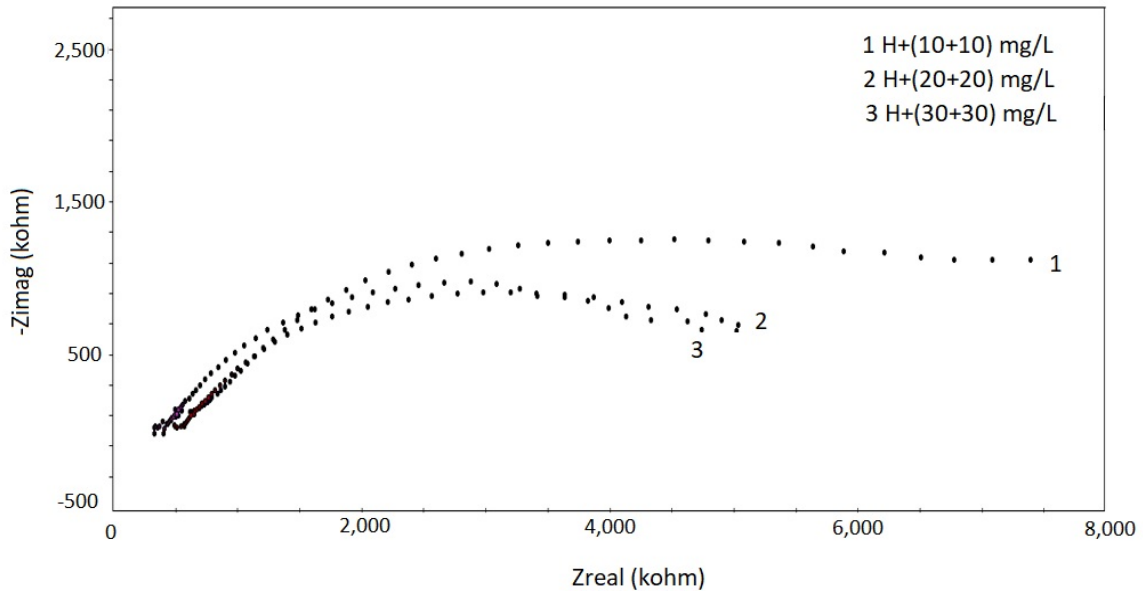


Fig. 8. Impedance diagrams obtained for treated water Hamma with (Quercetin+ Alginate)

Table 12. Evolutions of the high frequency capacity ( $C_{hf}$ ), high frequency resistance ( $R_{hf}$ ) and limescale inhibition efficiency with quercetin+alginate concentration

(Quercetin + Alginate) concentration (mg/L)	$R_{hf}$ ( $k\Omega.cm^2$ )	$C_{hf}$ ( $\mu F/cm^2$ )	Inhibition efficiency (%)
0	18.1	$1.1 \times 10^{-6}$	-
(10+10)	3.6	48.9	80.3
(20+20)	2.6	94.9	85.8
(30+30)	2.5	124.7	86.1

