Removal of Fluoride In Brackish Drinking Water From Senegal By Using KSF And K10 Montmorillonite Clays

Mouhamadou A. Diallo¹, Saidou N. Diop²*, Mohamad M. Diémé²., Courfiia K. Diawara²

¹ Faculté des Science Technique, Université Cheikh Anta DIOP B.P5005 Dakar-Fann, SENEGAL

² UFR Sciences et Technologies Université de Ziguinchor B.P 523 Ziguinchor, SENEGAL

Abstract - Access to safe drinking water is a major challenge for many countries globally for the twenty-first century. In fact, with water crisis issues, the development of research activities for local materials efficiency in improving water quality should be a priority in scientific research, technology, and innovation. Every year, over one million people died or suffered from diseases related to drinking water quality. In Senegal, most people living in the groundnut basin (center and west of Senegal) consume water containing high fluoride and salt levels. They are then exposed to serious health problems such as dental and/or skeletal fluorosis. Therefore, it becomes necessary to remove the excess of fluoride ions from drinking water to prevent health problems.

For this, two types of commercial clays named montmorillonite K-10 (250 m^2/g) and montmorillonite KSF (30 m^2/g) were tested.

In this work, we proposed to carry out two methods of filtration: the dynamic method (filtration with agitation) and the static one (filtration with a column) to study their influence on the efficiency of fluoride ions removal.

In dynamic filtration, 1 g of clay and 100 mL of water sample containing a concentration level of 3.70 mg/L were introduced into a beaker and stirred for 1 hour at 150 rpm by using a magnetic stirrer. Results obtained show fluoride retention rates varied between 74% and 84% for montmorillonite KSF and 26% to 52% for montmorillonite K-10.

In static filtration, 1 g of clay is put into a column equipped with a tap, and then 100 mL of the sample passes through the clay at a flow rate of 100 mL/h. This method results show fluoride retention rates varying between 49 to 67% for montmorillonite KSF and 30% for montmorillonite K-10.

Keywords : Fluoride, montmorillonite KSF, montmorillonite K-10.

I. INTRODUCTION

The twenty-first century has several issues and major challenges for many countries to access safe drinking water. In fact, within a context of water scarcity, the development of research activities on the effectiveness of local materials to improve water quality should prioritize research, technology, and innovation policies. Every year, over one million people die or suffer from diseases related to drinking water quality. In Senegal, most people living in the groundnut basin (center and west of Senegal) consume water containing high fluoride ions and salt levels. They then are exposed to serious health problems such as dental and/or skeletal fluorosis. It seems clear that the fixed amount of fluoride in the human body depends on the concentration of fluoride ions contained in drinking water and climatic conditions [1]. In Senegal's groundnut basin, the drinking water is carried out by the aquifers, namely the Oligo-Miocene, the Paleocene, the Eocene, and the Maastrichtian relatively high levels, higher than 1.5 mg/L and even reaching a peak of 13 mg/L in the region of Mbour [2]. These waters are the only available source of drinking water in the geographical area. Treatment of these brackish and fluorinated waters are then necessary to avoid dental and skeletal fluorosis. The choice of defluorination technique of water from the groundnut basin of Senegal must be guided basically by the physico-chemical quality of these waters, the country's economic constraints, the simplicity of process operation, and the availability of the implemented material.

Our work aims to test fluoride ions' retention efficiency by adsorption on two types of montmorillonite clays called KSF and K-10 in dynamic mode and static one.

II. RELATIONSHIP BETWEEN FLUORIDE INTAKE FROM WATER AND HEALTH

Consumption of highly fluorinated waters can manifest negatives effects on the health of populations that are exposed to these waters. So, the level of fluoride concentration in drinking water must respond to specific standards.

