ISSN 2349-7203
IJPPR
INTERNATIONAL JOURNAL OF PHARMACY & PHARMACEUTICAL RESEARCH
An official Publication of Human Journals

Human Journals
Research Article
September 2019 Vol.:16, Issue:2

Evaluation of the Adsorption Capacity of Calcine Bones for the Removal of Fluoride Ions in Water by Thomas Model Application

ISSN 2349-7203
IJPPR
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An official Publication of Human Journals

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Submission: 23 August 2019
Accepted: 28 August 2019
Published: 30 September 2019

HUMAN JOURNALS
www.ijppr.humanjournals.com

Keywords: Fluorides, Adsorbents, Binding Capacity, Calcined Bone, Ionometry

ABSTRACT

This study aims to propose a method for reducing the concentration of fluoride ions in the groundwater of the Bangui region by a simple and cheaper technique that is respectful of the environment through the use of calcined beef bones, accessible to developing countries. We applied ionometry for the determination of fluoride using an automatic ionometer controlled by software "Labcom" version 2.3. The results obtained in this work show a large capacity of these adsorbent materials to retain fluoride ions. We found a significant increase the fixing capacity as a function of particle size, and Thomas' model was finally used to determine the fixing capacity of the calcined materials. The values obtained experimentally on the support 0.4 mm in diameter is $q_{(eq)}$ = 116 mg/kg is clearly better compared to that obtained on the support 0.7 mm, $q_{(eq)}$ = 43 mg/kg. These results confirm the effectiveness of the size of the finest material (support 0.4 mm) to effectively remove fluoride ions.

1) INTRODUCTION

Water is an indispensable natural source in the lives of humans, animals and plants. To have it in sufficient quantity and quality contributes to the maintenance of health. But it can also be a source of diseases due to pollution by industrial discharges, wastewater, household waste and various organic waste [1]. The depletion of surface water forces water producers to diversify sources of supply by tapping into the basement. Although it is considered an important source for the nutrition of small towns, in some cases it's chemical composition can cause public health problems, especially when it contains in excess undesirable substances such as the fluoride ion. According to previous studies, the regular consumption of water with fluoride ion concentrations higher than 1.5 mg / l causes the appearance of dental fluorosis, which is characterized by tooth calcification [2]. Fluorides are naturally present in the Earth's crust and in the waters of the planet. They are released into the environment when minerals in soils are exposed to climatic elements (rain, erosion, etc.); volcanic activity and aerosols from marine waters can also emit fluorides. Fluorides in the environment are becoming more abundant. This is due in particular to their increasing use in industrial products and in dental health products. By considering fluoride levels in ambient air, drinking water, food, consumer goods and dental health products, the average amount absorbed by humans is about 20% below the level of adverse effects are generally felt in the skeleton. [3]

Some pictures on bone fluorosis

Image No. 1: **osteoporosis**

Image No. 2: **Spotted email**

2. MATERIALS AND METHODS

2.1 MATERIALS

Potentiometric measurements were made using the following sensors and equipment:

- Reference electrode Ag / AgCl / KCl 3M

- A fluoride ion selective electrode with Hach brand crystalline membrane;

- An oven EUROTHERM which is used to calcine the bones at a temperature of 600 ºC

for 5 h.

2.2 METHODS

In this study, we will use the ionometric or potentiometric method for the determination of fluoride ions in water. This technique is very easy to use and allows direct measurements. It uses specific electrodes having a sensitive and selective membrane for the fluoride ion. The electrode used in this study is of the HACH brand with a measurement range ranging from 0.02 to 2000 mg / l of fluoride at a temperature ranging from 5 to 50°C. The specific fluoride electrode is combined with a reference electrode (Ag / AgCl / 3M KCl). The measurements are made every minute when the drift is less than 2mV / min. It is equipped with a 1m cable and BNC connector.

2.2.1 PREPARATION OF THE FILTER MATERIAL

The samples of the bones of cattle used in this study were collected at the butcher's shop of a market in the city of Bangui, then washed with distilled water and dried in ambient air.

