Mater. Environ. Sci. 7 (10) (2016) 3875-3884 *Hayani et al.*
ISSN : 2028-2508
CODEN: JMESCN

Softening of hard water by ion-exchange with strongly acidic cationic resin. Application to the brackish groundwater of the coastal area of El Jadida province (Morocco)

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Received 10 Feb 2016, Revised 05 Jul 2016, Accepted 07 Jul 2016
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Abstract
In this work, the resin Duolite 206A has been tested for softening, on the one hand, synthetic water containing Ca^{2+} and Mg^{2+}, and secondly, brackish groundwater from the coastal area of El Jadida province (Morocco). After studying the effect of the feed rate on the treatment of synthetic waters based on $CaCl_2$, $2H_2O$ and $MgCl_2$, $6H_2O$, the effect of salinity and pH on the cationic exchange efficiency was evaluated. The obtained results revealed that the treatment of water by the resin Duolite 206A is not overly influenced by the NaCl concentrations below 2 $g.l^{-1}$. However, treatment of water strongly acidic on exchange resin is characterized by a decrease of Ca^{2+} and Mg^{2+} ions removal efficiency because of their competition with H^+ ions. Groundwater of the coastal area located between Sidi-Abed and Ouled-Ghanem of El Jadida province (Morocco) have pH close to neutral, thus competing with H^+ ions is nonexistent when softening on the resin. The treated water at 20 minutes from the start of the filtration, using 20 g of the resin and a flow rate of about 6.1 $l.h^{-1}$, is characterized by a reduction of approximately 63–70% and 54–55% of Ca^{2+} and Mg^{2+} ions, respectively. Beyond this time the residual ionic concentration increases to reach the initial concentration C_0. The regeneration tests showed that a solution of NaCl at 10 $g.l^{-1}$ seems very suitable to regenerate rapidly the resin Duolite 206A saturated with calcium or magnesium ions.

Keywords: Hard water; Groundwater; Salinity; Softening; Ion-exchange; Duolite 206A.

1. Introduction
The sources of water pollution are various and multiple. Currently, the increase in population and the intensification of socio-economic activities are accompanied by large discharges which cause pollution of ground and surface water [1-6]. Ground waters, often geologically protected, are exposed to several categories of pollution having agricultural, industrial and/or urban origins [7]. Surface waters are also threatened by pollutant discharges from different sources (industrial, domestic, agricultural, atmospheric, thermal, etc). On the other hand, the nature of traversed medium may substantially influence the water hardness expressed in terms of calcium and magnesium salts.
The implementation of water treatment systems is essential and urgent to meet the needs of increasingly rising of water requirement in different sectors (drinking water, agriculture, industries, etc.). Among the techniques that may can reduce or eliminate the salt contents of hard waters, the ion-exchange methods on synthetic resins can be cited [8-11]. The ion exchangers are insoluble macromolecules (resin) including ionizable groups having the property of reversibly exchanging and some of their ions, in contact with other ions from water. The synthetic resins have often been used on softening; they are based on a modified-polymer such that ionic groups are present on its chains. If the resin is a cation exchanger, the polymer attracts the positive ions by the presence of negatively charged groups. Treatment on resin ion exchangers is a process widely used currently in softening and demineralization of natural waters, in chemical separation for analytical purposes, in treatment of industrial

wastewater and also in the recovery and recycling of metals released by certain industries such as surface treatment workshops [12].

In this research work, Duolite 206A resin has been used for the softening of synthetic hard water and natural groundwater. The main goals of the present study is to perform treatments in dynamic mode in order to (i) justify the applicability of this ion exchange resin in hard water softening; (ii) determine the influence of sodium chloride concentration on softening; and (iii) develop applications on groundwater of the region located between Sidi-Abed and Ouled-Ghanem (El Jadida province) which have relatively high calcium and magnesium contents.

2. Materials and methods

2.1. Resin « Duolite 206A »

Duolite 206A is a polystyrene strong acid cation resin with sodium ion as exchangeable element. This resin is manufactured by Rohm and Haas from synthetic material. Its behavior and their characteristics in batch mode were studied in our previous works [13].

Before each use, the resin is immersed in NaCl solution, 0.1 mol l^{-1} during 12 h. Duolite 206A is then washed several times by distillated water at ambient temperature in order to eliminate all salt traces.

2.2. Filtration system

The experimental system used during treatment tests in continuous mode, is composed by a cylindrical Pyrex glass column of 27 cm as height and 1.5 cm as internal diameter (Figure 1). The height of the bed of the Duolite 206A is 25 cm which is equivalent to 16.5 cm^3 as volume and 20 g as mass of this resin. The water circulation through ionic exchange column has been ensured through a peristaltic pump with adjustable flow.

