Scaling Behavior and Softening Groundwater Assessment: A Representative Case Study in Algeria

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Abstract: This study investigates the scaling behavior of groundwater in the Touggouret region of South Algeria, which serves as the primary water supply source. The groundwater exhibits high salinity and temperature, posing challenges to its utilization. The research aims to understand the geochemical characteristics and scaling sources to facilitate effective water management strategies.Geochemical modeling using the PhreeqC model reveals positive saturation values for carbonate rocks (Dolomite, Calcite, and Aragonite) and negative saturation indices for evaporite rocks (Gypsum and Anhydrite). This suggests that scaling behavior primarily stems from carbonated rocks.The high salinity, temperature, and positive saturation values contribute to the accumulation of scale-forming substances. Mitigation strategies should focus on removing calcium and magnesium ions, the main scaling contributors, from the groundwater. Softening techniques involving lime and soda can be applied.Understanding the scaling behavior sources is crucial for developing appropriate treatment methods and water management practices. These practices should consider the geochemical characteristics of the aquifers, including temperature and salinity control. By addressing scaling issues, water quality and availability can be improved in the Touggouret region.This research provides insights into the scaling behavior of groundwater in Touggouret, addressing water quality challenges associated with high salinity and temperature. The findings inform decision-making processes for water treatment and management, facilitating the availability and quality of water resources while mitigating scaling issues.

Keywords: scaling behavior, groundwater, Touggouret, geochemical characteristics, softening techniques.

1. Introduction

Generally, when water is the main subject of scientific studies, two main axes will be discussed which they quantity and quality [1]. Even if the two terms are important, from the last three decades of the 20th century the concern of water quality has been extremely exceeds the scientific studies [1].

On of the most known problems related to water quality is scaling phenomena [2].

It's not hard to detect the existence of this problem in Tougouret region especially that the groundwaters of the study area characterized by a very high hardness amounts in addition of high temperature (60 ° C). Scaling phenomenon caused by precipitation in large quantities formed in the water pipes as well as in cooling towers. The town of Touggourt is supplied from the Albian aquifers as a main source of drinking water. Despite its availability, this water has a great disadvantage, a very high scaling and a concentration in certain ions exceeding the world health organization guidelines. It is a major concern of the local authoritiesthat a large budgetis mobilized each year to solve this problem. TheAlbian groundwatersare characterized by excessive hardness due mainly to the calcium and magnesium levels, as well as by high levels of chloride, sulphate, and sodium [3].

The groundwater quality in Touggouret region has been investigated by many researchers with different point of views, Kadri et al, 2022 treated the Suitability of using the Albian groundwaters in agricultural purposes based on indices such as sodium adsorption ratio (SAR), permeability index (PI), soluble sodium percent (SSP), residual sodium carbonate (RSC), magnesium hazard (MH), Kelley's ratio (KR) and irrigation water quality index (IWQI), where they found that the Albian groundwaters in Touggouret region could be used for irrigate the salt-tolerance crops in soils characterized with a high permeability[4].Benhaddya et al, 2020 take into consideration the pollution by heavy metals in surface and groundwater systems in Oued Righ region, where the authors based in their assessment on the heavy metal pollution index (HPI) and the heavy metal evaluation index (HEI) in addition of other statistical methods such as one-way ANOVA, principal component analysis (PCA) and cluster analysis (CA). The results revealed that groundwaters have no heavy metals contamination, otherwise thesurface waters show a significant correlation with groundwaters which indicate an existing relation between the two water resources [5].Berkani et al., 2019 studied the possibility of reuse of reverse osmosis concentrate. The results show that sulfate, bicarbonates, and calcium have inhibited effects on the removal of nitrates. Otherwise, the application of adsorption and chemical reduction shows an efficient removal rate[6].

Baouia and Messaitfa 2015 worked on the removal of fluoride from the groundwaters of Tougouret region, where the two main aquifers were assessed regarding fluoride concentrations. The results show that the fluoride contained in Tougouret groundwater exceeds the world health organization (W.H.O). For that, the authors tested four removal techniques to eliminate fluoride where the most efficient technique was found to be the Aluminum sulfates and lime [7]. In a larger scale, Mazigh et al., 2014 focused on the economic aspect of defluoridation in the northern part of the African sahara. The study compared the production costs of three types of treatment process which they, electrodialysis, reverse osmosis and the electrochemical bipolar reactor (EBR). The results show that the most efficient economic process was the EBR with an estimated production costs of 0.339 USD per cubic meter [8]. In the light of the previous litterateur review and in the limits of our knowledge, the assessment of scaling behavior of Tougouret groundwaters have been never studied. The novelty of our work presented in this paper consistin the combination between the assessment of scaling behavior and the treatment of the problem by an experimental work concerning the removal of high hardness values where the objectives of this work are: (1) Studying the existent geochemical processes to detect the main factors controlling groundwater quality from deferent aquifers. (2) the assessment of scaling behavior based on stability and aggressivity index such as Ryznar , Langlier, Packurios andAggressivity index. (3) the comparison between two economic techniques for groundwater softening, we speak here about softening by lime and soda and softening by lime and execs soda.

2. Methodology

2.1. Study area

2.1.1 Geographical Location

Touggourt region is placed in the Algerian Eastern Desert It is located between the wilayas of El Oued and Ouargla, confined to the geographic coordinates between longitude and latitude; 32∘54' to 34∘09' North and 05∘50', 05∘75' East. with the average altitude in relation to the sea level: 72 m. Palm Oases cover a considerable part of its area. The research area is part of the Lower Sahara, and characterized by an arid desert climate, the temperature is higher in summer, the average annual temperature is 23.8 ° C, with 35.5 ° C in July for the hottest month and 10.6 ° C in January for the coldest month, with extremes of temperature 42.2 ° C in July and Tm = 5.4°C in December; the annual rainfall is low and very irregular, are significantly lower than the annual evaporation. The climatic conditions of the region are insufficient to balance the excessive exploitation of groundwater by the population of the region, i.e., the recharge of groundwater is still negligible [4,9]. Figure 1 shows the study area location and sampling locations.
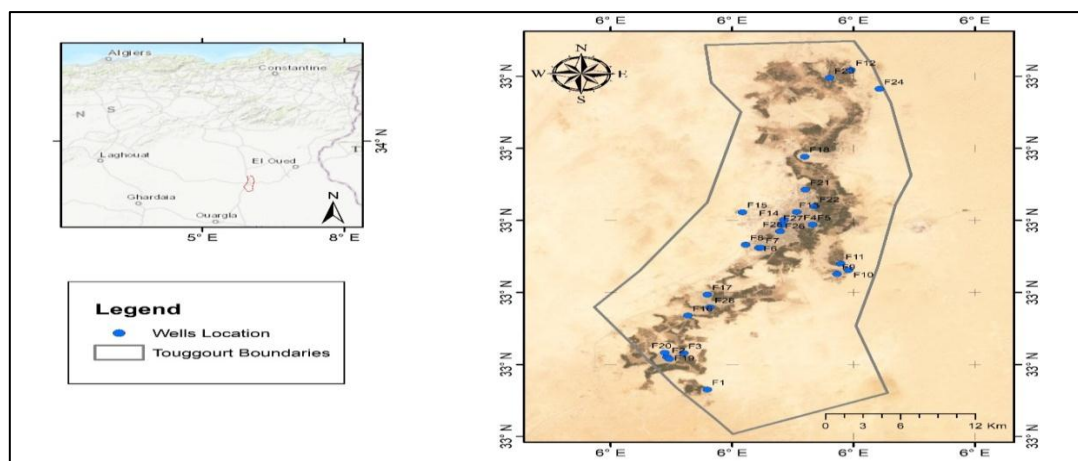
Figure 1: Study area localization.

2.1.2 Geological Aspect

The study area formed by the geological formations as follow: Tertiary age lands and Quaternary detrital deposits, a Miocene continental sandstone geological formation, siliceous sands, clays and occasionally marls, and Continental Pliocene constitute the structure of the regs in the form of a calcareous crust, with puddings or water limestones[10,11].The geological map of Touggourt highlights the geometry of the geological units that are identified and modeled from top to bottom: (1) Mio-Pliocene; (2) Eocene; (3) Cenomanian; (4) Turonian; (5) Cenomanian;(6) Albian;[12,13]. The Mio-Pliocene of the Sahara can be relatively thick 150 m. It is presented as sandy and clayey facies with gypsum. The Eocene has two lithological different sets that can be distinguished at the base: The carbonate Eocene is formed essentially by dolomites and dolomitic limestones with some intercalations of marl, clay and even anhydrite and salt. The thickness of this formation varies between 100 and 500 m, the maximum thickness being in the area of the lower Sahara. At the top, the evaporitic Eocene is formed by an alternation of limestone, anhydrite and marl. Its thickness reaches a hundred meters under the Chotts, [14]. The Cenomanian is individualized in two facies: the lower Senonian characterized by clayey and saliferous formations with anhydrite, it is very little permeable, [9,15]; the Upper Senonian is characterized by permeable carbonate formations.

