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Salinity Reduction from Saharan Brackish Water by Fluoride Removal on Activated Natural Materials: A Comparative Study

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***Abstract*—**The present study presents, firstly, to characterize the physicochemical quality of brackish groundwater of the Terminal Complex (TC) from the region of Eloued-souf and to investigate the presence of fluoride, and secondly, to study the comparison of adsorbing power of three materials, such as (activated alumina AA, sodium clay SC and hydroxyapatite HAP) against the groundwater in the region of Eloued-souf. To do this, a sampling campaign over 16 wells and consumer taps was undertaken. The results show that the groundwater can be characterized by very high fluoride content and excessive mineralization that require in some cases, specific treatment before supply. The study of adsorption revealed removal efficiencies fluoride by three adsorbents, maximum adsorption is achieved after 45 minutes at 90%, 83.4% and 73.95%, and with an adsorbed fluoride content of 0.22 mg/L, 0.318 mg/L and 0.52 mg/L for AA, HAP and SC, respectively. The acidity of the medium significantly affects the removal fluoride. Results deducted from the adsorption isotherms also showed that the retention follows the Langmuir model. The adsorption tests by adsorbent materials show that the physicochemical characteristics of brackish water are changed after treatment. The adsorption mechanism is an exchange between the OH^- ions and fluoride ions. Three materials are proving to be effective adsorbents for fluoride removal that could be developed into a viable technology to help reduce the salinity of the Saharan hyper-fluorinated waters. Finally, a comparison between the results obtained from the different adsorbents allowed us to conclude that the defluoridation by AA is the process of choice for many waters of the region of Eloued-souf, because it was shown to be a very interesting and promising technique.

***Keywords*—**Fluoride removal, groundwater, hydrochemical characterization, natural materials.

I. Introduction

IN developing countries, particularly Mediterranean countries considered to be semi-arid to arid, are increasingly confronted with water shortages as a result of climatic fluctuation, advancing deserts, as well as increased demands from agriculture, industry and people, which are substantial and growing [1], [2].

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The role of groundwater is especially important that they are often the only source of drinking water and are therefore vital to develop the country.

Current also bad management and the direct impact of urbanization pose a major problem especially in our country. Algeria lives at present this crucial problem, especially the regions of Northern Sahara affected by drought. This is the case of the waters of the El Oued-souf region with brackish water rich in fluoride ions for human consumption [3].

In recent years, much research has focused on the study of the quantity and quality of groundwater or surface water resources in semi-arid areas [2].

In Algeria, in general, the waters of northern Sahara are characterized by an excessive total mineralization, often associated with high hardness and fluoride concentrations that often exceed the guide values recommended by the WHO and values Algerian limits: 1.5 mg/L [3]-[6]. The region of the Sahara Algerian-Tunisian northern waters consists of significant resources. It consists of two large bunk aquifer systems of considerable power [7], [8]: The Intercalary Continental (IC) and the TC, which form one of the largest hydraulic tanks in the world with significant reserves estimated at $31{,}000 \times 10^9$ m^3. The aquifers of TC cover 350000 km^2 and that of IC covers 600,000 km^2 [7]. Groundwater load fluoride probably by dissolving the fluorinated apatite after leaching phosphate rocks whose solubility increases with the temperature of the considered water table (T> 35°C). The saturation level of the water depends mainly on the movement of the balance equation (1) forming the fluorine:

$$(CaF_2)\ Ca^{2+}+2F^- \rightarrow CaF_2 \quad (1)$$

The calcium content, the balance of water in calcite ($CaCO_3$), gypsum ($CaSO_4$, 2 H_2O), and the formation of calcium complexes ($CaSO_4$, $CaHCO_3$ +, $CaCO_3$) are important factors in the movement of this balance.

Fluoride is a universal scale of a geological origin of pollutants most commonly found in groundwater. It should be noted also that in these areas, contaminated water is consumed without any prior treatment. The adverse health effects of ingesting high doses of fluoride really only become apparent after several years of consumption. Indeed, in Algeria, and specially the Eastern-North Sahara, is the most exposed region to fluorotic risk: dental fluorosis and skeletal fluorosis [9]. Investigations were conducted that reveal that 80% of the

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population of El-Oued is affected by the teeth-bone fluorosis, Darmous [10], [11]. The excess fluoride issue was raised at the regional level through various studies on the quality of the Algerian Sahara waters [3], [12]. To this end, our interest in this work focuses fundamentally on the rich groundwater fluorides intended for human consumption.

Fluoride removal techniques in water intended for human food are quite numerous, but both poorly understood and poorly enforced due to their high operating costs. Currently, there are a significant number of fluoride removal methods. They can be classified into three large families: i) precipitation reactions [13], [14] (aluminum salt, silica gel, sodium aluminate, ferric salts, etc.), ii) the use of resins ion exchange [15]-[17] or materials on which there is the adsorption of fluoride (clay, AA, activated carbon, tricalcium phosphate, etc.) [18]-[21], iii) membrane techniques [22]-[27] (reverse osmosis, nanofiltration, electrodialysis, etc.).

Currently, the best results for the defluoridation of drinking water are those with AA, either in efficiency or in terms of economic cost; however, the cost remains very high in all cases.

The originality of this present work is to characterize on one hand, the quality of the physicochemical brackish groundwater aquifers of the TC from the city of El-oued, and secondly, to assess the fluoride removal of three materials such as (AA, clay and HAP) against the groundwater in the region of El-oued. The adsorption by the materials was carried out on synthetic fluorinated water and then secondly, on natural waters of the South Algerian region.