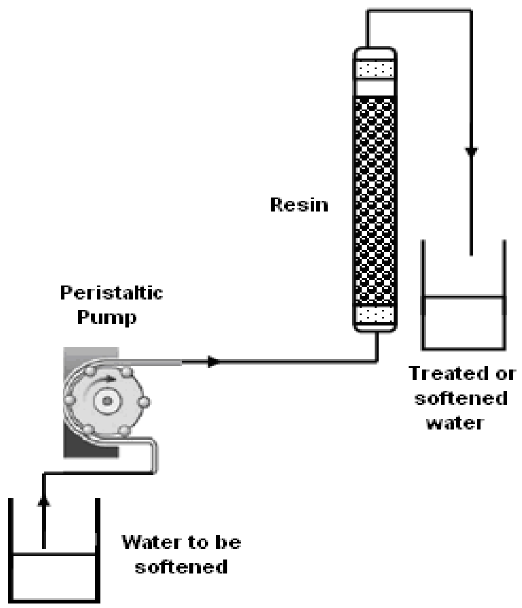

Figure 1: Scheme of the experimental system used in dynamic mode.

2.3. Softening tests

Firstly, the softening of synthetic solutions containing calcium chloride dihydrate $CaCl_2$, $2H_2O$ (98%, Prolabo) or magnesium chloride hexahydrate $MgCl_2$, $6H_2O$ (99%, Riedel-deHaën) was carried out. These solutions of appropriate concentrations and pH of about 6.5 were stored in a polyethylene feed tank with a capacity of 5 liters. The prepared solutions feed the column at ambient temperature, from down to upstream via a peristaltic pump which maintains a constant flow rate at the entrance to the experimental column. Water samples, after its softening, have been collected at the outlet of the column using glass bottles of 100 ml. They were carried out over 1 h for different feed rates (2.9, 6.1, 9.5 and 13.2 $l.h^{-1}$).

The reduction of the content of Ca^{2+} or Mg^{2+} ions was investigated at different concentrations of sodium chloride NaCl (99.5%, Riedel-deHaën) to evaluate the salinity impact on the softening of hard water. The pH effect was also studied to demonstrate the effect of this parameter on the treatment effectiveness.

The optimized parameters during synthetic water softening have been adopted for desalination study of groundwater from two wells located in the concerned area.

2.4. Water analysis

Different physicochemical parameters have been analyzed according to AFNOR (French Association of Normalization) standard [14]. The analytical determination has been realized in triplicate. The used chemical reagents have an analytical quality.

3. Results and discussion

3.1. Physicochemical characteristics of groundwater

The groundwater of 74 wells of the littoral zone, located between Sidi-Abed and Ouled-Ghanem of El Jadida province, has been analyzed in order to evaluate their physicochemical properties (Figure 2). The average values of the different physicochemical parameters analyzed are summarized in Table 1.

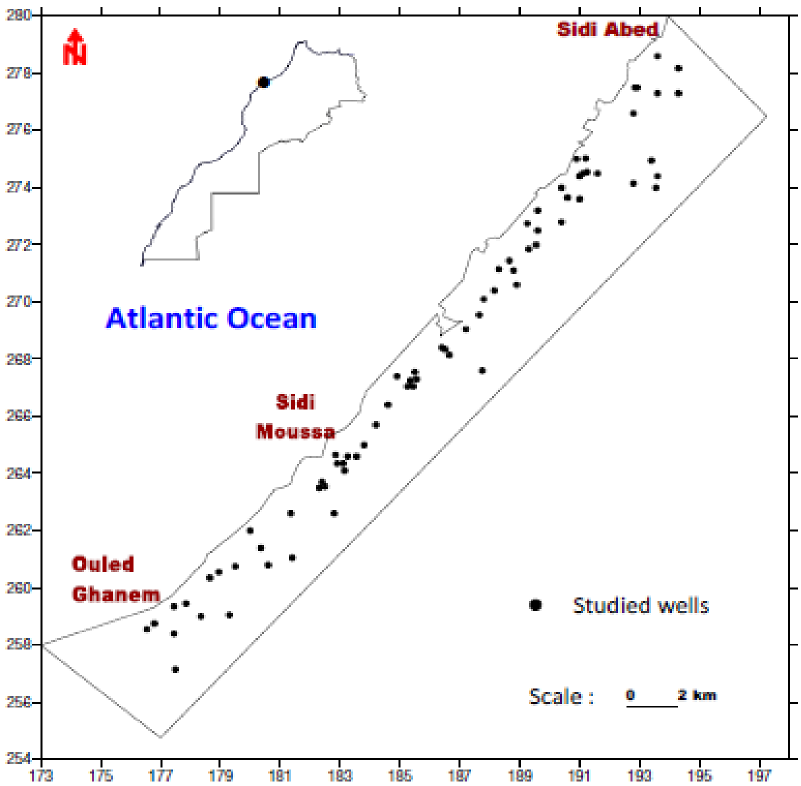

Figure 2: Spatial distribution of studied wells located between Sidi Abed and Ouled Ghanem.

The obtained results showed that the groundwater of the area studied in this work is particularly loaded by chloride and sodium; they have a hardness that exceeds the standard of drinking water. Thus, the analyzed groundwaters are not consumable and contribute to the reduction of agricultural production as a result of soil salinization caused by Na^+ contribution.