The Turonian consists of a thick bar of limestone and dolomite, which contrasts sharply with the evaporites and clays of the Cenomanian below and the Senonian above. It is, among all those of the eastern basin of the Algerian Sahara, the best characterized sedimentary formation. With a thickness ranging from 25 to 70m approximately, in the study area. The Cenomanian consists of alternating dolomites, dolomitic limestones, clays and anhydrite. The transition from the Vraconian to the Cenomanian is clear: frank sandy facies, related to the Albian, is followed by clays and evaporites, related to the Cenomanian. The Albian stage includes the mass of sands and clays between the Aptian bar and the overlying clay horizon attributed to the Cenomanian [16], the geological section of the study area is presented in figure 2.
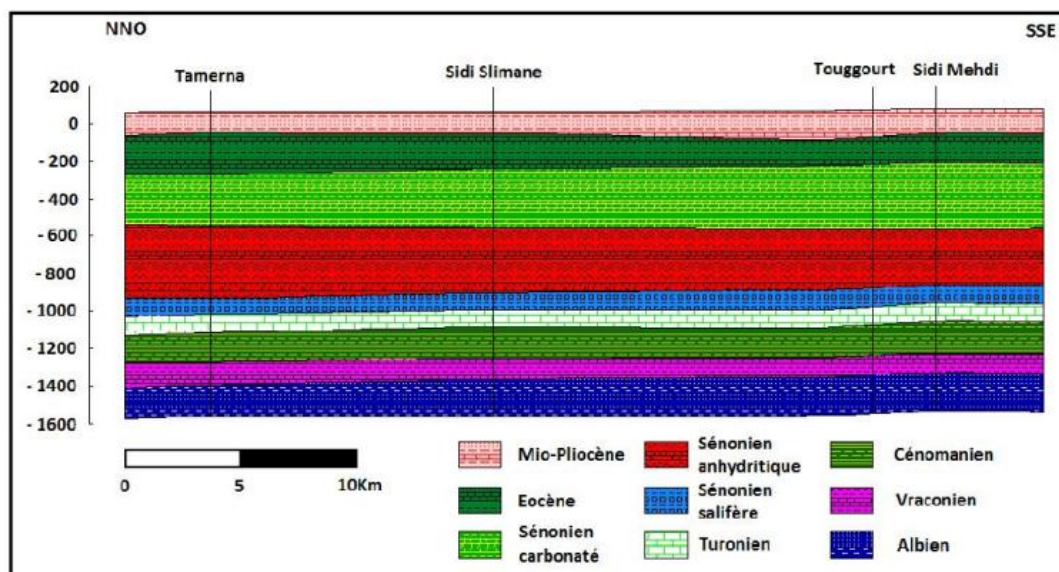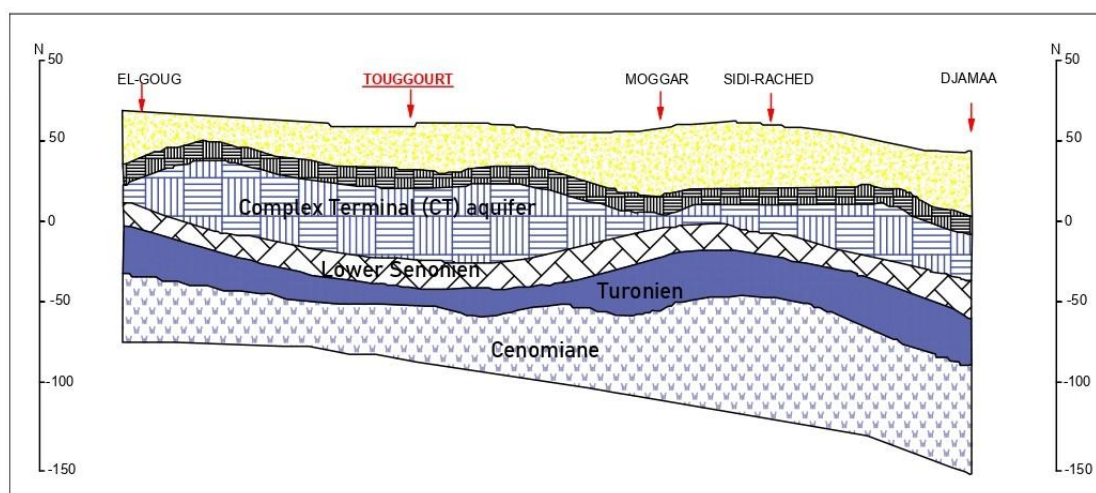
Figure 2: Geological section of the study area (HAOUARI, 2012)

2.1.3 Hydrogeological Aspect

From a hydrogeological perspective, the aquifer system in the study area is part of the (SASS) This basin contains a series of aquifer layers grouped into two reservoirs called: Continental Intercalary (CI) and Terminal Complex (TC). The Continental Intercalary is an aquifer of 1500m and more in depth; composed of sandstone or clayey sands, it is located between 700 and 2000 m in depth. [15,17].

Figure

3:The hydrogeological Cross-section layers in the study area.

From the lithological point of view, the intercalary continent is formed by a succession of layers of sand, sandstone, clayey sandstone and clay. The Albian water is relatively unmineralized, with an electrical conductivity of 3 mS/cm, the temperature is higher than 50°C when it gushes out, which poses problems of cooling prior to irrigation [18]. The Terminal Complex contains more

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than one aquifer (Mio-Pliocene, Senonian carbonates and Eocene) with a depth varies between 200 to 500 m. It is composed of three main aquifers Figure 3 shows the hydrogeological Cross-section layers in the study area.

a. The first aquifer: in the sands and clays of the Pliocene, which is in fact a network of small aquifers in communication.

b. The second aquifer: in the coarse sands and gravels of the upper Miocene.

c. The third layer: in the fissured and karstic limestones of the lower Eocene. [19]

2.2. Data Collection andData analyses

The study area has a multi-aquifer system. Precisely for aquifers TC1, TC2 and TC3 from the Terminal Complex aquifer system and the Albian from the Continental intercalary aquifer system. The collected data containing physical and chemical analysis results of 95 wells distributed as follows, 37 from TC1, 24 from TC2, 20 from TC3 and 14 from the Albian aquifer. Firstly, the collected data was analyzed to determine their suitability for use in this research paper by calculating the ionic balance (IB) of samples.Where all samples with an IB greater than +10 % or less than −10% have been removed from the collected data.Error values below ± 5% are the best analytical estimation [20-22]. For the assessment strategy, the use of several stability indices such as Langelier stability index (LSI), Ryznar stability index (RSI), Agressivity index (AI) andPakurios stability index (PSI) have been used to determine the scaling behavior amount in the groundwater of the study area. Furthermore, a chemical simulation using PhreeqC model was assessed to determine the main geochemical characteristics of the aquifer targeted in this study. In addition of that, a statistical analysis was held on for the aim of clarify the existent co-relations between the chemical component of groundwater and determine the main parameters controlling the interaction process.

2.3. Sampling and field preparation.

In order to start the laboratoryexperiments regarding groundwater softening, a sampling operation has been relied on from the wells supplying Touggouret water treatment station (four wells). The sampleshave been harvested in polyethylene bottles of 1.5-liter capacity. During field preparation, all the bottles have beenwashed with nitric acid, rinsed with distilled water, and rinsed a second time with sample water itself. As a final step before sampling,the chlorination of raw water was stopped, and the pipes drained for five minutes to insure representative groundwater sampling.

After collecting the necessary samples, they were mixed to obtain one sample which we called the Mixed Sample and we give it the label "MS", the "MS" represents the overall inflow water quality, the temperature, pH and EC of "MS" were measured in fieldusing a multiparameter referenced under "HANNA HI9829". All samples were transported to the "laboratory of water

and environment engineering in the Saharan environment, Ouargla" in a cool box for the aim of completing the physical and chemical analysis.

2.4. Laboratories experiments

all samples have been characterized regarding Calcium (Ca^{2+}), Magnesium (Mg^{2+}), Sodium (Na^+), Potassium (K^+), Bicarbonates (HCO_3^-), Sulphate (SO_4^{2-}), Chloride (Cl^-), Total Dissolves Solids (TDS) and Total hardness (TH) according to the standard methods water quality analysis described by RODIER et al. (2009) [23].

After that, two methods of softening have been selected to study the possibility of reducing the Total Hardness (TH) which they, the precipitation by addition of lime-Soda and the precipitation by addition of excess lime-Soda. The two methods have been oriented to reduce both permanent and non-permanent hardness [24]. The experimental protocol of precipitation by lime-soda addition, and precipitation by excess lime-soda addition is described in figure 4.
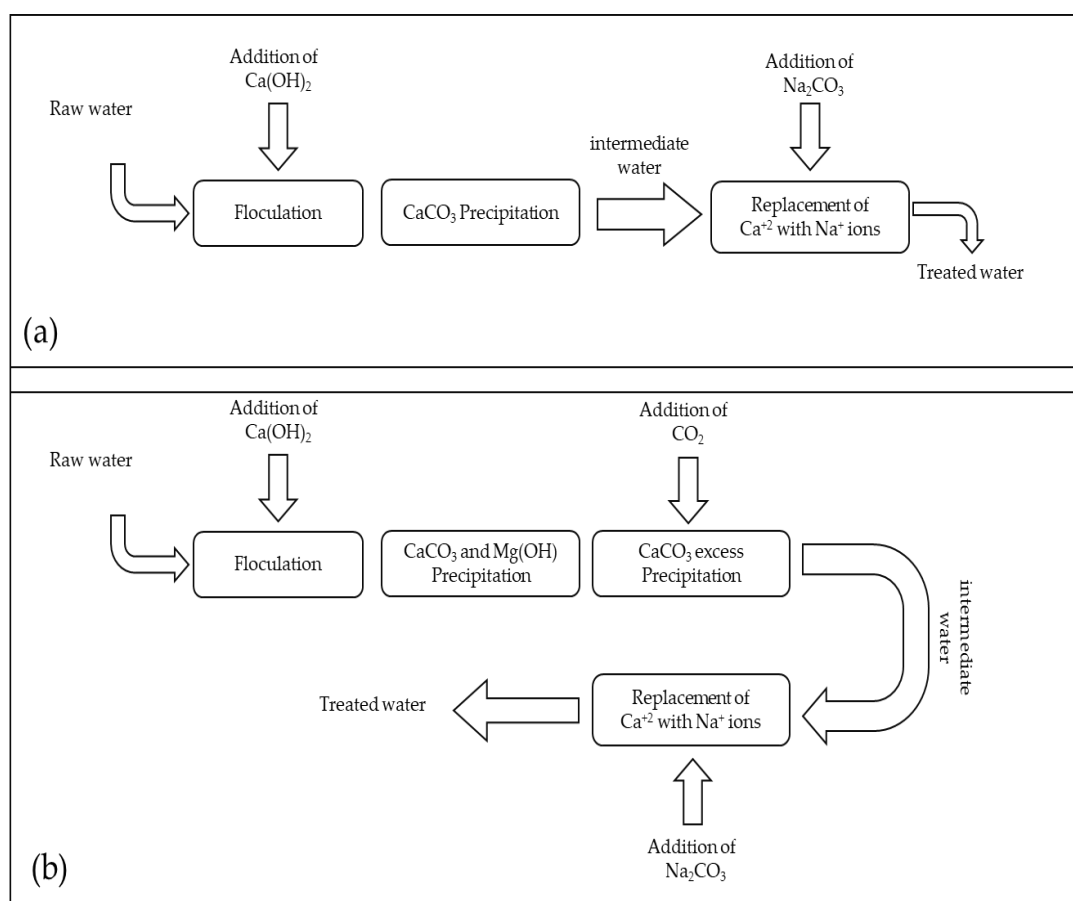

Figure 4: Process of softening by (a) lime and soda, (b) excess of lime and soda.

