



Environmental Science

An Indian Journal

Current Research Paper

ESAIJ, 9(1), 2014 [23-30]

Determination of calcium, magnesium, bicarbonate and sulfate in wells of Tiykomiyne area, Talsint region (Eastern Morocco) by ionic chromatography

H.Taouil^{1*}, S.Ibn Ahmed¹, A.El Assyry², A.Daagare³, R.Touir⁴

¹Laboratoire de Synthèse Organique et Procédés d'Extraction, Université Ibn Tofail.

Département de Chimie, B.P. 133, 14000 Kenitra, (MAROC)

²Laboratoire d'Optoélectronique et de Physico-chimie des Matériaux, Université Ibn Tofail,

Département de Physique, B.P. 133, Kénitra, (MAROC)

³Laboratoire des Essais Biologiques -Unité de Pharmacologie, Faculté des Sciences - Université Ibn

Tofaïl, Kénitra, Maroc, B.P. 133, Kénitra, (MAROC)

⁴Laboratoire des Matériaux, d'Electrochimie et d'Environnement, Université Ibn Tofail,

Faculté des sciences, BP 133, 14000 Kenitra, (MAROC)

E-mail : Hamidsup@yahoo.fr

ABSTRACT

Applications using supercritical water often encounter the presence of inorganic compounds in feed streams, most often with a minor concentration. These compounds can lead to damage of the equipment via erosion, scaling and corrosion or can influence and disturb the main reaction and processes inside the systems. In order to avoid these problems and to predict the influence of these compounds, it is vital to possess knowledge of the chemical composition of the most common inorganic compounds in supercritical water. For this, the spatial variation of calcium, magnesium, bicarbonate and sulfate were investigated during low flow periods of the year 2011 at five wells level in the Tiykomiyne area, Talsint region, eastern Morocco, using ionic chromatography method. The obtained results show that in the majority of wells, their values are higher than the values set by the WHO (Ca^{2+} : 270 mg L⁻¹; Mg^{2+} : 50 mg L⁻¹ and SO_4^{2-} : 500 mg L⁻¹). However, the total permanent hardness values in all studied stations were found higher indicating that these waters are very hard. These can be explained by the calcareous nature of the geological terrain where traversed by water. Finally, the majority of the studied water wells have a scale or corrosion character. This result limits the use of groundwater as drinking and cooling water in this area. © 2014 Trade Science Inc. - INDIA

KEYWORDS

Ionic chromatography method;
Wells water analysis;
Hardness;
Scale and corrosion;
Sulfate.

Current Research Paper

INTRODUCTION

Since its introduction in 1975 by Small et al.^[1], ion chromatography (IC) has emerged as a very powerful method for analysis of anions and cations in a variety of environmental samples, especially aqueous solutions^[2-5]. IC offers a number of advantages over alternative analytical methods in terms of speed, sensitivity, selectivity, simultaneous determination ability, stability and reliability^[2]. However, anions and cations cannot be separated simultaneously in the same column in a conventional ion chromatographic system. In fact, one of the most effective developments in ion chromatography has been the introduction of procedures that allow the simultaneous separation of metal cations and simple inorganic anions^[6,7]. These methodologies include both suppressed and non-suppressed techniques.

In addition, in most cases, scales are made of calcium salts: carbonate, sulfate or phosphate. Because of their poor thermal conductivity and their good adherence to the walls, these mineral compounds decrease the heat transfer rate, reduce the water flow rate and even shorten equipment life by corrosion. Calcium sulfate is the major constituent of scales in thermal desalination plants where brackish waters and sea waters are treated^[8-11]. There are three main forms of calcium sulfate: calcium sulfate dehydrate or gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), calcium sulfate hemihydrate ($\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$) and anhydrite (CaSO_4). When it is precipitated from an aqueous solution, gypsum is preferentially formed at temperatures at least as high as 100 °C.