The statistical analysis applied to the results of the physicochemical determinations (Tables 2 and 3) demonstrates that 97% of water wells have a sodium concentration ≥ 200 mg.l^{-1} and 100% of water wells posses a calcium concentration ≥ 100 mg.l^{-1}. However, 96% of water wells display a magnesium concentration ≥ 50 mg.l^{-1}. On the other hand, the results revealed that 99% of water wells have a magnesium loadings ≤ 150 mg.l^{-1} and 90% of them display a calcium loadings ≤ 275 mg.l^{-1}. These limits have been considered thereafter for the preparation of synthetic solutions to investigate the effect of some parameters such as the feed rate of the column, salinity and pH on the performance of the tested resin and the softening effectiveness.

On the other hand, the shape of the curve of Figure 3 showed that the concentrations of sodium and chloride ions are linearly correlated with a regression coefficient R^2 very close to the unit ($R^2 = 0.9932$). These ions are therefore present in groundwater as sodium chloride whose concentration varies from 0.44 g.l^{-1} to 1.75 g.l^{-1}.

This is caused by the intrusion of salt water due to the proximity of the sea. The study of the salinity effect on the water softening is therefore necessary.

Table 1: The physicochemical characteristics of groundwater of the studied area.

Chemical composition	Minimum ($mg.l^{-1}$)	Maximum ($mg.l^{-1}$)	Average ($mg.l^{-1}$)	WHO ($mg.l^{-1}$)
Cl^-	231.85	1245.87	734.57	250
SO_4^{2-}	211.20	600.48	294.48	500
Ca^{2+}	60.14	136.65	97.81	100
Mg^{2+}	17.67	114.21	59.47	50
Na^+	123.00	667	411.65	200

Table 2: Distribution of water wells of the studied area according to their salinity degrees.

Na^+ ($mg.l^{-1}$)	≥ 200	≥ 300	≥ 400	≥ 500	≥ 600	≥ 700
NaCl ($mg.l^{-1}$)	≥ 500	≥ 750	≥ 1000	≥ 1270	≥ 1526	≥ 1780
% water wells	97.3	75.5	50.7	15	3	0

Table 3: Distribution of water wells of the studied area according to their concentrations on magnesium and calcium.

Ca^{2+} ($mg.l^{-1}$)	≥ 100	≥ 150	≥ 200	≥ 250	≥ 275
% water wells	100	74	41	20	10
Mg^{2+} ($mg.l^{-1}$)	≥ 50	≥ 100	≥ 150	-	-
% water wells	96	22	1	-	-

The results of the physicochemical analysis of the studied groundwater show that the reduction of salinity, especially the hardness of these waters, is necessary to save the population health and to prevent the soil salinization during crop irrigation.

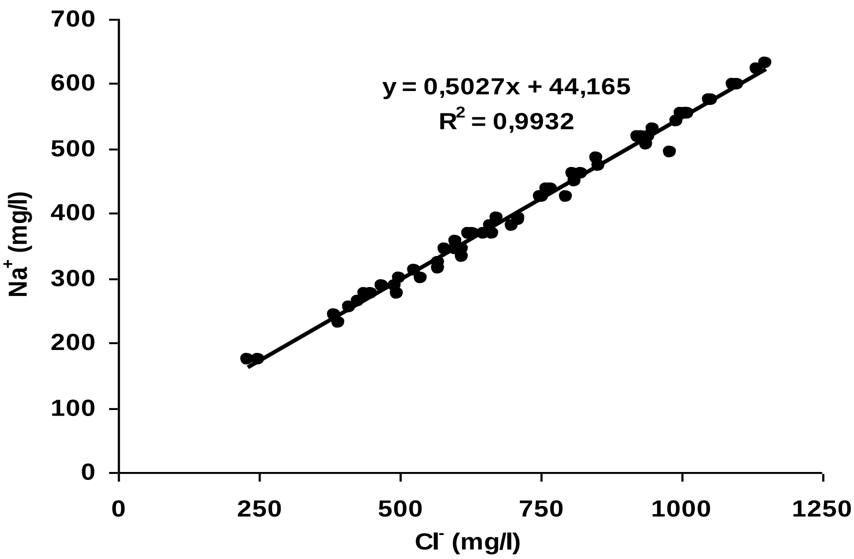

Figure 3: Correlation between the concentrations of Na^+ and Cl^- ions.

3.2 Softening of salt waters

3.2.1 Feed rate effect

By using $CaCl_2$, $2H_2O$ and $MgCl_2$, $6H_2O$, synthetic waters have been prepared with an average of ion concentrations relatively similar to those measured in groundwater in the studied area. Figures 4 and 5 showed the leakage evolution of calcium and magnesium ions as a function of time for different feed rates varied from 2.9 to 13.2 $l.h^{-1}$. As it can be seen, the curve representing the progress of the saturation on the resin varies with time. Initially, before the breakthrough, the residual concentrations of the ions to be removed are relatively constant. The breakthrough is the point of abrupt change which is corresponding to the beginning of the ionic leakage. After this point, there is an increase of the residual concentration that continues until the feed concentration C_0.