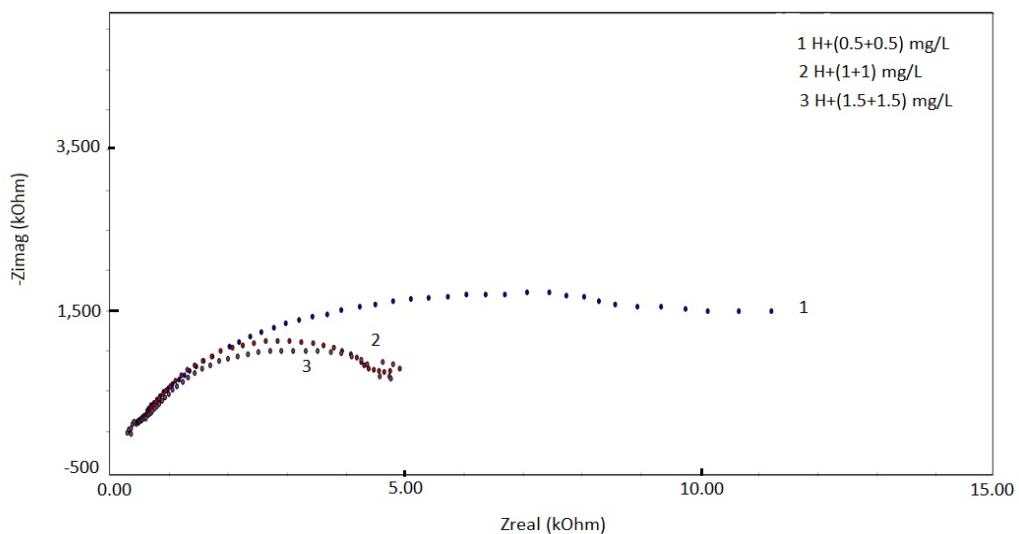


Fig. 9. Impedance diagrams obtained for the treated Hammawater with the mixture gallic acid+alginate

Table 13 shows that the addition of 1 mg/L of gallic acid+alginate to Hamma water results in a strong inhibition, with an efficiency of 73.53 %. Table 13 demonstrates that increasing the concentration of gallic acid+alginate beyond 2 mg/L causes a continuous rise in efficiency, reaching 84.9% at 3 mg/L. By comparing the mixtures (Quercetin + Gallic acid) and (Gallic acid + Alginate), (Quercetin + Gallic acid) was found to be the most effective with an inhibition efficiency of 84.78% at 6mg/L.

But if we compare the three mixtures, we find that (Gallic acid + Alginate) is more effective than the other two mixtures with an inhibition efficiency of 84.9% at 3mg/L.

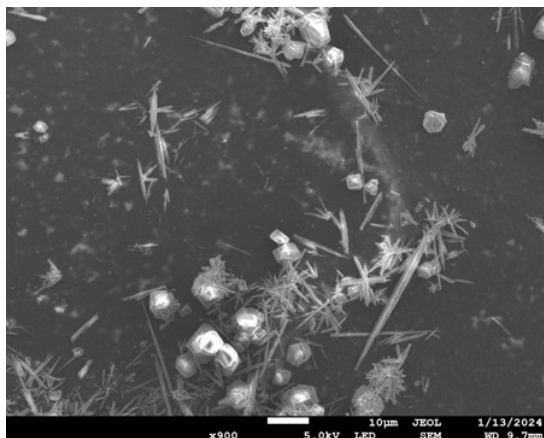
**Table 13.** Evolutions of the high frequency capacity ( $C_{hf}$ ), high frequency resistance ( $R_{hf}$ ) and limescale inhibition efficiency with gallic acid+alginate concentration

gallic acid+alginate (mg/L)	$C_{hf}(\mu F/cm^2)$	$R_{hf}(kohm.cm^2)$	Inhibition efficiency (%)
0	$1,1.10^{-6}$	18.1	-
(0.5+0.5)	9.8	4.8	73.5
(1+1)	42.5	3.0	83.3
(1.5+1.5)	58.6	2.7	84.9