In the area Tyikomiyne (people) region of Talssint, the water wells were used for drinking and irrigation, but the geological nature of the soil in this area is likely to cause contamination of the water by calcium, magnesium and sulfates ions. So this may be limited the opportunities to use the groundwater in the region. Indeed, these elements can migrate and reach groundwater, accumulate in the food chain and pose risks to human health^[12].

However, the calcium has beneficial effects. Indeed, it can block the absorption of heavy metals, increasing bone mass and prevent certain types of cancer. Then, at very high concentrations, the calcium can have negative effects on the absorption of other essential minerals for human body.

In addition, magnesium can provide drinking water an unpleasant taste. For some people, just a concentration of 100 mg L⁻¹, but for most people, this concentration should be about 500 mg L⁻¹. These concentrations are far superior to those that have the most water. In drinking water, magnesium can have a laxative effect, especially if the concentrations of magnesium sulfate are greater than 700 mg L⁻¹. However, the human body tends to adapt to the laxative effect.

In the other hand, sulfate is a major component of dissolved in rainwater compounds. High concentrations of sulfate in drinking water can have a significant laxative effect combined with calcium and magnesium, the two major components of water hardness. Sulfate can be attacked by bacteria which reduces hydrogen sulfide (H_2S).

For this purpose, the maximum sulfate level suggested by the WHO guidelines for the required quality of water intended for consumption, according to the Geneva Accords in 1993 is 500 mg L⁻¹. The EU standards which are more recent, 1998, complete and stringent than WHO standards suggesting a maximum of 250 mg L⁻¹ of sulfate in water intended for human consumption.

So, a complete analysis of the current situation of pollution calcium, magnesium and sulfates and rigorous monitoring of its evolution are needed to judge the quality of these waters and its impact on the environment state in this region.

Therefore, our work has focused on the impact study of calcium, magnesium, hydrogen carbonate and sulfates on the water wells quality using ion chromatography and on the environment of Tyikomiyne area of Talssint region.

MATERIALS AND METHODS

Study area

The Talssint region belongs to the Eastern High-Atlas domain, part of the eastern region, putting it in contact and regions Tafilalt-Meknes and Fes-Boulmane. Our medium study concerns the wells waters of the Tyikomiyne, region Talssint area, to our knowledge, has been no previous academic study^[13], and it is delimited by:

- Agglomerations Douars “Ezzaouia” south,
- The area “Affia” north
- The RP601 regional road towards “ Beni-Tadjit” west
- Jbal Alaajra, at the east.

In order to determine the quality of calcium, calcium, magnesium and sulfates on the water wells quality of Tyikomiyne area, five wells stations were selected. These stations are denoted such as shown in TABLE 1.

These stations are located on the map below (Figure 1), which represents the location of water wells of Tyikomiyne Talssint region (eastern Morocco).

Bioclimatic map

This region is characterized by pre-Saharan and Saharan environments. Thus, it was high in the summer and very cold in the winter. So, the average minimum of the coldest month (January) was $-5\text{ }^{\circ}\text{C}$ and the average maximum of the hottest month (July) was $47\text{ }^{\circ}\text{C}$.

The average annual rainfall was about 245 mm for 1983/2007 period with large inter-annual variations. It was about 500 mm for 2008/2010 period: the extremes recorded are 61 mm in 1998-1999 and 684.5 mm in 2009/2010^[15].