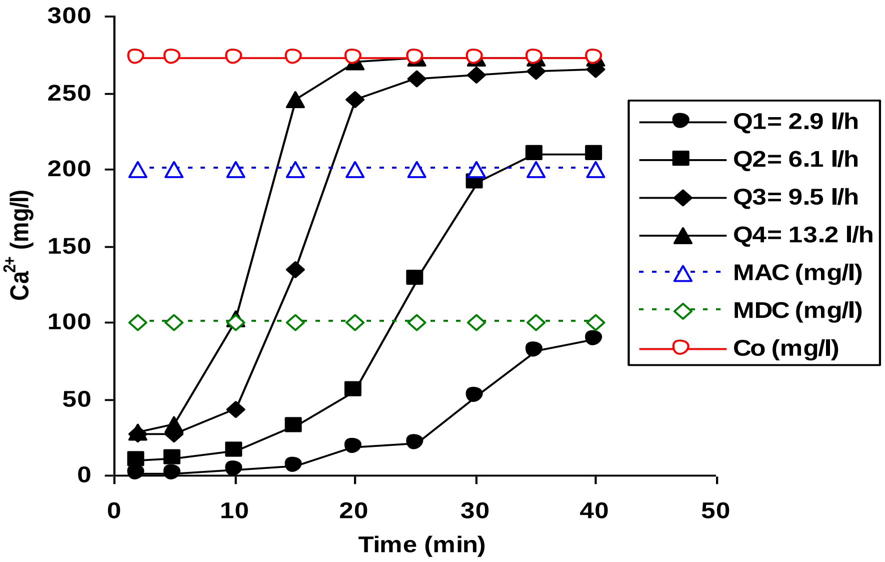

Figure 4: Evolution of the concentration of Ca^{2+} ions in the treated water versus time and feed rate. MAC: Maximum Admissible Concentration; MDC: Maximum Desirable Concentration.

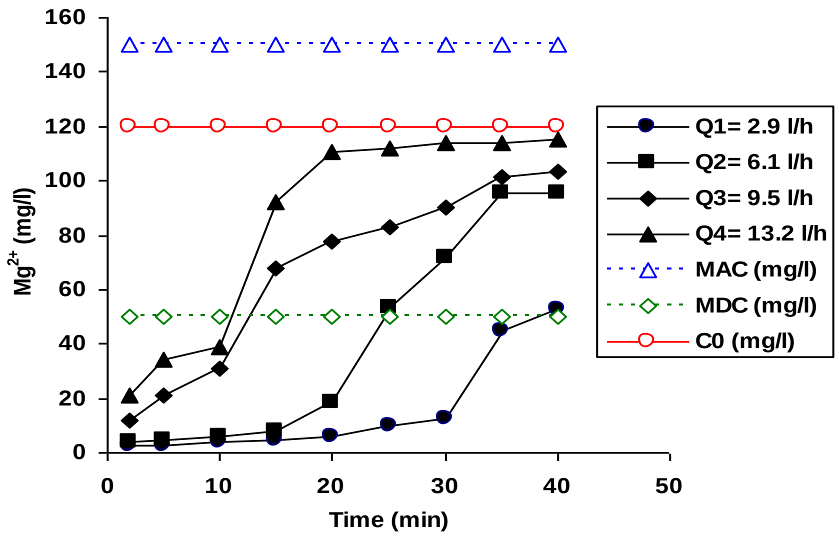

Figure 5: Evolution of the concentration of Mg^{2+} ions in the treated water versus time and feed rate. MAC: Maximum Admissible Concentration; MDC: Maximum Desirable Concentration.

It is apparent from the study of the effect of the treatment flux that the softening achieved at 9.5 and 13.2 $l.h^{-1}$ is characterized by an immediate breakthrough (<5 min). After the breakthrough time, the content of Ca^{2+} and Mg^{2+} ions in treated water increases rapidly to reach the feed concentrations. After 10 minutes of treatment, the loading of Ca^{2+} ion and Mg^{2+} ion of treated synthetic waters become greater than the maximum desirable concentration (MDC) recommended by World Health Organization for both ions [15]. Regarding the softening achieved with flow of 2.9 $l.h^{-1}$, the concentrations of Ca^{2+} and Mg^{2+} ions in the treated water remain inferior to the MDC during 30 to 35 minutes of treatment. By considering the obtained results with the filtration flow of 6.1 $l.h^{-1}$, it has been proved that during the first twenty minutes, the contents of treated water on Ca^{2+} and Mg^{2+} ions are below the MDC established by WHO. Over 20 minutes of treatment, a relatively significant breakthrough was observed and the contents of Ca^{2+} and Mg^{2+} ions increased quickly and exceeded the maximal concentration recommended by WHO. On the other hand, the breakthrough times are highly dependent on the feed rate. Increasing in the rate leads to decreasing in time and subsequently leads to increasing residual concentration of the ions in the treated solutions.

