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Use of Chemical Technical Rcp for the Inhibition of Scaling from Hard Water by a Green Inhibitor: Quercitine

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Abstract: Groundwater of Negrine, Fourchi and Hamma that supply the cities of Tébessa, Ain M'lila and Constantine with drinking water are from limestone reservoirs.

These water are very hard as they are loaded with calcium hydrogenocarbonate and may deposit large quantities of calcium carbonate (82% in weight). The incrusting deposits formed on the walls of pipes and on the industrial installations consist primarily of $CaCO_3$ as calcite.

The techniques and economic impacts of tartar consequences are:

- Partial or total obstruction of pipes together with weakening of water flow rates,
- Decreasing of heat transfer,
- Jamming stopping devices (valves, taps)
- Clogging of heat exchangers, filters etc..

The anti-scale struggle has several scale inhibitors (phosphates, carboxylates) that are not used for drinking water. It also has several processes that are used to prevent the precipitation of tartar.

A number of chemicals, electrochemical and nanofiltration treatments have been used to limit the precipitation of tartar. Other studies have focused on the influence of metal cations (Cu, Fe, Zn and Mn) on the precipitation of calcium carbonate by using the scaling potentiality, RCP and polyethylene test.

The aim of our work is to evaluate and inhibit the furring Hamma hard waters by using the RCP test (rapid controlled precipitation) use for softening hard water with green inhibitor: Quercitine.

Key words: Water · Hardness · $CaCO_3$ · Inhibition · RCP · Quercitine

INTRODUCTION

Uncontrolled formation of compact and adherent deposits of calcium carbonate on the walls of pipes for industrial or domestic installations (scaling), supplied with natural waters or distribution of technical and economic consequences are disastrous. This is the case of groundwater Hamma supplying the city of Constantine in drinking water. During their movement within the distribution system, this water gives rise to scale. Increasing the thickness of this layer leads to reductions in throughput and can lead to jamming of the valves and taps.

For this, several chemical processes [1-2], electrochemical [3-4], nanofiltration treatments [5-6], the scaling potentiality [7], fast controlled precipitation method [8-10] and polyethylene test [11], were used to limit the precipitation of tartar.

Studies have focused on the influence of foreign ions precipitation of calcium carbonate [12-13], but the experimental conditions were often different from those encountered in natural waters.

The main goal that we have set ourselves is to determine the possible changes in the furring hard water power (Hamma) by a green inhibitor quercitine using a chemical process of rapid controlled precipitation.

We chose quercitine because it is a green scale inhibitory molecule, non-toxic and biodegradable. The test speed controlled precipitation was developed by Ledion *et al.*,[10] allows to follow the kinetics of the process of germination - growth of calcium carbonate in specific water.

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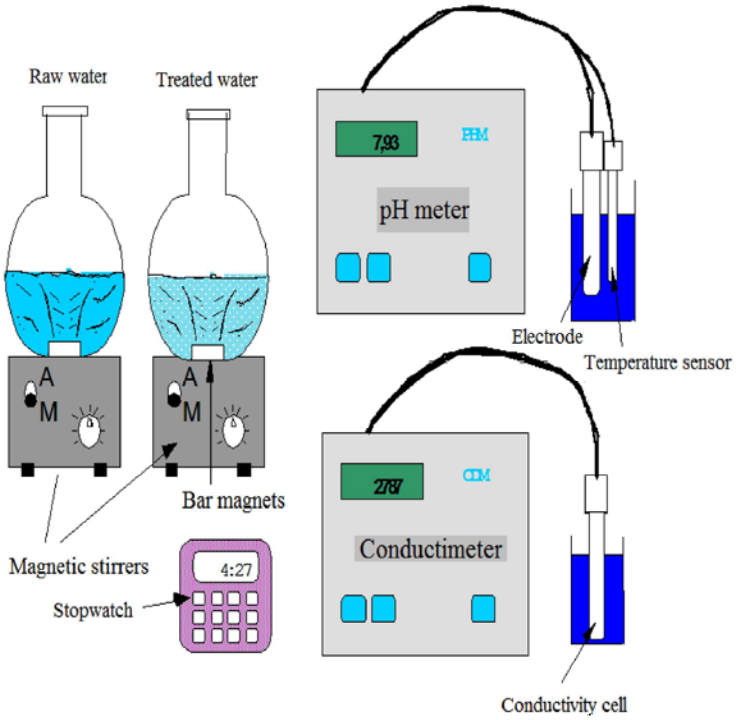