II. Hydrogeological Context of the Wilaya of Eloued-Souf

The wilaya (province) of El Oued is located in northeastern of septentrional Sahara; it occupies an area of 54,573 km^2. The climate of the region of El Oued is a hyper arid Saharan type, characterized by a hot summer and a dry and mild winter. The aquifer system of El-Oued is composed of three aquifers (Fig. 1); an unconfined aquifer, and two confined aquifers (the TC and IC) [28]-[30]. This work focuses on the groundwater aquifer of the TC. The aquifer of T TC is between 200 meters and 600 meters deep. The number of operated wells for irrigation and drinking water supply is 172. TC formations are very heterogeneous, and include seating permeable limestone Senonian and Mio-Pliocene. Indeed, it is possible to distinguish three main aquifers body, separated locally by semi-permeable or impermeable horizons. These three bodies are represented by limestones and dolomites of the Senonian and Eocene, by sand, sandstone and gravel from Pontian, and by the sands of Mio-Pliocene [31]. The water temperature of the IC can reach proximity 50 °C, while the waters of TC are around 30 °C. The fluoride concentration of those waters is up to 6 mg/L, while hardness is around 33 mEq/L, and mineralization can reach 3 g/L [3].

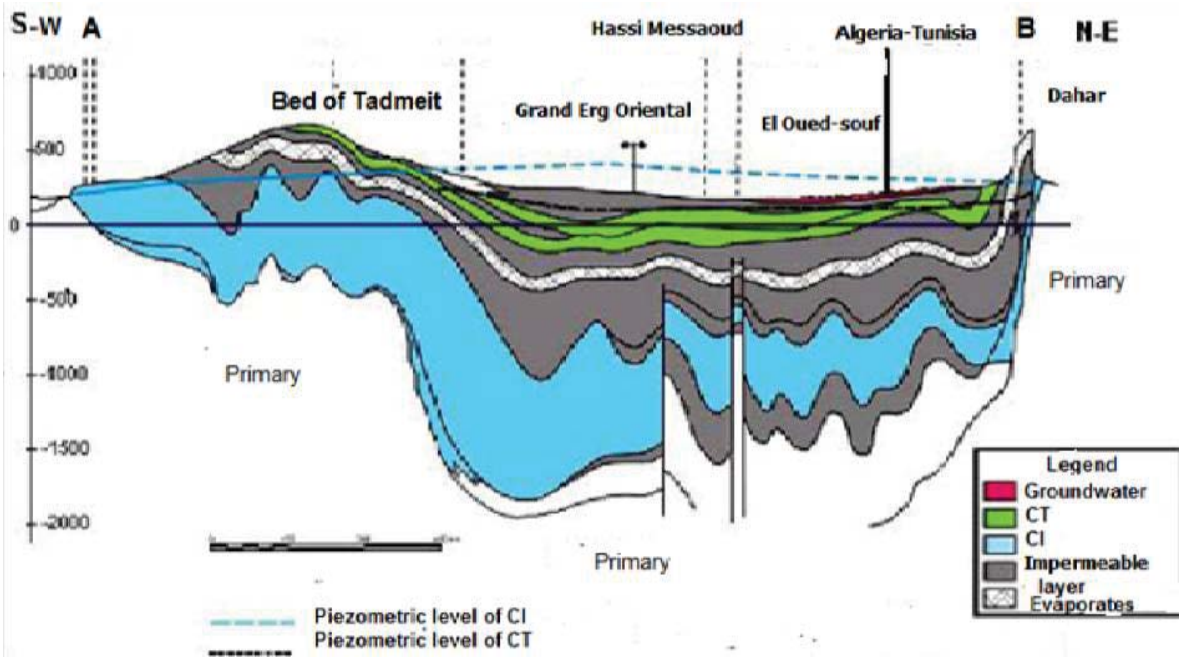


Fig. 1 Hydrogeological section through the Sahara [28], [31]. AB geological and hydrogeological section from the South-West to the North-East

III. Methods and Materials

A. Sampling and Analysis Methods

The 16 water samples analyzed were collected from 12 wells and four consumer taps. The water in this study comes from the groundwater TC for the City of El Oued. The measurements of temperature, potential hydrogen and electrical conductivity were performed in situ. The pH of water is analyzed using a pH meter WTW inoLab level LD82362. The electrical conductivity was measured by a

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conductivity meter model WTW inoLab level LD82362, and the temperature was measured by a mercury thermometer. Analyses of the elements Cl^-, HCO_3^-, SO_4^{2-}, Ca^{2+}, Mg^{2+}, Na^+ and K^+, were performed by volumetry, UV-Visible spectrometry and flame spectrophotometry [32]. The potentiometry method was used to determine the level of fluoride, F^-. These parameters were analyzed according to the AFNOR standards.

B. Experimental Studies

Adsorption experiments were performed by agitating a specific quantity of adsorbent (AA, SC, and HAP) with 100 mL of synthetic fluoride solutions and natural waters with desired concentrations of fluoride in different flasks in a shaking thermostat bath at selected temperatures. After stabilization (equilibrium), the sorbate is filtered and analyzed. Adsorption equilibrium studies were conducted by varying: the initial fluoride concentration, 2 mg/L; contact time solid–liquid, 5–120 min; adsorbent dose, 1–10 g/L; pH, 2–10; and temperature, 25-50 °C. Fluoride was analyzed using a combination of the fluoride-specific electrode ELIT 8221 and the reference electrode 001 ELIT N (calomel), which was connected to a potentiometer (CyberScan pH/Ion 510). The meter was calibrated using 10 sodium fluoride solutions with concentrations ranging 0.1– 10 mg/L, a range in which the electrode exhibits a true Nernstian behavior. Before any measurements were carried out, aliquots of 10 mL experimental solutions were mixed with 10 mL of total ionic strength adjusting buffer [4], [33], [34].