3.2.2. Effect of NaCl on softening

To evaluate the salinity effect on the softening of the synthetic waters (pH = 6.5), ionic exchange treatment tests were conducted using the same experimental system described above with a feed rate of 6.1 $l.h^{-1}$ at room temperature. The NaCl effect has been evaluated by varying its initial concentration from 0 to 10 $g.l^{-1}$. The results obtained and illustrated in Figures 6 and 7 showed the evolution of calcium and magnesium ions concentrations in the treated water (softened water) as a function of time and NaCl content in feed solution. As can be seen, NaCl contents varied between 6 and 10 g l^{-1} lead to residual concentrations of Ca^{2+} and Mg^{2+} that exceed the WHO standard [15] during the first 5 minutes. Nevertheless, the softening curves related to the NaCl concentrations varied from 2 and 4 $g.l^{-1}$ showed that the residual contents on Ca^{2+} and Mg^{2+} ions in the treated water remain less or equal to the MDC established by WHO, during 20 and 15 minutes, respectively. The leakage of Ca^{2+} and Mg^{2+} ions is strongly pronounced in agreement with salinity increasing, this indicates that the natural water having high NaCl concentrations cannot be effectively softened because the Na^+ ions compete with Ca^{2+} and Mg^{2+} ions.

From the obtained results, a concentration of 2 g NaCl l^{-1} (or 786 mg Na^+ l^{-1}) provides a softening efficiency very close to that found using the synthetic water-free NaCl. However, the NaCl contents of water wells of the studied area remain inferior to 2 $g.l^{-1}$ (0.44-1.75 $g.l^{-1}$). Thus, it is expected that the NaCl effect on resin efficiency is minimal in our case.

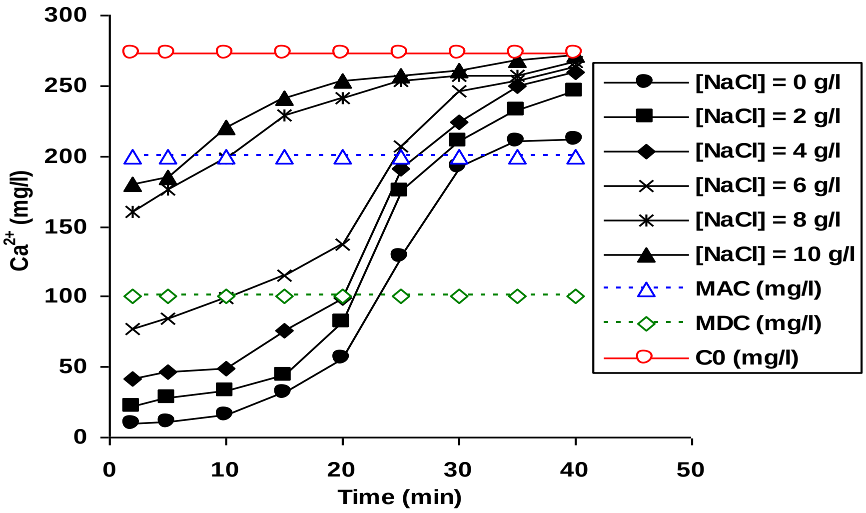

Figure 6: Evolution of the concentration of Ca^{2+} in the treated water versus time and NaCl concentration. MAC: Maximum Admissible Concentration; MDC: Maximum Desirable Concentration.

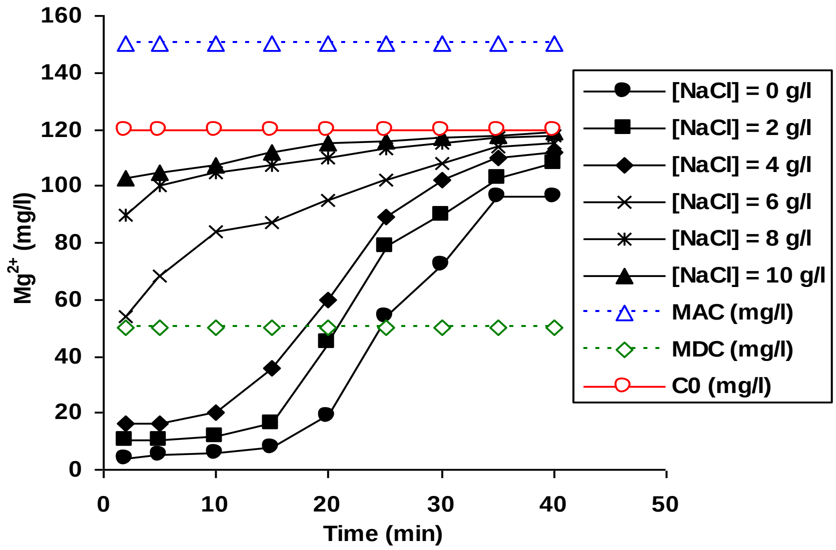

Figure 7: Evolution of the concentration of Mg^{2+} in the treated water versus time and NaCl concentration. MAC: Maximum Admissible Concentration; MDC: Maximum Desirable Concentration.