3. Results

3.1. Hydrochimistry

Potential of hydrogen (pH) mainly represents the alkalinity or the acidity of a solution. The obtained result from the analyzed samples shows that all the studied aquifers have a neutral groundwaters. The minimum pH values registered in the TC 1 aquifer with a value equal to 6.74, whereas the maximum values found in Albian wells with a value of 8.05. the comparison of the mean values shows that the pH values was greater in the deeper aquifers where the Albian and TC 3 aquifers have mean values of pH equal to 7.59 and 7.38 respectively, in the other hand TC 1 and TC 2 have lower mean values of pH equal to 7.24 and 7.18 respectively.

Electrical conductivity (EC), an important parameter describes the groundwater salinity. Very high values of EC caused a serious problem for agricultural practices and negatively affect soil permeability. The measured values of EC founded with very high amount exceeding the World Health Organization guidelines (1500 µS/cm) the minimum values registered in TC 1 aquifer with a value equal to 2210 µS/cm, where the maximum value registered in the TC 2 aquifer with a value achieved 10200 µS/cm.

Total hardness (TH), the amount of calcium and magnesium dissolution cause mainly the variation in groundwater hardness values. In the studied samples we registered groundwater classes from slightly hard to very hard groundwaters. The minimum values founded as follow 113, 163, 211.48 and 102 mg/l as CaCO3 in TC 1, TC 2, TC 3 and Albian aquifers respectively. In contrast, the maximum values achieved 2200, 3820, 326.4 and 2060 mg/l as CaCO3. The High values of hardness have no reported issues related to human health, in the other hand the high amounts of hardness have other related problems in irrigation, industrial domains in addition to the related problems at water supply networks.

Calcium ion (Ca^{2+}) analysis results shows an exceeding of WHO guidelines (200 mg/l) in 35%, 25%, 100% and 50% of TC 1, TC 2, TC 3 and Albian aquifers respectively. The highest value registered in TC 2 aquifer with a value of 841.6 mg/l, while the minimum value registered in TC 1 aquifer with a value of 80 mg/l.

Magnesium ion (Mg^{2+}): the average values of Mg^{2+} founded as 258.6, 409.9, 435.5 and 190.3 mg/l in TC 1, TC 2, TC 3 and Albian aquifer. The highest value (573 mg/l) registered in TC 3 aquifer while the minimum value of Mg2+ founded in TC 1 aquifer with a value equal to 58.3 mg/l. compared to WHO guidelines, we found that 81.08% of samples from TC 1 exceed the standards value (150 mg/l), for TC 2, TC 3 and Albian 100%, 100% and 71.42 % of samples founded exceeding the guideline value respectively.

Sodium ion (Na^+): the sodium ions presence plays a main role in the related effects of water on mediums n contact such as soils, pipes, reservoirs… etc. generally the values of Sodium in the analyzed samples founded with relatively high amounts. In the TC 1 aquifer the maximum value was 1600 mg/l which is the highest registered value in all the aquifers samples. The minimum value in the same aquifer founded as 200 mg/l while the mean value was 596.2 mg/l. the lowest value of Na^+ (105.8 mg/l) registered in TC 2 aquifer, where the maximum and the mean value in

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the same aquifer founded as 551.8 and 319.8 mg/l respectively. The TC 3 aquifer was found to have Na+ values near to registered ones in TC 2, where the minimum, maximum and mean values founded as follow 132.1, 440.6 and 291.7 mg/l respectively. For the Albian aquifer, the minimum, maximum and mean values were found to equal 162.3, 299.9 and 680 mg/l respectively.

Table 1: Descriptive statistics of groundwater analysis results.

Variable	Aquifer	N	Mean	StDev	Minimum	Q1	Median	Q3	Maximum	Skewness
pH	TC 1	37	7.2392	0.2594	6.7400	7.1000	7.2100	7.3250	8.0000	0.87
	TC 2	24	7.1779	0.1263	6.9000	7.1000	7.2000	7.2875	7.4100	-0.15
	TC 3	20	7.3780	0.2716	7.0700	7.1650	7.2700	7.6100	7.9100	0.86
	Albian	14	7.587	0.395	7.010	7.210	7.610	7.963	8.050	-0.17
EC (µS/cm)	TC 1	37	5162	1699	2210	3545	5500	6550	7900	-0.27
	TC 2	24	7070	1670	3260	5925	6900	7975	10200	0.06
	TC 3	20	7072	1007	5780	6290	6715	7948	9180	0.63
	Albian	14	4521	1601	2450	2923	4575	5485	8270	0.85
TH (mg/l as CaCO3)	TC 1	37	643	648	113	166	189	1050	2200	1.00
	TC 2	24	615	989	163	203	228	259	3820	2.45
	TC 3	20	276.90	35.75	211.48	246.16	281.87	301.56	326.40	-0.40
	Albian	14	705	687	102	104	460	1424	2060	0.64
Ca^{2+}(mg/l)	TC 1	37	200.6	106.4	80.0	129.6	159.4	242.5	456.9	1.17
	TC 2	24	219.8	167.0	109.0	138.0	166.5	200.5	841.6	2.86
	TC 3	20	391.3	50.0	293.0	358.0	389.0	414.3	477.0	-0.00
	Albian	14	264.6	126.6	176.0	191.1	199.2	333.0	573.1	1.76
Mg^{2+}(mg/l)	TC 1	37	258.6	112.1	58.3	166.1	295.6	355.4	458.9	-0.34
	TC 2	24	409.9	86.5	155.6	352.8	414.0	467.8	543.0	-0.91
	TC 3	20	435.5	77.2	293.0	401.5	442.0	485.3	573.0	-0.26

	Albian	14	190.3	64.6	80.2	129.4	206.1	236.4	284.6	-0.39
Na^+ (mg/l)	TC 1	37	596.2	306.5	200.0	310.0	551.8	814.8	1600.0	0.99
	TC 2	24	319.8	119.4	105.8	230.6	289.8	407.3	551.8	0.68
	TC 3	20	291.7	80.0	132.1	245.5	279.7	368.0	440.6	-0.04
	Albian	14	299.9	164.2	162.3	212.7	232.4	326.1	680.0	1.60
K^+ (mg/l)	TC 1	37	37.05	15.18	15.96	21.94	39.56	45.88	74.81	0.62
	TC 2	24	64.8	152.3	16.0	21.9	39.6	39.8	778.0	4.86
	TC 3	20	74.3	166.3	16.0	22.2	39.6	45.9	778.0	4.42
	Albian	14	85.1	199.5	19.0	30.4	30.9	39.6	778.0	3.73
HCO_3^- (mg/l)	TC 1	37	135.33	24.84	71.00	119.75	134.50	150.84	195.20	0.16
	TC 2	24	155.81	47.26	113.00	128.25	139.00	165.00	315.16	2.16
	TC 3	20	111.35	15.36	83.00	97.25	113.50	123.75	136.00	-0.39
	Albian	14	165.83	21.37	136.47	151.90	164.14	175.22	217.77	1.11
Cl^- (mg/l)	TC 1	37	1087.2	414.7	414.0	787.1	1052.9	1488.6	1847.4	0.12
	TC 2	24	1572	753	742	1183	1333	1786	4399	2.52
	TC 3	20	1054.9	259.6	523.0	869.8	1018.5	1307.8	1486.0	-0.31
	Albian	14	626.4	302.1	410.5	445.1	498.4	686.9	1429.6	1.89
SO_4^- (mg/l)	TC 1	37	1057.3	285.9	480.0	937.5	1090.0	1286.0	1575.0	-0.76
	TC 2	24	1283.1	205.8	756.0	1168.3	1330.0	1374.0	1625.0	-0.63
	TC 3	20	2219.2	317.9	1516.0	1995.8	2165.0	2499.8	2746.0	-0.21
	Albian	14	826.1	249.7	400.0	704.2	817.5	1014.3	1350.0	0.08

The results revealed that the highest value of Bicarbonates (HCO_3^-) registered in TC 2 aquifer with a value equal to 315.16 mg/l where the lowest value (71 mg/l) was found in TC 1 aquifer. The mean values in the studied aquifers founded as 135.33, 155.81, 111.35 and 165.83 mg/l in TC 1, TC 2, TC 3 and Albian aquifer respectively. Chloride ions (Cl^-) ions variate between 410.5 mg/l as a minimum value in Albian aquifer and 1847.4 mg/l in TC 1 aquifer. The mean values achieved 1087.2, 1572, 1054.9 and 626.4 mg/l in TC1, TC 2, TC 3 and Albian aquifers

respectively. For Sulphate ions (SO_4^{2-}) presence in studied aquifers, the analysis results shows that the TC 3 aquifers contain the highest v lues with a maximum value achieved 2746 mg/l and a minimum value equal to 2219.2 mg/l, the TC 1 and TC 2 aquifers have similar patterns of sulphates distribution which is low than the amounts founded in TC 1 aquifer, while the lowest values registered in the Albian wells aquifer with a minimum of 400 mg/l, maximum of 1350 mg/l and a mean value of sulphate equal to 826.1 mg/l. the Table 1 present a statistical overview of the obtained results.