IV. Result and Discussion

A. Physical and Chemical Characteristics of the Sampled Waters

The results obtained show high values of conductivity from 2490-5340 µS/cm and a fluoridation beyond the drinking water standards, or higher contents of fluoride of 0.8 mg/L to 3.8 mg/L, pH tend to alkalinity, with values between 7.1 and 8.1. Three chemical elements (SO_4^{2-}, Cl^- and Na^+) present dominant and higher contents followed by (Ca^{2+}, Mg^{2+} and HCO_3^-) and with varying concentrations. The wealth of elements in water (SO_4^{2-}, Cl^- and Na^+) is related to the dissolution of evaporite formations. In addition, the elements Ca^{2+} and Mg^{2+} come from two sources, namely the gypsum formations (evaporites) and limestone in the case of carbonates. The waters of El-oued appear as highly concentrated water fluoride ions. With the concentrations of sulfates and chlorides measured, we can classify these waters as chloro-sulfated water. The results show that these waters are rich in mineral salts and particular fluorides.

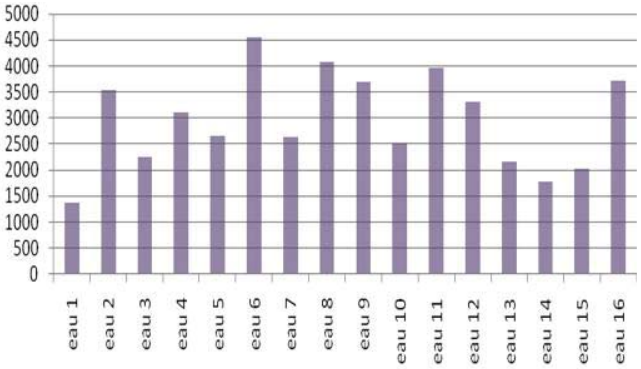


Fig. 2 Histogram of conductivity values of water analysis

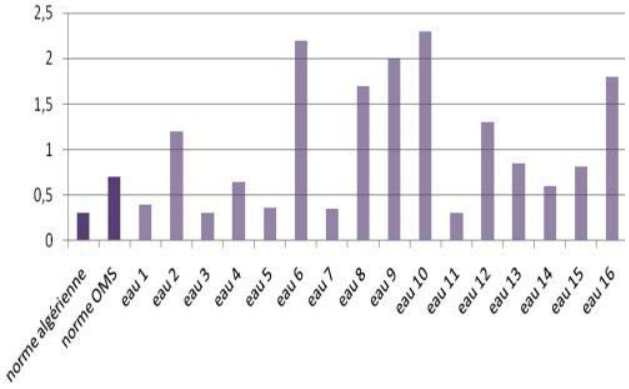


Fig. 3 Histogram of fluorides values of water analysis

B. Defluoridation of Synthetic Fluoride Water

Three different materials (AA, SC, and HAP) have been investigated in this study aiming to enhance Saharan groundwater quality by reducing its high fluoride concentration. The adsorption rate of AA was found to be faster compared to that of HAP and SC, and the equilibrium time for fluoride removal is 60 min. Maximum adsorption is achieved at 90%, 83.4% and 73.95% and with an adsorbed fluoride content of 0.22 mg/L, 0.318 mg/L and 0.52 mg/L for AA, HAP and SC, respectively (Fig. 4). Indeed, the acidity of the medium significantly affects the adsorption of fluoride ions. The graphical representation of the adsorption data of the fluoride ions for the different adsorbents over the studied pH range is shown in Fig. 5.

The maximum adsorption is reached at pH 4 for the AA and SC. Moreover, the adsorption of HAP increases with pH up to pH 3. Hence, the defluoridation capacity of the adsorbent is effective in acidic range. This can be explained due to the change in surface charge of the adsorbent. This is attributed to a greater increase in the attractive force between positively charged surface and negatively charged fluoride ions [35]. On the other hand, at high pH there is a sharp drop in adsorption, which is due to the negative charge of the materials surface. It can be concluded that the fluoride adsorption is explained by anion exchange. In addition, the ion exchange mechanism is also involved in the fluoride removal by AA, SC, and HAP.

