HOUSEHOLD PURIFICATION OF FLUORIDE CONTAMINATED MAGADI (TRONA)

J M Nielsen* and E Dahi*
Copenhagen, Denmark

SUMMARY: Purification of fluoride contaminated magadi is studied using bone char sorption and calcium precipitation. The bone char treatment is found to be workable both in columns and in batches where the magadi is dissolved in water prior to treatment. The concentrations in the solutions were 89 g magadi/L and 95 and 400 mg F/L respectively in natural and synthetic solutions. The fluoride removal capacities observed were 4.6 mg F/g bone char for the column system and 2.7 mg F/g bone char for the batch system in case of synthetic magadi solution. It is however concluded that the batch system is the best treatment method. A procedure for purification of fluoride contaminated magadi at household level is described.

Key words: Trona; Magadi; Fluoride; Fluoride removal; Magadi purification; Household treatment.

INTRODUCTION

The World Health Organisation's guideline for the maximum fluoride concentration in drinking water is 1.5 mg/L. However, WHO stresses that the climatic conditions and daily water intake should be taken into consideration when adopting fluoride standards for countries. Especially in fluorosis afflicted areas in East Africa drinking water is not the only source of fluoride intake. The naturally occurring mineral trona ($Na_2CO_3 \cdot NaHCO_3 \cdot 2H_2O$), locally called magadi, is known to contain relatively high amounts of fluoride.[1,2] Magadi is used in the household mainly as a tenderiser to shorten the cooking time of legumes and vegetables. The frequency of magadi use for food preparation in households in Arusha Region, Northern Tanzania ranges from daily use to a couple of times per week.[3-6] The fluoride content of magadi is subject to considerable variation. In Tanzanian magadi, concentrations from 0.1 mg F^-/g magadi to 18 mg/g have been reported.[4,6-8] The fluoride concentration in magadi originating from Lake Magadi and harvested by the Magadi Soda Company also varies.[8] However, a concentration of 4.0 mg F^-/g magadi has been reported to be typical.[9]

Since drinking water in most cases is the major contributor to the total fluoride intake efforts have been put in development of methods for defluoridation of drinking water. Promising methods which are now in use in Northern Tanzania are the contact precipitation technique and the bone char filter technique.[10] The human fluoride intake through magadi may under certain circumstances be significant, even compared to the intake through water and other sources.[3,4] The aim of this investigation is to develop a method for purification of fluoride contaminated magadi. For this purpose two processes are tested: A bone char sorption process in batch as well as in column and a precipitation process based on addition of calcium chloride.

MATERIALS AND METHODS

Column Experiments. Synthetic magadi solution and natural magadi solution were filtered through two glass column filters in series, the first containing bone char, the second containing activated carbon. Gravel was placed at the inlet and the outlet of both columns. The filters were connected with a plastic tube and closed with stoppers of rubber. Distilled water was filtered through the columns to clean the filter materials. Hereafter the filter columns were filled with magadi solution and left for 24 hours before

* Endeco, Thulevej 16, DK-2860 Søborg, Denmark. E-mail: jmn@image.dk , endeco@image.dk

the filtration was started. The flow through the filters was kept constant during the whole experiment. Samples from the outlet of both the bone char filter and the activated carbon filter were taken at regular intervals of 6 to 8 hours. The column design parameters are listed in Table 1 and the design is illustrated in Figure 1.

Jar test experiments using bone char. Experiments were carried out in one litre plastic beakers containing 500 ml synthetic magadi solution. Amounts of 50 and 100 g bone char were added, respectively. The solutions were stirred in the Jar test apparatus (Phipps & Birds Stirrer 7790-402) at a speed of 50 and 100 rpm, respectively. After 24 hours of stirring samples were taken, filtered through a 0.45 µm Minisart GF filter and fluoride concentration and alkalinity were tested.