After drying, the bones were put in an oven for three (3) days at a temperature of 105 ° C. An amount of known mass is introduced into the oven at a temperature of 600 ° C for five (5) hours and protected from oxygen and then cooled in the desiccator for 24 hours. The raw coal is then crushed and sieved to different grain sizes (0.7 mm and 0.4 mm).

These retentas are then washed with distilled water and then dried in an oven at 105 ° C for three days (image 3 and 4).

Image No. 3: retentas 0.7mm

Image No. 4: retentas 0.4mm

For the treatment of elimination of fluoride ions in water, we used as the filter materials prepared at different particle sizes.

This device is composed of:

- a 5-liter plastic container serving as a water tank contaminated with 5 ppm sodium fluoride NaF in fluoride.

- A 25 cm high column containing the filter materials, connected to the contaminated water container via a DINKO D-21V brand pump which regulates the filtration flow rate. The flow rate is regulated at 10 ml/min.

- A KERN EMB 5.2KI electronic scale, which is used to measure the filtered water mass (see diagram of the device below).

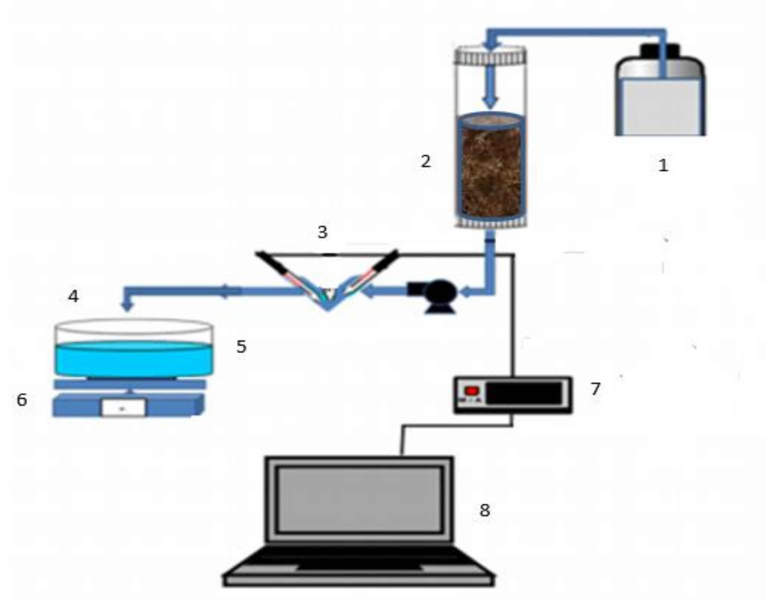

Image No. 5: Filtration device

1: Contaminated water tank

2: the column filled with calcined bone

3: the specific fluoride electrode and the reference electrode

4: treated water tank

5: peristaltic pump

6: the ionomètre

7: Labcom software

3. DATA EXPLOITATION METHOD

The evolution of the residual concentrations of the fluoride ion in the effluent as a function of the volume of filtered water makes it possible to determine experimentally the total amount retained in the Q total column. The latter corresponds quantitatively to the area of the evolution curve of the fluoride ion concentration as a function of the filtered volume or the filtration time. The concentration adsorbed on the support Cads, with Cads = (Co-Ct).

The total adsorbed quantity (Qtotal) is determined by numerical integration of the curve given by the following equation:

$$\mathbf{Q_{totale}} = F\frac{A}{1000} = \frac{F}{100}\int_0^t (C_{ads}dt), \qquad (1)$$

Where F is the flow rate of the filtration (in ml/min); A represents the area of the evolution curve of the fluoride adsorption as a function of time (saturation curve of the column) (Adsorbed concentration); (t total) is the total elapsed time in minutes, which is necessary to obtain the exhaustive time (te), the time required to reach 90% of saturation of the column.