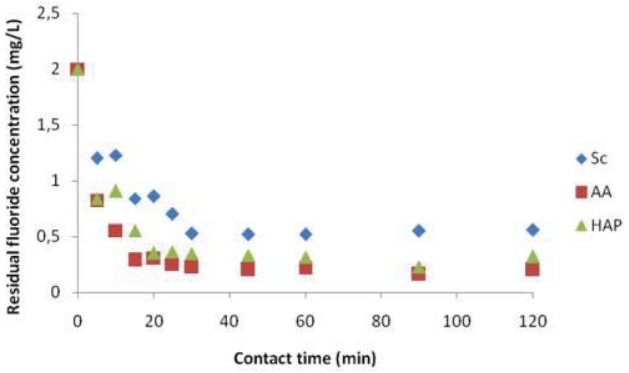


Fig. 4 Adsorption kinetics of fluoride ions on AA, HAP and SC

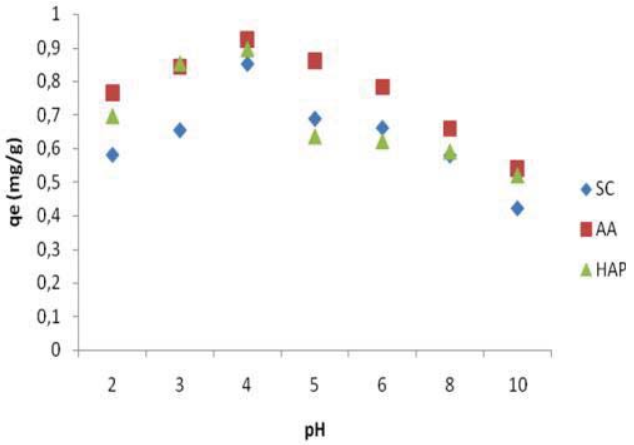


Fig. 5 Effect of pH on the adsorption of fluoride

The effect of adsorbent mass on the removal of fluorides showed that significant removal percents were obtained at a minimum mass of 0.2, 0.25 and 0.4 for AA, HAP and SC, respectively (Fig. 6). Any further addition of the adsorbent beyond this value did not cause any significant change in the adsorption. Moreover, the percentage of adsorption rises with the increase of the adsorbent content. As shown in Fig. 7, the amount of fluoride ions adsorbed decreases with the increasing of the temperature of the three adsorbents. This increase is not important; nevertheless, it can be concluded that the adsorption of fluorides ions is exothermic.

To check the effect of stirring speed on mass transfer toward the surface of sorbent, various stirring speeds (w= 250, 500, 1000, 1200 rpm) were investigated. According to the series of experiments performed on the three sorbents (AA, HAP, and SC), it was found that the amount of ions absorbed fluorides increases with increase of speed, particularly in the early process. The rate of appropriate agitation should be neither too high or too low, but moderate and adapted to each reactor type (type, size, etc.). Thus, according to our operating conditions, the optimum speed for defining the yield/rate should be 500 ppm. The nature and dimensions of the reactor are decisive parameters on the stirring speed.

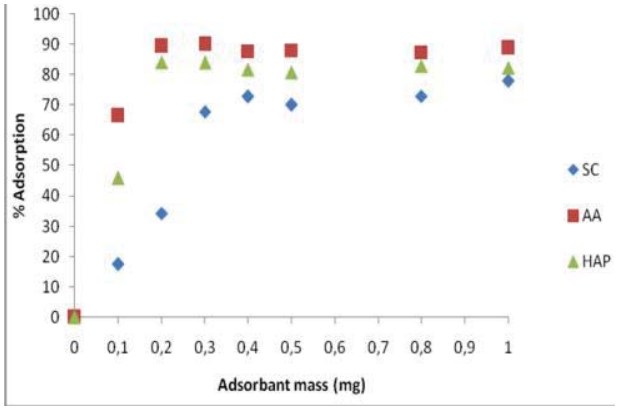


Fig. 6 Effect of mass adsorbent on the adsorption of fluoride

C. Adsorption Isotherm

Figs. 8-10 clearly show the different adsorption capacities for the isotherm models in the non-linear form of the experimental data with two isotherm models (Langmuir, Freundlich). Analysis of the isotherm results shows that the adsorption capacity increases with the initial concentration.

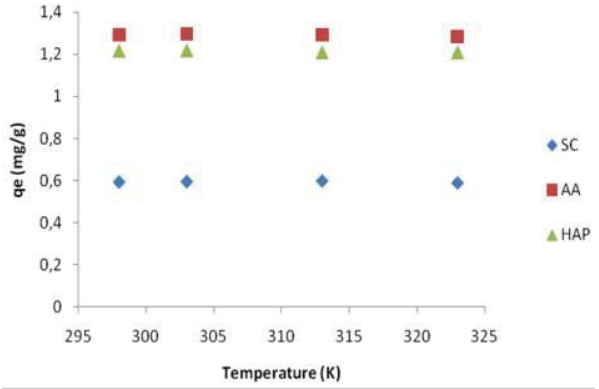


Fig. 7 Effect of temperature on the adsorption of fluoride

A remarkable difference was observed in the amount adsorbed with the nature of the adsorbent. The recorded highest rate of adsorption was observed for AA. We find on the graphs expressing the adsorbed amount based on the equilibrium concentration qe= f(Ce) that the inflection observed towards the end of the first layer proves more additional adsorption facilitated by the interactions of the adsorbate-adsorbed sublayer than by adsorbate-adsorbent surface interaction. For concentrations of F^- ions below 2 mg/L, the adsorption is at maximum on the first layer of the material. Due to the obtained results values of correlation coefficients (R^2). Most of the R^2 values exceed 0.98 for the Langmuir, suggesting that both the models closely fit the experimental results. A good linear regression was obtained for the Langmuir model, which confirms the results of the isotherm models in the non-linear form. This indicates the probable formation of a monolayer of fluorides without mutual interactions of localized sites whose energy is identical. The results compare competitively with some published results [36], [37].

