NVEO
Natural Volatiles &
Essential Oils

Removal Of Fluoride Ions From Drinking Water Using Organic Matrix "OM" (Date Seeds-Deglet Nour) : Analyze The Effect Of Experimental Conditions

Difallah Ahmed[1]*, Messaïtfa Amar[2] , Saggaï Sofiane[3]

[1]* Water and Environmental Engineering in Saharan Milleau (GEEMS) Laboratory. Kasdi Merbah University,
30,000 Ouargla (Algeria) difallah.ahmed@univ-ouargla.dz
[2] Water and Environmental Engineering in Saharan Milleau (GEEMS) Laboratory. Kasdi Merbah University,
30,000 Ouargla (Algeria) a_messaitfa@yahoo.fr
[3] Water Water and Environmental Engineering in Saharan Milleau (GEEMS) Laboratory. Kasdi Merbah University, 30,000 Ouargla (Algeria) sofianeaero@yahoo.fr

Received: 11/2022 Published: 11/2022

Abstract:

The purpose of this study is to Défluoruration of groundwater in the region of Ouargla south-east Algeria whose concentration of fluoride ions increased more than 2.78 mg/l that exceeded WHO standards. Procedure in- volves adsorption of organic matrix were prepared from a new lignocellulosic biomass source: date seeds without the addition of any chemicals and analyze the effect of experimental conditions (contact time -temperature- granular di- ameter diversity -PH- adsorption dose) in enhancing the adsorption capacityof fluoride ions The best results were conducted using spectrophotometer type DR 6000, (λ = 580nm) The effect of the reaction time was observed from 5to 1440 minutes, temperature and adsorption dose between raw water and the organic matrix. Indicated a maximum removal percentage (98.56 %) with an initial concentration of F ions 2.78 mg/l and the fluoride removal temperature appeared to be between 105–400 °C was 200 m, 60 min, 6 and 1 g/40 mL, respectively, may be used of organic matrix as sustainable, low-cost and efficientadsorbents for F- removal from aqueous solution. Overall, the results conducted in the present research indicated that the water treatment in the region ofOuargla may favorably affect the water availability, lifestyle and Public healthof the population in this Saharan region.

Keywords: Defluorination, Ouargla, Fluorosis, Northern Sahara, Date seeds

1. Introduction

Unwanted metal ions are classified as micro-elements present in the environment in different concentrations in the environment Humans, animals and plants, where fluoride is classified as an essential substance because it contributes tothe development and maintenance of dental health.

This element is very useful in the mineralization of bones and teeth endemic to calcified tissues with a concentration of up to 99%in the body (Liu et al. 2017) and its advantage in theattraction to calcium in teeth and bones due to its electronic strength (Susheela et al.1993) Its concentration ranges from 0.05 to 2 mg/l It is considered vitalfor the human body (Bhatti et al. 2010) and contributes to the cohesion of bonetissue and teeth (Acharya, 2005) when its concentration is between 0.5 to 1.5 mg/l according to the World Health Organization (WHO.2006),it can be acquired through water fluoridation when fluoride (NaF) is added to drinking water (Fouskaki et al. 2003; Konieczka, Zygmunt, and Namieśnik ,2000).As it is found in the food chain, water (CaF_2), air, rocks and soil($Na_5Al_3F_{14}$) are in the form of compounds. However, it is toxic in high concentrations, and exposureto fluoride may lead to effects on teeth (Warren and Levy, 2003)and infection with dental fluorosis (Chavaissieux and Meuinier ,1995) to extend the effect to bone density and deformation (Onyango et al. 2004) and may have a longereffect From this it reaches paralysis (Veressinina et al.2001) and in casesof toxicity is fatal (Tokaliogˇlu, Kartal, and S¸ahi˙n 2004). Pollution with fluoride in the environment occurs naturally in the earth's crust and in the waters of the planet (Goyer, 1981).They are released into the environment when minerals in the soil are exposed to climatic factors (rain, erosion, etc.); Most of the natural resources have a geological origin (Travi ,1993). This is the case with groundwater from granite reservoirs and some sedimentary basinsas well as geothermal water that concentrates high levels of fluoride ions. volcanic activity According to a UNICEF report, tens of millions of people are infected with fluorosis, which is endemic in 25 countries worldwide; Especially countries in volcanic regions (Petrone et al. 2013) the abundance of fluoridein the environment is increasing. This is due in particular to the increased use and improper disposal of waste products by various industries, including nickel smelting, steel, aluminum and magnesium mining, copper, iron and steel, zinc and lead, production of boronium, glue and adhesives, phosphate fertilizers, petroleum and Handicrafts, ceramics, pottery, cement and brick factories, flu- oride factories, coal combustion, storage of fluoroapatite in leak sheds and useof fluorinated pesticides (Environnement Canada et Sant´e Canada, 1993 ;Goyer 1981; World Health Organization, 2002; Sant´e Canada, 2007; Marier, 1977) and industrial manufacturing of building materials, ceramics, semiconductors, phos- phate fertilizers and glass(Cai et al. 2018; Rasool et al. 2018); Tovar-Gómez et al. 2013); Waghmare et al. 2015). Given the adverse effects of such metals, their concentrations should be limited to levels acceptable by environmental regulatory agencies. Over the past decades, many works have adopted several Removal of fluoride ions from drinking water using organic matrix "OM" (dateseeds-Deglet Nour)

Removal of fluoride ions from drinking water using organic matrix "OM"
(date seeds-Deglet Nour):
analyze the effect of experimental conditions

methods for removing fluoride in water, including the classic chemical treat- ment (Paulson,1977; Maxime P, 1996; Comte, 2004; Rabosky J.K, 1975) or theuse of lime(Achour and Youcef, 2001; Scott et al. 1937; Boruff, 1934). In Algeria the few experimental works carried out on southern waters showed the effectiveness of water defluoridation by chemical precipitation with lime. How- ever, this technique results in the use of high doses of lime to reach acceptable levels of fluoride (Achour and Youcef, 2001). or by fusion-coagulation technique(sintering), as many studies have shown (Achour and Youcef, 2001; Scott et al. 1937; N'DAO, Lagaude, and Travi, 1992; Mazounie and Mouchet,