3.2. Hydro chemical facies

The relationship between the different dissolved ions and the hydrogeochemical facies of groundwater can be analyzed by plotting the chemical analyzed data on a Piper diagram (Piper 1944). Figure 5 present the plotted data on a Piper diagram where we could define three main parts, the triangle at the left lower side, which is present the cations ions, the triangle at the right lower side which presented the anions ions and the diamond form in the upper middle which present the groundwater facies types. Each aquifer has been presented with a deferent symbol in order to make distinguishing between deferent aquifers easier. Based on figure 5 the hydro chemical facies in 84.24 % of samples was the Cl-SO4-Ca-Mg divided on the four aquifers as follow, 64.87% from TC 1, 100% from TC 2, 100% from TC 3 and 85.72% from Albian aquifer. Cl-Na-K was detected as secondary facies in 35.13% of TC1 wells and 14.28% of Albian wells.From the results, it is observed also that alkaline earths (Mg^{2+} and Ca^{2+}) expressively higher than the alkalis (Na+, K+) and Strong acids (Cl⁻and SO_4^{2+}) exceed the weak acids (CO_3^{2-}, HCO_3^{-}).
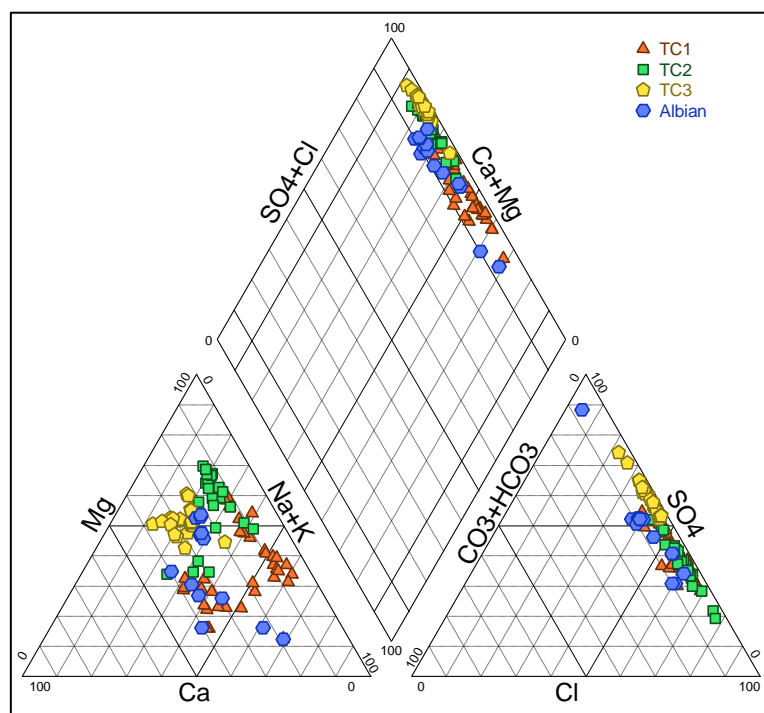

Figure 5: Piper diagramme.

From 37 wells of TC 1 aquifer, we found that Sodium (Na⁺) and Magnesium (Mg²⁺) were the dominant cations in 13 and 7 wells respectively, while 17 wells founded with non-dominant cations. Which is concerning TC 2 aquifer, 1 sample founded to have Calcium as dominant cation, while Magnesium was the dominant cation in 18 samples where 5 samples founded wit no dominant cation. In TC 3 aquifer the wells divided in two types, the majority (15 wells) have Magnesium as dominant cation in the other hand the rest of wells (5 wells) have no dominant cation. The Albian aquifer wells have Sodium and Magnesium as dominant cations in 2 and 3 wells respectively; otherwise, 9 wells founded with no dominant cations. Actually, the number of wells with no dominant cation in all the aquifer was 36, which represent about 38% of wells, this ratio has been minimized to 7.3% in the case of dominant anions where we register the Sulphate as dominant anions in 7, 1, 20, 8 in TC1, TC 2, TC 3 and Albian aquifers respectively; Also, the Chloride was the anion dominant in 26, 21 and 5 wells from TC 1, TC 2 and Albian wells respectively. In the other hand the no dominant anion case registered in 4 wells from TC 1, 2 wells from TC 2 and 1 well from the Albian aquifer.

3.3.   Groundwater Geochemistry

From the widely used methods in the investigations about groundwater dominance process we find Gibbs plot. Even if Gibbs himself has developed his theory for surface waters, but at the same time there is nothing incorrect about using Gibbs plot to investigate groundwater hydrochemistry. In a query from Web of Science database, 382 out of 720 publications have citing Gibbs diagram and have the keyword "Groundwater" [25]. Gibbs diagrams describe the evolution of water chemistry, where three parts could be defined, the upper, middle, and lower parts which represent evaporation, rock dominance and precipitation governing process. The plot of data on Gibbs diagram on his first part be based on the total dissolved salts (TDS) in the Y axis versus the ratio between sodium and the sum of sodium and calcium in the X axis, while in the second part the X axis contain the ratio between Chloride and the sum of Chloride and Bicarbonates. Figure 6presents the plotted data of the studied aquifers on Gibbs diagram where each aquifer has been presented with an independent symbol in order to easily distinguish between them. As Figure6 shows, we can see that all the points situated in the upper part of the diagramindicate that the groundwaters of the studied aquifers are of a very ancient age. Also, the high salinity presented by TDS values, indicate that there is no recent contact between rainfall waters in the groundwater in the study area and that groundwater have a sufficient contact time with reservoir rocks in order to react and acquire the chemical characteristics of the actual state.
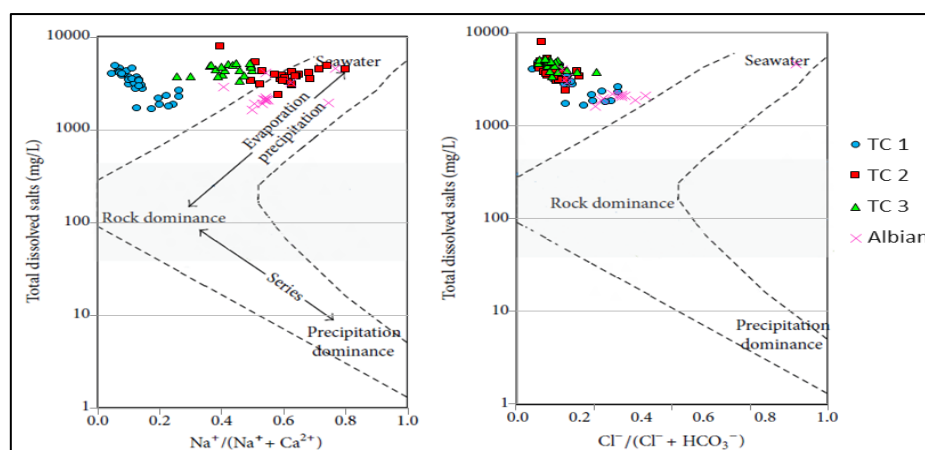
Figure 6: Gibbsdiagram.

Even if the previous mentioned results take an important place in this paper, the Gibbs diagram have not the answers forall related questions about geochemistry mechanism processes. For that, a deeper investigation based on thermodynamic and saturation equations offered by the PhreeqC model has been taken in order to get more comprehensive results about the geochemistry of the studied aquifers. In addition, geochemistryassessment helps to get more knowledge about the aquifer medium from a geological perspective, this led to better understand the main sources of groundwater quality. As figure 7 and Table 2 shows, two types of rocks could be defined in Tougouret aquifers, carbonate rocks presented as Calcite, Dolomite and Aragonite; and Evaporate rocks presented in

Gypsum and Anhydrite. As a first observation we note that all of Calcite, Dolomite and Aragonite were foundin supersaturated state in all studied aquifer. In the other hand, the Anhydrite and Gypsum founded as undersaturated. The mineral saturation indices were found in deferent levels in the studied aquifers, but the pattern of varietywas found to be the same in all aquifers.The Dolomite saturation indices was the highest regarding the supersaturated state in comparison with Calcite and Aragonite where the mean values of the previous mentioned minerals were 1.25, 0.42 and 0.31 in TC 1aquifer, 1.47, 0.42 and 0.30 in TC 2, 1.69, 0.70 and 0.59 in TC 3, 2.18, 0.99 and 0.88 in Albian aquifer respectively. Otherwise, all aquifers groundwaters found as undersaturated with Gypsum more than Anhydrite with mean values equal to -0.79 and -0.58 in TC 1, -0.78 and -0.56 in TC 2, -0.27 and -0.047 in TC 3, -0.69 and -0.49 in Albian aquifer respectively.
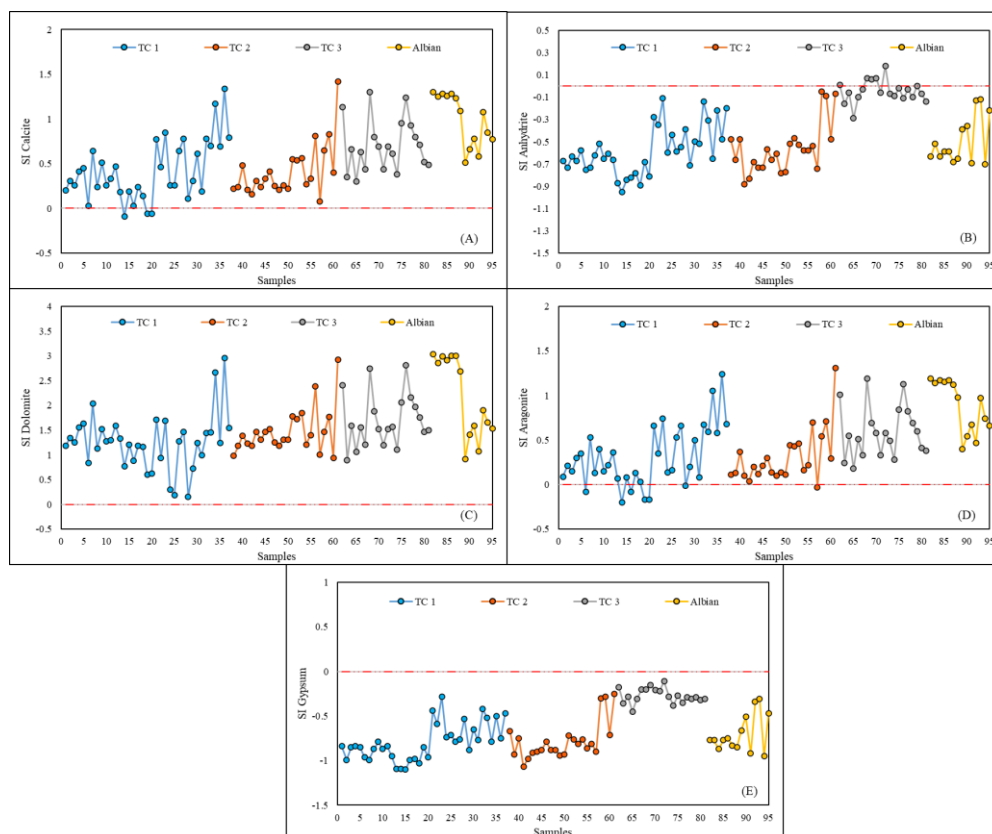
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Figure 7: Saturation indices of deferent rocks.