Fluoride is necessary and beneficial to the human body at standards levels but toxic at higher doses. Water plays a prophylactic role from 0.5 mg/L of fluoride ions, but the risk of fluorosis begins and becomes stronger when the concentration is above 1.5 mg/L [**3**]. A relationship between the concentration of fluoride in water and risk of fluorosis

was established, therefore between 0.5 mg/L and 1.5 mg/L, good dental health is promoted; between 1.5 mg/L and 4 mg/L, there is a risk of dental fluorosis; between 4 mg/L and 10 mg/L, fluorosis affects the teeth and/or bones; and beyond 10 mg/L an advanced stage of fluorosis, namely crippling fluorosis is reached [3].

In Senegal, as in many other countries worldwide, studies show that from a level of 2 mg/L of fluoride in water, all children are affected by fluorosis and that 60% of them have severe fluorosis for concentrations close to 4 mg/L [**3**].

World Health Organization (WHO) recommends a guideline value of 1.5 mg/L. It states that specific standards for each country should take into account the climatic conditions, the amount of daily water consumed, and other possible fluoride intakes [4].

A. Dental fluorosis

The immediate consequences of regular water consumption containing excessive fluoride ions are dental and skeletal fluorosis [5,6]. Dental fluorosis has been described in many countries worldwide, including Morocco, Kenya, Tanzania, Senegal, India, especially in countries where people consume water with high fluoride content [7].

The severity and distribution of dental fluorosis depend on the concentration of fluoride in water, the duration of exposure, the stage of ameloblasts activities, and the variation in individual susceptibility to fluoride [7].

The enamel may be mottled in brown or white with streaks, bands and can still exhibit the characteristic aspect of "chalky" teeth. In moderate forms, only the surface layer of enamel is affected. As the severity increases, the deeper layers are affected, and the porosity becomes more important, and the teeth show a chalky white appearance [8,9]. The stain on the teeth is one of the most recognizable dental fluorosis symptoms (figure 1) [10].





Fig. 1 Cases of dental fluorosis

B. Skeletal fluorosis

Skeletal fluorosis is osseous damage due to chronic intoxication to highly fluorinated water (figure 2).

Skeletal fluorosis occurs after a regular and prolonged exposure (at least 10 years) of water with fluoride concentrations above 4 mg/L. Prolonged and high exposure,

around 10 to 40 mg/d, may cause osteopathic effects observed in the skeleton [11].

The fluoride ions (F) replace the hydroxyl ions (OH) from the hydroxy-apatite of the bone to form fluorapatite [3Ca₃(PO₄)₂.CaF₂], which is less soluble than the hydroxyapatite [3Ca₃(PO₄)₂.Ca(OH)₂], the main component of bones. The substitution of OH⁻ ions by F⁻ ions results in an accumulation of fluoride in bone, which causes skeletal fluorosis [**10**].





Fig. 2 Cases of skeletal fluorosis

III. MATERIALS AND METHODS

The work presented in this paper was performed in three regions of the groundnut basin in Senegal, namely Diourbel, Fatick, and Kaolack. In each region, we chose a site in the rural area and urban area to take samples for water treatment.

Identification of a site is done using either the letter U for the urban site or R for the rural site, followed by the region's first letter. For example, UD means a sample taken from the urban site of Diourbel, while RK means a sample taken from the rural site of Kaolack.

Samples were periodically taken at intervals of 20 days during a sampling period of 12 months to monitor the evolution of physicochemical parameters of the water depending on the period of the season.

The experiments were conducted using two methods of filtration: the dynamic method and the static one. We introduced 1 g of montmorillonite clay and 150 mL of water in dynamic filtration to be treated with a fluoride content of about 3.70 mg/L in a 250 mL beaker. The mixture is stirred for 1 hour at 150 rpm using a magnetic stirrer. After 1 hour of stirring, the solution was allowed to settle for 10 minutes and then filtered through a microfilter, and finally, the concentration of fluoride ions in the filtrate was measured.

In static filtration, 1 g of clay is placed in a Pyrex column, then 100 mL of water to be treated passes through the clay with a flow rate of 100 mL/h.