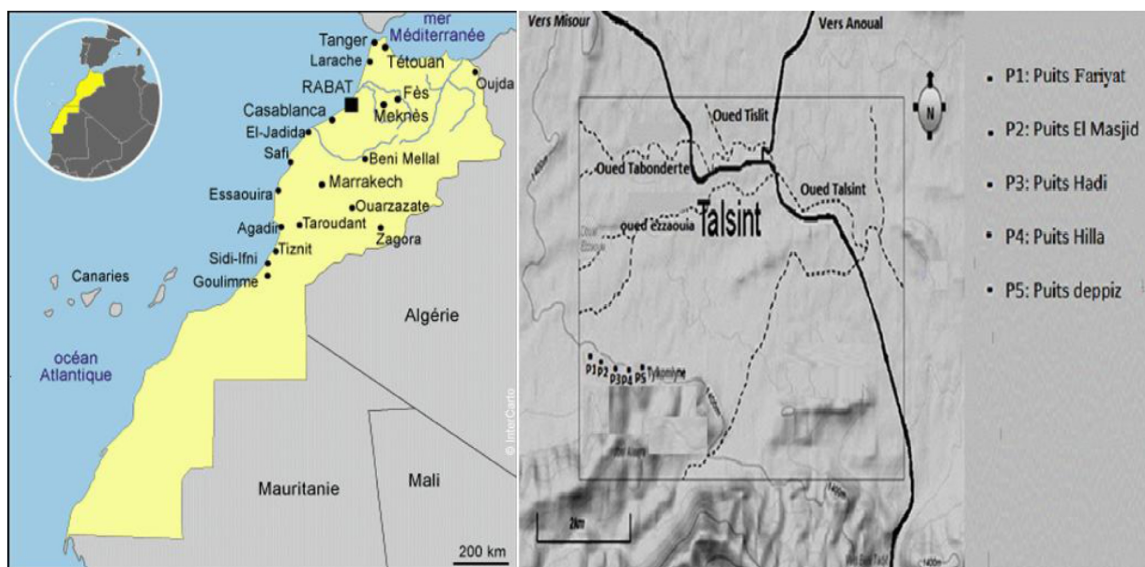


Figure 1 : Location water wells of Tyikomiyne Talssint region

TABLE 1 : Names of wells in the Tyikomiyne area^[14].

Well 1 : P1	Well 2 : P2	Well 3 : P3	Well 4 : P4	Well 5 : P5
Faryat	El Masjid	Hadi	Hilla	Deppiz

Analysis method

The water samples were stored in polyethylene bottles thoroughly cleaned beforehand with a slightly acidified solution, then rinsed several times with distilled water^[16]. These Water samples, used for the determination of heavy metals, are treated in the terrain with ultra pure HNO_3 .

An ICS-3000 system (UATRS, Morocco), which offers a range of modules without reactive ion chromatography (Reagent FreeTM, RFITM). This system combines the automatic generation of eluents and removing self regenerated to make the ion chromatography easier and more efficient. Also, ICS -3000 is characterized

by the presence of three

detectors, two conductivity and amperometric; ability to facilities several types of separation columns for different applications and automatic sample. All elements were determined using this method after filtration of the water by a filter with $0.45\text{ }\mu\text{m}$ of porosity.

RESULTS AND DISCUSSION

Calcium

Calcium is an alkaline earth metal, the major water hardness component, its content varies largely depending on the traversed terrain nature. It is the most common element in the nature (carbonates, etc.), especially in the form of bicarbonates, sulfates or chlorides. It holds its overall value from the geological nature of the environment in particular large masses of the organogenic rock^[17].

Current Research Paper

Therefore, it is necessary, to note that the Ca^{2+} content is high where the water flows through the carbonate facies. So, the Ca^{2+} contents seem to be so closely linked to the land nature^[17].

However, the calcium ions result from attack by water containing carbon dioxide of limestone or simple dissolution of sulfates such as gypsum^[18]. In addition, this element plays an essential role in the skeletons and shells formation, and the phenomena of cell permeability, it is concentrated by organisms from water or food^[18].

It can not in any way problematic for drinking water, the only disadvantage of domestic high hardness scaling while very soft water can cause problems such as pipes corrosion^[19]. It is responsible for water hardness. The water hardness is expressed by total hardness in French degrees ($20^\circ \text{F} = 4 \text{ mg L}^{-1} \text{ calcium}$)^[20].

For this, analyses of five wells have been studied in this region. The obtained results are presented in Figure 2. It is noted that calcium ion content are highly variable from one well to another. So, the highest content (396.49 mg L^{-1}) was recorded in well 2, while the lowest value (257.69 mg L^{-1}) was recorded in well 3. In addition, it is remarked that all measured values are higher compared to the values reported in other regions of Morocco^[18,21-22]. This water is hardness scaling and corrosive such as mentioned in our previous works^[21-25].