1984)The efficacy of aluminum sulfate in a specific treatment such as defluoridation of water. The process is based on the hydrolysis of aluminum sulfate and the for- mation of a precipitate of Al (OH) $_3$ with the ability to adsorb fluoride ions. The fluoride binding capacity of aluminum hydroxide, determined by mg of fluoride bound per mg dose of aluminum, increases with the fluoride content of raw water for constant aluminum concentration (Mazounie and Mouchet,1984). Ion ex- change (Desjardins, 1997) and electrocoagulation (Mameri et al. 1998). These are classic techniques. As for the modern physical methods (Yang and Dluhy, 2002) such as membrane techniques (Farcy M, 2008; Mazet ,2002) electrodial- ysis (Hichour et al. 1999) and microfiltration (Pontie et al. 2003; Tahaikt et al. 2007).However, most of these techniques It consumes high energy and chemicals, in addition to producing large quantities of sludge making it expensive and difficult to handle. Adsorption is one of the most widely used methods. Adsorbents, such as activated carbon (AC) are the most popular adsorbent, but they are still very expensive and also require regeneration and this limits their use in developing countries. Which represents a real challenge motivating the search to explore more economical alternatives (Inyang et al. 2016; Pellera et al. 2012)Recently research has turned to treatment methods using cheaper, potentially environmentally friendly natural materials for water and wastewater purification (Pellera et al. 2012; Chen et al. 2011) including plant and ani-mal wastes, but the preparation of activated carbon from organic waste is very exciting from an economic point of view of environmental importance because we We take advantage of simple transformations, a way to value and manage unwanted waste into a value-added product, and the direct application of these raw materials. It can be used to remove organic and inorganic pollutants, to improve its adsorption power and its ability to remove mineral pollutants from aqueous solutions. It can be prepared from various organic sources, including agricultural waste, Biochars prepared from anaerobically digested sludge (Jinet al. 2016),canola straw and soybean straw, Peanut straw (Tong et al. 2011)

date seed (Mahdi Yu, and El Hanandeh,2018),rice husk (Masih, Anthony, and Siddiqui, 2018), orange pomace (Santos et al. 2015), animal manure (Wang et al. 2020), macroalgae (Park et al. 2016) hermaphrodite and wheat-straw (Bogusz, Oleszczuk, and Dobrowolski, 2015),walnut (Ding et al. 2016),orange droppings and olive pomace (Pellera et al. 2012) Most of the previous stud- ies showed that the biomass of turmeric seeds showed remarkable adsorption abilities to remove methyl bromide and Cu^{2+} and Ni^{2+} ions in aqueous solu- tion (Mahdi, Hanandeh, and Yu, 2017;Mahdi, El Hanandeh, and Yu, 2017; Mahdi, Yu, and El Hanandeh, 2018), which included several aspects of sorption

including kinetics, isotherms, ability of Adsorption, and the effect of the pH ofthe solution. Also, some studies focused on the adsorption efficiency of biochar, such as pyrolysis conditions, particle size, and reaction temperature. Many of the published literature has used very popular isothermal variables such as Langmuir and Freundlich models for their simplicity and ease of application. This paper presents the removal of fluoride ions from the drinking water of the inhabitants of southeastern Algeria, Ouargla region, using the organic matrix ”OM”(date seeds - Deglet Nour) and an analysis of the effect of experimental conditions. What was confirmed by the National Institute of Public Health in 1980, In gen- eral, the groundwater of the Northern Sahara of southeastern Algeria is highly mineralized with high levels of fluoride, which led to a high rate of dental fluoride poisoning among the inhabitants of the northern desert. The problem of fluoride in drinking water affected a large part of the population of the region, where44% (mondiale de la Santé Bureau régional de

l'Europe Copenhague, 1981) of fluoride (Achour and Youcef, 2001) is endemic. Among the reasons for the difference in fluoride concentrations, the geological composition in the study area, and the nature of the population's diet for their excessive consumptionof tea and dates (Baouia K. 2017; Belmabdi A, 2014; Messa¨ıtfa 2008) are rich in fluorine,and the concentrations of this water in fluorine are considered high and require treatment. Dental and skeletal problems, associated with the presence of fluoride ions in excess of the recommended standard from the World Health Organization(1.5 mg/L), affect many areas of the northern Sahara. The high concentrationof fluoride ions in drinking water represents a real public health concern and problems for the population of the area (Fig. 1). The concentration of fluoridein drinking water was determined for the most important areas of the cityof Ouargla in terms of population density and the exploitation of date seedsin the drinking water treatment process, after converting their seeds into an organic matrix. The main objectives of the current study were (1) to remove fluoride ions from drinking water (2) Determination of optimal conditions for preparing an organic matrix including pyrolysis temperature (100, 200, 400 °C), and particle size (< 50µm 200µm 500µ > 1mm); (3) to determine the optimal operating conditions including solution pH, initial metal concentration, temperature and contact time using batch adsorption experiments; Through the physical adsorption of fluoride ions, we use waste raw materials that are widely available in southeast Algeria as an effective alternative way to remove fluoride ions. We have taken into account the possibility of defluoridation, the availability of the product, economical and biotechnological, easy to apply, without risk to health and an acceptable yield.

2. Materials and Methods

Study area

The study area comprises the wilaya of Ouargla , which is situated in the north- east of the Algerian Grand Sahara it is 850 km from the capital Algiers between the latitudes 31.95 North and the longitudes 5.33 East, at the Sahara desert- the largest hot desert and the third largest desert in the world. The basin drains anarea of 99 thousand hectares for a perimeter of 45 km.

Removal of fluoride ions from drinking water using organic matrix "OM" (date seeds-Deglet Nour): analyze the effect of experimental conditions

Figure 1. A sample from a resident of the study area infected with dental fluorosis

Raw materials

Degla Nour date seeds, natural lignocellulosic residues from palm waste, theraw material used in this study, and the process of preparing these materials include the stages of washing, drying, calcination, grinding, and sieving. The amount of raw material from date kernel collected from the study area starting from October and continuing until January when the dates harvest season. 6 kg were collected (Fig. 2) and washed well with boiling water in the range of 60C0 until the wash water became colorless. The main characteristics of date seedsare presented in (Table 1).