Table 2: Descriptive statistics of geochemical saturation indices.

Variable	N	Mean	StDev	Minimum	Q1	Median	Q3	Maximum	Range	Skewness
Terminal complex system "TC 1 aquifer"										
Anhydrite_TC1	37	-0.5811	0.2146	-0.95	-0.73	-0.62	-0.46	-0.11	0.84	0.57
Aragonite_TC1	37	0.3059	0.3342	-0.2	0.08	0.21	0.555	1.24	1.44	0.77
Calcite_TC1	37	0.4159	0.3342	-0.09	0.19	0.31	0.665	1.34	1.43	0.77
Dolomite_TC1	37	1.253	0.5691	0.15	0.91	1.25	1.53	2.96	2.81	0.67
Gypsum_TC1	37	-0.79	0.2062	-1.1	-0.96	-0.84	-0.68	-0.28	0.82	0.66

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Terminal complex system "TC 2 aquifer"

Mineral	N									
Anhydrite_TC2	24	-0.5629	0.2233	-0.88	-0.73	-0.58	-0.48	-0.05	0.83	1.17
Aragonite_TC2	24	0.3042	0.2918	-0.03	0.1125	0.205	0.4375	1.31	1.34	2.01
Calcite_TC2	24	0.4158	0.2911	0.08	0.225	0.32	0.5475	1.42	1.34	2.03
Dolomite_TC2	24	1.4671	0.4459	0.94	1.1875	1.35	1.67	2.92	1.98	1.86
Gypsum_TC2	24	-0.7779	0.2149	-1.07	-0.9075	-0.835	-0.7275	-0.25	0.82	1.56

Terminal complex system "TC 3 aquifer"

Mineral	N									
Anhydrite_TC3	20	-0.047	0.1001	-0.29	-0.1	-0.06	0.0075	0.18	0.47	-0.05
Aragonite_TC3	20	0.5915	0.2884	0.18	0.3425	0.565	0.7875	1.19	1.01	0.68
Calcite_TC3	20	0.703	0.2887	0.3	0.4525	0.675	0.8975	1.3	1	0.67
Dolomite_TC3	20	1.699	0.532	0.89	1.272	1.565	2.038	2.81	1.92	0.68
Gypsum_TC3	20	-0.2735	0.0831	-0.45	-0.3175	-0.285	-0.2025	-0.11	0.34	0.02

Continental intercalary system "Albian aquifer"

Mineral	N									
Anhydrite CI	14	-0.4929	0.2098	-0.7	-0.6575	-0.59	-0.325	-0.12	0.58	0.87

Aragonite CI	14	0.8836	0.2917	0.4	0.63	0.975	1.155	1.19	0.79	-0.44
Calcite CI	14	0.9943	0.2909	0.51	0.7425	1.085	1.265	1.3	0.79	-0.44
Dolomite CI	14	2.181	0.809	0.92	1.5	2.295	2.993	3.03	2.11	-0.24
Gypsum CI	14	-0.6979	0.2091	-0.95	-0.855	-0.77	-0.5	-0.31	0.64	0.82

3.4.   Groundwater stability behavior.

The stability of the studied samples had been assessed based on five indices LSI, RSI, PSI, LSSI and AI. This variety in the selected indices aims to a better clarification about the groundwater behavior.

3.3.1 Langelier Stability Index (LSI) **(Langelier 1936 ; Langelier 1946)**

Is an equilibrium model of water saturation versus calcium carbonate used to predict water stability [26, 27]. Langelier Stability Index (LSI) takes the form:

ISL = pH - pHs

Where:pH: the pH of the measured water.

pHs: the pH at which water with a given calcium content and alkalinity is in equilibrium with calcium carbonate.

pHs = (9.3+A+B) - (C+D)

Where:A = [log10 (TDS) - 1] / 10

B = -13.12 × log10(°C+273) + 34.55

C = log10 (Ca as CaCO3) – 0.4

D = log10 [Alcalinity as CaCo3]

3.3.2 Ryznar Stability Index (**Ryznar 1949**)

Considered an empirical method to predict scaling trends in water. John Ryznar in 1944 used the Langelier index to develop a new stability index called the Ryznar index [28], the Ryznar index used to predict scaling or water aggressiveness tendencies and expressed as follows:

ISR = 2pHs – pH = pHs - ISL

3.3.3 Aggressiveness Index (AI)(**Millette et al. 1980**) [29].

Originally developed to monitor water in asbestos pipes, is sometimes replaced by the Langelier index as an indicator of water stability behavior.

AI = pH + C +D

Where:C = log10 (Ca as CaCO3) – 0.4

D = log10 [Alcalinityas CaCO3]

3.3.4 Puckorious Saturation index(**Puckorius& Brooke, 1991**) [31].

Is an important tool to establish a relationship between the state of saturation and the formation of scale by incorporating the buffering capacity of water into the index, the index can be calculated by the following formula:

ISP = 2. pHs - pHeq

Where:pHs: the pH at which water with a given calcium content and alkalinity is in equilibrium with calcium carbonate (used in Langlier index)

pHeq = 1.465 x Log [Alk] + 4.54

Alk: Alkalinity as $CaCO_3$.

Table 3: Water conditions based on aggressivity indices.

Index	Value	Water condition
LSI	> 0	The water is supersaturated with calcium carbonate (CaCO3).
	0	Saturated, the CaCO3 is in equilibrium.
	< 0	The water is undersaturated with respect to calcium carbonate.
RSI	≤ 6	Supersaturated, tend to precipitate CaCO3.
	6 < RSI < 7	Saturated, the CaCO3 is in equilibrium.
	≥ 7	Under saturated, tend to dissolve CaCO3.
AI	> 12	The water is not aggressive.
	10 < AI < 11.9	The water is moderately aggressive.

	< 10	The water is very aggressive.
	> 6,5	Water tends to corrode.
PSI	4,5 < PSI < 6,5	Optimal interval.
	< 4,5	Water tends to precipitate.

Figure 8 presents the variation of calculated aggressivity indices, where associated water conditions of each index is presented in table 3.The calculation results revealed to the existence of supersaturation regarding calcium carbonate in the groundwater of TC1 and based on LSI, where all the values were greater than 0 with a minimum value of 0.31 and a maximum value of 1.87, the average of calculated results was 0.83 which indicated the possibility of calcium carbonate precipitation. In a confirmation of the previous observation, the results of RSI found to have an average of 5.58 which indicates a saturation of groundwaters regarding the calcium carbonate only one well (F14) present an equilibrium state with a value of 6.59. in the other hand, the aggressiveness indices shows that the TC1 groundwaters don't have the aggressiveness behavior as well as they more likely precipitate where the values of AI variate between 11.12 and 12.47 with an average value of 11.52 otherwise, the values of PSI founded to variate between 4.20 and 6.31 with an average of 5.30.
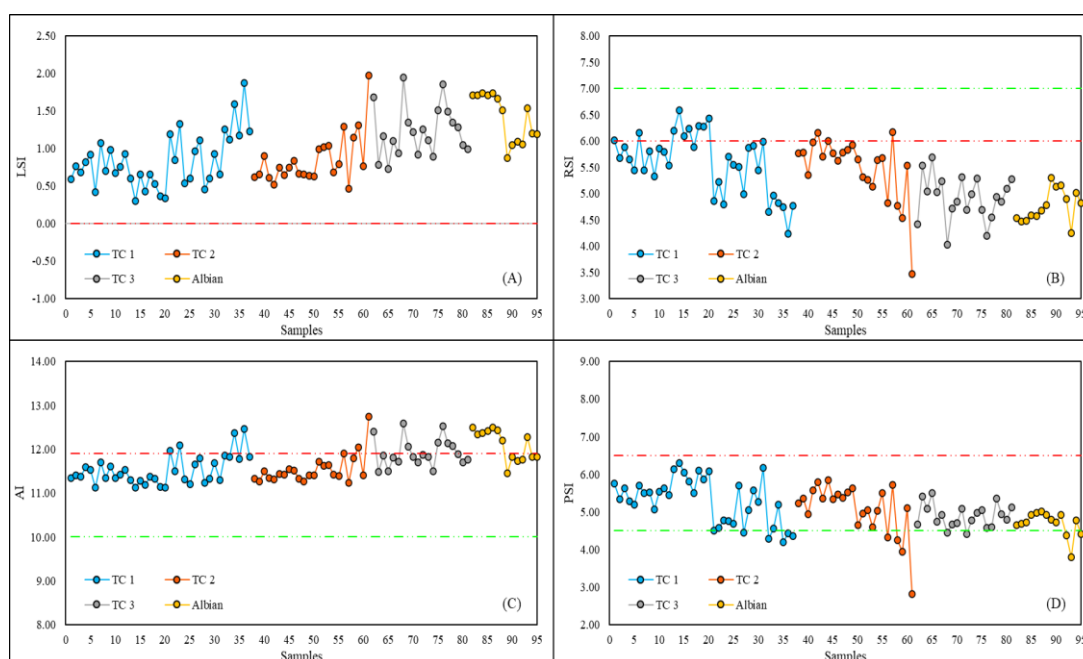

Figure 8: Aggressivity indices variation.

