



## Adsorption of fluoride ions on hydroxyapatite-modified *Corbula trigona* shell waste: Effect of coexisting anions, temperature and regeneration

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### ARTICLE INFO

#### Article history:

Received 19 April 2023

Received in revised form 15 June 2023

Accepted 16 June 2023

Available online 10 August 2023

#### Keywords:

*Corbula trigona* shells  
Hydroxyapatite  
Fluoride ions  
Groundwater

### ABSTRACT

Hydroxyapatite (HAp) synthesized using *Corbula trigona* shell powder (CTSP) in the presence of 0.3 mol/L phosphoric acid solution was used to evaluate the influence of some parameters such as coexisting anions, temperature and regeneration. Cl<sup>-</sup> and NO<sub>3</sub><sup>-</sup> ions have no significant effect on fluoride removal efficiency in the studied concentration range while sulfates have a detrimental effect on fluoride removal efficiency. The removal efficiency increases with temperature for all the different concentrations studied (2.2; 5.2; 10.5 and 16.8 mg/L). The thermodynamic results showed that the adsorption process was spontaneous, endothermic and irreversible in nature. The maximum adsorption capacity of fluoride ions was 89.3% in the first cycle and gradually decreased with increasing number of regeneration cycles. HAp could be used up to 5 times during fluoride ion removal with a loss of nearly 56% of its adsorption efficiency. The obtained results showed that HAp derived from *Corbula trigona* shell waste can be a promising adsorbent for groundwater defluoridation in developing countries.

### 1. Introduction

The double equation of drinking water supply and sanitation of the living environment of the populations represents a major challenge for developing countries, all of which are confronted with a galloping demography and a rapid socio-economic development. The most affected countries remain those of Africa, in general, and particularly those of sub-Saharan Africa [1]. According to the United Nations, 800 million people in Sub-Saharan Africa do not have access to safe drinking water [2]. Therefore, these challenges related to the provision of safe drinking water and sanitation are likely to be further exacerbated by the climate change crisis in Africa. Moreover, this situation is more deplorable in rural areas where more than half of the population is affected. As a result, people in rural areas are forced to consume raw water from lakes, rivers, wells or boreholes without any prior treatment and therefore of questionable quality. In recent decades, the scarcity of quality resources can be explained by water pollution due to activities of

anthropic and/or natural origin. Fluorine pollution of groundwater is due to the degradation of apatite minerals, wastewater from semiconductor industries, metallurgy, fertilizers, pesticides and glass manufacturing [3]. Thus, in countries such as India, China, Mexico as well as in some African countries, mainly the countries located in the East African Rift Valley such as Ethiopia, Uganda, Kenya and Tanzania, surface and groundwater are highly loaded with fluoride ions [2,4]. In Côte d'Ivoire, studies have shown that groundwater from hand-dug wells in the slums of southern Abidjan (Anoumabo and Adjouffou slums) contains fluoride levels ranging from 1.86 to 16.78 mg/L [5,6]. Consumption of water containing doses above 1.5 mg/L of fluoride ions can cause numerous health problems such as dental and skeletal fluorosis [7]. In addition, other adverse effects such as cancer, nervous and digestive disorders due to the formation of hydrofluoric acid (HF) in the stomach, lowered hemoglobin levels, reduced immunity, urinary and respiratory problems, female sterility and Alzheimer's syndrome have also been reported [8–12].

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<https://doi.org/10.22034/JCHEMLETT.2023.393828.1112>

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In order to avoid public health problems related to the consumption of drinking water rich in fluoride ions, the treatment of these waters must be considered before their availability to consumers. Therefore, many techniques for defluoridation of drinking water have been developed. Among these, adsorption [13], precipitation-coagulation [14,15], ion exchange [16], membrane separation [17–20], electrocoagulation [21], have been implemented to reduce the excess of fluoride ions to concentrations respecting the recommendations of the World Health Organization (WHO). Several researchers have devoted their studies to many natural and synthetic materials such as limestone, snail shells, cuttlebone, hydroxyapatite for the reduction of fluoride ions [22–26]. Some of the adsorbents introduced in recent years have a high potential for defluoridation of fluoride ion rich waters. Among them, hydrothermally modified limestone made of hydroxyapatite (HAp) has shown high efficiency for the treatment of fluoride waters [22,27].