Table 1. Physiological and physiological properties of Deglet-Nour date seeds

Elements	Ca^{++}	P	Mg^{+}	K^{+}	ABDUL et al. (2013)
Date seeds (100mg/g)	38.8	68.3	51.7	22.9	
Physiological	weight (g)	Ø(cm)	pH	length (cm)	Ash(%)
Value (ranges)	0.6 -1.69	0.58-1	5.76 -6.12	2.9 -3.15	0.80 - 1.08
ingredients %	Water	Fibers	Fatty substances	Protein	sugars
	6.37-12.42	13.54 - 16.27	8.72-10.39	6.51 - 8.59	6.02 - 7.41
	KHALI et al. (2014)				

Prepare the organic matrix

The biomass (date seeds) was washed with distilled water several times to re- move dirt particles and water soluble materials. The washed materials were then completely dried in an oven at 105°C, 200°C and 400 °C for 24 hours. They were crushed using a rotary jaw crusher. The latter was ground using a ball mill and then sieved using two sieves to retain only particles with a particle size between 50µm and 1 mm respectively. without the addition of any chemicals (Fig 3).

Figure 2. Photographs of organic matrix preparation The raw material (a) After the carbonization process (b) organic matrix (c)

Procedures

The initial concentration of fluoride ions solution was 2.79 mg/l for all experi- ments. For fluoride ions removal kinetic experiments, the batch method was usedbecause of its simplicity. About 1 g to 6 g of organic matrix was contacted with40 mL of fluoride ions at PH = 7.49 solution in a sealed flask agitated vigorously by a magnetic stirrer controlled shaker at a speed of 150 rpm. At predetermined intervals of time, samples filtrate of the mixture was withdrawn analysed by a UV–Vis spectrophotometer in λ = 580nm for the concentration of fluoride ions. The adsorption capacity was calculated by using the following equation:

$$qe = \frac{(C0-Ce)*v}{m} \quad (1)$$

Where q_e (mg/g) is the adsorption capacity, C_0 and C_e (mg/l) are the initial and equilibrium concentrations of F- , and any time, respectively, V (L)is the volume of the solution and m (g) is the weight of used biosorben For the calculation of fluoride ions rate adsorption (R %), the following expression was used Al (Sagheer et al. 2009; Balarak et al. 2016):

$$R(\%) = \frac{(C0-Ce)*100}{C0} \quad (2)$$

Removal of fluoride ions from drinking water using organic matrix “OM” (date seeds-Deglet Nour):
analyze the effect of experimental conditions

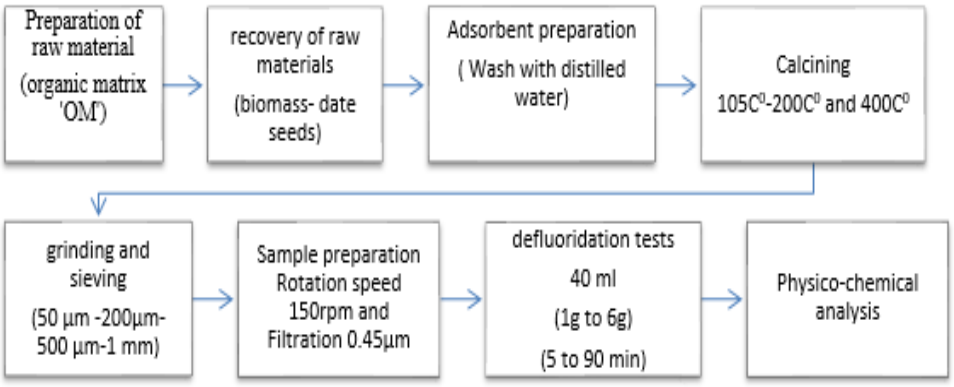

Figure 3. Step-by-step procedure followed for Adsorbent Preparation and Defluoridation Tests

3. Results and Discussion

Effect of granular diameter diversity

As for the difference in the granular diameter diversity of the date seeds at the diameters (50µm, 200µm, 500µm and 1 mm) .The (Fig. 4-5-6) , it did not have a clear effect in this process, although the increase in the specific area of the matrixis related to the granular diameter , where the lower the granular diameter, the higher the specific area and accordingly the number of active sites increases and thus increases the efficiency of adsorption, (Abe et al. 2004) but in this case weconsider it unimportant So that the diameters converge from each other, and thismeans convergence in the specific space of the adsorbent, and the convergence of the specific behavior of the matrix made our experiments possible to reach minimum levels of fluoride ions less than the limit recommended by the WHO. And the polarization of fluoride in the reaction medium, where it is possible to take the particle diameter Ø = 50µm selected for the (OM) in this study.