Fig. 1: Experimental apparatus used in the process of rapid controlled precipitation

MATERIAL AND METHODS

Device Used: The test apparatus, is shown in Fig.1 composed of:

- Two magnetic P SELECTA stirrers
- Two bar magnets.
- A digital pH meter JENWAY 3505 pH meter equipped with a saturated calomel electrode and a temperature sensor. It has a measurement accuracy of 1/100 of pH.
- A conductivity meter HANNA EC214 equipped with a conductivity cell with integrated temperature sensor,
- A stopwatch.
- A thermostatic bath.

Experimental Procedure: The two balloons are cleaned before used in a diluted hydrochloric acid bath at 50% and then rinsed with water Hamma. Before the sampling, each of the two containers is rinsed with water during the test that contain (raw or treated). Both magnetic stirrers are set to exactly the same rotational speed (800 rev/min). The pH meter is calibrated with two buffer solutions of pH = 4 and pH = 7, the meter is being calibrated beforehand. The electrodes of the pH meter and conductivity are rinsed with distilled water prior to each measurement. To test a tartar treatment Quercitine (0,05, 0,2, 1, 10, 20, 30 and 40) mg/L, is performed by comparing treated and untreated water. Thus collects a treated water sample and a sample of untreated water, which are then brought to the same temperature 30 °C in a thermostated bath. The two samples are then identifies the values ??of initial pH and resistivity, then the two samples stirred at 800 rev/min at the same time. The tap frequency measurements are also identical to the two waters every 5 minutes. The maximum duration of the test is 100 minutes. To avoid pollution of water to the other, the electrode is rinsed with distilled water after each test.

RESULTS AND DISCUSSIONS

Evaluation of the Quality of Raw Water Hamma:

Table 1: Analysis of water Hamma

Parameter	Hamma Water	Standards WHO
T°C	32	25
pH	7.35	6.5-8.5
EC mS/cm	0.899	1.25
Dissolved oxygen mg/L	6.68	-
HCO_3^- mg/L	417	200
The oxygen consumed by organic matter	2	2
TH mg/L $CaCO_3$	554	350
Ca^{2+} mg/L	148	100
Mg^{2+} mg/L	45	50
Cl^- mg/L	145	250
SO_4^{2-} mg/L	190	400
NO_3^- mg/L	2.3	50

Temperature: It is important to know the water temperature with a good precision (it should be measured in situ). Indeed, it plays a role in the solubility of gases in the dissociation of dissolved salts and pH determination, to know the origin of the water and any mixtures, etc.... In addition, this measurement is very useful for limnological studies. In general, the water temperature is influenced by the source from which it comes from (superficial or deep) [14]. In our study area the water temperature Hamma is 32 ?, which shows that its origin is a thermal spring.

pH: The pH of water is presenting its acidity or alkalinity. The pH of natural waters is related to the nature of the terrain traversed. In most natural waters, the pH dependent equilibrium calcocarbonic. The pH is an important parameter to define how aggressive or embedding is the water. It is involved in these phenomena with other parameters such as hardness, alkalinity and temperature.

The pH is an indicator of the water quality. WHO advocates for drinking water pH between 6.5 and 8.5. This is verified for Hamma water with a pH of 7.35.

Conductivity: The water conductivity is a measure of its ability to conduct electrical current. The conductivity measurement allows to determining quickly but very roughly mineralization of the water and follow the change. Table (2) establishes a relationship between the degree of mineralization and conductivity according to French regulations. The conductivity of Hamma water is 0.899 mS/cm, resulting in significant mineralization.

Dissolved Oxygen: The content of oxygen in water depends on the origin of the water. Surface waters may contain relatively large amounts near the saturation (8-10) mg/L at 20 °C. His role in this case is predominant in the assimilative pollutant loads. Compared with groundwater, it does contain usually a few mg/L. We know that for a high temperature, the oxygen content decreases, due to its lower solubility and this is not always confirmed by the pumping station Hamma where agitation is important. For Hamma (6.68 mg/L).