It is therefore important to look for alternative, natural adsorbents that have good fluoride ion adsorption properties. Bivalve shell wastes offer this alternative. These under-exploited adsorbents are locally available in large quantities, inexpensive, easy to regenerate and are non-toxic [28]. Indeed, bivalve shells are mainly composed of calcium carbonate (95%) [29]. Recently, these materials have been the subject of some research work for the removal in aqueous solution of thorium [30], malachite green [31], methylene blue [32], Congo red dyes and copper ions [38].

The objective of this study is to evaluate the effects of temperature and coexisting anions on the removal of fluoride ions from groundwater intended for human consumption using HAp. Then, by the batch method, HAp was put in contact with a quantity of groundwater to follow the effects of temperature and coexisting anions.

## 2. Materials and methods

### 2.1. Synthesis of hydroxyapatite

The operating conditions of phosphoric acid treatment of limestone powder by Gogoi and Dutta [34] and Mohan and Dutta. [22] were used as the basis for the synthesis of hydroxyapatite (HAp) in this study. A phosphoric acid ( $\text{H}_3\text{PO}_4$ ) solution with concentrations of 0.30 mol/L was prepared. Thus, to one liter of each  $\text{H}_3\text{PO}_4$  solution is added 63.5 g of CTSP. These suspensions are stirred and refluxed in a flask for 10 hours at 110 °C. Throughout the experiment, the Ca/P molar ratio was kept constant at 1.67. The precipitate thus obtained is hot filtered on Büchner using Wattman filter paper of 0.45  $\mu\text{m}$

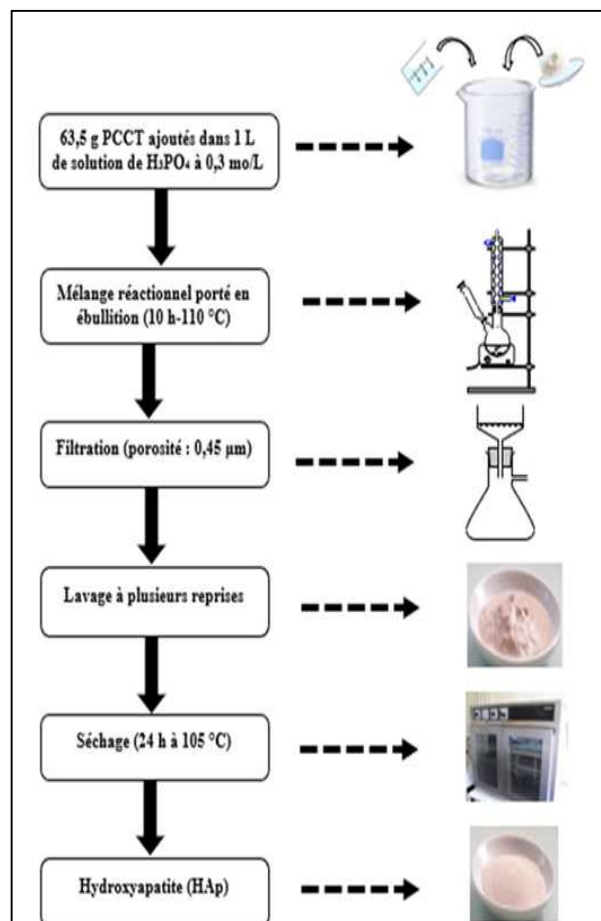
porosity, then washed with distilled water until a pH around 7 is obtained. Finally, the modified CTSP is oven dried at 105 °C for 24 hours and cooled in a desiccator (Fig 1).

### 2.2 Groundwater spiked with fluoride

Groundwater from a borehole in the Bogueúdia Sub-Prefecture (Côte d'Ivoire), was sampled in polyethylene bottles of 1 liter capacity each. A fluoride stock solution was prepared by dissolving an appropriate mass of NaF in distilled water and daughter solutions were prepared from the stock solution by dilution.

### 2.3 Regeneration of hydroxyapatite

Regeneration of HAp was performed using NaOH solution as a regenerant. Thus, a 10 g mass of fluoride-saturated HAp was contacted with 500 mL of 0.3 mol/L NaOH solution to release the active sites. After 2 hours of stirring, HAp was separated from the solution using a 0.45  $\mu\text{m}$  pore size filter paper and the filtrates were analyzed to determine the desorbed fluoride concentration. Recovered HAp was washed 5 times with distilled water and dried at 105 °C for 2 hours in the oven for reuse. Five adsorption-desorption cycles were also performed.