For the TC2 aquifer, the same results were found. A groundwater supersaturated regarding calcium carbonate based on LSI and RSI with an average value equal to 0.85 and 5.48 respectively. The minimum and maximum values were 0.46, 1.97 for LSI and 3.47, 6.18 for

RSI. The Aggressiveness index AI founded to have a maximum value of 12.74 and a minimum value of 11.23 which indicate that the TC2 have a groundwater have no aggressiveness behavior, the same result could be confirmed by PSI where the average value founded to be 5.06 which indicate an equilibrium stat of TC2 groundwater.

Based on LSI, the results showed that there was calcium carbonate saturation in the TC3 groundwater, where all the values were greater than 0, with a minimum value of 0.7 and a maximum value of 1.94. The average of the calculated results was 1.23, which suggested that calcium carbonate precipitation might occur. The results of RSI found to have an average of 5.68, which suggests a saturation of groundwaters regarding the calcium carbonate, are a confirmation of the earlier observation and show that no well exhibits an equilibrium state. The aggressiveness indices, on the other hand, indicate that the TC3 groundwaters do not exhibit aggressive behavior and are more likely to precipitate where the values of AI range between 11.49 and 12.58 with an average of 4.89.

Regarding the Continental intercalary system, the calculation results show to the existence of a saturation regarding calcium carbonate in the groundwater of the Albian aquifer, where all the values of LSI were greater than 0 with a minimum value of 0.87 and a maximum value of 1.74, the average of calculated results was 1.41 which indicated the possibility of calcium carbonate precipitation. In a confirmation of the previous observation, the results of RSI were found to have an average of 4.76 which indicate a saturation of groundwaters regarding the calcium carbonate, no well present an equilibrium state. in the other hand, the aggressiveness indices shows that the Albian groundwaters don't have the aggressiveness behavior as well as they are more likely to precipitate where the values of AI variate between 11.46 and 12.49 with an average value of 12.10 otherwise, the values of PSI founded to variate between 3.80 and 5.00 with an average of 4.69. the obtained results are summarized in table 4.

<p align="center">**Table 4: Descriptive statistics of aggressivityindices.**</p>

Variable	N	Mean	StDev	Minimum	Q1	Median	Q3	Maximum	Range	Skewness
		Terminal complex system "TC 1 aquifer"								
LSI TC_1	37	0.8277	0.3550	0.3056	0.5960	0.7526	1.0931	1.8685	1.5629	0.87
RSI TC_1	37	5.5838	0.5723	4.2330	5.1057	5.6703	6.0017	6.5889	2.3558	-0.44
PSI TC_1	37	5.2976	0.6073	4.1971	4.7254	5.4413	5.7332	6.3080	2.1109	-0.24
AI	37	11.524	0.334	11.118	11.299	11.400	11.735	12.467	1.349	1.13

TC_1

Terminal complex system "TC 2 aquifer"

LSI TC_2	24	0.8467	0.3302	0.4623	0.6414	0.7466	1.0111	1.9691	1.5068	1.94
RSI TC_2	24	5.485	0.604	3.472	5.278	5.663	5.825	6.175	2.704	-1.85
PSI TC_2	24	5.058	0.692	2.808	4.727	5.292	5.517	5.845	3.037	-1.71
AI TC_2	24	11.542	0.330	11.233	11.338	11.418	11.631	12.744	1.511	2.41

Terminal complex system "TC 3 aquifer"

LSI TC_3	20	1.2296	0.3358	0.7277	0.9539	1.1892	1.4536	1.9429	1.2152	0.63
RSI TC_3	20	4.9188	0.4240	4.0243	4.6848	4.9660	5.2640	5.6846	1.6603	-0.33
PSI TC_3	20	4.8905	0.3083	4.4194	4.6596	4.8557	5.0821	5.5000	1.0806	0.42
AI TC_3	20	11.920	0.317	11.491	11.708	11.848	12.114	12.580	1.089	0.71

Continental intercalary system "Albian aquifer"

LSI CI	14	1.4112	0.3174	0.8722	1.0832	1.5208	1.7087	1.7393	0.8672	-0.39
RSI CI	14	4.7647	0.3060	4.2541	4.5229	4.7286	5.0412	5.3056	1.0516	0.26
PSI CI	14	4.6907	0.3188	3.8045	4.5894	4.7473	4.9253	5.0036	1.1991	-1.81
AI CI	14	12.102	0.348	11.456	11.805	12.236	12.424	12.492	1.036	-0.43

3.5.   Groundwater Softening

Before starting the laboratory experiments, it is recommended to apply the theoretical bases of each method to get an idea about the expected softening rates. The equations involved in the precipitation by addition of lime-soda are shown in formulas 1-4:

$$Ca(HCO_3)_2 + Ca(OH)_2 \rightarrow 2CaCO_3 \downarrow + 2H_2O \dots\dots\dots\dots\dots\dots\dots\dots(1)$$

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$$Na_2CO_3 \ + \ CaSO_4 \rightarrow CaCO_3 \downarrow + Na_2SO_4 \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots..\ldots\ldots..(2)$$

$$Na_2CO_3 \ + \ Ca(OH)_2 \rightarrow CaCO_3 \downarrow + 2NaOH \ \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots..(3)$$

$$2Na(OH) + \ Ca(HCO_3)_2 \rightarrow CaCO_3 \ \downarrow + Na_2CO_3 + 2H_2O\ldots\ldots\ldots\ldots..(4)$$
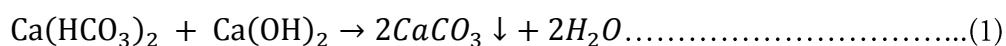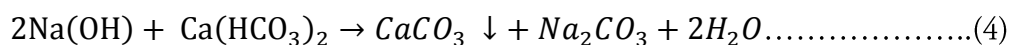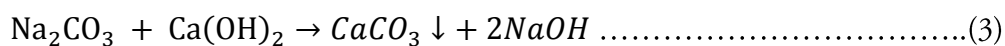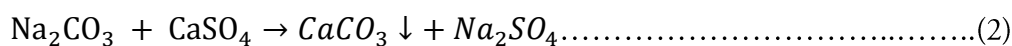
As it is shown in equationsfrom 1 to 4, the initial state of water where the association of calcium (Ca) and bicarbonates (HCO_3) ions presents the carbonatehardness, which is the main problem in our water, the lime (Ca $(OH)_2$) was added in order to get chemical reactions generate calcium carbonates (CaCO3 as a precipitate) and two water molecules(2(H2O)). After that, the addition of soda in form of Na_2CO_3helps in eliminating the second type of hardness which is non-carbonate hardness (hardness related to sulphate association). Thetheoretical reactions are presented in figure 9 using bare diagrams to describe reactions in each step from step 01 (initial water) to step 07 (final water) where all concentrations are in mg/l as $CaCO_3$as described in Desjardin guide [24].
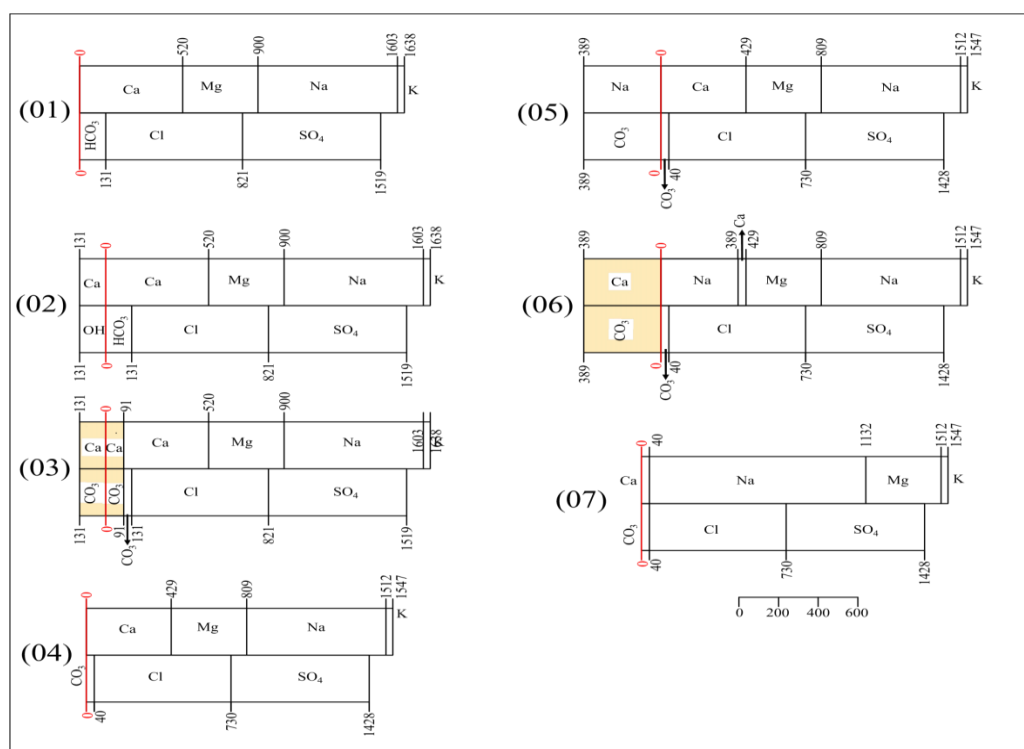
Figure 9: Softening by lime and soda process.