However, in the majority of stations, the obtained values of calcium are relatively higher than the standards guideline value set by WHO (270 mg L^{-1}) and the Algerian potability water (200 mg L^{-1})^[26]. Another study was carried out on North-East of the web Makian (Northeast Algeria)^[27], they found the most wells (92.85%) have higher content of the standard water potability some values reached 845 mg L^{-1} .

Magnesium

Magnesium is one of the most common elements in the nature. It constitutes about 2.1% of the Earth's crust. This is a significant component of water hardness. The magnesium ions content in the water depends on the nature of the terrain where it crosses and can be high in water through the rich in MgSO_4 ^[17]. He showed that the contents magnesium ions are related to the presence of magnesium-sedimentary rocks which enrich the

existing sources in the Bou Regreg area. So, these ions come, as calcium ions, from the carbonated compounds dissolution rich in magnesium^[27].

Figure 3 shows the obtained results analysis for five wells. It is observed that that the average contents of magnesium ions was between 53.08 mg L^{-1} (well 3) and 80.96 mg L^{-1} (well 2). These values are relatively low compared to other studies reported in the Morocco (regions of Tafilalet and Marrakech) where the average contents of Mg^{2+} are very high in the majority of water wells^[18] and are greater than indicated by the WHO (50 mg L^{-1}). This may be due to the dolomitic nature of the region through by water^[18].

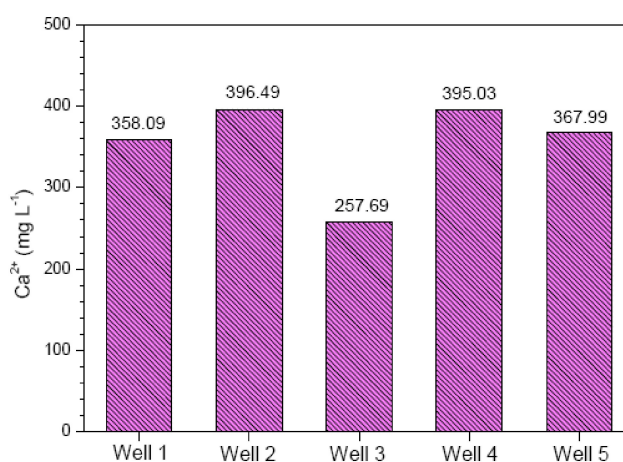


Figure 2 : Spatial variation of the average content of calcium ions in the water wells of Tyikomiyne

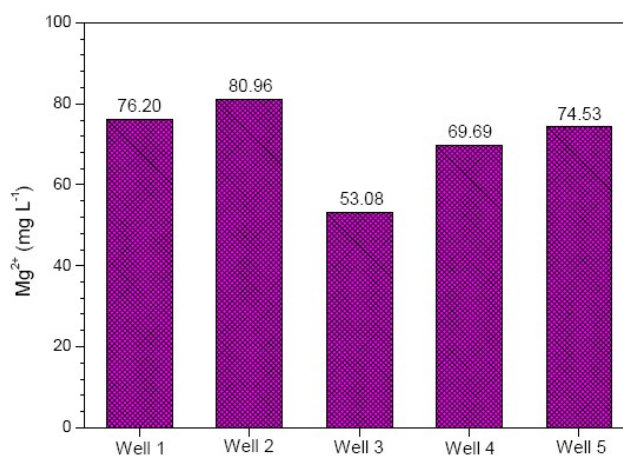


Figure 3: Spatial variation of the average content of magnesium ions in the water wells of Tyikomiyne

Total permanent hardness

Total hardness of water is the sum of the metal cations concentrations other than alkali metal and hydrogen ions^[18]. The water hardness is due to the presence

of divalent metal ions such as Ca^{2+} , Mg^{2+} , Fe^{2+} , Mn^{2+} , Sr^{2+} , etc. the most abundant ions are Ca^{2+} et Mg^{2+} ions^[28].