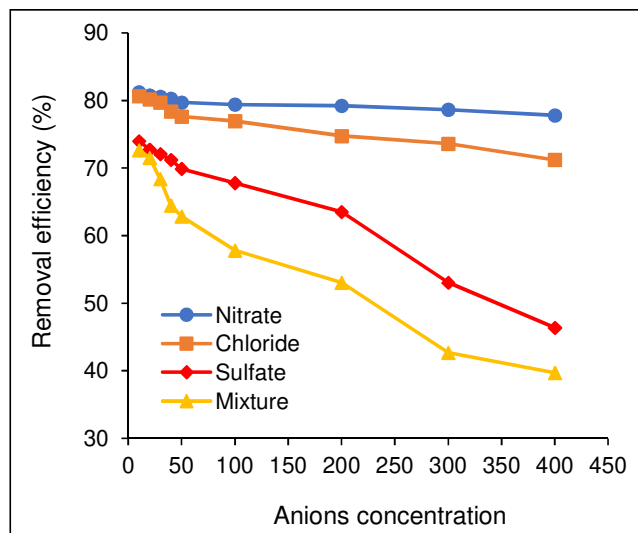
**Fig 1.** Synoptic diagram of the preparation of hydroxyapatites from *Corbula trigona* shell powder

### 3. Results and Discussion

#### 3.1 Effects of factors influencing fluoride removal

##### 3.1.1. Effect of coexisting anions

The concentration of  $\text{Cl}^-$ ,  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$  anions was maintained in the range of 10–400 mg/L by adding appropriate amounts of NaCl,  $\text{NaNO}_3$  and  $\text{Na}_2\text{SO}_4$ . From this study (Fig 2), it can be seen that  $\text{Cl}^-$  and  $\text{NO}_3^-$  ions do not have a significant effect on the removal efficiency of fluoride in the range of concentrations studied. This is probably due to the fact that these ions are low affinity ligands, interacting with the active adsorption sites through weak bonds at the outer sphere complexation [35]. On the other hand, sulfates have a detrimental effect on the removal efficiency of fluoride. This could be explained by the competition between  $\text{SO}_4^{2-}$  and  $\text{F}^-$  for the available active sites on the HAp surface.  $\text{SO}_4^{2-}$  being divalent may also increase the coulombic repulsion forces thus reducing the chances of fluoride interaction with the active sites [26].

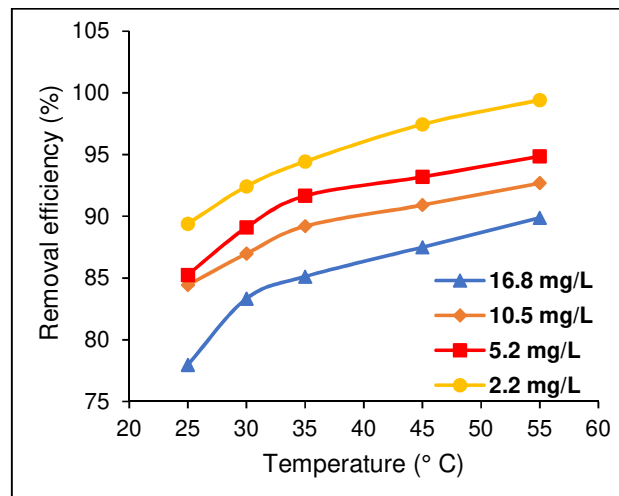


**Fig 2.** Effect of co-anion on fluoride adsorption by HAp (16.8 mg/L of fluoride initial concentration, HAp dose: 5 g/L, pH 7.5 and temperature 25° C)

##### 3.1.2. Effect of temperature

To investigate the influence of temperature on the removal efficiency of fluoride ions, tests were performed at different temperatures between 30 and 55°C. The results are shown in Fig 3. The results show that for the different concentrations, the removal efficiency increases with temperature. It varies from 89.39% to 99.78% for 2.2 mg/L, from 85.26% to 96.21% for 5.2 mg/L, from 84.44% to 93.46% for 10.5 mg/L and from 77.59% to 89.38% for 16.8 mg/L fluoride. This could be due to activation of the

adsorbent surface or to the opening of new pores for fluoride ion binding. The increase in fluoride ion removal efficiency with temperature shows that the adsorption process of fluoride ions on HAp is endothermic. This indicates that the removal of fluoride ions is disadvantaged at low temperature.