Table 2: Relationship between conductivity and mineralization

Conductivity (is/cm)	Mineralization
0 -100	Very low mineralization
100 - 200	low mineralization
200 - 333	Accentuated average mineralization
333 – 666	mineralization accentuated
666 - 1000	significant mineralization
>1000	high mineralization

Bicarbonates: The bicarbonate or calcium bicarbonate, present in hard water is one of the causes of the water hardness. It is unstable in solution in water and tends to turn into calcium carbonate (calcite) to form scale encrusting. The baking stability is related to the water temperature and the presence of dissolved carbon dioxide. Concentration must be held between 100 and 300 mg/L and ideally 200 mg/L to approximately maintain a stable pH and to avoid having scaling waters. For the waters of Hamma it is to 417 mg/L.

The Oxygen Consumed by Organic Matter: Determining the amount of oxygen transferred by $KMnO_4$ to oxidize the organic matter contained in water expressed as O_2 mg/L of water, represents the total organic matter content.

High organic matter content should always be suspected microbial contamination.

Observations on the waters of Hamma, we indicate a value of 2 mg/L of O_2. Which is a common value. WHO recommends admitted to drinking water limit value of 2 mg/L.

Total Hardness: Hardness expressed the ability of water to react with soap. Or the hardness (TH) of water essentially corresponds to the total content of calcium and magnesium. It is directly linked to the geological nature of the terrain traversed. Thus, a limestone soil give a "hard" water (strongly mineralized with calcium and magnesium), while water passing through a crystal soil (granite) as the sand will be "soft". Groundwater is generally harder than the water surface. This is the case of water having a hardness of Hamma 554 $CaCO_3$ mg/L (55.4 °F). Refer to Table (3) for the classification of hardness. In fact, groundwater is rich in carbonic acid, they have a high solubilizing power towards soil and rocks. Hard water cover about a third of calcium and magnesium needs of a man. There is a correlation between the consumption of fresh water and the frequency of appearance of cardiovascular diseases. Thus, hard water, provide protection against these diseases.

Table 3: Ranking of the hardness

Hardness	Hardness concentration in mg/L of $CaCO_3$
Fresh	0 – 60
Moderately sweet	60 – 120
Lasts	120 – 180
Very hard	180 and more

Calcium: Calcium is an important element of the hardness is usually the dominant element of drinking water. It is especially in the form of bicarbonates and in less important amounts in the form of sulfates, chlorides. Calcium salts are obtained mainly during the attack by limestone dissolved carbon dioxide (CO_2). It is the dominant element cationic water. The presence of calcium in the water of Hamma is 148 mg/L, is directly related to the geological nature of the terrain traversed.

Magnesium: Magnesium is an important element of the hardness of water and widely distributed in nature. In many minerals and limestone (2.1 % of the Earth's crust). Geological abundance, its high solubility, its industrial use are their levels in water may be important (a few mg/L to several hundred mg/L) for Hamma (45 mg/L).

Chlorides: Chlorides are present in almost all waters. The concentrations vary widely, passable to ten mg/L to more than a thousand mg/L. The origin of chlorides is natural, it is due to contact with certain geological formations. The chlorides which are easily soluble in water and do not participate to say, the biological process. They play no role in the phenomena of decomposition. They are conservative. However, their presence does not necessarily indicate a pollution of human or animal origin, when an increase in their concentration is observed. The maximum concentration of chloride is given 250 mg/L, because at higher concentrations, water can have a salty taste. Chlorides are also corrosive agents at high concentrations. Groundwater Hamma concentration is around 145 mg/L to the standard for drinking water.

Sulfates: Sulfates come from gypsum rocks and sulphide oxidation found in rocks such as pyrite. The most frequently encountered sulfates are sodium sulfate, ammonium sulfate and magnesium sulfate.

It is known that the concentration of sulfate ions in water is variable depending on the nature of the ground crossed. According to our test results, Hamma contains 190 mg/L. Overall, our waters meet standards (WHO) where the sulphate concentration is limited to 400 mg/L. Beyond this value of diarrheal disorders may occur especially in children.

Nitrates: Nitrates are the most oxidized form of nitrogen. And increasing the nitrate content in water causes a development of algal flora and therefore eutrophication of aquatic phenomenon. In natural waters, the rate of nitrate is very variable depending on the season and the origin of the water. Acceptable values ??are the order of 2 to 3 mg/L. They should not exceed 20 mg/L for fish life. Their origin is mainly anthropogenic (fertilizer use in agriculture...). For drinking water at Hamma, it is 2.3 mg/L and it meets the standards.