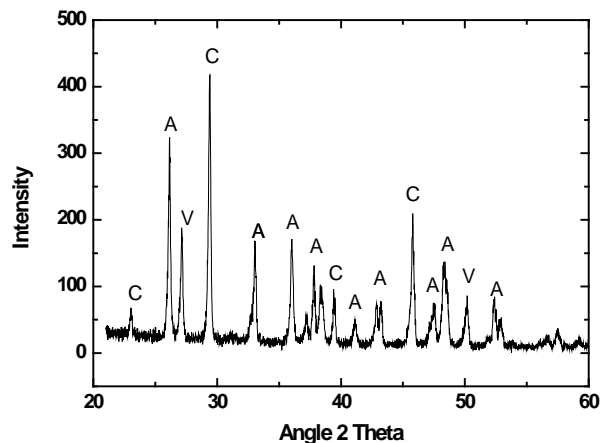
### 3.5. Characterization of crystals

According to Fig 10A, the Hamma raw water is essentially constituted of calcite and aragonite. This result is consistent with the XRD spectrum (Fig 10B). As shown in Fig 11, there are mostly aragonite formed in the presence of the mixture of quercetin and alginate. In the presence of the mixture alginate + gallic acid,  $CaCO_3$  crystals precipitate under calcite form (Fig 12A). This is confirmed by the result obtained by XRD (Fig 12B).

In the presence of the mixture quercetin + gallic acid,  $CaCO_3$  crystals precipitate under calcite form (Fig 13A). This is confirmed by the result obtained by XRD (Fig 13B).