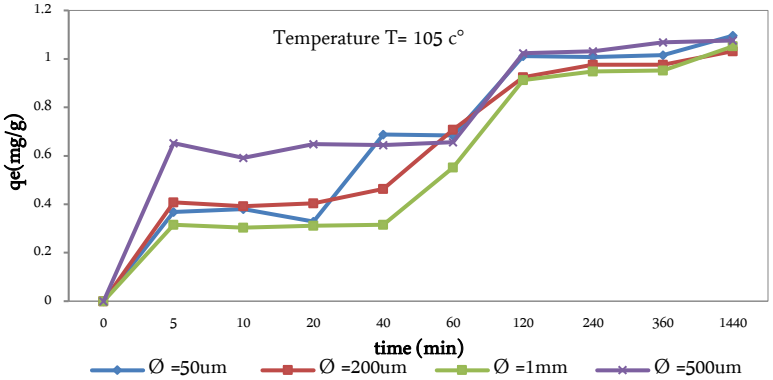

Figure 4 Effect of granular diameter diversity at a temperature105 C0

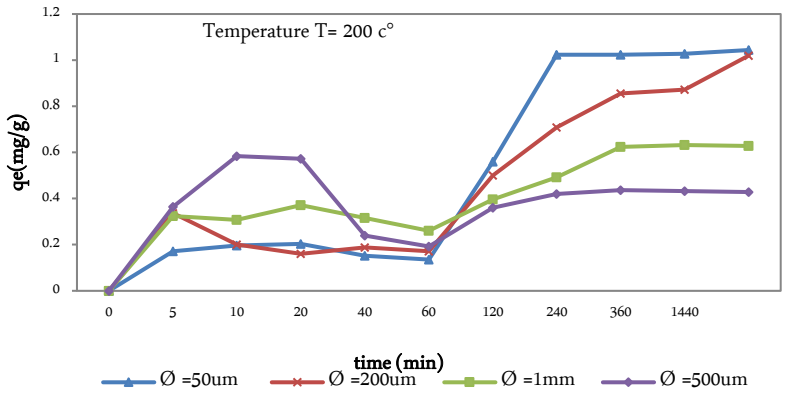

Figure 5 Effect of granular diameter diversity at a temperature 200 C^0

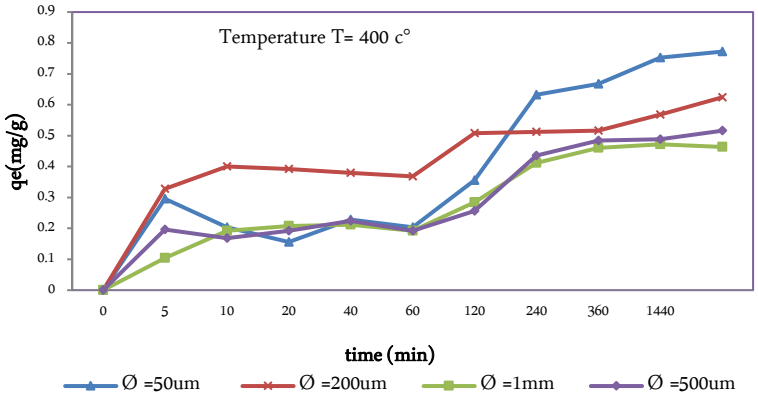

Figure 6 Effect of granular diameter diversity at a temperature 400 C^0

Effect of contact time

Results depicted in (Fig. 7) clearly show that the adsorption of fluoride ions on the (OM) prepared at different temperatures and granular diameter diversity, One of the factors affecting adsorption. shows the effect of contact time on F- ionuptake by the selected adsorbent adsorption material (OM). Perform adsorption experiments to find the optimal time by varying the contact time from 5 to 1440 minutes.

When the (OM) is prepared at a temperature of 105 and 400 C^0. Except(OM) prepared at temperatures of 200 C^0,Equilibrium contact time was foundto be 120 min at a 105 C^0 Nearly 98 % of the fluoride ion was adsorbed within the 1440 min of contact and 69.42 % at a 400 C^0, In the case of 200 C^0 that the polarization amount of fluoride ions increases and decreases 12.23 % was absorbed during the first hour of contact, and it may be due to the liberation of fluoride in the reaction medium and then an increase in the amount of polar- ization of fluoride ions with the passage of the reaction time, where the amount of polarization increases at 240 min to reach 92.08 % and then prove over time. As we note that the adsorption process is proportional to the reaction time

Removal of fluoride ions from drinking water using organic matrix “OM” (date seeds-Deglet Nour):

analyze the effect of experimental conditions.

The removal of the fluoride ion increases with the reaction time between the solution (water) and the (OM) granules. The sorption is first followed by the linear rise in the three samples together (Fig. 7) in which instantaneous, extremely fast uptake takes place in the first 5 minutes, Initially, The results obtained are in agreement with the kinetic models, where the system approaches equilibrium, moving from a higher absorption phase at the beginning, followed by a slower phase (Mahdi, Yu, and El Hanandeh, 2018; Naghizadeh et al. 2017) at a temperature of 105 and 400 C0. the rate of F- uptake was higher because all sites on the adsorbent were vacant and the F- concentration was high, The fast initial uptake was due to accumulation of metal ions on surfaces of OM adsorbents which is a rapid step (Mohan, Singh, and Singh, 2006; Abe et al. 2004) but then a decrease of sorption sites reduced the uptake rate. From this, it was concluded that 120 min were sufficient to reach 0.25 mg/l (Fig. 8) These results can be interpreted according to(Tripathy, Bersillon, and Gopal, 2006), By a cross reaction between the hydroxyl groups of the surface proteins and the fluoride ions according to

the following reaction −COH + F ⟷ CF + OH

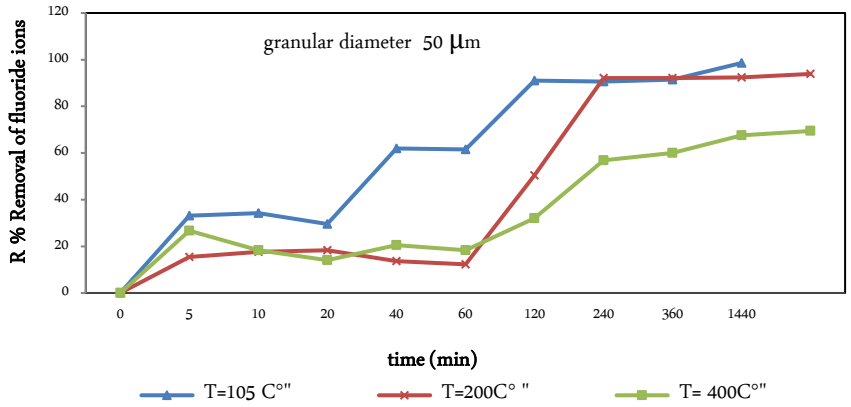

Figure 7 Effect of contact time on F- adsorption by OM (concentration: 2.79 mg/ Solution pH: 7.46 Agitation speed: 150 rpm, Dose 1 g/ 40 mL).