The adsorption capacity of the adsorbent at equilibrium is given by the amount of solute adsorbed per mass of the adsorbent (in mg / g); it is calculated experimentally from the equation:

$$Q_{exp} = Q_{total}/m_{os}, \qquad (2)$$

Or mos represents the mass of the filter material inside the column (in grams).

The total solute mass passing through the column during the experiment can be calculated the equation:

$$M = C_o\, F_{total}\ / 1000 \qquad (3)$$

From equations (1) and (3), it is then possible to reach the percentage of solute retained on the column according to:

$$Y\% = Q_{total}\, 1000/ m \qquad (4)$$

Or Qtotal is the total amount of solute retained in the column expressed in mg; the total mass of solute circulating through the column throughout the experiment.

3.1 MATHEMATICAL MODEL OF THOMAS

The Thomas model is a model used for the theoretical column adsorption / desorption study. It makes it possible to calculate the mass of solute adsorbed by the column. The basic assumption is that there is a state of equilibrium between the adsorbent and the solute. Thomas proposed the following equation:

Thomas equation

$$\frac{C_0}{C_t} = \frac{1}{1 + \exp\left[\frac{k_{Th}}{F}(Q_{eq}m - C_o V_{eff}\right]}$$

Where: represents Thomas's rate constant (mL.mg-1.min-1); Qeq the theoretical adsorption capacity of the column (mg.g-1); m adsorbent mass in column (g)

Q the filtration rate (mL.min-1) and Veff represents the volume of solute that has passed through the column (mL)

This equation can be linearized in this way:

Linearized Thomas equation

$$Ln\left(\frac{C_0}{C_t} - 1\right) = \frac{k_{Th}Q_{eq}m}{F} - \frac{k_{Th}C_o}{F}V_{eff} \quad (6)$$

If the flow rate is constant throughout the filtration this equation can also be reduced to the equation of a straight line y = ax + b

Where y = ln (C0 / Ct - 1), and x = Veff (7)

The slope a = (KTh × C0) / Q (8)

The ordinate at origin b = (KTh × Qeq × m) / Q. (9)

From this line the theoretical capacity of the Qeq column can be determined.

4. RESULTS AND DISCUSSION

4.1 Development of fluoride ion dosing technique

4.1.1 Calibration

The calibration makes it possible to determine the actual slope and to compare it with the theoretical value of Nernst. We can also with this method check the range of linearity of the sensors. For this, we have prepared a range of standards whose fluoride ion (F-) concentrations are between 0.2 and 1.5 ppm. Standards are prepared from a salt of sodium fluoride (NaF). Potentiometric measurements of the standards are made at different ionic strengths by stability using Labcom software.

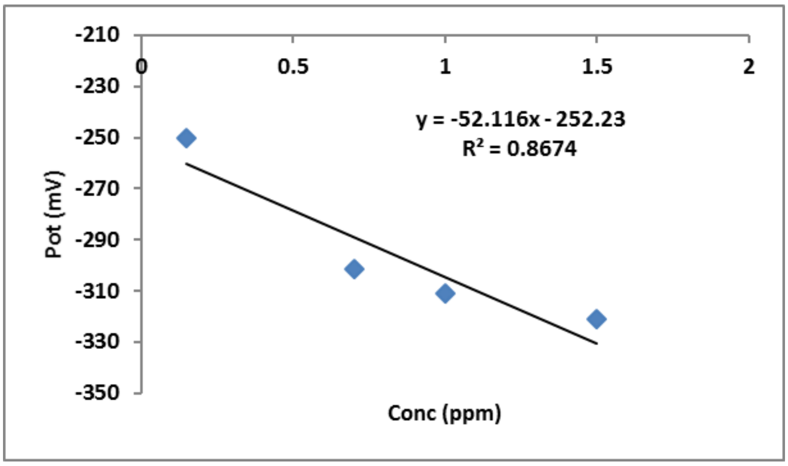

Figure No. 1: Calibration of the fluoride electrode

The slope of Nernst UN indicates the theoretical value of the slope of the electrode. It corresponds to the variation of the tension created by the activity of the fluoride ions in solution as a function of its concentration. It depends on the temperature and the charge z of the ion to be measured.