Thus, water hardness was calculated from measured Ca and Mg concentrations using the method described in APHA et al. (i.e. $2.5 [\text{Ca}] + 4.1 [\text{Mg}]$)^[29].

Figure 4 shows the obtained results of the total permanent hardness of water for five wells. It is noted that the total hardness of water of the studied stations varies from one station to another and all water are very hard. It is also found that these values are higher which may be due to the calcareous nature of the geological terrain traversed by water. It can say that the majority of the studied waters are very hard ($> 300 \text{ mg L}^{-1}$) [30]. The same result was obtained by Alami when he studied the groundwater in the region M'nasra located in the Gharb region (northwestern Morocco)^[28].

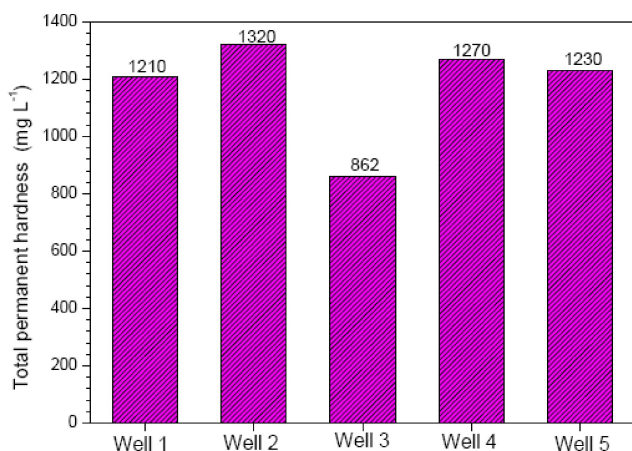


Figure 4 : Spatial variation of the average of total permanent hardness in the water wells of Tyikomiyne

Bicarbonate

Figure 5 shows the obtained results of the bicarbonate (hydrogen carbonate) of water for five wells. It is noted that the bicarbonate values in the studied stations varies from one station to another. It is also found that these values are higher which may be due to the calcareous nature of the geological terrain traversed by water.

However, the pH of the water well is generally between 7 and 9 (TABLE 2) which it is shown that at the pH from 7 to 8, less than 2% of the carbonates are in the form of CO_3^{2-} and the majority is HCO_3^- ion^[31].

In the previous results, all wells water contains calcium and bicarbonate ions, the reaction shifts to the calcium carbonate precipitate formation according to

the reaction:



This is a fundamental thermodynamic condition for the formation and dissolution of scale. Thus, it can see that the scale phenomenon is controlled by the equilibrium concentration of Ca^{2+} ions and CO_3^{2-} ions. This depends mainly on the temperature, pressure and the concentration of free ions in the water.

In addition, the chemical reaction causing the precipitation of calcium carbonate is widely promoted by increasing of temperature, releasing carbon dioxide, accelerates the scale formation. So, there is little or no scaling on cold water. In contrast, hot water circuits represent a favorable field of scale

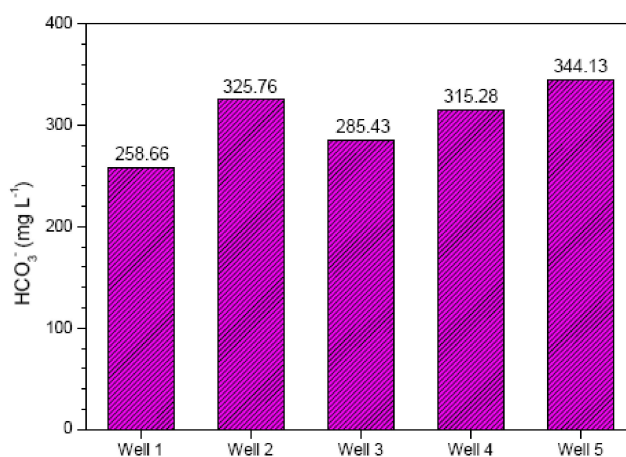
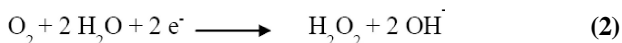