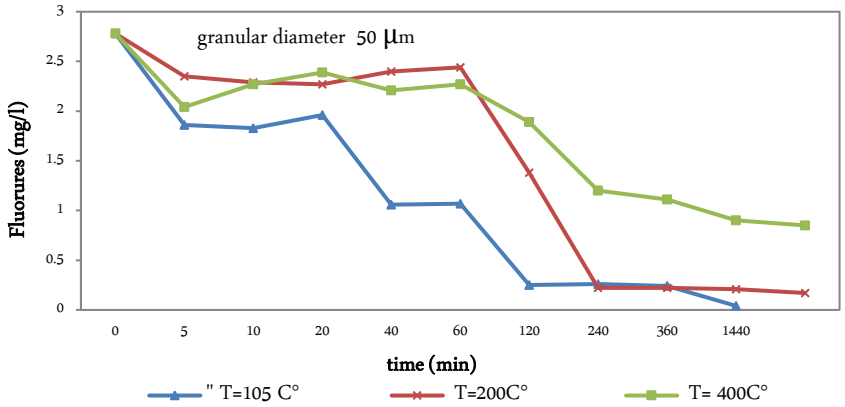

Figure 8 Evolution of fluoride concentration (mg / L) in treated water on date seeds calcined

Effect of the temperature

The effect of temperature It is possible to rely on the organic matrix in the natural state after the process of sterilization and drying at a temperature of105 as a first stage in a treatment to reduce fluoride ions in the water of the region, which gave the highest removal rate of 98.56% in a time of 1440 minutes,

according to (Fig 7). And we must take into account the organic matter produced in the reaction medium due to the use of the date seeds in its natural form, which must be removed.

Effect of adsorbent dosage

The effect of adsorbent dosage on removal of F- ion concentration was studied by varying dosage from 1 to 6 g as shown in Fig 9. Adsorbent dosage is one of the important parameter studied while conducting batch adsorption studies. It was found that adsorption increased with increase in mass of adsorbent (OM) That is, increasing the active sites and thus increasing the percentage of fluoride ions removed (Hanumantharao, Kishore, and Ravindhranath, 2012) Maximum removal efficiency of 100% for F- (from initial concentration of 2.79 mg/l) was observed when 4g of (OM) was used.

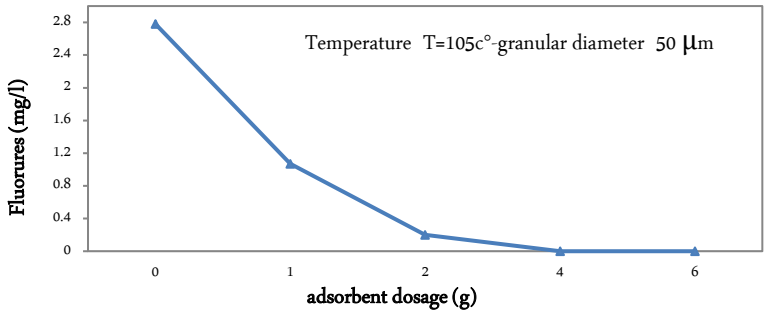

Figure 9 Effect of adsorbent dosage on F- adsorption by OM (concentration: 2.79 mg/L, Solution pH: 7.46 Agitation speed: 150 rpm, Temperature T=105c°, granular diameter 50 µm).

Effect of PH

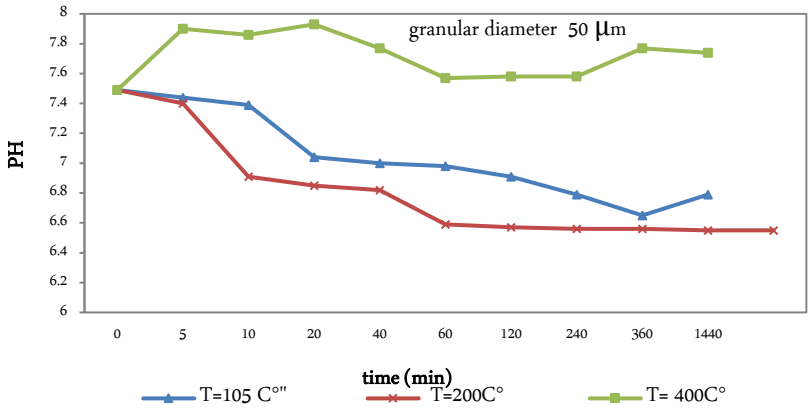

Figure 10 The PH evolution of the reaction of date seeds calcined and treated water

Monitoring of variations in (PH) During the reaction, (Fig 10) shows it. At the beginning of the reaction, the pH increases, which is logical due to the release of Hydroxide ions (OH^-) from the carbon in the solution. As for its decrease, with the exception of (MO) prepared at a temperature of 400 °C, so with the difficultyof understanding this, this can be explained by the possibility of reaction of the hydroxide (OH^-) released with minerals dissolved in water (Ca_2, Na^+ , K^+, . .) or
to the reaction of hydrogen peroxide released with hydrogen potentially released
from proteins, from the (MO) Since the fluoride ion has an affinity (Adler, Klein, and Lindsay, 1938) for tricalcium phosphate $Ca_3(PO_4)2$ and is replaced by

Removal of fluoride ions from drinking water using organic matrix “OM” (date seeds-Deglet Nour):
analyze the effect of experimental conditions.
carbonate ions according to the reaction

$$3Ca_3(PO_4)2CaCO_3 + 6NaF \leftrightarrow 3Ca_3(PO_4)2CaF_2 + 3NaCO_3$$

Thus, the lower pH can be attributed to this reaction.