The theoretical slope value is -59.16; the value of the slope calculated on Excel -52.116 and that obtained by the software is -57.32. The values of the slopes obtained are all close to -59.16 the theoretical slope of Nernst. This result validates the calibration of the device and leads to obtaining reliable results.

4.1.2 Reliability of the method

Any analytical method must be reliable, this reliability is related to the range of linearity between the potential difference and the concentrations of the element in solution. The potential evolution curve as a function of fluoride ion concentration is given in the following figure 2.

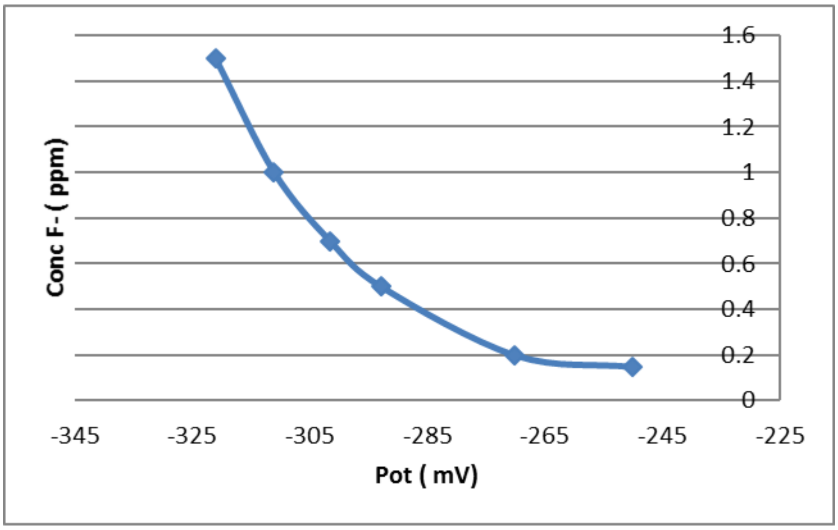

Figure No. 2: Reliability of the method

We note that the evolution of the potential difference as a function of the concentration is not always linear over the chosen measurement range. There is a linearity between concentrations ranging from 1.5 mg / l to 0.2 mg / l. a breakout occurred at the level of 0.2ppm, which explains that the analysis method is reliable only from 0.2 mg / l of fluoride in the sample. Below this value detection is difficult in our experimental conditions. This result corresponds to the detection limit (LD) of measurement given by the manufacturer.

4.2 Removal of fluorides ions on different fixed bed column

In a 5L plastic bottle used as a reservoir, the water was contaminated with 5 ppm NaF. The removal is by filtration on a filter material contained in a 250 ml flask. This vial is connected directly to the 5 L vial of contaminated water. A pump connected to the 250 ml flask, it allows to suck and regulate the filtration rate of water to 10 ml/min. A weigh scale allows you to weigh the amount of filtered water. Two granulometries of the filter materials had been retained 0.7mm and 04 mm in diameter.

The filtrates are taken periodically at the outlet of the filtration column for the determination of fluoride ions. The samples are taken every 100 ml of filtered water.

FIG. 3 shows the evolution of the concentration of the fluoride ions after passing on the two supports 0.7 mm and 0.4 mm, this allows the determination of the retention percentage of the filtering materials. The application of the mathematical model of Thomas will make it possible to determine the retention capacity of the fluoride ions as a function of the adsorbent materials.