3.2.3 Effect of pH on softening

To evaluate the pH effect on the softening effectiveness, tests have been performed in the static or discontinuous mode at ambient temperature by stirring for 1h 30 min a mass of 0.5 g of resin in 100 ml solutions containing 0.5 g of $CaCl_2$, $2H_2O$ or $MgCl_2$, $6H_2O$ per liter. The pH of the solution is adjusted by appropriate solutions of HCl or NaOH depending on the desired value. The obtained results presented in Figure 8 showed that the softening efficiency decreases especially if the pH is less than 5, this is probably due to the excess of H^+ ions which compete with Ca^{2+} or Mg^{2+} ions.

The groundwater in the studied area contains HCO_3^-, they have pH between 7 and 8. Therefore, no pH correction will be required during a prospective application of the tested resin.

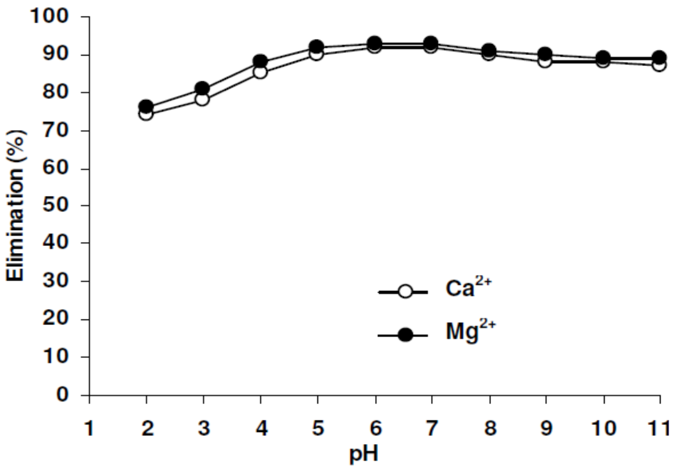

Figure 8: Effect of pH on the softening of synthetic waters.

3.2.4. Softening of groundwater by the resin

To demonstrate the possibility of groundwater softening through Duolite 206A, water samples were taking from two wells in which Mg^{2+} and Ca^{2+} loadings are higher than those recommended by WHO. Table 4 illustrates the average of physicochemical characteristics of groundwater to be treated by the resin exchanger-cation. The present analysis show that water issued from both wells are neutral, their pH are suitable for softening on resin denoted Duolite 206A.

Table 4: The average physicochemical characteristics of groundwater to be soften.

	Water well n° 1	Water well n° 2
Coordinate	X1= 188.65 et Y1=271.45	X2= 186.65 et Y2=268.15
pH	7.3	7.4
EC ($mS.cm^{-1}$)	2.5	4
Cl^- ($mg.l^{-1}$)	539	991
TAC ($mg.l^{-1}$)	204	233
NO_3^- ($mg.l^{-1}$)	65	84
Na^+ ($mg.l^{-1}$)	300	540
K^+ ($mg.l^{-1}$)	3.9	5.9
Mg^{2+} ($mg.l^{-1}$)	110	130
Ca^{2+} ($mg.l^{-1}$)	168	332

On the other hand, we find that the conductivity of the water from the well 2 is higher than that of water from the well 1, this is in good accordance with the concentrations of chemical elements present in the both mediums. In fact, water originally issued from well 2 is concentrated by chemical elements (Cl^-, NO_3^-, Na^+, K^+, Mg^{2+} and Ca^{2+}) compared to that of well 1.

As for the synthetics water, the resin had shown its efficiency in softening ground waters in the studied area. The obtained results in the case of the two wells (Figure 9 and 10), with 6.1 $l.h^{-1}$ as feed rate, had revealed that the treatment for 20 minutes leaded to treated waters which had contents of Ca^{2+} and Mg^{2+} ions lower or close to the maximal concentrations values recommended by WHO. In the case of the first well, the treated water at the first 20 minutes of the treatment have been characterized by a reduction of the concentrations of Ca^{2+} and Mg^{2+} ions of approximately 63% and 54%, respectively. On the other hand, elimination yields of approximately 70% and 55% have been recorded respectively for Ca^{2+} and Mg^{2+} ions in the case of the second well. Beyond 20 minutes, ion leakage increased to join the initial concentration C_0 for the two ions.