4. Conclusion

From our tests, it appears that the granular diameter diversity and calcification temperature used had no clear effect of adsorption, under the conditions ofthe experiments carried out in this research. We concluded that the adsorption process is affected by the contact time from the ideal moment and adsorbent dosage to the degree of calcination of 105 °C. The results are very distinct, as the fluoride concentration was reduced by 98.56%, from 2.74 mg/l to 0.25 mg/l ,within 1 h after the reaction using 1g of biomass source (OM), and 0 mg/l When increasing the adsorbent dosage to 4 g.The results are satisfactory in relationto the amount of adsorbent and the concentration of fluoride ions. Adsorptionis one of the effective techniques used in the water treatment process despite the development of many methods and techniques in the process of reducingthe concentration of fluoride in water, but its operation and maintenance costs are high, especially in less industrialized countries. In the current study, thelimit already recommended by the World Health Organization (WHO) has been reached. Taking into account several factors such as diet and climatic conditions, especially the effect of humidity, temperature and the amount of water consumed

per day, as the World Health Organization (WHO) has indicated that in hotregions, the appropriate concentration of fluoride in drinking water should be less than 1 mg/l and 1.2 mg/l in cold regions, and this is due to the consumption of large amounts of water in hot climates. And as specialists always we have madestudies (research) to choose the best method requires for our project at the sametime the least cost method, that is to say we have always estimated the technical- economic and environmental part. Thanks to this study, it was concluded that date seeds-Deglet Nour has a high efficiency as an easy to use, low cost, availableand suitable for local use and not harmful to the environment. The adsorbent material to improve its effectiveness in the context of sustainable development. This product can be used as a radical solution to the high concentrations of fluoride in the desert regions of northern Algeria between the eastern and western regions.

List of symbols

C_e — equilibrium metal ion concentration, mg/L
C_0 — initial metal ion concentration, mg/L
m — mass of adsorbent, g
q_e — equilibrium solid-phase concentration,mg/g
V — liquid-phase volume, L

Declarations

This study was funded by Water and Environmental Engineering in Saharan Milleau (GEEMS) Laboratory. Kasdi Merbah University, 30,000 Ouargla-Algeria.

Conflicts of interest

All authors certify that they have no affiliations with or involvement in any organization or entity with any financial interest or non-financial interest in the
subject matter or materials discussed in this manuscript. Authors are responsible for correctness of the statements provided in the manuscript. See also Authorship Principles.

Data availability statement

The datasets generated during and/or analysed during the current study are available from the corresponding author on reasonable request.

References

Abe, I., Iwasaki, S., Tokimoto, T., Kawasaki, N., Nakamura, T., Tanada, S.: 2004, Adsorption of fluoride ions onto carbonaceous materials. Journal of colloid and interface science **275**(1),35. [abe2004adsorption]

Acharya, S.: 2005, Dental caries, its surface susceptibility and dental fluorosis in south india. International dental journal **55**(6), 359. [acharya2005dental]

Achour, S., Youcef, L.: 2001, Excès des fluorures dans les eaux du sahara septentrional oriental et possibilité de traitement. EIN International **6**, 47. [achour2001exces]

Adler, H., Klein, G., Lindsay, F.: 1938, Removal of fluorides from potable water by tricalcium phosphate. Industrial & Engineering Chemistry **30**(2), 163. [adler1938removal]

Al Sagheer, F., Al-Sughayer, M., Muslim, S., Elsabee, M.: 2009, Extraction and characteri- zation of chitin and chitosan from marine sources in arabian gulf. Carbohydrate polymers **77**(2), 410. [al2009extraction]

Balarak, D., Mahdavi, Y., Bazrafshan, E., Mahvi, A.H., Esfandyari, Y.: 2016, Adsorption of fluoride from aqueous solutions by carbon nanotubes: determination of equilibrium, kinetic, and thermodynamic parameters. Fluoride **49**(1), 71. [balarak2016adsorption]

Baouia K.: 2017, Analyse et distribution des ions fluorure dans les eaux et les aliments consommés dans le sud Algérien : cas de la wilaya de Ouargla.Thèse de Doctorat, Université de Ouargla, 76.

BELMABDI, A.: Distribution des ions fuorures dans les eaux et les principaux aliments, evaluation du risque de la fluorose dans deux communautés du sud est algérien (ouargla et el oued). PhD thesis, Université de Ouargla-Kasdi Merbah. [belmabdidistribution]

Bhatti, M., Al-Rashdan, A., Boota, A., Al-Rashid, Z., Al-Ruwaih, S., et al.: 2010, De- termination of fluoride levels in soft drinks, fruit juices and milk consumed by the population in kuwait using an ion-selective electrode. Kuwait J. Sci. Eng **37**(2A), 75. [bhatti2010determination]

Bogusz, A., Oleszczuk, P., Dobrowolski, R.: 2015, Application of laboratory prepared and commercially available biochars to adsorption of cadmium, copper and zinc ions from water. Bioresource technology **196**, 540. [bogusz2015application]

Boruff, C.: 1934, Removal of fluorides from drinking waters. Industrial & Engineering Chemistry **26**(1), 69. [boruff1934removal]

Cai, Q., Turner, B.D., Sheng, D., Sloan, S.: 2018, Application of kinetic models to the designof a calcite permeable reactive barrier (prb) for fluoride remediation. Water research **130**, 300. [cai2018application]

Chavaissieux, P., Meuinier, P.: 1995, bénéfique et risque des aorts fluorés. Arch Pédiatre **2**.
[chavaissieux1995benefique]

Chen, X., Chen, G., Chen, L., Chen, Y., Lehmann, J., McBride, M.B., Hay, A.G.: 2011, Adsorption of copper and zinc by biochars produced from pyrolysis of hardwood and corn straw in aqueous solution. Bioresource technology **102**(19), 8877. [chen2011adsorption]

Comte, S.: 2004, Couplage de la chromatographie gazeuse inverse à un générateur d'humidité. etude de l'hydrophilie de surface de solides divisés et des limites de la technique. PhD thesis. [comte2004couplage]

Desjardins, R.: 1997, Le traitement d'eaux, 2ème édition de l'ecole polytechnique de montréal. P242 P **6**, P241. [desjardins1997traitement]

Ding, Z., Hu, X., Wan, Y., Wang, S., Gao, B.: 2016, Removal of lead, copper, cadmium, zinc, and nickel from aqueous solutions by alkali-modified biochar: Batch and column tests. Journal of Industrial and Engineering Chemistry **33**, 239. [ding2016removal]

Environnement Canada et Santé Canada.: 1993, Fluorures inorganiques. Ottawa, Environnement Canada, Collection Liste des substances d'intérêt prioritaire.