As it is shown in figure 9, the initial state of water (Step 01),the addition of lime (Ca$(OH)_2$) in step 02 need to be in an equivalent amount of existing bicarbonates (131 mg/l as $CaCO_3$ in our case) in order to create an association with initial calcium and bicarbonates, this association produce calcium carbonates($CaCO_3$) as a precipitate which make it easy to removed (Step 3). The step 04 represents the intermediate water state where the next step (Step 05) shows the addition of soda (NaCO3), the amount of added soda needs to be lower than existing calcium amount with 40 mg/l as $CaCO_3$(389 mg/l as $CaCO_3$ in our case) where we register in step 06 the

exchange between calcium and sodium ions. The final concentration of calcium (Ca^{2+}) was found to be 40 mg/l as CaCO3, where the initial concentration was 520 mg/l as CaCO3 which represents an elimination rate of 92.31 %.
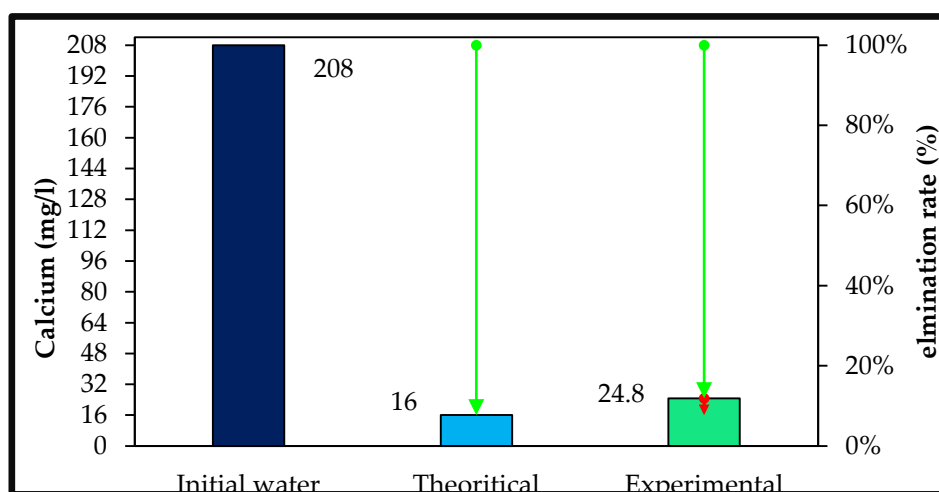

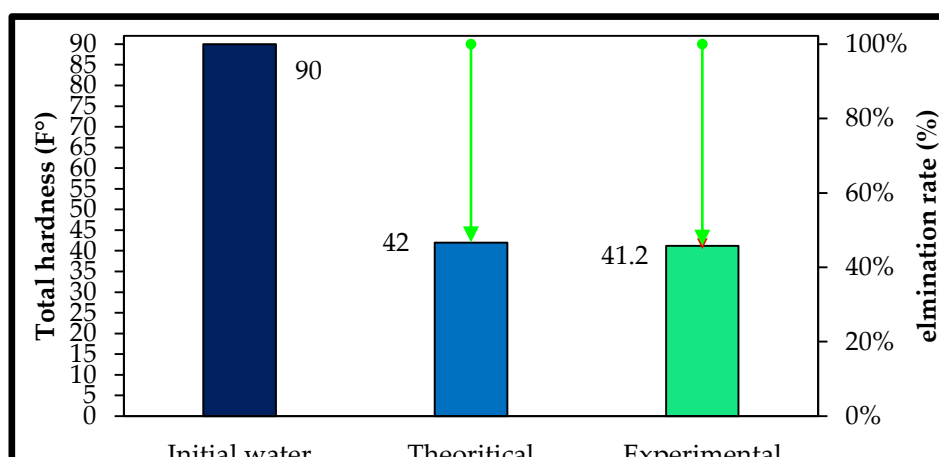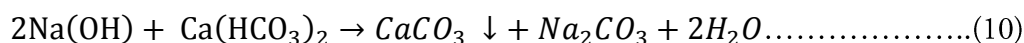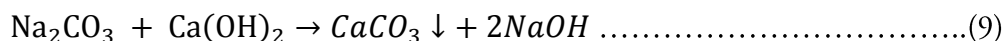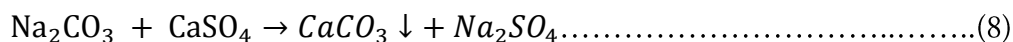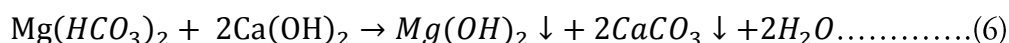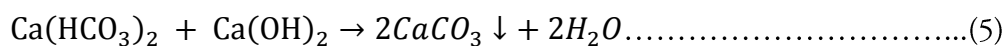Figure 10:Calcium reduction after softening with lime and soda addition.

Figure 11: Total hardness reduction after softening with lime and soda addition.

The theoretical estimation of removal rates was tested with an experimental work. Figures 10 and 11 present initial, theoretical, and experimental results founded for calcium and total hardness removal rates. The left and right axis present concentration and percentages respectively, where the removal rate was presented with a green arrow oriented from top to bottom and the error rate between theoretical and experimental was presented with a red arrow oriented from bottom to top. It's clear from figures that the lime soda process gives great results where the removal rates achieved 88.08% and 54.22% for calcium and total hardness respectively, the error rate between theoretical and experimental results was relatively low with values of 4.23% and 0.89 % for calcium and hardness respectively.

The equations involved in the precipitation by addition of excess lime-soda are shown in formulas 5-10:

$$Ca(HCO_3)_2 \; + \; Ca(OH)_2 \rightarrow 2CaCO_3 \downarrow + 2H_2O\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(5)$$

$$Mg(HCO_3)_2 \; + \; 2Ca(OH)_2 \rightarrow Mg(OH)_2 \downarrow + 2CaCO_3 \downarrow + 2H_2O\ldots\ldots\ldots\ldots(6)$$

$$Ca(OH)_2 \; + \; CO_2 \rightarrow CaCO_3 \downarrow \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(7)$$

$$Na_2CO_3 \; + \; CaSO_4 \rightarrow CaCO_3 \downarrow + Na_2SO_4\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(8)$$

$$Na_2CO_3 \; + \; Ca(OH)_2 \rightarrow CaCO_3 \downarrow + 2NaOH \ldots\ldots\ldots\ldots\ldots\ldots\ldots(9)$$

$$2Na(OH) \; + \; Ca(HCO_3)_2 \rightarrow CaCO_3 \downarrow + Na_2CO_3 + 2H_2O\ldots\ldots\ldots\ldots(10)$$

Reactions steps of excess lime-soda addition are presented in figure 12, where step 01 describes the initial state of groundwater. This method targeted the reduction of calcium and magnesium both. For that, the added quantity of excess lime needs to be 50 mg/l as CaCO3 in addition of the concentration of bicarbonates (HCO_3^-) and magnesium (Mg^{2+}) in the sample, in our case:

Excess lime = [50 + HCO_3^- + Mg^{2+}] = [50 + 131 + 380] = 561 mg/l as $CaCO_3$

Step 02 in the figure presented the addition of the calculated amount of excess lime. After reactions, we see that hydroxide (OH^-) react with bicarbonates (HCO_3^-) which led to the dissolution of this last and the presence of carbonates (CO_3^{2-}), which result a precipitation of bounded ions of calcium (Ca^{2+}) and carbonates (CO_3^{2-}) as shown in step 04,The treated water state after elimination of precipitated $CaCO_3$ is presented in step 5. Parallelly, a reaction between magnesium (Mg^{2+}) and hydroxide (OH^-) occurring (step 06). According to Desjardins recommendation, we leave 40 mg/l from precipitated ($CaCO_3$) and 10 mg/l from precipitated ($Mg(OH)$). Step 07 presentedthe water state after eliminating the recommended quantities of precipitates. In order to dissolute the remaining quantities of precipitates, we proceed to the addition of 50 mg/l of carbon dioxide (CO_2) as shown in step 08. This step results in the presence of 50 mg/l of carbonates after the bound of added CO_2 and the existing OH^-, as we see in step 09, an additional 50 mg/l of $CaCO_3$ precipitate was eliminated. The intermediate water state before adding soda is presented in step 10. The addition of sodium carbonates ($NaCO_3$) in step 11 considered as a second step of reducing calcium amounts where the exchange between sodium and calcium ions and the new created bounds between exchanged calcium and carbonates resulted the presence of calcium carbonates as precipitate as shown if step 12, the final water state presented in step 13 shows final concentrations of calcium and magnesium equal to 40 mg/l and 10 mg/l as CaCO3 respectively.Applying the second softening method (addition of excess lime and soda) resulted in further reductions in the concentrations of calcium, magnesium, and total hardness. The treated water exhibited concentrations of 47.9 mg/l as CaCO3 for calcium, 8.61 mg/l as CaCO3 for magnesium, and 5.7 French degrees for total hardness. Figures 13, 14 and 15 present the expected (theoretical) and the real (experimental) reduction of calcium, magnesium and total hardness respectively.