**Fig 3.** effect of temperature on fluoride removal at different concentrations (2.2, 5.2, 10.5 and 16.8 mg/L fluoride)

#### 3.2. Determination of thermodynamic parameters

The influence of temperature on the adsorption process was investigated. The adsorption of fluoride ions on HAp was evaluated at different temperatures, 298, 303, 308, 3018 and 328 K, under optimal conditions. The thermodynamic function parameters, namely standard free energy variation ( $\Delta G^0$ ), standard entropy variation ( $\Delta S^0$ ) and standard enthalpy variation ( $\Delta H^0$ ) were calculated using Equation 1 [36]:

$$\Delta G^0 = -RT \ln K_{eq} \quad (1)$$

Where  $K_{eq}$  is the dimensionless equilibrium constant derived from the equilibrium constant ( $K_e$ ) of the best-fit adsorption isotherm model at a given temperature.  $R$  is the gas constant ( $8.314 \text{ J mol}^{-1} \text{ K}^{-1}$ ), and  $T$  is the temperature (K).  $K_{eq}$  is given by the following equation [37,38]:

$$K_{eq} = \frac{1000 * K_e * \text{molecular weight of adsorbate} * [\text{Adsorbate}]^0}{\gamma} \quad (2)$$

Where  $\gamma$  is the activity coefficient and is equal to 1.00,  $[\text{Adsorbate}]^0$  is the standard concentration which is equal to  $1 \text{ mol L}^{-1}$ . Therefore, from the Van't Hoff equation (3), the values of  $\Delta H^0$  ( $\text{kJ mol}^{-1}$ ), and  $\Delta S^0$  ( $\text{J mol}^{-1} \text{ K}^{-1}$ ) are obtained from the slope and intercept of the line  $\ln K_{eq}$  as a function of  $1/T$ .

$$\ln K_{eq} = \frac{\Delta S^{\circ}}{R} - \frac{\Delta H^{\circ}}{RT} \quad (3)$$

The graphs are shown in Fig 4 and the thermodynamic values at different temperatures were presented in Table 1. The negative values of  $\Delta G^{\circ}$  for all concentrations suggest that the adsorption process is physisorption and spontaneous in nature. The positive values of  $\Delta H^{\circ}$  also indicate that the adsorption process of fluoride ions on HAp was endothermic in nature. The positive values of  $\Delta S^{\circ}$  obtained for the different concentrations, show the increased randomness at the adsorption/solution interface during the adsorption of fluoride onto the materials [39].

### 3.3. Fluoride ion desorption and adsorption cycles

From the point of view of cost-effectiveness, the recovery of HAp after each adsorption event is necessary. In order to report the feasibility of adsorbent reuse, the adsorption-desorption cycles were performed five times. Fig 5(a) and Fig 5(b) show SEM photograph of raw HAp and regenerated HAp (b), respectively. The SEM images of HAp after regeneration indicate structural changes in the adsorbent.

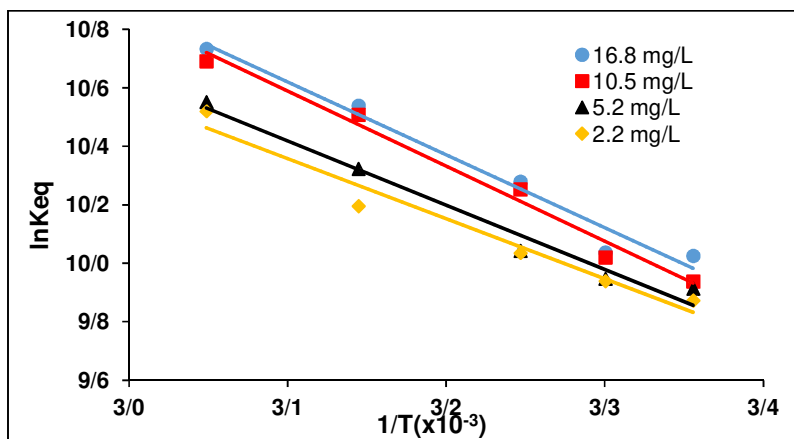


Fig 4. Variation of lnKeq as a function of 1/T

Table 1. The standard thermodynamic parameters of the sorption of fluoride on HAp adsorbent