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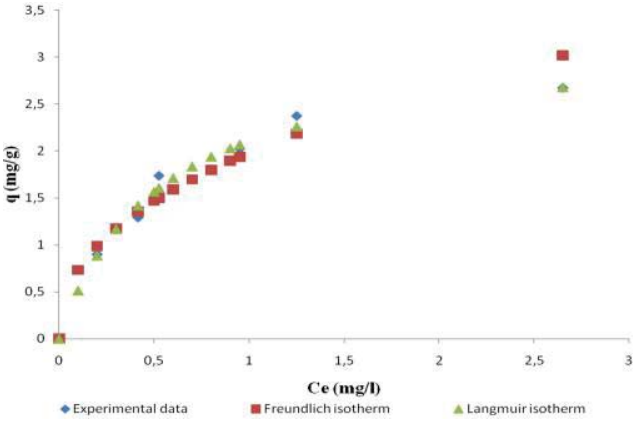


Fig. 8 Adsorption isotherm of fluorides by AA

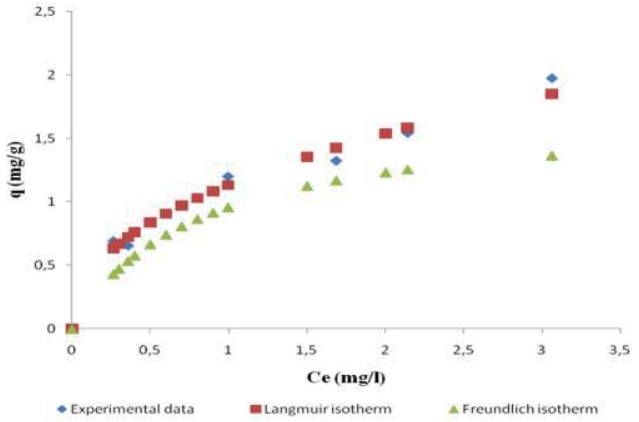


Fig. 9 Adsorption isotherm of fluorides by HAP

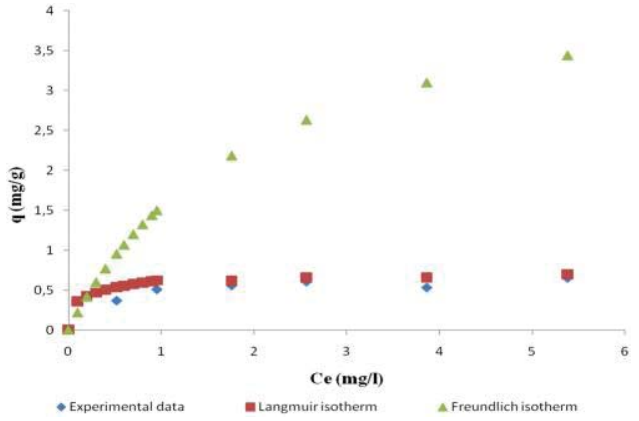


Fig. 10 Adsorption isotherm of fluorides by SC

D. Characterization Studies

1. FTIR Analysis

Fig. 11 shows the comparison of the FTIR spectra of AA before and after adsorption AA and AAA, respectively. We can raise a disappearance in the range 3200-3750 cm^{-1}, characteristic of groups stretching vibration aluminols Al-OH and a band at 1640 cm^{-1} attributed to vibrations valence of the OH group of incorporation of water over the water binding vibration adsorbed. These results then show the retention of F^- ions present in the aqueous solution by AA. In addition, a weakening of the band's intensity of Al-OH deformation vibrations appear between 775 cm^{-1} and 800 cm^{-1}.

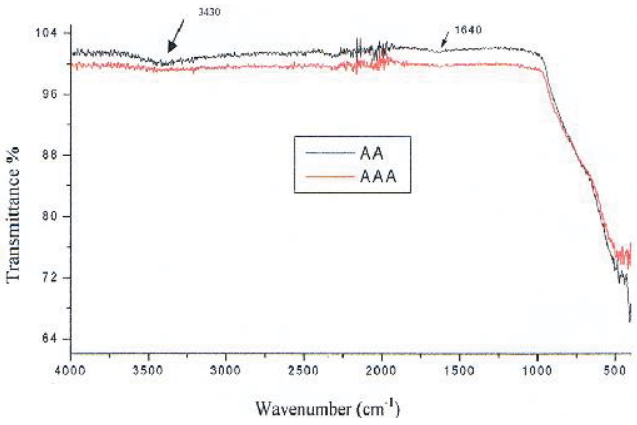


Fig. 11 IR spectra of AA, AAA before and after adsorption of fluorides

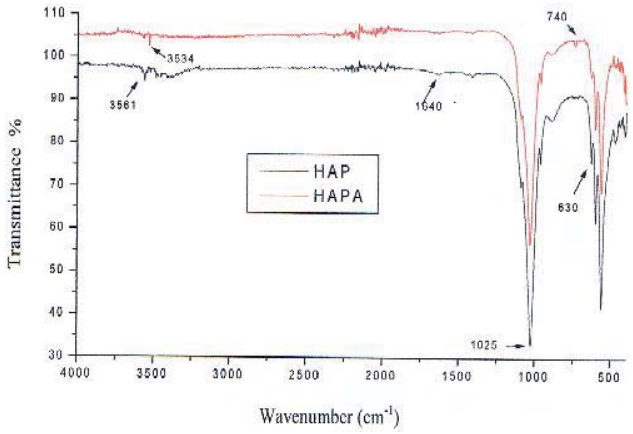


Fig. 12 IR spectra of HAP, HAPA before and after adsorption of fluorides

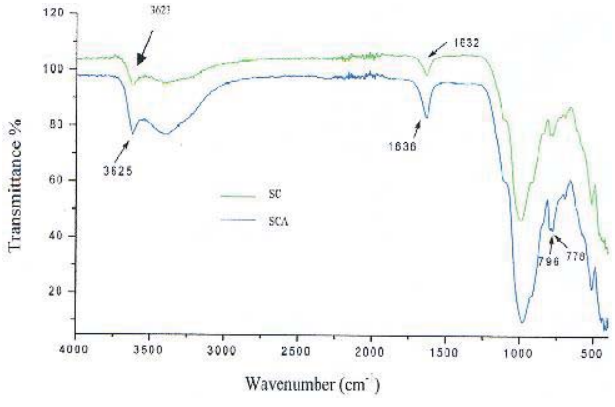


Fig. 13 IR spectra of clays SC, SCA before and after adsorption of fluorides

As shown in Fig. 12, which illustrates the comparison of HAP before absorption and HAPA after adsorption, no change is noted in the absorption bands related to PO_4^{-3} ions, However, we note the presence of two bands located at 3530 cm^{-1} and 630 cm^{-1} attributable to OH^- ions. Indeed, the