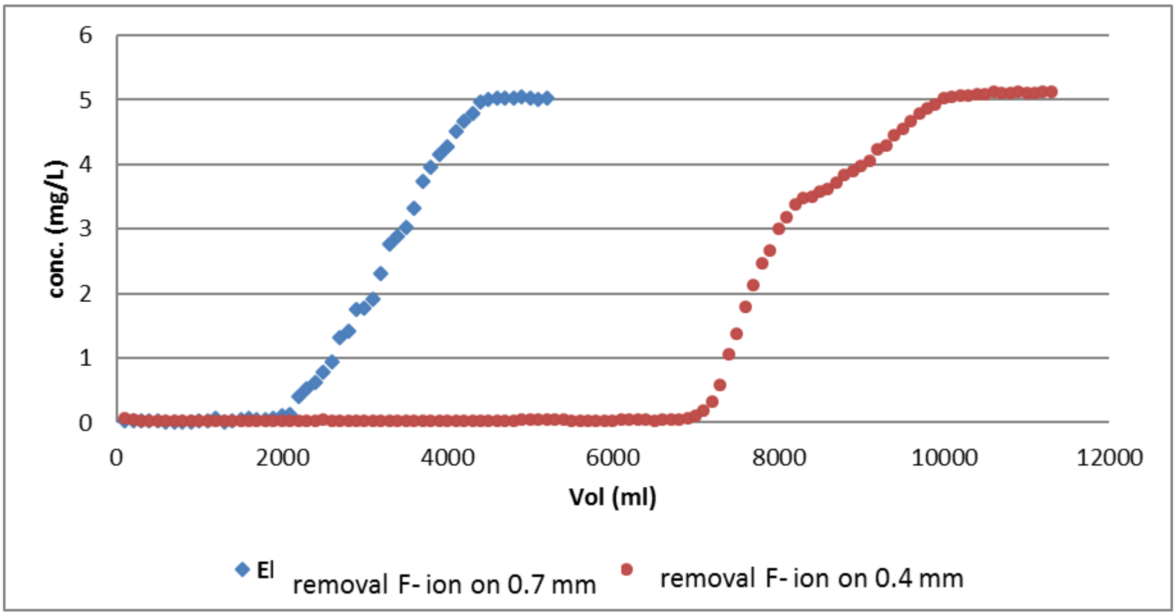

Figure No. 3: Comparison of the retention capacity of the F- ions on the two supports 0.7mm and 0.4mm as a function of the volume of filtered water

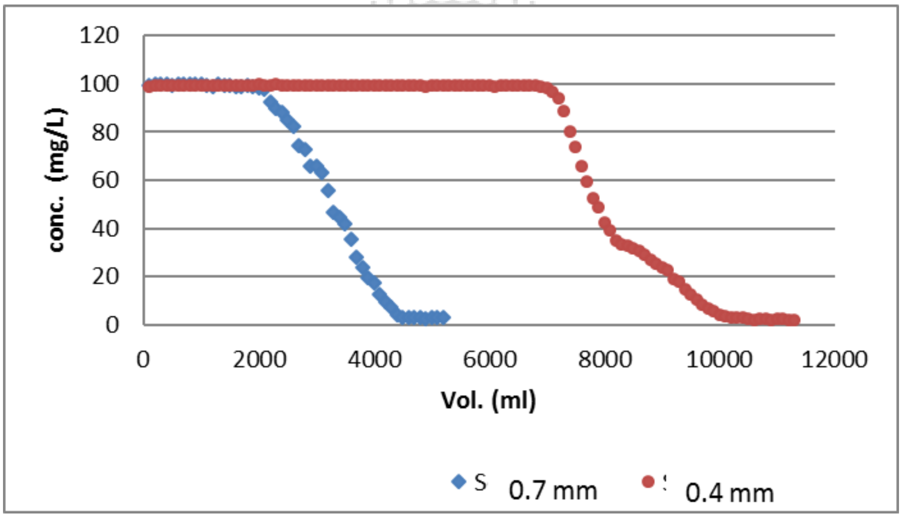

Figure No. 4: Percent removal of fluoride ions on both supports

The curves in FIG. 4 clearly show that at the beginning of the filtration, the supports 0.7 mm and 0.4 mm retain between 99% and 100% of the fluoride ions in the water to be treated. After filtration of a volume of 2100 ml of contaminated water on the different materials, there is a decrease in the retention percentage of the support 0.7 mm while the support 0.4 mm remains effective at 100% retention of the contaminant up to 7100 ml.