TABLE 1. Design parameters for filtration of synthetic and natural magadi solutions through bone char and activated carbon filters

Parameters	Unit	Synthetic magadi solution		Natural magadi solution	
		Bone Char	Activated Carbon	Bone Char	Activated Carbon
Cross sectional area, A	cm^2	7.07	7.07	7.07	7.07
Length of filter bed, L	m	0.80	0.80	0.40	0.40
Surface loading, Darcy velocity, v_s	m/hour	0.10	0.10	0.06	0.06
Porosity of filter bed, ε	-	0.55	0.62	0.55	0.62
Contact time, T_C	hours	4.3	4.9	3.9	4.4
Grain size of filter bed, GS	mm	2.0-2.8	1.0-3.0	2.0-2.8	1.0-3.0
Mass of filter bed, M	g	335	150	170	75

Precipitation experiments. Experiments were carried out in one litre plastic beakers containing 500 ml synthetic magadi solution. Aliquots of 1.00, 2.00, 3.00, and 4.00 ml of calcium chloride solution were added, respectively. The solutions were stirred in the Jar test apparatus (Phipps & Birds Stirrer 7790-402) at a speed of 50 rpm for 5 minutes. After 1 hour of settling the solutions were decanted. Samples were taken, filtered through a 0.45 µm Minisart GF filter and fluoride concentration and alkalinity were tested.

Bone char preparation. The bone material was delivered from the Danish bone meal factory DAKA, where the bone material has been boiled, washed, dried and crushed into small particles d_{BC}<4.0mm. The bone material was pyrolysed in a programmable ceramic oven (Scandia Oven, Type SK 355) in a closed steel container, where the access of atmospheric oxygen was restricted. The temperature was raised at a rate of 4°C/minute from room temperature to 600°C and then kept constant for 10 hours. The charred bone material was allowed to cool down to room temperature before the oven was opened. The bone char was divided into fractions d_{BC}<0.50 mm, 0.50-1.0 mm, 1.0-1.4 mm, 1.4-2.0 mm, 2.0-2.8 mm, and d_{BC} >2.8 mm using a test sieve shaker (Endecotts EFL2 mk3). The grain size 2.0-2.8 mm fraction was selected and used as bone char in all experiments. The specific surface area of the bone char was measured according to the BET method and found to be 116 m^2/g.

Calcium chloride solution. The calcium chloride solution was prepared by addition of analytical $CaCl_2$ to distilled water with a dosage of 2.5 mol/L.

Synthetic magadi solution. The synthetic magadi solution was prepared by addition of analytical chemicals to distilled water as follows: 0.393 mol/L Na_2CO_3, 0.393 mol/L $NaHCO_3$, 21.1 mmol/L NaF, and 28.6 mmol/L NaCl. The dosage of sodium carbonate and sodium bicarbonate equals a concentration of 89 g/L pure trona.

Natural magadi solution. Magadi collected at Lake Natron, Tanzania was dissolved in distilled water (89 g/L) and the concentration of carbonates and fluoride equals a concentration of 1100 meq/L and 5.0 mmol/L, respectively.

Fluoride and alkalinity measurements. The fluoride concentrations were measured using a Metrohm fluoride ion selective electrode and a Metrohm Ag/AgCl reference electrode with a sleeve type diaphragm connected to a Metrohm potentiometer (692 pH/Ion Meter). Aliquots of 5.0 mL of the sample were mixed with 5.0 mL distilled water and 10.0 mL CDTA-tisab and the fluoride concentrations were measured using the standard addition procedure, according to Standard Methods.[11]

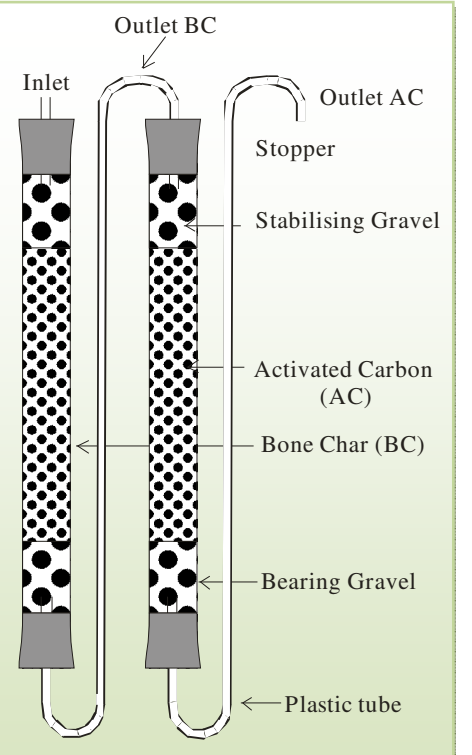

FIGURE 1. Experimental set-up for column design experiments in case of synthetic and natural magadi solutions.