For feed and filtered water, the concentration of fluoride ions is measured by using a MULTIDIRECT

spectrophotometer. We used two commercial clays called montmorillonite KSF and K-10, which have a specific surface area of 250 m²/g and 30 m²/g, respectively. Their chemical composition is presented in table 1.

Table 1: chemical composition of montmorillonite K-10 and KSF

Compounds	SiO ₂	Al_2O_3	CaO	MgO
Montmorillonite K-10 (%)	73	14	0,2	1,1
Compounds	Na ₂ O	K ₂ O	Fe ₂ O ₃	H_2SO_4
Montmorillonite K-10 (%)	0,6	1,9	2,7	-
Compounds	SiO ₂	Al_2O_3	CaO	MgO
Montmorillonite KSF (%)	53,2	18,8	2,9	2,8
Compounds	Na ₂ O	K ₂ O	Fe ₂ O ₃	H_2SO_4
Montmorillonite KSF (%)	-	-	5,1	6

IV. RESULTS AND DISCUSSIONS

A. Dynamic method

a) Dynamic filtration versus time

Figure 3.A and Figure 3.B represent the evolution of fluoride in the filtrate by using montmorillonite KSF and K-10, respectively, in dynamic mode. Results of fig 3.A show that the concentration of fluoride in the filtrate decreases considerably. With concentration levels between 2.62 (UK) and 3.8 mg/L (RD) at the beginning, values were less than 1 mg/L for all samples, leading to retention rates varying from 74 to 79%. Concentrations lower than 1 mg/L in the filtrate were obtained within 15 minutes of agitation time. Fluoride concentration in the filtrate gradually decreases till 30 minutes agitation time and then remains uniform beyond this agitation time, and similar results were reported elsewhere **[12-18]**.

For fig 3.B, the decrease of fluoride concentration in the filtrate is not monotonous. We notice that the maximum retention is obtained after 1 hour of agitation for all samples. Retention rates varying from 26 to 52% were obtained. We also note that fluoride retention varies along with the initial concentrations of fluoride in water samples. The fluoride concentration in the filtrate always exceeds 1.5 mg/L except for the sample with an initial concentration of 2.62 mg/L (UK), decreasing until 1.2 mg/L in the filtrate.



Fig.3 evolution of concentration fluoride infiltrate versus agitation time

b) Fluoride removal versus initial concentration of fluoride

Figure 4 depicts the initial concentration of fluoride in samples and the final concentration after filtration with KSF and K-10 montmorillonite clays in the sampling period's function. The results are shown in the fig4 (A, B, C, D, E, and F) emerge that the concentration of fluoride in the water samples is higher than WHO guidelines, which is 1.5 mg/L. This concentration varies between 2.62 (UK) and 5,6 mg/L (RK). It reaches its maximal value in September, corresponding to strong haste during the rainy season. The increase in the concentration of fluoride is due to the washing of the rocks by rainwater. We notice that the fluoride concentration in the filtrate depends on fluoride's initial concentration in water samples. In all figures, we notice that whatever is the value of the initial concentration of fluoride in water samples, the montmorillonite KSF remove the fluoride ions partially until concentrations lower than 1.5 mg/L. While for the montmorillonite K-10, we notice a reduction in the fluoride concentration, but the values always stay above 1.5 mg/L except for the UK sample taken on 21/04/2011 below 1.5 mg/L. Fluoride concentration for this date is low compared to the others; we can conclude that the montmorillonite K-10 could be effective for low fluoride concentrations in water.