It can therefore be concluded that the saturation of the grains of the calcined bones at 0.7 mm in diameter is very fast compared with grains having 0.4 mm in diameter.

4.2.1 Evaluation of the fixing capacity of the supports by Thomas model application

To determine the fixing capacity of the supports applies to the Thomas model described above. The representation of y = ln (C0 / Ct - 1) and x = Veff; allows to linearize the model and to obtain the following figures 5 and 6.

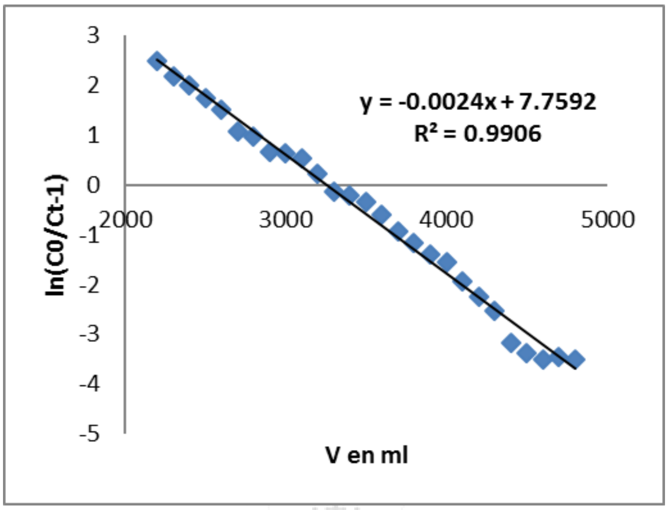

Figure 5: Thomas model application for 0.7 mm

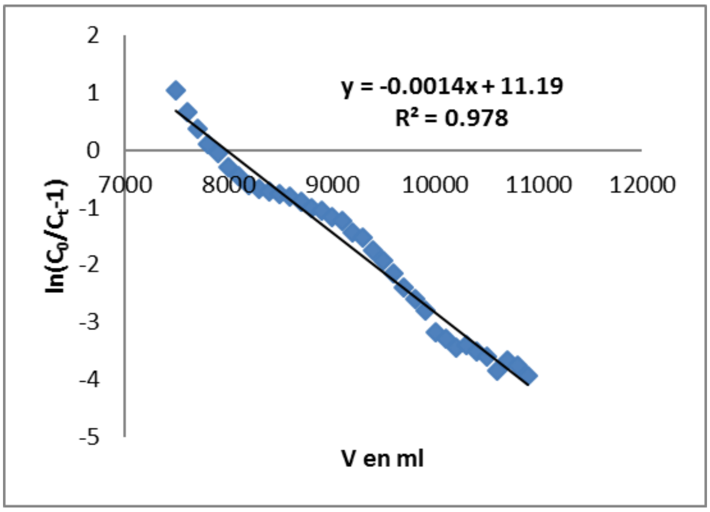

Figure 6: application for 0.4 mm

From the slope and the ordinate at the origin one can determine the various parameters according to model of Thomas. The obtained values recorded in the following Table 1.

Table No. 1: Parameter calculation from Thomas model

	Parameter calculation from Thomas model								
	Q	**W**	**X**	**q total**	**Y**	**qo (calc)**	**q (eq)**	**Kth**	**R**
size	ml/min	mg	g	mg	%	mg/g	mg/g	L/mg/min	
0.7mm	**10**	**26,936**	**390**	**17,006**	**63,134**	**0,043**	**0,044**	**4,633**	**0,9906**
0.4mm	**10**	**59,099**	**360**	**42,730**	**72,302**	**0,116**	**0,119**	**2,677**	**0,9780**

- Q is the flow rate of the filtration;

- W represents the total mass of the fluoride having passed on the column;

- X is the total mass of the grains of calcined bones in the column;

- total, the total quantity fixed on the column;

- Y is the percentage of the retention of the fluoride ions on the column;

- qo (calc) capacity of the column obtained experimentally;

- qo (eq) capacity of the column obtained by the Thomas model.