Farcy M, D., A.: 2008, Systèmes membranaires de potabilisation de l'eau dans les villages et centres non viabilisés. viabilisés. Journal des Sciences et Technologies **7** (2), 51.

Fouskaki, M., Sotiropoulou, S., Koĉı, M., Chaniotakis, N.: 2003, Morpholinoethanesulfonic acid-based buffer system for improved detection limit and stability of the fluoride ion selective electrode. Analytica chimica acta **478**(1), 77. [fouskaki2003morpholinoethanesulfonic]

Goyer, N.: 1981, Vue d'ensemble sur les substances toxiques: rapport sectoriel rédigé pour le bureau d'étude sur les substances toxiques, environnement québec. Québec, Environnement Québec. Bureau d'étude sur les substances toxiques. [goyer1981vue]

Hanumantharao, Y., Kishore, M., Ravindhranath, K.: 2012, Characterization and defluoridation studies of active carbon derived from typha angustata plants. J Anal Sci Technol **3**(2), 167. [hanumantharao2012characterization]

Hichour, M., Persin, F., Sandeaux, J., Molénat, J., Gavach, C.: 1999, Défluoruration des eaux par dialyse de donnan et électrodialyse. Revue des sciences de l'eau/Journal of Water Science **12**(4), 671. [hichour1999defluoruration]

Inyang, M.I., Gao, B., Yao, Y., Xue, Y., Zimmerman, A., Mosa, A., Pullammanappallil, P., Ok, Y.S., Cao, X.: 2016, A review of biochar as a low-cost adsorbent for aqueous heavy metal removal. Critical Reviews in Environmental Science and Technology **46**(4), 406. [inyang2016review]

Jin, H., Hanif, M.U., Capareda, S., Chang, Z., Huang, H., Ai, Y.: 2016, Copper (ii) removal potential from aqueous solution by pyrolysis biochar derived from anaerobically digested algae-dairy-manure and effect of koh activation. Journal of Environmental Chemical Engineering **4**(1), 365. [jin2016copper]

k, B.: 2017, Analyse et distribution des ions fluorure dans les eaux et les aliments consommés dans le sud algérien : cas de la wilaya de ouargla. Thèse de Doctorat, Université de Ouargla,

76. [BaouiaK2017]

Konieczka, P., Zygmunt, B., Namieśnik, J.: 2000, Effect of fluoride content in drinking water in tricity on its concentration in urine of pre-school children. Toxicological & Environmental Chemistry **74**(1-2), 125. [konieczka2000effect]

Liu, Y., Maguire, A., Tianqui, G., Yanguo, S., Zohoori, F.V.: 2017, Fluoride concentrations in a range of ready-to-drink beverages consumed in heilongjiang province, north-east china. Nutrition and health **23**(1), 25. [liu2017fluoride]

Mahdi, Z., El Hanandeh, A., Yu, Q.: 2017, Date seed derived biochar for ni (ii) removal from aqueous solutions. In: MATEC Web of Conferences **120**, 05005. EDP Sciences. [mahdi2017date]

Mahdi, Z., Hanandeh, A.E., Yu, Q.: 2017, Influence of pyrolysis conditions on surface characteristics and methylene blue adsorption of biochar derived from date seed biomass. Waste and Biomass Valorization **8**(6), 2061. [mahdi2017influence]

Mahdi, Z., Yu, Q.J., El Hanandeh, A.: 2018, Investigation of the kinetics and mechanisms of nickel and copper ions adsorption from aqueous solutions by date seed derived biochar. Journal of environmental chemical engineering **6**(1), 1171. [mahdi2018investigation]

Mameri, N., Yeddou, A., Lounici, H., Belhocine, D., Grib, H., Bariou, B.: 1998, Defluoridation of septentrional sahara water of north africa by electrocoagulation process using bipolar aluminium electrodes. Water research **32**(5), 1604. [mameri1998defluoridation]

Marier, J.: 1977, Some current aspects of environmental fluoride. Science of the Total Environment **8**(3), 253. [marier1977some]

Masih, M., Anthony, P., Siddiqui, S.H.: 2018, Removal of cu (ii) ion from aqueous solutions by rice husk carbon-chitosan composite gel (ccrh) using response surface methodology. Environmental nanotechnology, monitoring & management **10**, 189. [masih2018removal]

Mazet, P.: 2002, Les eaux souterraines riches en fluor dans le monde. [mazet2002eaux]

Mazounie, P., Mouchet, P.: 1984, Procédés d'élimination du fluor dans les eaux alimentaires. Revue française des sciences de l'eau **3**(1), 29. [mazounie1984procedes]

Messaïtfa, A.: 2008, Fluoride contents in groundwaters and the main consumed foods (dates and tea) in southern algeria region. Environmental geology **55**(2), 377. [messaitfa2008fluoride]

Mohan, D., Singh, K.P., Singh, V.K.: 2006, Trivalent chromium removal from wastewater using low cost activated carbon derived from agricultural waste material and activated carbon fabric cloth. Journal of hazardous materials **135**(1-3), 280. [mohan2006trivalent]

mondiale de la Santé Bureau régional de l'Europe Copenhague, O.: 1981, La technologie appropriée de déminéralisation de l'eau potable rapport sur un séminaire de l'oms. [organ]

Naghizadeh, A., Shahabi, H., Derakhshani, E., Ghasemi, F., Mahvi, A.H.: 2017, Synthesis of nanochitosan for the removal of fluoride from aqueous solutions: a study of isotherms, kinetics, and thermodynamics. Fluoride **50**(2). [naghizadeh2017synthesis]

N'DAO, L., Lagaude, A., Travi, Y.: 1992, Défluoruration expérimentale des eaux souterraines du sénégal par le sulfate d'aluminium. Sciences et Techniques de l'Eau **26**, 243. [n1992defluoruration]