The alkalinity was measured using the end point titration procedure according to Standard Methods.[11] The end points were pH=8.3 and pH=4.5. Samples of 1.00 mL were diluted to 50.0 mL and titrated automatically with 0.1 N H_2SO_4 at a maximum titration rate of 1.00 mL/min. pH values were monitored continuously (5 seconds interval) using a Metrohm pH-electrode connected to a Metrohm 719S Titrino (potentiometer/dosimat). The values of pH and the amount of acid added were recorded on a PC. The calibration of the pH-electrode was carried out using Metrohm buffer solutions having pH=4.0 and pH=9.0.

RESULTS

The results of the measurements of the total alkalinity and the fluoride concentration in the effluent solution from the bone char columns and from the activated carbon columns are shown in Figure 2. The upper figure concerns the treatment of the natural magadi solution while the lower one concerns the synthetic solution. The results are plotted, for both the fluoride and the total alkalinity, as the ratio between the concentrations of the outlets and the concentration of the inlet to the bone char column. The abscissa is drawn as the fluoride loading on the bone char column. For the activated carbon column, the initial pore water is however neglected, as it has not been treated in the bone char column.

During the filtration the removed fluoride is taken up by the bone char. In Figure 3 the estimated fluoride concentration in the bone char, f_t is plotted versus the fluoride loading on the column. The fluoride concentration in the bone char is calculated as the sum of the

differences between the inlet and the effluent concentrations, S_i-$S_{e,t}$, in the different samples multiplied by the differential part volumes of treated solutions, ΔV_k, divided by the mass of bone char, M_{BC} in the column:

$$f_t = \frac{1}{M_{BC}} \sum_{k=0}^{V_t} (S_i - S_{e,t}) \cdot \Delta V_k$$

Table 2 shows the experimental data and the results from the jar test experiments. X_{BC} is the amount of bone char added to 1 litre of synthetic magadi solution and the ΔTAL is the change in alkalinity between the treated and the untreated magadi solution. Table 3 shows the experimental data and the results from the bone char column experiment where synthetic magadi solution is treated. The dosage of bone char, X_{BC}, is calculated as the amount of bone char in the column divided by the amount of treated water at a selected effluent fluoride concentration corresponding to different filtration times. The average effluent fluoride concentration, $S_{e,average}$, is calculated as the sum of the effluent concentrations, $S_{e,t}$, in the different samples multiplied by the differential part volumes of treated solutions, ΔV_k, divided by the cumulative volume of treated solution, V_t, at the sampling time:

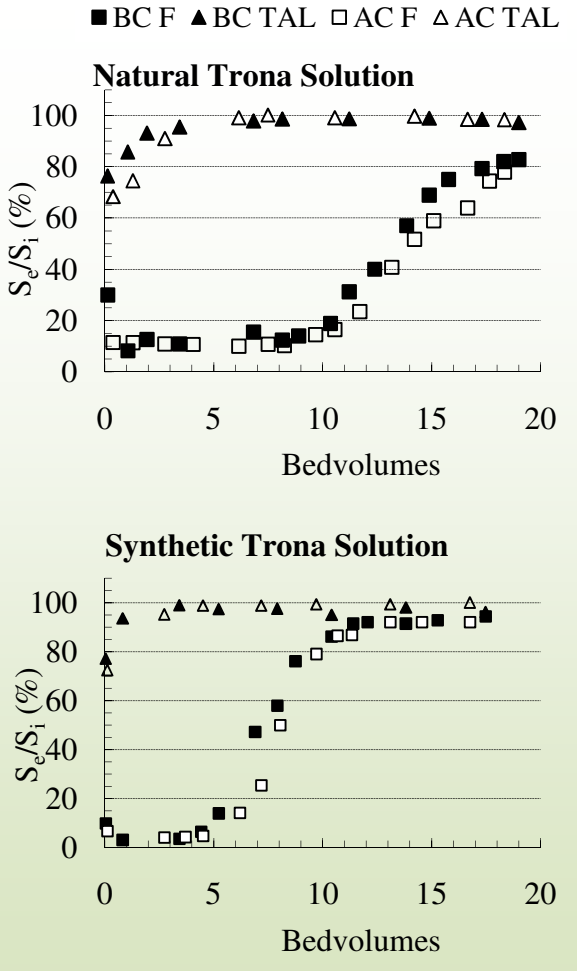

FIGURE 2. The ratio between the effluent (e) and the inlet (i) concentration of fluoride (F) and the total alkalinity (TAL) versus the number of bedvolumes of filtered solution for bone char (BC) and activated carbon (AC) column using natural and synthetic trona solutions.