Fig.4 Fluoride removal efficiency of KSF and K-10 montmorillonite clays

Results depicted in Figure 5 show that fluoride concentration in raw water samples studied ranged from 2.75 mg / L (UK) and 4.42 mg / L (RK). Results obtained after 1 hour of stirring show that montmorillonite KSF effectively retains fluoride ions from water samples. The concentration of fluoride ions obtained after filtration is less than 1 mg/L, which gives rejection rates of fluoride ranging between 74% (UK) and 84% (RK). Similar results were reported by [14-16]. However, montmorillonite K-10 eliminates fluoride ions with relatively low retention rates ranging from 33% (UK) and 45% (RK) [17]: the concentration of fluoride ions in the filtrate is higher than the maximum value of 1.5 mg/L recommended by the World Health Organization (WHO) in all sites except the sample from the urban area of Kaolack (UK) where the fluoride concentration in the filtrate is less than 1.5 mg/L.



Fig.5 Fluoride removal efficiency by using KSF and K-10 montmorillonite in a dynamic method

B. Static method

Figure 6 and Figure 7 show the results obtained after a passage of the raw water through the column filled with montmorillonite KSF and montmorillonite K-10 clays, respectively.

Figure 6 shows that the concentration of fluoride ions in the filtrate gradually decreases during the filtration until a volume of 40 mL. Beyond a volume of 40 mL, the concentration of fluoride ions begins to increase in the

filtrate to reach almost its initial value for a volume of 140 mL. This means that from a filtrate volume of 140 mL, montmorillonite KSF clay does not adsorb any fluoride ions from water. The maximum retention of fluoride ions was obtained for a volume of 40 mL and vary between 49% and 67% for the different sites, and similar results were reported by Kusrini and al. **[15]**.



Fig.6 Filtration of raw water with montmorillonite KSF in the static method

The results displayed in Figure 7 show that the concentration of fluoride ions in the filtrate decreases progressively at the beginning of filtration until a volume of 20 mL. Beyond a volume of 20 mL, the concentration of fluoride ions in the filtrate gradually increases to reach almost its initial value for a volume of 100 mL. From 100 mL of montmorillonite K-10 no longer retains the fluoride ions containing in the water to be treated. Maximum retention rates of fluoride ions were obtained for a filtered volume of 20 mL with values ranging between 51% and 64% depending on the sample's initial concentration.



Fig.7 Filtration of raw water with montmorillonite K-10 in a static method

V. CONCLUSION

Access to safe drinking water is a major challenge for many countries globally due to the water crisis that is growing increasingly. Despite water availability in some countries, water resources are often contaminated by chemical elements at excessive levels. In Senegal, most people living in the groundnut basin consume brackish and highly fluorinated water and are faced with dental and/or bone fluorosis. To avoid these public health problems, it is necessary and urgent to provide effective and inexpensive treatment methods. Thus, we undertook to test local materials such as clays to study their effectiveness in treating brackish and fluorinated water in Senegal.

The results show rejection rates of fluoride ions of 75% with montmorillonite KSF and 40% with montmorillonite K-10 in dynamic filtration. For montmorillonite KSF, a 30 minute agitation time was sufficient to provide fluoride concentration less than 1.5 mg/L, correspondings to WHO guidelines. The study shows that the effectiveness of fluoride retention depends on the initial concentration in the raw sample. Then, montmorillonite K-10 is suitable for a low initial concentration of fluoride. The observed results show rejection rates of fluoride ions of 35% with montmorillonite KSF and 30% with montmorillonite K-10 in static mode.

These results show that montmorillonite KSF effectively removes fluoride excess in drinking water from the groundnut basin in Senegal.