Initial concentration	$\Delta S^{\circ}$ (kJ/K/mol)	$\Delta H^{\circ}$ (kJ/mol)	$\Delta G^{\circ}$ (kJ/mol)			
			298 K	308 K	318 K	328 K
2.2 mg/L	0.139	16.67	-24.46	-25.70	-26.96	-28.69
5.2 mg/L	0.143	18.27	-24.56	-25.72	-27.29	-28.78
10.5 mg/L	0.154	21.36	-24.62	-26.26	-27.78	-29.16
16.8 mg/L	0.153	20.73	-24.84	-26.32	-27.86	-29.27

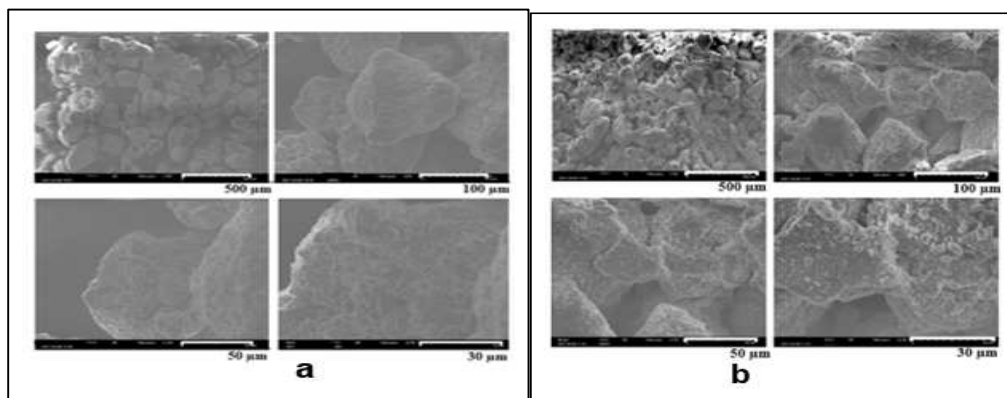


Fig 5. (a) SEM photograph of raw HAp ; (b) Regenerated HA

These results are supported by EDS analysis and mapping of the chemical elements present in the adsorbent (Fig 6(a) & (b)). After analysis of these results, we note a decrease in the weight fraction of carbon, phosphorus, calcium and an increase in oxygen following the regeneration of the adsorbent (Fig 7(a)). On the other hand, copper and aluminium, initially present in HAp, have disappeared. The non-presence of the latter in the adsorbent could be explained by the formation of precipitates in the form of  $\text{Al}(\text{OH})_3$  and  $\text{Cu}(\text{OH})_2$  during the different recycling cycles [40]. The mapping of the observed chemical elements shows a clustering of these elements by location after the different regeneration cycles in Fig 7(b). This is probably due to the progressive degradation of our adsorbent following the adsorption-desorption cycles. The removal and desorption efficiency of fluoride ions is shown in Table 2. The results of this study show

a progressive decrease in the removal efficiency of fluoride ions on HAp during the different regeneration cycles. Indeed, the maximum adsorption capacity was 89.3% during the first cycle and gradually decreased with the increase of the number of cycles. Thus, HAp could be used up to 5 times during fluoride ion removal with a loss of nearly 56% of its adsorption efficiency. The decrease in desorption efficiency could be explained by the non-desorption of fluoride ions on active sites during regeneration of the adsorbent. On the other hand, similar results were obtained by Nagaraj *et al* [41] when defluorinating water with PAHs in five regeneration cycles of adsorption/desorption of fluoride ions with a loss of adsorption capacity of the adsorbent. Indeed, the results obtained in this study confirm that HAp could remove up to 33.33% of fluoride ions after the fifth cycle.