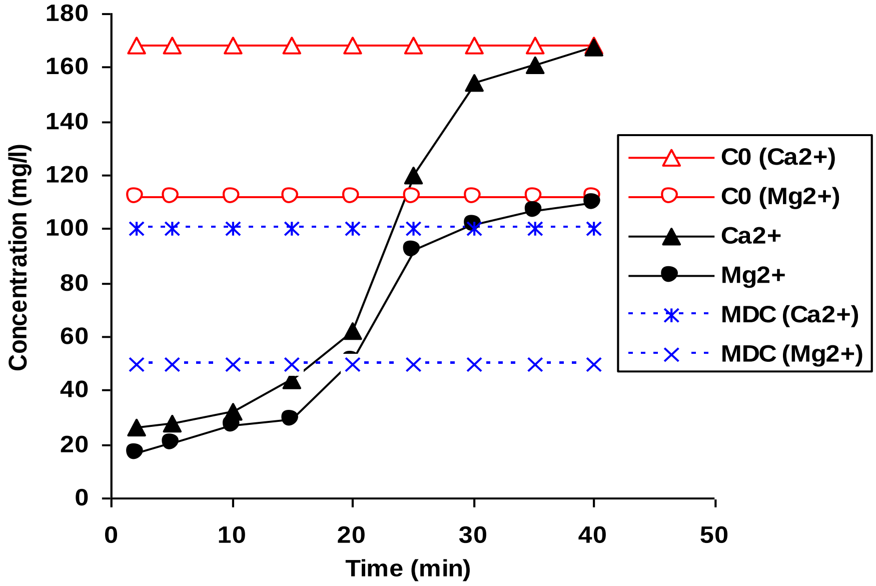

Figure 9: Softening of water from well n°1 by filtration on Duolite 206A.
MDC: Maximum Desirable Concentration.

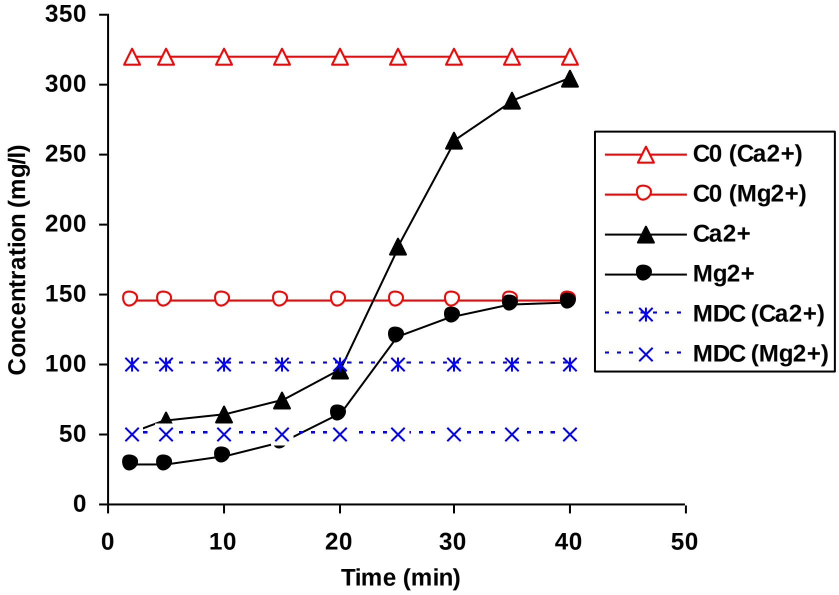

Figure 10: Softening of water from well n°2 by filtration on Duolite 206A.
MDC: Maximum Desirable Concentration.

3.3. Regeneration tests

The exchange capacity, specific to each resin is limited. After saturation of the resin, it must be regenerated to give it all its original exchange potential. There are two main modes of regeneration: the co-current regeneration and regeneration at backward current or at reversed flow. In the first case, the resin saturation and its generation take place in the same direction. However, at "backward current" mode, these both operations are performed in opposite directions.

During this study, the results of continuous regeneration tests with NaCl solutions at various concentrations were allowed us to draw the curves presented in Figures 11 and 12, showing the evolution of calcium ion and magnesium ion contents leached during washing time. For different studied cases, the maximum concentrations of leached calcium and magnesium ions are reached after one minute of regeneration. Generally, regeneration curves have similar appearances, as can be seen, the contents of calcium or magnesium ions leached increase by increasing the concentration of the regenerating solution containing NaCl. The highest concentration of Ca^{2+} or Mg^{2+} was observed for a concentration of regenerating NaCl of about 10 or 12 $g.l^{-1}$. This maximum concentration is about 836.71 $mg.l^{-1}$ of Mg^{2+} and 2047.5 $mg.l^{-1}$ of Ca^{2+} for both NaCl contents: 10 and 12 $g.l^{-1}$. At the end of the regeneration cycle, a stabilization of the concentration of leached Ca^{2+} or Mg^{2+} ions was revealed. This concentration is about 56.01 $mg.l^{-1}$ of Mg^{2+} and 145.37 $mg.l^{-1}$ of Ca^{2+} for both regenerating NaCl solutions with concentrations of 10 and 12 $g.l^{-1}$. Therefore, a regenerating NaCl solution with 10 $g.l^{-1}$ as concentration seems very suitable for the regeneration of Duolite 206A resin saturated by calcium or magnesium ions.