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decreased intensity of the band observed at 3530 cm $^{-1}$ characteristic of the symmetric vibration of OH^- translated substitution of OH^- tunnels by the F^- ions [37]. A weakening of the band that lies between 1600 cm^{-1} and 1700 cm^{-1} is attributed to stretching vibrations of OH constitution of water over the water binding vibration adsorbed. The intensity of the band characteristic of hydroxyl ions OH^- for HAPA after adsorption has fallen sharply. Besides, we also detect the presence of a new band whose position varies, but on average located about 740 cm^{-1}. The latter band is characteristic of the ions vibrating movement OH^- related to F^- ions by a hydrogen bridge. Accordingly, the hydrogen bonds formed HF type are responsible for a movement and a reduction in the intensity of the band of 3560 cm^{-1} (pure HAP) at 3530 cm^{-1} (fluorapatite partially hydroxylated) causing a weakening the strength of the OH bond and also the movement of the band at 630 cm^{-1} (pure HAP) towards higher frequencies until sometimes in HAP fluorinated, the position of 740 cm^{-1} [38]. This movement is therefore testament to the introduction of F^- ions in tunnels by substitutions to OH^- ions.

The FTIR spectra shown in Fig. 13 of the SC before and after adsorption of Fluorides (SC and SCA), indicates a decrease in the intensity of OH groups of elongation of the vibration band located between 3625 cm^{-1} and 3640 cm^{-1}, and between 3250 cm^{-1} and 3430 cm^{-1} [39], [40]. A weakening of the intensity of the deformation band of OH bound to an aluminum atom and an iron atom located at 778 cm^{-1} and 796 cm^{-1}. The spectra also detect a reduction and a shift of stretching vibration bands of the OH groups centered around 1632 cm^{-1} to 1636 cm^{-1} [39].

2. The BET Specific Surface

The BET specific surface area is shown in Table I for the three sorbents. The results obtained for AA and HAP showed that the specific surface area is quite large compared to SC (250 m^2/g). Moreover, we can note that the specific surface for three adsorbents after adsorption (is smaller compared to that which was initially.

TABLE I
VALUES OF THE BET SPECIFIC SURFACE OF DIFFERENT SORBENTS

sorbent	AA (m^2/g)	HAP (m^2/g)	SC (m^2/g)
Before adsorption	250	150	96
After adsorption	168	108	72

E. Application of Adsorption to Saharan Groundwater

After the experiments with synthetic solutions, it is interesting to study the removal of fluoride ions by adsorption on different materials AA, HAP, and SC and technique of nanofiltration from three Saharan groundwater samples collected from wells and consumer taps in Mih Ouansa (Wat1) and Kouinine (Wat2). They are used for irrigation and drinking water supply, as shown in Table II. From Table II, we note that the physicochemical characteristics vary after application of adsorption. Indeed, the concentration of fluoride ions decreases after treatment, there was a slight increase in pH and a decrease in conductivity. Ions such as sodium, potassium, etc., decreased after treatment. For example, the residual concentration does not exceed 0.524 mg/L, 0.647 mg/L and 1.05 mg/L for AA, HAP and SC, respectively for the water sample from Mih Ouansa. The rates of adsorbed fluoride ions are very high with AA compared to the adsorbents. Ca^{2+} decrease can be explained by the formation of fluorine CaF_2. This contributes to the reduction of fluoride ions. The formation of the fluorine CaF_2 is the main cause of the increase of percentage of the defluoridation [40]. The slight increase in pH may be explained by the release of the OH^- ions during adsorption. It appears from the results that the optimal retention of fluoride ions which determine the standards for drinking water is obtained at a time longer than that obtained in the case of synthetic water. This explains the coexistence of SO_4^{2-} and HCO_3^- anions, which reduce the retention of fluoride ions.

TABLE II
CHARACTERISTICS OF WATER SAMPLES BEFORE AND AFTER TREATMENT

Parameters	Raw water		AA		HAP		SC	
	Wat1	Wat2	Wat1	Wat2	Wat1	Wat2	Wat1	Wat2
Conductivity, µS/cm	4530	4070	4430	3806	4456	388.4	4497	3986
pH	7,59	7.46	7.82	7.51	7.89	7.55	7.79	7.49
Ca^{2+}, ppm	336	256	312	238	329.4	246.27	310.13	224.8
Mg^{2+}, ppm	123..93	104.49	117.9	99.8	120.4	98.7	109	95
Na^+, ppm	300	180	268	162	257.9	175.8	228	142
K^+, ppm	39.2	6.6	36.7	4.1	32.8	3	28	2.4
Cl^-, ppm	940.75	843.75	891.9	832.9	938.6	827.3	941	845.5
F^-, ppm	2.2	1.9	0.524	0.35	0.647	0.448	1.05	0.98
SO_4^{2-}, ppm	593.96	383.92	590	380.1	938.6	381.75	599.05	384.8
HCO_3^-, ppm	158.6	231.8	146.8	228.5	148	229	157.7	231.6

V. CONCLUSION

The results of the present investigation reveal some important observations of fluoride adsorption mechanisms.