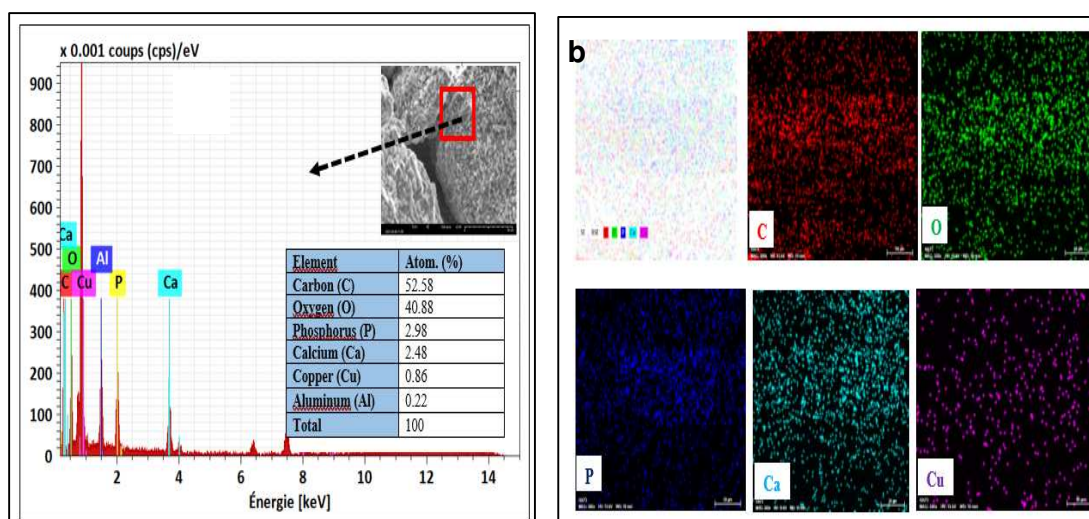


Fig 6. (a) Energy dispersive X-ray spectrum of crude HAp ; (b) Chemical element mapping of crude HAp

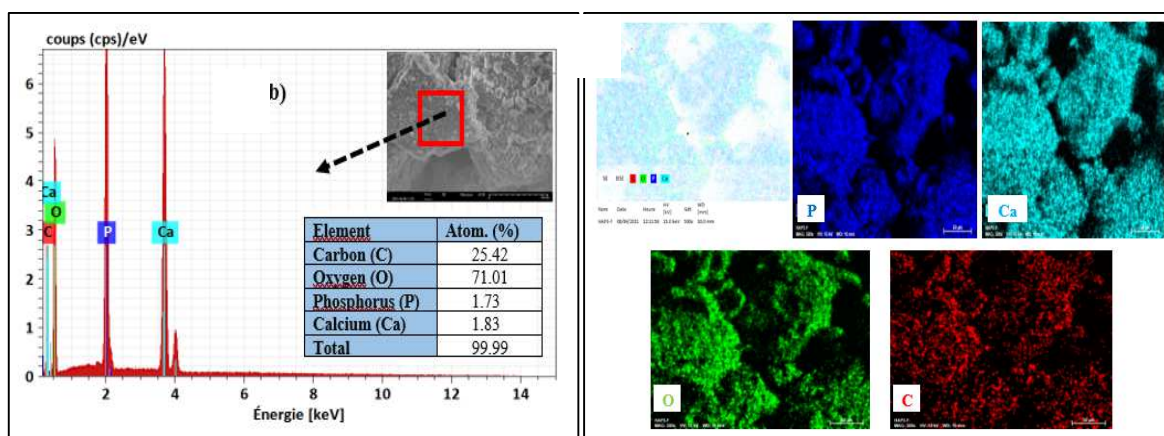


Fig. 7. (a) Energy dispersive X-ray spectrum of regenerated HAp; (b) Chemical element mapping of regenerated HAp

**Table 2.** Removal and desorption efficiency of fluoride ions (Initial concentration: 2.2 mg/L, HAp dose: 10 g/L, temperature: 25°C and contact time: 2 hours 55 minutes)

Number of cycles	Removal efficiency (%)	Desorption efficiency (%)
Cycle 1	89.30	-
Cycle 2	65.15	98.37
Cycle 3	57.58	97.11
Cycle 4	43.94	88.97
Cycle 5	33.33	77.73

#### 4. Conclusion

Hydroxyapatite was successfully synthesized using biological waste, *Corbula trigona* shells by hydrothermal method for adsorption of fluoride from groundwater by adsorption. The removal of fluoride ions from groundwater improved with increasing temperature. Cl<sup>-</sup> and NO<sub>3</sub><sup>-</sup> ions do not have a significant effect on fluoride ion removal efficiency for concentrations between 10 and 400 mg/L while sulfates have a detrimental effect on fluoride removal efficiency. Overall, hydroxyapatite modified *Corbula trigona* shell waste could be a promising alternative adsorbent for groundwater defluoridation at levels below the WHO allowable value.

#### Acknowledgements

The authors would like to thank the Laboratoire des Procédés Industriels de Synthèse, de l'Environnement et des Energies Nouvelles of the Institut National Polytechnique Félix Houphouët-Boigny of Côte d'Ivoire for the material means put at our disposal for the realization of experimental tests.

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