Figure 5 : Spatial variation of the average of bicarbonate in the water wells of Tyikomiyne

However, scale formation is determined using one of the three indices of incrustation. For this, we determined the Langelier Saturation Index (LSI) and Rysnar Saturation index (RSI) using the parameter values listed in the literature^[32-34]. The obtained results of different water wells are presented in Table 2. It is remarked that the Langelier Saturation Index (LSI) values are positive which justified by the calcium carbonate formation in these conditions. In addition, the Rysnar Saturation index values indicate that all water wells have a little scale or corrosion excluding wells 2 and 4 which have a little scale. These can be explained by the large amount of dissolved oxygen diffusion while increasing the hydroxyl OH^- amount formed according two reactions:



Current Research Paper

However, the OH⁻ ions formed induce an increase in the pH values of all water well, which causes the calcium carbonate precipitation^[35]. Lee et al.^[36] are observed at pH = 7.9 the scale deposits are thinner

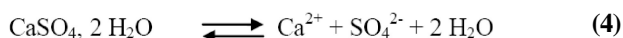
than those formed in solutions with a pH of 8.3. According our previous study for the use of water in cooling system where our conditions are T= 32 °C and pH = 7.35, these water are very scaling^[21-25].

TABLE 2 : Scaling and corrosion severity of the studied wells water

Wells	T (°C)	pH	Conductivity (μS/cm)	pH _s (LSI /RSI)	LSI	RSI	Characteristics
1	12.9	8.01	1320	7.2/7.1	0.77	6.1	LSI : Scale forming but non corrosive RSI :Little scale or corrosion
2	13	8.17	1290	7.1/6.9	1.1	5.7	LSI : Scale forming but non corrosive RSI :Little scale
3	12.6	8.04	1300	7.3/7.2	0.70	6.3	LSI : Scale forming but non corrosive RSI :Little scale or corrosion
4	12.4	8.00	1420	7.1/7.0	0.86	5.9	LSI : Scale forming but non corrosive RSI :Little scale
5	12.9	7.73	1250	7.1/6.9	0.64	6.1	LSI : Scale forming but non corrosive RSI :Little scale or corrosion

Sulfate

The presence of sulfates in water may be related to the dissolution of gypsum, according to the following reaction:



or to sulphide oxidation or it can be to anthropogenic in connection with an industrial or urban pollution^[18]. The wells surveyed by Boutin and Dias^[37] in the area of wastewater application from the Marrakech city of showed that the sulfate content ranging from 100 to 200 mg L⁻¹ while these values were less which their ranging from 20 to 120 mg L⁻¹ in the Tiznit region^[38]. The work have shown that the highest values of sulfate ion are recorded during the low water period in the water of Meskiana (North-eastern Algeria) with an average of 472 mg L⁻¹, following the evaporation phenomenon and 83.5 % of the wells exceeded the standard value (250 mg L⁻¹) for drinking water^[27].

In our case, the SO₄²⁻ contents vary from one well to another and their values from 680.80 mg L⁻¹ in the well 3 to 1267 mg L⁻¹ in well 2 (Figure 6). These values are very higher where the Moroccan standards of water quality for the drinking water production require a 'limit' of 200 mg L⁻¹ of sulfate. Indeed, according to WHO, all wells do not meet the standard value (250 mg L⁻¹). Therefore, the levels of sulfate may contribute to the contamination of water wells and springs in the area.

However, the sources of pollution by sulfates are many such as food, agricultural oil industry, and textile.

Since the locality Tyikomiyne has no industrial activity, therefore the source of pollution by sulfate in the studied waters may be related to the dissolution of gypsum according to equation (4).