- The adsorption kinetics was fast enough: 45min for the three adsorbents, and equilibrium was reached after 60 min. Indeed, the maximum adsorption is achieved with at a rate of 90%, 83.4% and 73.95% for AA, HAP and SC, respectively.
- The maximum fluorides adsorption was reached at pH 4 for the AA and SC, while, HAP is at pH 3.
- The minimum mass was obtained at 0.2, 0.25 and 0.4 for AA, HAP and SC, respectively.
- The fluoride adsorption isotherm is in agreement with the Langmuir model.
- The adsorption of fluorides ions is exothermic.
- A slight increase in pH and a decrease in conductivity is obtained. Ions such as fluorine, sodium, potassium, calcium, decreased after treatment.
- Different methods (FTIR and BET) of materials characterization after adsorption clearly confirm the adsorption of fluoride ions.
- AA proved to be the best adsorbent among those studied in this work in removing fluorides from synthetic and natural waters.

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REFERENCES

[1] N. Bouchahm, Samia Achour, "Qualité des Eaux Souterraines des Aquifères de la Région Orientale du Sahara Septentrional Algérien, Journal Algérien des Régions Arides", vol. 04, pp. 19 -27, 2005.

[2] N. Sedrati, "Origine et caractéristiques physico-chimiqurs des eaux de la wilaya de Biskra Sud-Est Algerian", thése de doctorat, Option Hydrogéologie, Badji Mokhtar-Annaba University, 2011.

[3] S. Achour, "La qualité des eaux du Sahara septentrional en Algérie : étude de l'excès en fluor". Tribune de l'Eau, vol 42, 542, pp.53-57, 1999.

[4] A. Ramdani; S. Taleb; A. Benghalem, N. Ghaffour. "Removal of excess fluoride ions from Saharan brackish water by adsorption on natural materials", Desalination, vol 250, pp. 408-413, 2010.

[5] H. M. Djellouli; S. Taleb; D. Harrache-Chettouh; S. Djaroud. Qualité physico - chimique des eaux de boisson du Sud algérien: étude de l'excès en sels minéraux". Journal du Cahiers d'études et de recherches francophones/ Santé, vol 2, pp. 109-112, 2010.

[6] A. Ramdani, H. M. Djellouli, N. Aït Yala, S. Taleb, A. Benghalem, B. Mahi, A. Khadraoui. "Physico-chemical water quality in some regions of southern Algeria and pretreatment prediction". Procedia Engineering. Procedia Engineering, vol 33, pp.335 – 339, 2012.

[7] I. Nezli, S. Achour, B. Hamdi-Aïssa, "Hydrogeochemical approach to study the water fluoridation of the Terminal Complex aquifer in the low algerianValley of M'ya (Ouargla), Courrier du Savoir, vol 09, pp. 57-62, 2009.

[8] L. Youssef, S. Achour, "Defluoruration des eaux souterraines du Sud Algerien par la chaux et le sulfate d'aluminium", Courrier du Savoir, 01(2001) 65-71.

[9] R. Meenakshi, R.C. Maheshwari, "Fluoride in drinking water and its removal", Journal of Hazardous Materials, vol B137, pp. 456–463, 2006.

[10] N. Mameri, A.R. Yeddou, H. Lounici, D. Belhocine, H. Grib, B. Bariou, "Defluoridation of septentrional Sahara water of North Africa by electrocoagulation process using bipolar aluminium electrodes", Water Res. Vol 32, pp.1604–1612, 1998.

[11] G.M. Witford, "Determinants and mechanisms of enamel fluorosis", Ciba Found Symp, vol 205, pp. 226-241, 1997.

[12] A, Guendouz; A. S. Moulla, W.M. Edmunds; K. Zouari, K; P. Shands; A. Mamou. "Hydrogeochemical and isotopic evolution of water in the complex terminal aquifer in Algerian Sahara". Hydogeology Journal, vol 11, pp. 483-495, 2003.

[13] M. Mohapatra, K. Rout, P. Singh, S. Anand, S. Layek, H.C. Verma, B.K. Mishra, "Fluoride adsorption studies on mixed-phase nano iron oxides prepared by surfactant mediation-precipitation technique". Journal of Hazardous Materials, vol 186, pp. 1751–1757, 2011.

[14] M.A. Menkouchi Sahli, S. Annouar, M. Tahaikt, M. Mountadar, A. Soufiane, A. Elmidaoui, "Fluoride removal for underground brackish water by adsorption on the natural chitosan and by electrodialysis", Desalination, vol 212, pp. 37– 45, 2007.

[15] A. Tor, "Removal of fluoride from water using anion-exchange membrane under Donnan dialysis condition", Journal of Hazardous Materials, vol 14, pp. 814-818, 2007.

[16] C. Castel, M. Schweizer, M.O. Simonnot and M. Sardin, "Selective removal of fluoride ions by a two-way ion-exchange cyclic process", Chem. Eng. Sci., vol 55, pp. 3341, 2000.

[17] M. Hichour, F. Persin, J. Mol6nat, J. Sandeaux, C. Gavach, "Fluoride removal from diluted solutions by Donnan dialysis with anion-exchange membranes", Desalination, vol 122 pp.53-62, 1999.