CONCLUSION

It should be noted that water at Hamma is well mineralized naturally rich in calcium and magnesium and it is with high hardness.

RCP Assays:

pH: The values obtained during the test allow us to trace the curves pH = f (time). An example of a curve is given in Figure (2). For given water, three distinct phases is observed.

Initially, there was an increase in the pH: degassing of CO_2 that predominates on the precipitation of $CaCO_3$, since it has not reached a sufficiently high degree of supersaturation ($\delta < 40$) generates an ion consumption H^+. In a second step, the pH tends to decrease due to the precipitation of calcium carbonate, which takes over the degassing according to the reaction:

$$Ca^{2+} + CO_3^{2-} \rightleftharpoons CaCO_3\ (s)$$

In a third step, degassing of CO_2 and the precipitation of $CaCO_3$ tend to balance, so pH stabilization is observed. Note that the pH of the raw water before generally decreases the treated water (to delay the precipitation) and decreases more rapidly (differential precipitation kinetics) during use of Quercitine as inhibitor of scaling. Figures (3 and 4). It may be noted that this method is especially sensitive to pH delays the precipitation (small difference in kinetics). The shape of the curve changes for 100% efficiency (Figure 5).

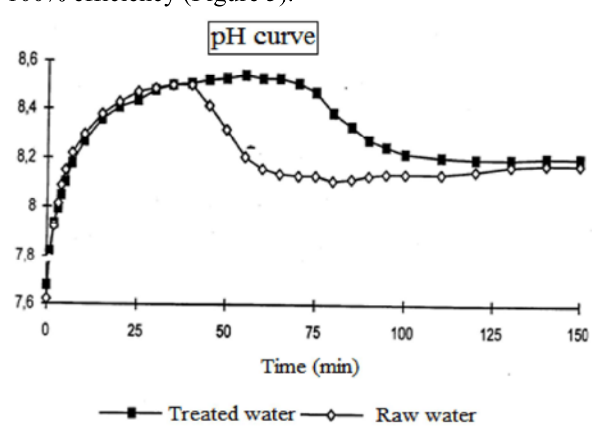

Fig. 2: pH curve using the RCP test

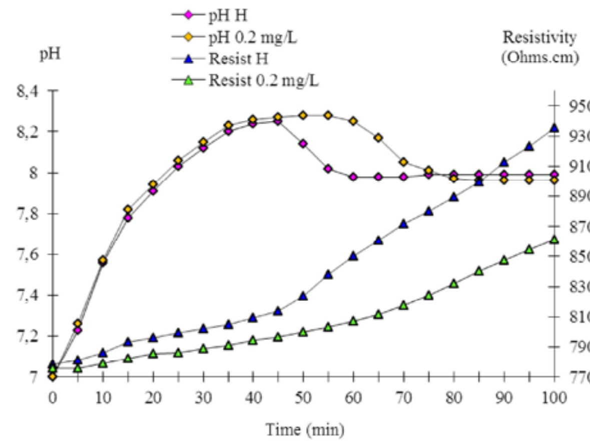

Fig. 3: Variation of the pH and resistivity with time for Hamma water without and with 0.2 mg/L of quercitine

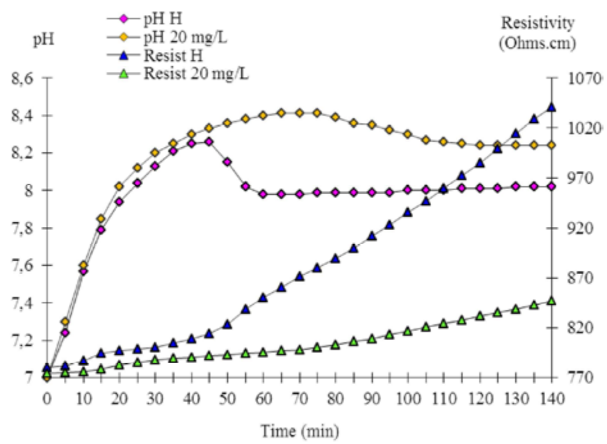

Fig. 4: Variation of the pH and resistivity with time for Hamma water without and with 20 mg/L of quercitine