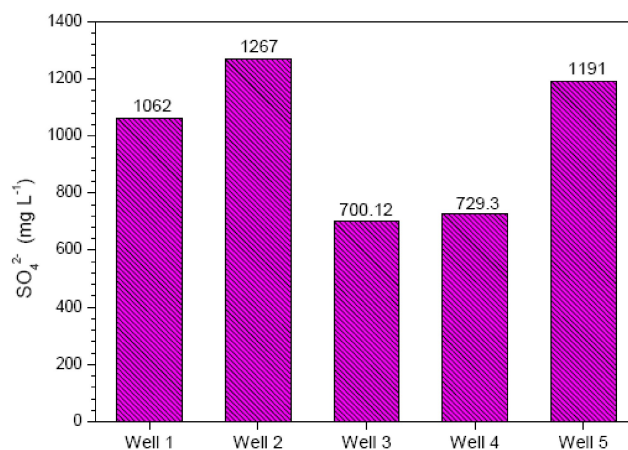


Figure 6 : Spatial variation of the average content of sulfates ions in the water wells of Tyikomiyne

CONCLUSION

The spatial variation of calcium, magnesium, bicarbonate and sulfate were investigated during low flow periods of the year 2011 using ionic chromatography method. The obtained results show that in the majority of wells, their values are higher than the values set by the WHO. In addition, the total permanent hardness values in all studied stations were found higher indicating that these waters are very hard. The determination LSI and RSI indicated that the studied waters have

scale character. These results limit the use of ground-water as drinking and cooling water in this area.

ACKNOWLEDGMENTS

Thanks are due to the National Centre of Scientific and Technical Research (CNRST)-Morocco.