REFERENCES

- Youcef L., Achour S. Étude de l'élimination des fluorures des eaux de boisson par adsorption sur bentonite. Larhyss Journal. ISSN 1112-3680 (03) (2004) 129-142.
- Pontié M., Rumeau M., Ndiaye M., DIOP C. M. Sur le problème de la fluorose au Sénégal : bilan des connaissances et présentation d'une nouvelle méthode de défluoruration des eaux de boisson. Cahier Santé.
 (6) (1996) 27-36.
- [3] Pontié M., Schrotter J. C., Lhassani A., Diawara C. K. Traitement des eaux destinées à la consommation humaine. Elimination domestique et industrielle du fluor en excès. Fluor et Environnement. L'actualité chimique (301-302) (2006) 2-7.
- [4] Viswanathan G., Jaswanth A., Gopalakrishnan S., Ilango S. S., Aditya G. Determining the optimal fluoride concentration in drinking water for endemic fluoride regions in South India. Science of the Total Environment. (407) (2009) 5298–5307.
- [5] Mandinic Z., Curcic M., Antonijevic B., Lekic C. P., Carevic M. Relationship between fluoride intake in Serbian children living in two areas with different natural levels of fluorides and occurrence of dental fluorosis. Food and Chemical Toxicology. (47) (2009) 1080– 1084.
- [6] Kumar H., Boban M., Tiwari M. Skeletal fluorosis causing high cervical myelopathy. Journal of Clinical Neuroscience. (16) (2009) 828–830.
- [7] Cutress T. W., Suckling G. W. Differential diagnosis of dental fluorosis J. Dent. Res. (69) (1992) 714-721.
- [8] Fejerskov O., Manji F., Baelum V. The nature and mechanisms of dental fluorosis in man. J. Dent. Res. (69) (1990) 692-700.
- [9] Evans R. W., Stamm J. W. An epidemiologic estimate of the critical period during which maxillary central incisors are most susceptible to fluorosis. J. Public Health Dent. 4 (51), (1991) 251-259.
- [10] Diawara C. K. Nanofiltration process efficiency in water desalination. Separation & Purification Reviews. (37) (2008) 303– 325.
- [11] Rodier J. L'analyse de l'eau, eaux naturelles, eaux résiduaires, eaux de mer. Dunod 8ème édition (2005) 981-984.
- [12] Kumar Yadava A., Abbassi R, Gupta A, Dadashzadeh M. Removal of fluoride from aqueous solution and groundwater by wheat straw, sawdust and activated bagasse carbon of sugarcane, Ecological Engineering. (52) (2013) 211–218.
- [13] Vázquez-Guerrero A, Alfaro-Cuevas-Villanueva R, Guadalupe Rutiaga-Quinones J, Cortés-Martínez R. Fluoride removal by aluminum-modified pine sawdust: Effect of competitive ions. Ecological Engineering. (94) (2016) 365–379.
- [14] Ramirez-Montoya L.A., Hernandez-Montoya V., Bonilla-Petriciolet,

Miguel A. Montes-Moran A., Tovar-Gomez R., Moreno-Virgen M.R. Preparation, characterization and analyses of carbons with natural and induced calcium compounds for the adsorption of fluoride. Journal of Analytical and Applied Pyrolysis. (105) (2014) 75–82.

- [15] Kusrini E., Sofyan N., Suwartha N., Yesya G., Rianti Priadi C., Chitosan-praseodymium complex for adsorption of fluoride ions from water. Journal of rare earth. 33 (10) (2015) 1104-1113.
- [16] Cai H., Xu L., Chen G., Peng C., Ke F., Liu, D Li Z., Zhang Z., Wan X. Removal of fluoride from drinking water using modified ultrafine tea powder processed using a ball-mill. Applied Surface Science. (375) (2016) 74–84.
- [17] Cai H., Chen G., Peng C., Zhang Z., Dong Y., Shang G., Zhu X., Gao H., Wan X. Removal of fluoride from drinking water using tea waste loaded with Al/Fe oxides: A novel, safe and efficient biosorbent. Applied Surface Science. (328) (2015) 34–44.
- [18] Sitti Aminah, Buchari, B., Amran, M. B. Preparation and Characterization of Surfactant Modified Bentonite for Adsorption of Cr(VI) from Aqueous Solution. International Journal of Applied Chemistry 14 (1) (2018) 1-10.
- [19] Saravanan J, Rajasekar J, Sai Krishna R, Sathish Kumar G, Defluoridation of Groundwater using Corn Cob and LECA Balls SSRG International Journal of Civil Engineering 4(3)(2017) 1-3.