[18] A. Ramdani; S. Taleb; A. Benghalem; N. Ghaffour. "Removal of excess fluoride ions from Saharan brackish water by adsorption on natural materials", Desalination, vol 250, pp. 408-413, 2010.

[19] Y. Ma; F. Shi; X. Zheng, J. Ma, C. Gao. "Removal of fluoride from aqueous solution using granular acid-treated bentonite (GHB): Batch and column studies", Journal of Hazardous Materials, vol 185, pp.1073–1080, 2011.

[20] W. Takaaki ; U. Yuta; N. Shuji; S. Katsuyasu, " Adsorption behavior of fluoride ions using a titanium hydroxide-derived adsorbent", Desalination, vol 249; pp. 323–330, 2009.

[21] M. Mourabet ; A. El Rhilassi; H. El Boujaady; M. Bennani-Ziatni; R. El Hamri; A. Taitai. "Removal of fluoride from aqueous solution by adsorption on Apatitic tricalcium phosphate using Box–Behnken design and desirability function", Applied Surface Science, vol. 258, pp. 4402–4410, 2012.

[22] M. Tahaikt; R. El Habbani; A. Ait Haddou; I. Achary; Z. Amor; M. Taky; A. Alami; A. Boughriba; M. Hafsi; A. Elmidaoui. "Fluoride removal from groundwater by nanofiltration", Desalination, vol. 212 , pp. 46–53, 2007.

[23] K. Hu, J. M. Dickson, "Nanofiltration membrane performance on fluoride removal from water" Journal of Membrane Science, vol 279, pp. 529–538, 2006.

[24] M. Tahaikt, A. Ait Haddou, R. El Habbani, Z. Amor, F. Elhannouni, M. Taky, M. Kharif, A. Boughriba, M. Hafsi, A. Elmidaoui, "Comparison of the performances of three commercial membranes in fluoride removal by nanofiltration. Continuous operations", Desalination, vol 225, pp. 209–219, 2008.

[25] A. H. Bannoud; Y. Darwich. "Elimination des ions fluorures et manganèses contenus dans les eaux par nanofiltration", Desalination, vol 206 , pp. 449–456, 2007.

[26] B. Van der Bruggen, M. Manttari, M. Nystrom, "Drawbacks of applying nanofiltration and how to avoid them: A review", Separation and Purification Technology, vol 63, pp. 251–263, 2008.

[27] D. Dolar, K. Košutić, B. Vučić, "RO/NF treatment of wastewater from fertilizer factory — removal of fluoride and phosphate", Desalination, vol 265, pp. 237–241, 2011.

[28] UNESCO. Projet ERESS. "Etude des ressources en eau du Sahara septentrional. Rapport sur les résultats du projet", Paris (1972). 100 p.

[29] A. Cornet. "Introduction à l'hydrogéologie saharienne. Géographie Physique et Géologie Dynamique" Vol.VI. fascl, pp. 5-72,1992.

[30] B. Bouselsal; N. Kherici. "Effets de la remontée des eaux de la nappe phréatique sur l'homme et l'environnement : cas de la région d'El-Oued (SE Algérie)", Afrique SCIENCE 10(3), pp.161 – 170, 2014.

[31] F. Bel; D. Cuche. "Etude des nappes du Complexe Terminal du bas Sahara. Données géologiques et hydrogéologiques pour la construction du modèle mathématique. DHW, Ouargla, 1970.

[32] J. Rodier, "The analysis of water: natural water, waste water, sea water: physical chemistry, bacteriology and biology." Ed Dunod, Paris, France, 8 pp-1383, (1996).

[33] A. Ramdani, S. Taleb, A. Benghalem, Study of the optimization of the potential of adsorption of the local montmorillonite for the reduction of the excess of ions Fluorides of Saharan water", Phys. Chem. News, vol 52, pp. 89–97, 2010.

[34] A. Tor, "Removal of fluoride from an aqueous solution by using montmorillonite", Desalination, vol 201, pp. 267–276, 2006.

[35] G. Karthikeyan, A. Shunmuga Sundarraj, S. Meenakshi, K.P. Elango, "Adsorption dynamics and the effect of temperature of fluoride at alumina solution interface", J. Indian. Chem. Soc., vol 81, pp.461–466, 2004.

[36] Y. Ku; H.M. Chiou. "The adsorption of fluoride ion from aqueous solution by activated alumina". Water Air Soil Pollut. Vol 133 (1), pp. 349–361, 2002

[37] W. Wei; X. Wang; Y. Wang; M. Xu; J. Cui; Z. Wei. "Evaluation of removal efficiency of fluoride from aqueous solution using nanosized fluorapatite", Desal. Wat. Treat. Vol 52 (31-33), pp. 6219-6229, 2014.

[38] L. El Hammari; A. Laghzizil; P. Barboux; K. Lahlil; A. Saoiabi. Crystallinity and fluorine substitution effects on the proton conductivity of porous hydroxyapatites, J. Solid State Chem. 177, pp.134-138, 2004.

[39] R. Sennour; G. Mimane; A. Benghalem; S. Taleb. "Removal of the persistent pollutant chlorobenzene by adsorption onto activated montmorillonite", Applied Clay Science, vol 43, pp.5003 – 506, 2009.

[40] M.G. Sujana, S. Anand, "Iron and aluminium based mixed hydroxides: A novel sorbent for fluoride removal from aqueous solutions, Appl. Surf. Sci., vol 256, pp.6956–6962, 2010.