REFERENCES

- [1] H.Small, T.S.Stevens, W.C.Bauman; *Anal.Chem.*, **47**, 1801 (1975).
- [2] P.R.Haddad, P.E.Jackson; *Ion Chromatography-Principles and Applications*, Elsevier, Amsterdam, (1991).
- [3] B.López-Ruiz; *J.Chromatogr. A*, **881**, 607 (2000).
- [4] G.Fernández, J.I.García-Alonso, A.Sanz-Medel; *Journal of Chromatography A*, **1033**, 127–133 (2004).
- [5] T.Williams, N.W.Barnett; *Analytica Chimica Acta*, **259**, 19–23 (1992).
- [6] V.K.Jones, J.C.Tarter; *Analyst*, **113**, 183 (1988).
- [7] P.V.Nesterenko; *Trends Anal. Chem.*, **20**, 311 (2001).
- [8] S.Ben Ahmed, M.M.Tlili, M.Ben Amor, H.Ben Bacha, B.Elleuch; *Desalination*, **167**, 311–318.
- [9] H.A.El Dahan, H.S.Hegazy; *Desalination*, **127**, 111–118.
- [10] M.M.Tlili, A.Korchef, M.Ben Amor; *Chemical Engineering and Processing*, **46**, 1243–1250.
- [11] M.M.Tlilia, P.Rousseau, M.Ben Amor, C.Gabrielli; *Chemical Engineering Science*, **63**, 559–566 (2008).
- [12] B.Jourdan, P.Piantone, C.Lerouge, D.Guyonnet; *Atténuation des métaux à l’aval de sites de stockage de déchets, Synthèse bibliographique. Rapport BRGM/RP-54417-FR*, 110 (2005).
- [13] H.Taouil, S.Ibn Ahmed, N.Hajjaji, A.Srhiri, A.El Assyry, F.El Omari; *ScienceLib*, **5(130401)**, 2111–4706 (2013).
- [14] H.Taouil, S.Ibn Ahmed, A.El Assyry, N.Hajjaji, A.Srhiri, F.Elomari, A.Daagare; *International Journal of Agricultural Policy and Research*, **1(5)**, 150–155 July (2013).
- [15] H.Taouil, S.Ben Ahmed, N.Hajjaji, A.Srhiri; *ScienceLib*, **4(120111)**, 2111–4706 (2012).
- [16] AFNOR; *Echantillonnage. Précaution à prendre pour effectuer, conservé et traiter les prélèvements*, T90-100 (1972).
- [17] R.Kourradi; *Thèse de Doctorat national, Université Mohammed V-Agdal, Faculté des sciences Rabat, Maroc*, (2007).
- [18] Ali Ait Boughrous; *Thèse de Doctorat national, Université Cadi Ayyad, Marrakech, Maroc*, 46 (2007).
- [19] D.Gaujous; *La pollution des milieux aquatiques : aide-mémoire. 2^{ème} Edition*, 217 (1995).
- [20] P.Queneau, J.Hubert; *Place des eaux minérales dans l’alimentation. Rapport de l’académie national de médecine. Société française de l’hydrologie et climatologie médicale. France.*, 175-220 (2009).
- [21] R.Touir, M.El Bakri, N.Dkhireche, M.Ebn Touhami, A.Rochdi; *J.Mater. Environ. Sci.*, **1(S1)**, 317-328 (2010).
- [22] R.Touir, N.Dkhireche, M.Ebn Touhami, M.Lakhrissi, B.Lakhrissi, M.Sfaira; *Desalination*, **249**, 922–928 (2009).
- [23] R.Touir, M.Cenoui, M.El Bakri, M.Ebn Touhami; *Corrosion Science*, **50**, 1530–1537 (2008).
- [24] N.Dkhireche, A.Dahami, A.Rochdi, J.Hmimou, R.Touir, M.Ebn Touhami, M.El Bakri, A.El Hallaoui, A.Anouar, H.Takenouti; *Journal of Industrial and Engineering Chemistry*, <http://dx.doi.org/10.1016/j.jiec.2013.03.012>, (2013).
- [25] N.Dkhireche, R.Abelhadi, M.Ebn Touhami, H.Oudda, R.Touir, M.Elbaoui, M.Sfaira, B.Hammouti, O.Senhaji, R.Taouil; *Int.J.Electrochem. Sci.*, **7**, 5314 - 5330 (2012).
- [26] E.Vierling; *Aliment et boissons : filière et produit. 3^{ème} Edition. Centre régional de documentation pédagogique d’Aquitaine. France.*, 230 (2008).
- [27] L.Gouaidia; *Thèse de Doctorat, Université Badji Mokhtar –Annaba- Algérie*, (2008).
- [28] I.Alami; *Thèse de Doctorat, discipline : science de l’environnement, université Ibn Tofail*, (2004).
- [29] Apha, Awwa, Wef; *Standard Methods for the Examination of Water and Wastewater*, 20th ed. American Public Health Association, American Water Works Association and Water Environment Federation, Washington, DC, (1998).
- [30] ONEP : *Traitement de l’eau potable, caractéristiques physico-chimique des eaux*, Maroc Mars (1998).
- [31] S.F. Mulford; *School control in sea water Evaporators Saline Water conversion progress report, n°133, OSW, Dep. Of the nation, Nov.* (1964).
- [32] W.F.Langelier; *J.Am.Water Works Assoc.*, **28**, 1500 (1936).
- [33] K.Rafferty; *Scaling in geothermal heat pump systems*, U.S. Department of Energy, July (1999).

Current Research Paper

- [34] Metcalf, Eddy; Wastewater Engineering Treatment and Reuse, (2003).
- [35] R.Ketrane, L.Leleyter, F.Baraud, O.Gil, B.Saidani; 12^{ème} Colloque National de la Recherche en IUT, Brest, 1-2 juin (2006).
- [36] R.U.Lee, J.R.Ambrose; Corrosion congress, paper n°294, (1986).
- [37] C.Boutin; Sensibilité à la pollution et répartition de quelques espèces de Crustacés phréatobies à Marrakech (Maroc occidental). Mém. Biospéol., Moulis, **11(38)**, 55-64 (1984).
- [38] M.BoulalL; Thèse de 3ème Cycle, Faculté des sciences, Semlalia, Marrakech, Maroc, 228 (1988).