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Both softening methods effectively reduced the concentrations of calcium and magnesium ions, resulting in decreased total hardness. However, the second method, which involved the addition of an excess of lime and soda, demonstrated slightly better performance in terms of achieving lower concentrations of calcium, magnesium, and total hardness. The addition of lime and soda in the first method led to the precipitation of calcium and magnesium ions as insoluble compounds, thereby reducing their concentrations. However, the excess of lime and soda in the second method ensured the complete precipitation of these ions, resulting in even lower concentrations and improved softening efficiency. The findings of this study suggest that the second softening method may be preferred for applications where stringent limits on calcium and magnesium concentrations, or total hardness are required. However, factors such as cost, availability of reagents, and the specific requirements of the water treatment system should be considered when selecting the most suitable softening method.
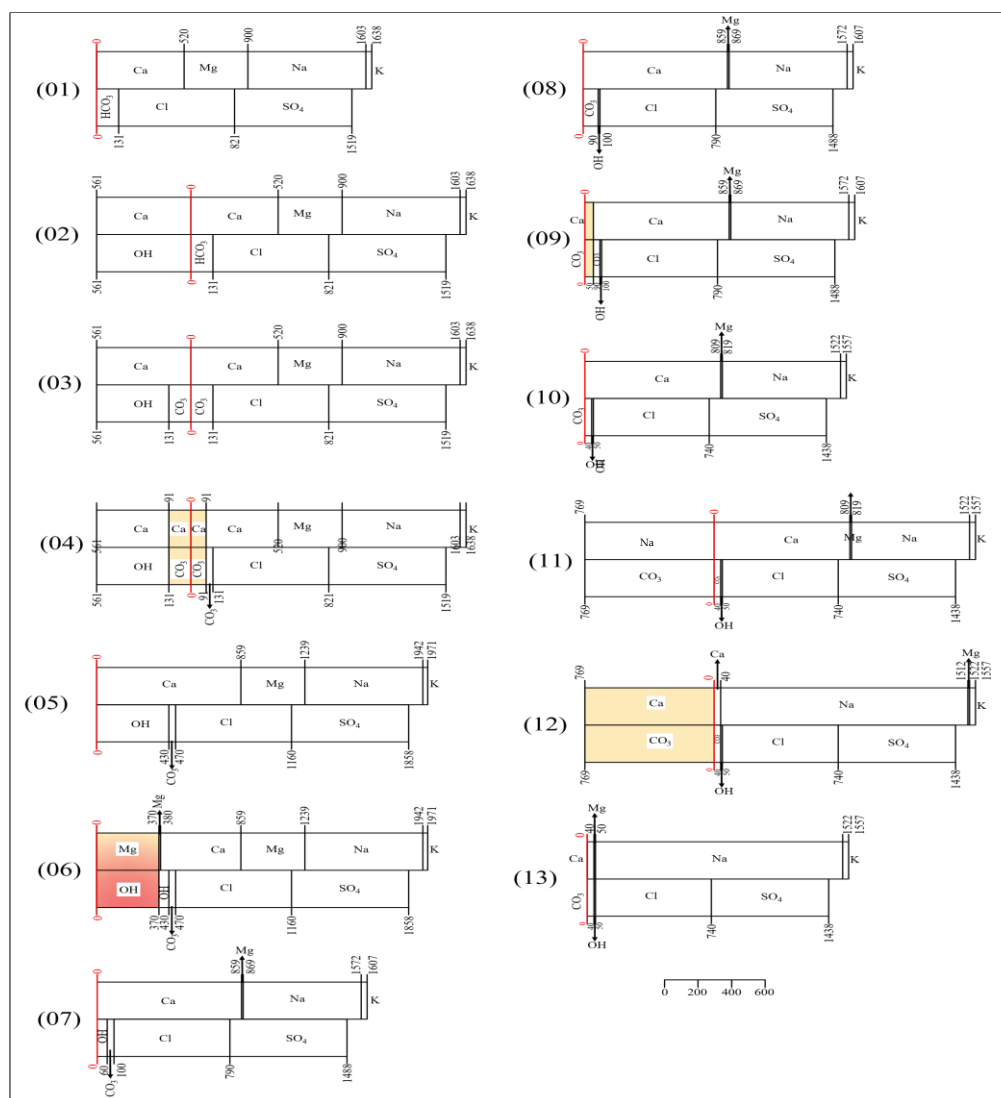

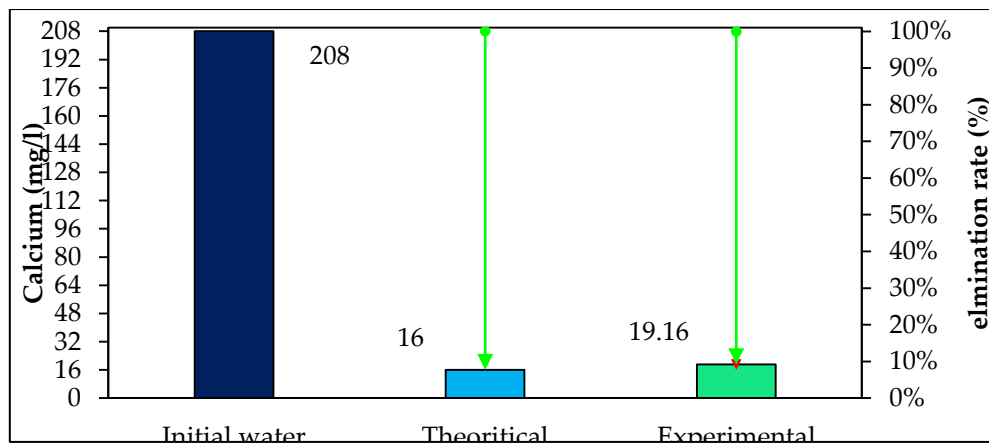**Figure 12:Softening by excess lime and soda process.**

Figure 13: Calcium reduction after softening with excess lime soda addition.
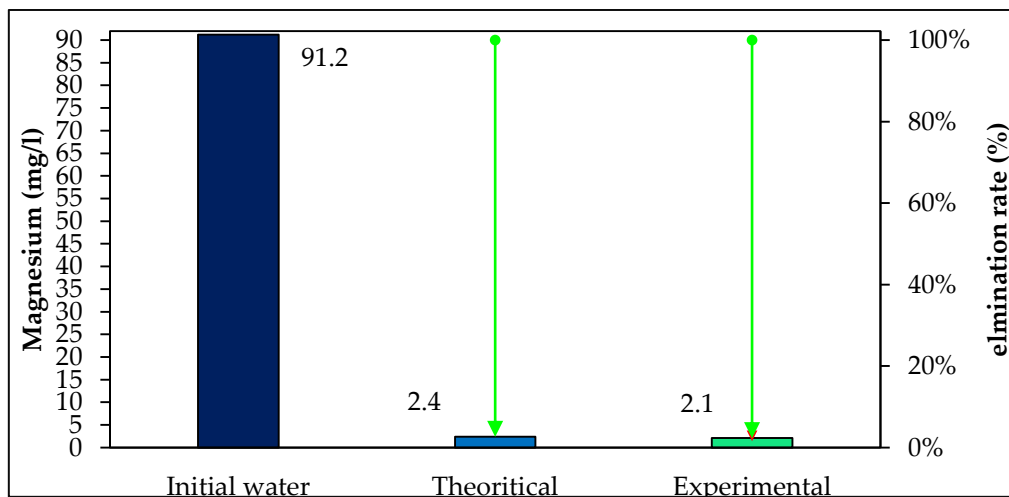

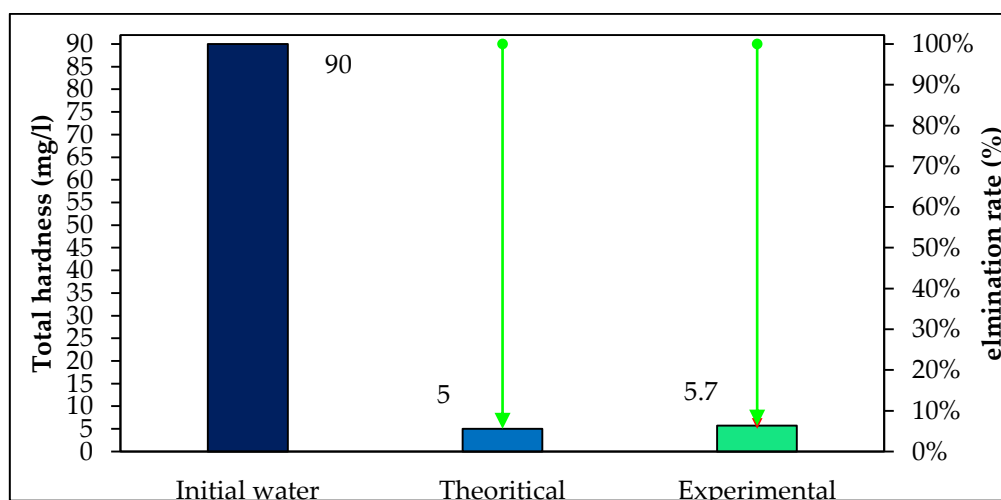Figure 14: Magnesium reduction after softening with excess lime and soda addition.

Figure 15: Total hardness reduction after softening with excess lime and soda addition.

4.   Conclusion

Geological characteristics largely affected the groundwaters quality, where those waters acquire several behaviors based on the geochemical process and interactions conditions. In the south Algerian the groundwater is the main source of water supply where the present study described the Scaling behavior of Touggouret region groundwaters exploited from four aquifers TC1, TC 2, TC 3 and Albian. The results revealed that Touggouret groundwaters characterized with high salinity and high temperature which make the exploitation of such groundwaters difficult. The results of geochemical modeling using PhreeqC model shows that Tougouret groundwaters have a positives saturation value regarding Carbonate rocks presented in Dolomite, Calcite and Aragonite, in the other hand negative saturation indices founded for evaporates rocks (Gypsum and Anhydrite) this results indicate that scaling behavior source is the carbonate rocks.

The comparative study of two softening methods, namely the addition of lime and soda and the addition of an excess of lime and soda, revealed their effectiveness in reducing the concentrations of calcium and magnesium ions, as well as total hardness, in the treated water sample. Both methods successfully achieved substantial reductions in these parameters compared to the initial concentrations in the untreated water. The first softening method, involving the addition of lime and soda, resulted in a considerable decrease in calcium concentration from 520 mg/l as $CaCO_3$ to 62 mg/l as $CaCO_3$. Additionally, the total hardness decreased from 90 French degrees to 41.2 French degrees. This method effectively precipitated calcium and magnesium ions, leading to improved water quality. The second softening method, which utilized an excess of lime and soda, demonstrated even better performance. It resulted in lower concentrations of calcium, magnesium, and total hardness compared to the first method. The treated water exhibited concentrations of 47.9 mg/l as $CaCO_3$ for calcium, 8.61 mg/l as $CaCO_3$ for magnesium, and 5.7 French degrees for total hardness. The excess of lime and soda ensured complete precipitation of calcium and magnesium ions, resulting in superior softening efficiency. Based on the findings, the second softening method appears to be more effective in achieving lower concentrations of calcium, magnesium, and total hardness. Therefore, it may be preferred in applications where strict limits on these parameters are required. However, practical considerations such as cost, availability of reagents, and system requirements should also be taken into account when selecting the appropriate softening method.

Further research can be conducted to optimize the softening process, explore the long-term stability of the treated water, and investigate the potential impacts on other water quality parameters. Additionally, economic analyses should be performed to evaluate the cost-effectiveness of both methods for large-scale implementation in water treatment facilities. In conclusion, this study highlights the successful elimination of calcium and magnesium ions, as well as the reduction of total hardness, through the application of lime and soda in two different softening methods. These findings contribute to the understanding of effective water treatment

techniques for the removal of hardness-causing ions, ultimately leading to improved water quality and various practical applications.

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