Onyango, M.S., Kojima, Y., Aoyi, O., Bernardo, E.C., Matsuda, H.: 2004, Adsorption equilibrium modeling and solution chemistry dependence of fluoride removal from water by trivalent-cation-exchanged zeolite f-9. Journal of Colloid and Interface Science **279**(2), 341. [onyango2004adsorption]

Park, S.H., Cho, H.J., Ryu, C., Park, Y.-K.: 2016, Removal of copper (ii) in aqueous solution using pyrolytic biochars derived from red macroalga porphyra tenera. Journal of Industrial and Engineering Chemistry **36**, 314. [park2016removal]
Paulson, E.G.: 1977, Reducing fluoride in industrial wastewater.. [paulson1977reducing]

Pellera, F.-M., Giannis, A., Kalderis, D., Anastasiadou, K., Stegmann, R., Wang, J.-Y., Gidarakos, E.: 2012, Adsorption of cu (ii) ions from aqueous solutions on biochars pre- pared from agricultural by-products. Journal of Environmental Management **96**(1), 35. [pellera2012adsorption]

Petrone, P., Guarino, F.M., Giustino, S., Gombos, F.: 2013, Ancient and recent evidence of endemic fluorosis in the naples area. Journal of Geochemical Exploration **131**, 14. [petrone2013ancient]

Pontie, M., Buisson, H., Diawara, C.K., Essis-Tome, H.: 2003, Studies of halide ions mass transfer in nanofiltration—application to selective defluorination of brackish drinking water. Desalination **157**(1-3), 127. [pontie2003studies]

Rasool, A., Farooqi, A., Xiao, T., Ali, W., Noor, S., Abiola, O., Ali, S., Nasim, W.: 2018, A review of global outlook on fluoride contamination in groundwater with prominence on the pakistan current situation. Environmental geochemistry and health **40**(4), 1265. [rasool2018review]

Santos, C.M., Dweck, J., Viotto, R.S., Rosa, A.H., de Morais, L.C.: 2015, Application of orange peel waste in the production of solid biofuels and biosorbents. Bioresource Technology **196**, 469. [santos2015application]

santé Canada.: 2007, Santé de l'environnement et du milieu de travail, fluorures inorganiques LSIP1, In Santé Canada. Site internet de Santé Canada, Information sur le fluor sa provenance, les fluorures, leurs effets sur la santé, sur la terre, eau, sol.

Scott, R., Kimberly, A., Van Horn, A., Ey, L., Waring, F.: 1937, Fluoride in ohio water supplies—its effect, occurrence and reduction. Journal (American Water Works Association) **29**(1), 9. [scott1937fluoride]

Susheela, A., Kumar, A., Bhatnagar, M., Bahudur, R.: 1993, Prevalence of endemic fluorosis with gastro-intestinal manifestations in people living in some north-indian villages. Fluoride **26**(2), 97. [susheela1993prevalence]

Tahaikt, M., El Habbani, R., Haddou, A.A., Achary, I., Amor, Z., Taky, M., Alami, A., Boughriba, A., Hafsi, M., Elmidaoui, A.: 2007, Fluoride removal from groundwater by nanofiltration. Desalination **212**(1-3), 46. [tahaikt2007fluoride]

Tokaliog˘ LU, S¸., Kartal, S¸., S¸AHI˙N, U.: 2004, Determination of fluoride in various samples and some infusions using a fluoride selective electrode. Turkish Journal of Chemistry **28**(2), 203. [tokaliouglu2004determination]

Tong, X.-j., Li, J.-y., Yuan, J.-h., Xu, R.-k.: 2011, Adsorption of cu (ii) by biochars generated from three crop straws. Chemical Engineering Journal **172**(2-3), 828. [tong2011adsorption]

Tovar-Gómez, R., Moreno-Virgen, M., Dena-Aguilar, J., Hernández-Montoya, V., Bonilla-Petriciolet, A., Montes-Morán, M.: 2013, Modeling of fixed-bed adsorption of fluoride on bone char using a hybrid neural network approach. Chemical Engineering Journal **228**, 1098. [tovar2013modeling]

Travi, Y.: 1993, Hydrogéologie et hydrochimie des aquifères du sénégal. hydrogéochimie du fluor dans les eaux souterraines **95**, Persée-Portail des revues scientifiques en SHS, ???. [travi1993hydrogeologie]

Tripathy, S.S., Bersillon, J.-L., Gopal, K.: 2006, Removal of fluoride from drinking water by adsorption onto alum-impregnated activated alumina. Separation and purification technology **50**(3), 310. [tripathy2006removal]

Veressinina, Y., Trapido, M., Ahelik, V., Munter, R.: 2001, Fluoride in drinking water: the problem and its possible solutions. In: Proceedings of the Estonian Academy of Sciences, Chemistry **50**, 81. [veressinina2001fluoride]

Waghmare, S., Arfin, T., Rayalu, S., Lataye, D., Dubey, S., Tiwari, S.: 2015, Adsorption behavior of modified zeolite as novel adsorbents for fluoride removal from drinking water: surface phenomena, kinetics and thermodynamics studies. International Journal of Science, Engineering and Technology Research **4**(12), 4114. [waghmare2015adsorption]

Wang, S., Kwak, J.-H., Islam, M.S., Naeth, M.A., El-Din, M.G., Chang, S.X.: 2020, Biochar surface complexation and ni (ii), cu (ii), and cd (ii) adsorption in aqueous solutions depend on feedstock type. Science of the Total Environment **712**, 136538. [wang2020biochar]

Warren, J.J., Levy, S.M.: 2003, Current and future role of fluoride in nutrition. Dental Clinics **47**(2), 225. [warren2003current]

WHO.: 2006, Guidelines for drinking-water quality **1**, world health organization, . [world2006guidelines]

World Health Organization.: 2002, Environmental Health Criteria for Fluorides. WHO Library Cataloguing-in-Publication Data édition.

Yang, C.-L., Dluhy, R.: 2002, Electrochemical generation of aluminum sorbent for fluoride adsorption. Journal of hazardous materials **94**(3), 239. [yang2002electrochemic