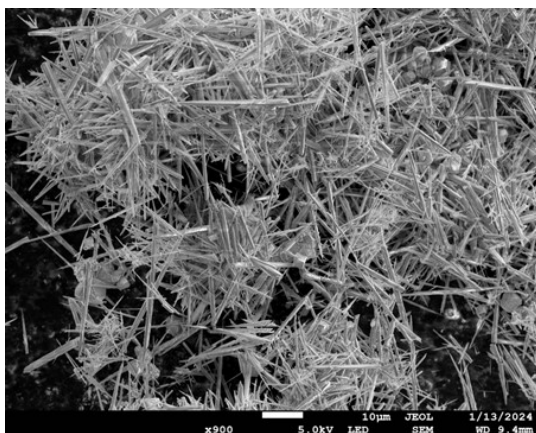


A

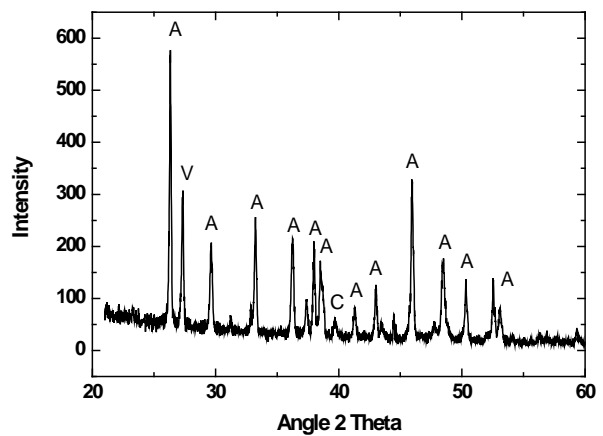


B

**Fig. 10.** Raw water of Hamma: (A) SEM image and (B) XRD spectrum: A: aragonite; C: calcite; V: vaterite



A



B

**Fig. 11.** Quercetin + alginate, (A) SEM image and (B) XRD spectrum

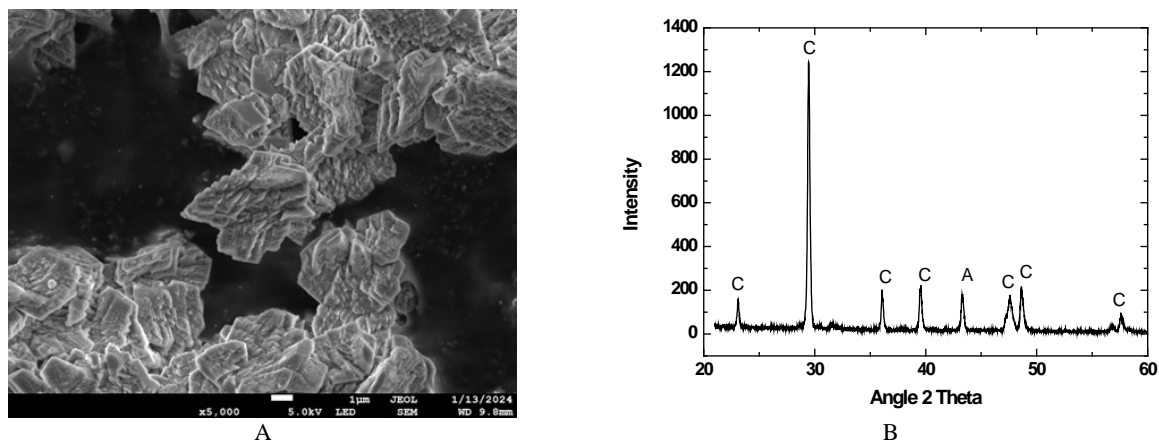


Fig. 12. Alginate + gallic acid, (A) SEM image and (B) XRD spectrum

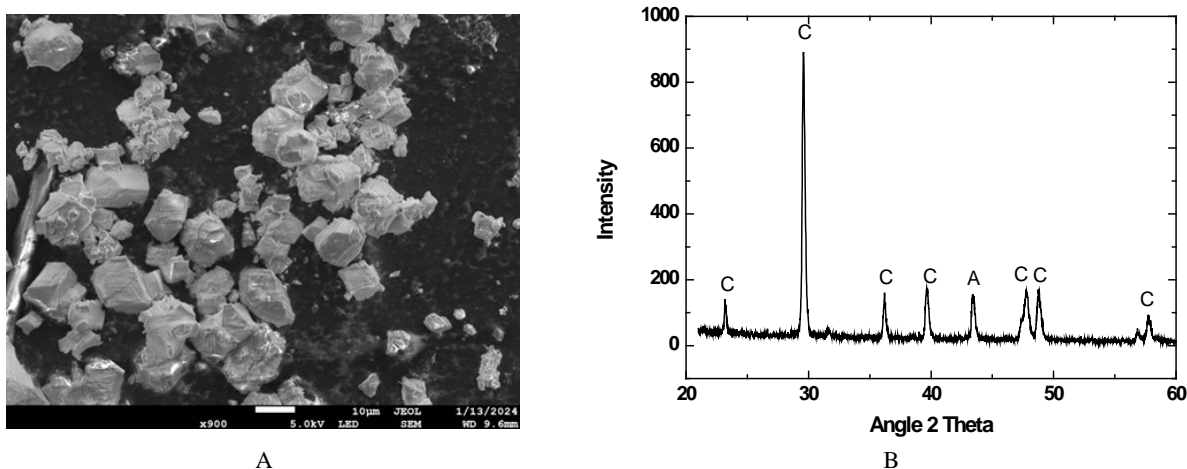


Fig. 13. Quercetin + gallic acid, (A) SEM image and (B) XRD spectrum

#### 4. Conclusions

According to the results obtained by chronoamperometry, the Hamma groundwater is identified as a very scaling water, with a scale index of  $83.1 \text{ min}^{-1}$  at  $30^\circ\text{C}$ , which explains the severe calcium carbonate currently generated on water pipes.

Furthermore, impedance measurements were used to determine the compactness and the adhesion of deposits, formed in raw water and in water treated with (gallic acid+quercetin), quercetin+alginate, and gallic acid+alginate. The high frequency capacity ( $C_{hf}$ ) increases with the added concentration of each inhibitor, resulting in the formation of more porous deposits and this reflects the effectiveness of the treatment used.

The mixture of gallic acid+alginate, (Gallic acid+Quercetin), and quercetin+alginate were shown in laboratory tests to be entirely effective agents to prevent limescaling at doses of just 3 mg/L, 6 mg/L, and 60 mg/L. They should be considered green inhibitors since they are reportedly cheap and safe, and they might be used to safely prevent limescale build up on domestic appliances and the water distribution system. The mixture (Gallic acid+Alginate) has a more pronounced inhibitory effect than

(Gallic acid+Quercetin) and quercetin+alginate because it acts at lower concentrations to achieve high efficiency (84.9% at 3 mg/L).

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