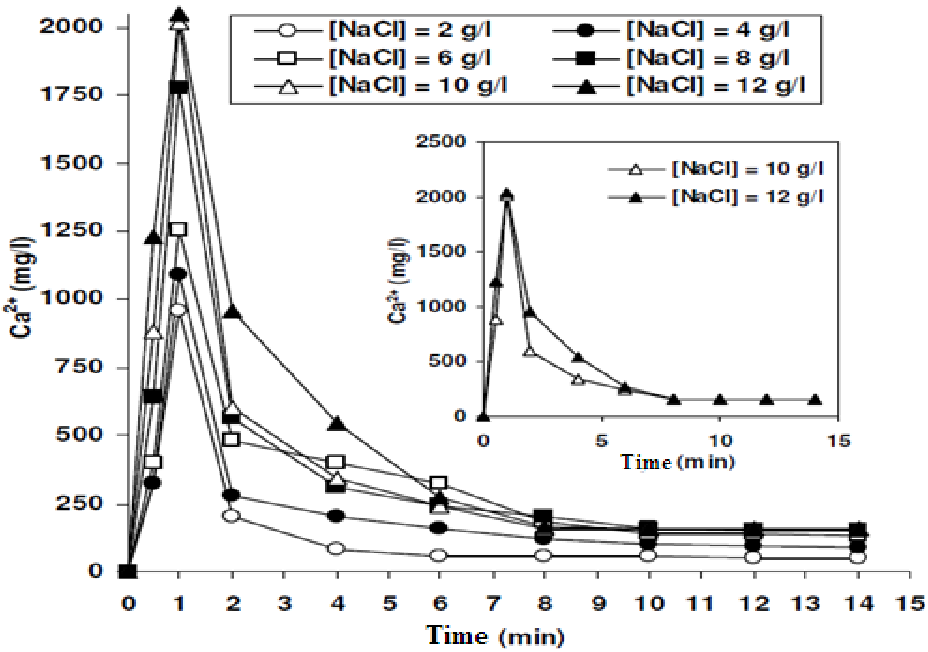

Figure 11: Regeneration of Duolite 206A by NaCl solutions at different concentrations (case of Ca^{2+} ion).

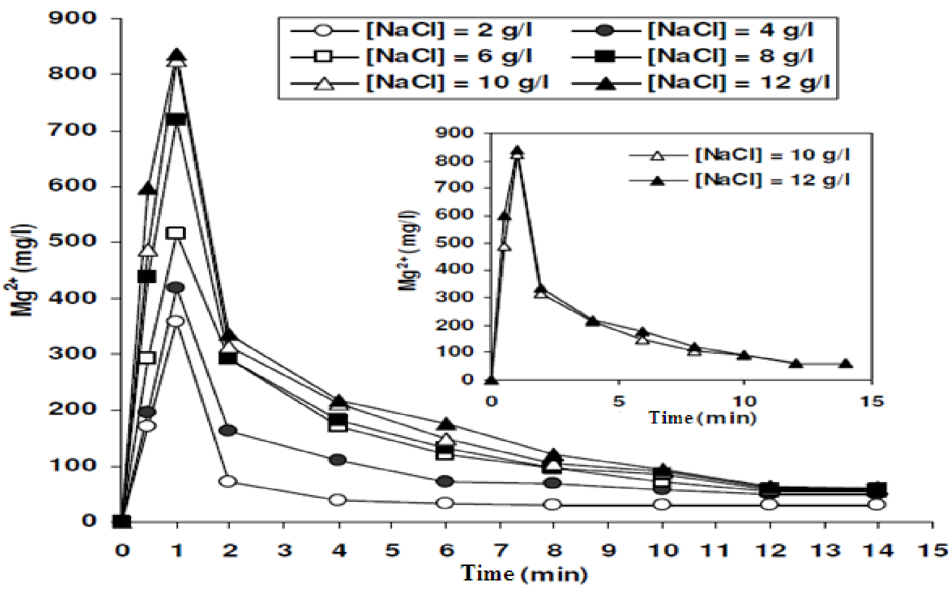

Figure 12: Regeneration of Duolite 206A by NaCl solutions at different concentrations (case of Mg^{2+} ion).

ISSN : 2028-2508
CODEN: JMESCN

Conclusions

The main objectives of this study were optimization of parameters which influenced the softening of water in dynamic mode by using the strong acid cationic resin "Duolite 206A". This resin was applied to soften synthetic hard water and groundwater of the area located between Sidi-Abed and Ouled-Ghanem (El Jadida - Morocco). The physicochemical analysis demonstrates that the groundwater of the studied zone is hard and saline; they therefore require a pretreatment before utilization.

It is founded that the softening rates are heavily influenced by the feed rates. On the other hand, the results showed that the leakage of Ca^{2+} and Mg^{2+} ions in the treated water is quite important for high salinities; this may limit the resin use during a prospective application of groundwater heavily loaded with NaCl. pH also can be considered as another parameter which can influence the softening efficiency. The results showed a negative effect of this parameter on the treatment in acidic medium, this may be caused by the competition of H^+ ions with Ca^{2+} and Mg^{2+} ions to be removed.

The results of the softening feasibility of groundwater by the resin, denoted Duolite 206A, are very satisfactory. The resin regeneration after its saturation is easily and quickly achieved by a concentrated NaCl solution. The strong acid cationic resin tested in this study is therefore a high-performance material which can be used for softening and/or demineralization of groundwater at large scale.

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