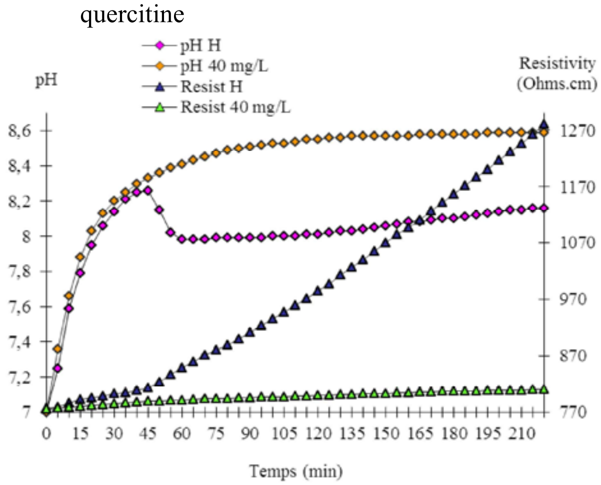

Fig. 5: Variation of the pH and resistivity with time for Hamma water without and with 40 mg/L of quercitine

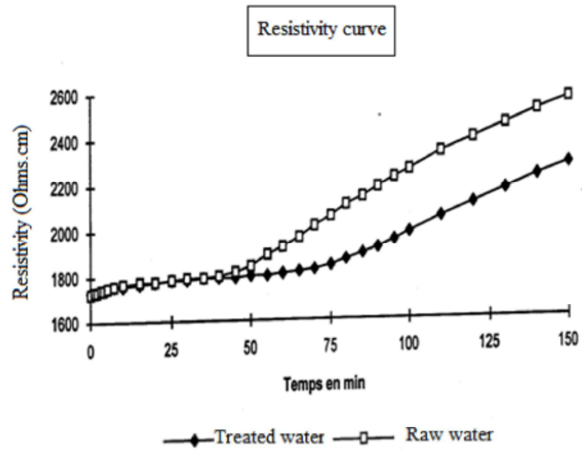

Fig. 6: Resistivity curve using the RCP test

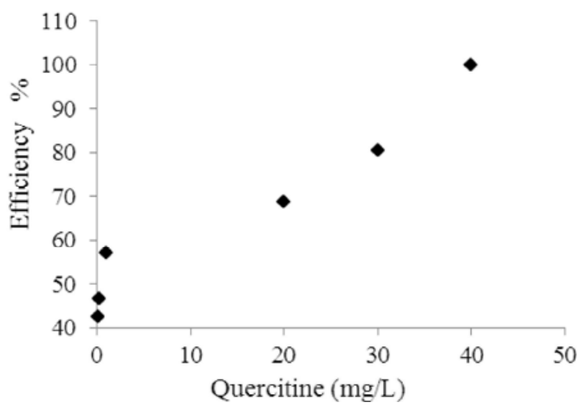

Fig. 7: Evolution of the efficiency as a function of the concentration of quercitine

Resistivity: The course of the curve Res =f(t) reveals that, during the precipitation, the Ca^{2+} and CO_3^{2-} ions cause a decrease in conductivity, thus increasing the resistivity of raw water against the (Figure 6) treated water. As for pH, an antiscalant treatment causes a delay in precipitation. It is also seen through which the resistivity starts to increase after the raw water. It also slows down the kinetics of precipitation (least significant formation of calcium carbonate). This enables the complete resistivity of pH because it best describes the kinetics of precipitation of the slopes of the lines change (Figures 3-5).

Tests at 30 presence of quercitine and provide a curve of increasing effectiveness in function of the amount added, see Figure 7. It is seen that with addition of 0.05 mg/L, the efficiency is about 42.46 % and from 40 mg/L of the blocking-growth process of germination of the calcium carbonate is higher and reaches 100 %.

CONCLUSION

Our work consisted of studying methods to prevent encrustation of calcium carbonate on the walls of pipes carrying hard water Hamma. For this, a rapid precipitation method (RCP) has monitored the implementation of the process of nucleation-growth of calcium carbonate. The addition of quercitine at low concentrations (0.05 mg/L) has demonstrated significant role for the antiscale- effect.

The total scale inhibition is reached for an addition of 40 mg/L of quercitine. It can be concluded that the test (RCP) is easy to implement and quercitine has inhibitory effect of scaling.

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