$$S_{e,average} = \overline{S_e} = \frac{1}{V_t} \sum_{k=0}^{V_t} S_{e,t} \cdot \Delta V_k$$

It was investigated to what extent the addition of $CaCl_2$ to magadi solution would reduce the fluoride contamination. The results of the measurements of fluoride and carbonates concentrations can be seen in Figure 4. The reductions in carbonate and bicarbonate alkalinity and fluoride concentration are plotted versus the amount of calcium added. It is concluded that the idea of using $CaCl_2$ for removal of fluoride from highly alkaline solutions is not feasible. Even though the solubility product for fluorite (CaF_2) is

exceeded, $K_{fluorite}=10^{-10.57}$ at 25°C, the reduction in the fluoride concentration is minor compared to the reduction in carbonate alkalinity, i.e. aragonite ($CaCO_3$) is more likely to precipitate than fluorite.

Discussion

In Figure 2 it is observed that bone char is able to remove fluoride from highly alkaline waters (magadi solutions) without any major changes in the total alkalinity of the treated solution. However, focusing on the initial few bedvolumes of treated solution there seems to be a minor but significant removal of alkalinity in the bone char column. The alkalinity removed in case of natural and synthetic magadi solutions are equal to 308 meq and 125 meq, respectively. This removal is probably caused by precipitation of $CaCO_3$, as the bone char is known to contain varying amounts of free calcium. The same phenomenon is observed in the jar test experiments. The total alkalinity of the treated solution is lower than the initial total alkalinity. It is seen from Table 2 that the higher the dosage of bone char, the higher is the reduction of the total alkalinity.

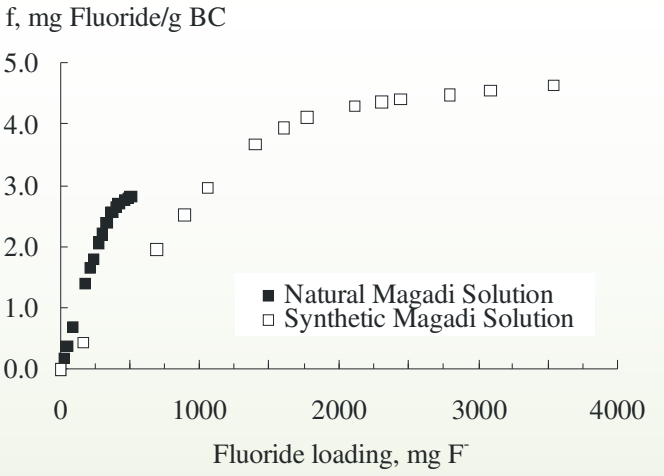

FIGURE 3. The fluoride concentration in bone char versus the fluoride loading for column experiments in case of natural and synthetic magadi solutions containing 89 g magadi/L.

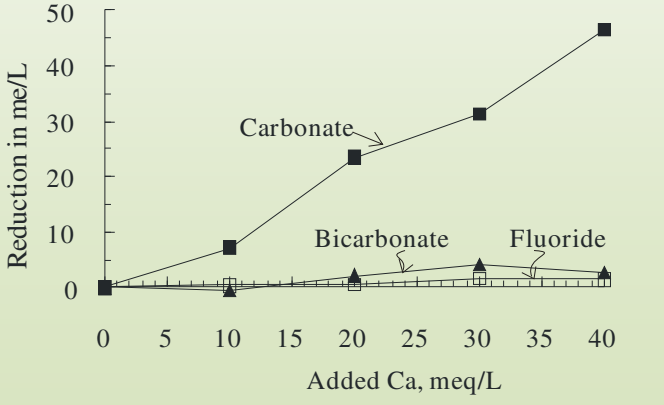

FIGURE 4. The reduction in carbonate and bicarbonate alkalinity and fluoride concentration versus the addition of calcium in precipitation experiments in case of synthetic magadi solution containing 89 g magadi/L.