The fixing capacity of the column obtained experimentally q (eq) is close to that obtained by the model of thomas q0 (calc). These results show the applicability of thomas model to our filtration system. The values of the fixing capacity obtained experimentally on the support 0.4 mm q (eq) = 116 mg / kg is clearly better compared to that obtained on the support 0.7 mm q (eq) = 43 mg / kg. These results confirm the effectiveness of the 0.4 mm support in eliminating fluoride ions.

4.2.2 Comparison of the adsorption capacity according to the granulometry of the supports

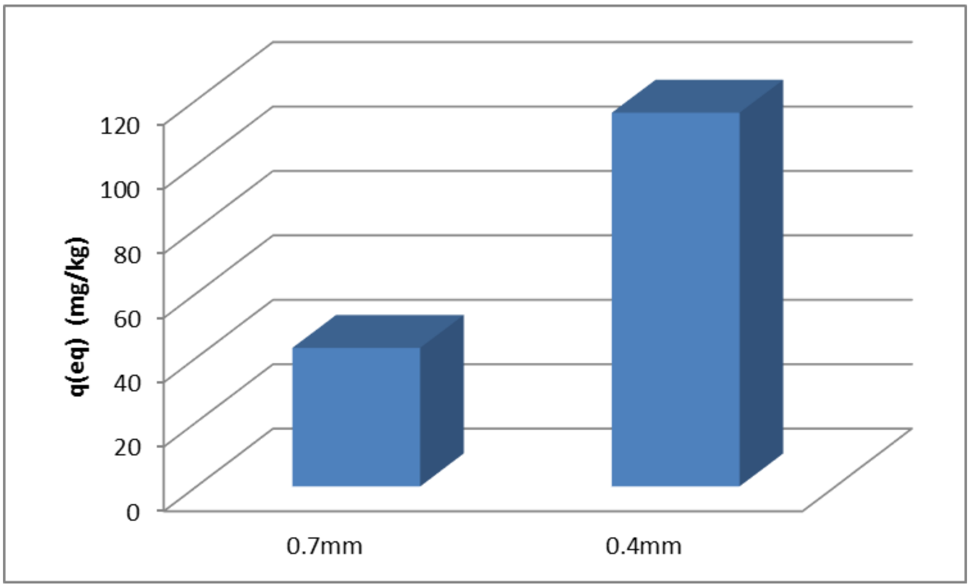

Figure No. 7: Comparison of the adsorption capacity according to the granulometry of the supports

Figure 7 shows that the adsorption capacity is very significant for grains of 0.4 mm, its value is about 3 times higher than that of materials of 0.7 mm. This leads us to confirm that the finer the grains are the contact surface is important and the elimination is effective.

CONCLUSION

The main results obtained in this work have shown that (i) the technique of fluoride ion dosing by potentiometer is reliable, the values of the slope obtained are after calibration close to the theoretical value of the Nernst relation (-59.16 mV), Excel (-52,166 mV) and Labcom software (-57.32 mV). The process developed in this work shows a large capacity of the materials used to retain fluoride ions. Also, we have observed a significant increase in the fixing capacity of the filter materials according to their grain size, the finer the grains are, the more the filtration is effective. We can conclude that the maintenance and improvement of water quality remains one of the basic measures of public health. While the quality of this water appeared to be acquired in the industrialized countries, the development of knowledge on the toxic effects of contaminants and the upsurge of certain epidemics made it possible to highlight that it is a permanent threat which not be forgotten. This process has the advantage of being cheap and requiring no chemical treatment products. In addition, the design of this system has been to use local materials (beef bone) often left behind in developing countries and which constitute a source of environmental pollution.

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