From Figure 3 it can be seen that the concentration of fluoride in the bone char increases linearly until the effluent fluoride concentration starts to increase, i.e. the break point. This takes place in the bone char columns after loading of 300 and 1200 mg F^- from the natural and synthetic magadi solutions, respectively. Figure 3 shows that achieved bone char capacities in case of natural and synthetic magadi solutions are 2.8 and 4.6 mg F^-/g BC as the inlet fluoride concentrations are 95 and 400 mg F/L, respectively.

TABLE 3. Experimental data and results from jar test experiments in case of synthetic magadi solution containing 89 g magadi/L and 400 mg F/L.

Batch test no.	X_{BC} g/L	Stirring rpm	S_e mg/L	f mg/g	$f_{average}$ mg/g	ΔTAL meq/L
1	50	50	234	3.24	3.20	39.0
2	50	100	238	3.16		32.0
3	100	50	126	2.74	2.69	104
4	100	100	137	2.63		65.0

TABLE 4. Experimental data and results from bone char column experiment in case of synthetic magadi solution containing 89 g magadi/L and 400 mg F/L. The figures in bold, X_{BC} should be compared with the same figures in table 2.

V	X_{BC}	S_e	f_t	$S_{e,average}$
l	g/L	mg/L	mg/g	mg/L
3.35	**100**	177	3.55	45.0
6.72	**50**	367	4.46	177

The results are in agreement with the sorption isotherms theory, where the maximum sorption capacity is higher, the higher the inlet concentration.

When using the bone char as a fluoride removal media in the jar test experiments, it has been necessary to add more than 100 g/L bone char to the synthetic magadi solution to obtain an acceptable residual fluoride concentration of less than 1 mg F^-/g magadi. An addition of 100 g BC per litre synthetic magadi solution resulted in a residual fluoride concentration of 1.4 mg/g magadi.

Tests were conducted to elucidate if the mixing of bone char and magadi solution is of any significance. Twenty five grams of bone char were added flasks containing 250 ml synthetic magadi solution and shaken for 0, 5, 10, 15, and 30 minutes, respectively. After 24 hours of contact time the residual fluoride concentrations were measured to be within the same range, 151-168 mg F/L. From these results it is concluded that when sufficient contact time is provided, the mixing is of minor importance.

When comparing the column and the batch test's possibilities for being utilised at household level in developing countries the column method has 2 main drawbacks. The operation of the columns is quite troublesome, as the flow must be controlled at a very low rate. Furthermore, the breakpoint has to be checked which is an almost impossible task at household level. On the same line the batch treatment results in approximately 20 % lower sorption capacity and hence a higher consumption of bone char, cf. Table 2 and 3. However, this drawback seems to be minor compared to the major advantage of simple operation, where no breakpoint needs to be checked. Compared with the column method the batch method is much more preferable for use in developing countries, especially at household level.

In defluoridation of drinking water small grain sizes have shown higher efficiency compared to larger grain sizes.[12] However, in this study not less than 30 % higher defluoridation efficiency is achieved in batch tests when using large grain sizes, the initial concentration of fluoride being 400 mg/L. The batch experiments showed that the fluoride removal is about 70 % when using bone char grains of 2.0-2.8 mm compared to

60 % for grains of 0.5-1.0 mm. Thus, it is important to avoid crushing the bone char into small grains when dealing with solutions containing high fluoride concentrations. This is quite opposite the recommendation in normal water defluoridation.

This study shows that defluoridation plants based on bone char for treatment of magadi solutions may be efficient both as batch systems and as column systems. When taking the drawbacks of the systems into consideration it is concluded that the batch system is superior to the column system at household level. The set-up of the batch system may be recommended as follows:

- About 100 mL of clean drinking water is transferred into a 200 mL container.
- A small amount of magadi, ca. 10 g, is added and the solution is stirred until complete dissolution apart from possible dirt.
- About 1.5 times as much of bone char (ca. 15 g) is added.
- The mix is stirred gently a few times and left overnight.
- The next day the purified magadi solution is decanted and then ready for use.

As the solution is durable larger batches can be prepared for use over a week or even a month.

Raw natural magadi, especially scooped magadi, may contain insoluble fractions: clay particles, organic matter and alike. The utilised settling over night was observed to result in a good separation of this dirt.

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