

ARTÍCULOS ORIGINALES / *Originals*

DEVELOPMENT OF A HOUSEHOLD METHOD FOR TREATMENT OF HIGHLY FLUORIDATED WATER USING PROCESSED EGGSHELL

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Abstract

High intake of fluoride generates a clinical entity called fluorosis. The World Health Organization has recommended a limit for water consumption of 1.5 mg/l. When this limit is exceeded water needs remediation. Eggshell is a calcium rich waste that could be used as a resource for the reduction of water fluoride because the fluoride reacts with calcium to form calcium fluoride. The objective of this work was to develop an eco-friendly method for the elimination of fluoride from water. Upon investigating different variables of this method the following was established: 1. Incineration of eggshell increases 5.6 times fluoride uptake. 2. Time required to complete 50% of the uptake process is 0.52 ± 0.12 min. 3. Fluoride uptake increases significantly as the size of particles decreased: thick (1.72 ± 0.55), thin (1.59 ± 0.30) and ultra thin (2.37 ± 0.35) (ANOVA, LSD test $p < 0.05$). 4. The remediated water is neutralized using compressed CO_2 and CO_2 from air. 5. The organoleptic characteristics were determined and, remediated water was: colorless, tasteless and odorless. No differences were found when comparing the remediated solution with tap water of Rosario, Santa Fe, Argentina. In conclusion,

the method developed in this work is suitable for the remediation of fluoride in water on a laboratory setting; further studies need to be done to apply this methodology at a household level.

Keywords: fluoride, water remediation, eggshell, groundwater.

Resumen

DESARROLLO DE UN MÉTODO HOGAREÑO PARA EL TRATAMIENTO DE AGUAS CON ALTA CONCENTRACIÓN DE FLUORURO USANDO CÁSCARA DE HUEVO MOLIDA.

La alta ingesta de fluoruro genera una entidad clínica denominada fluorosis. La Organización Mundial de la Salud recomienda que el límite para el agua de consumo sea de 1.5 mg/l. Cuando se supera este límite es necesario remediar el agua. La cáscara de huevo es rica en calcio, y podría ser utilizada como un recurso para la disminución de fluoruro de agua, por reacción con el calcio para formar fluoruro de calcio. El objetivo de este trabajo fue desarrollar un método de remediación ecológica para la eliminación de flúor del agua. Se inves-

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tigaron diferentes variables de este método. 1. Incineración de cáscara de huevo, lo que aumentó 5,6 veces la absorción de fluoruro. 2. Tiempo requerido para completar el 50% del proceso de captación, se obtuvo: 0.52 ± 0.12 min. 3. La captación de fluoruro aumenta significativamente a medida que el tamaño de las partículas disminuye: grueso ($1,72 \pm 0,55$) y fino ($1,59 \pm 0,30$) y ultra fino ($2,37 \pm 0,35$) (ANOVA, test LSD $p < 0.05$). 4. El agua remediada se neutralizó usando CO_2 comprimido y CO_2 del aire. 5. Las características organolépticas se determinaron y, el agua obtenida es: incolora, insípida e inodora. No se encontraron diferencias al comparar el agua remediada con agua de red de la ciudad de Rosario, Santa Fe, Argentina. En conclusión, el método desarrollado en este trabajo es adecuado para la remediación de fluoruro en el agua a nivel hogareño o de laboratorio.

Palabras claves: fluoruro, remediación de agua, cáscara de huevo, agua de pozo.

Introduction

Fluoride (F) is an ion widely distributed in nature, and intakes of more than approximately 0.07 mg/kg/day of F generates a clinical entity called fluorosis that can produce from mottled teeth to the modification of the secretion and action of several hormones. The World Health Organization (WHO)¹ has established an acceptable upper limit for water consumption of 1.5 mg F/l, although these values are under discussion worldwide depending on the average maximum temperature.² Coincident with numerous studies in different parts of the world,^{3,4} the authors of this study have found a high percentage of well water with F concentration exceeding the limit set by the WHO in the center of Argentina. In addition, the levels of F depend on "macrovariation" and "microvariation" over time for a well, and also on the distance between wells. These results indicated that F concentration in well water varies significantly through time and changes

when distances are equal or greater than 500 m between two wells. More surprising is the finding that water F concentration of a single well can change 100% in few days.⁵ Whereas in the central-western Chaco it was found that 9% of the samples exceeded the limit proposed by the WHO,⁶ in other regions of Argentina the percentage of wells with F concentrations exceeding 1.5 mg/l, was close to 100%.⁷ The establishment of regional low-F river water aqueducts, reverse osmosis plants and consumption of bottled water significantly reduces the exposure of the population to excessive amounts of F. However, in areas far from urban centers or lower economic resources, exposure to F is a problem still unsolved. In Argentina the effects of fluorosis have been scarcely studied, and a study from our laboratory showed insulin resistance in people of southern Buenos Aires province.⁸ While current studies indicate that the effects of water intake with high content of F increases directly with the concentration of F, a recent study shows that the effects of F may be present with lower concentrations in rats with moderate deficit in renal function.⁹

Research into new methods of remediation of water with high content of F is abundant. Sixteen papers were presented on this topic in the XXXth Congress of the International Society for Fluoride Research venue in Szczecin (Poland).¹⁰ Several researchers have developed F removal techniques using different compounds, from alumina absorption techniques to industrial or agricultural waste materials.¹¹ In these studies the search for abundant resources, especially waste from the area, for water F removal was observed.

In our laboratory, tests were conducted to use eggshells, a waste product in the general population, as a source of calcium.¹² The chemical composition of eggshell is about 95% of calcium carbonate, and preliminary studies indicate that eggshell could be used as a resource for the elimination of F from water, by reaction with calcium to

form calcium fluoride, which is an insoluble compound. Eggshell incineration transforms calcium carbonate in calcium oxide which reacts with water to form calcium hydroxide.

The following reactions provide the theoretical background supporting the use of incinerated eggshell for the remediation of fluoridated water.

Reactions:

| | | | | |
|-----------------------------------|--|---------------|-----------------------------------|--|
| dissociation of calcium hydroxide | $\text{Ca}(\text{OH})_2$ | \rightarrow | $\text{Ca}^{++} + 2(\text{OH})^-$ | $K_{\text{sp}}_{\text{Ca}(\text{OH})_2} = [\text{Ca}^{++}][\text{OH}^-]^2 = 7.9 \times 10^{-6}$ |
| precipitation of calcium fluoride | $2 \text{F}^- + \text{Ca}^{++}$ | \rightarrow | CaF_2 | $1/K_{\text{sp}}_{\text{CaF}_2} = 1/4 \times 10^{-11}$ |
| global chemical reaction | $\text{CaO} + \text{H}_2\text{O} + 2 \text{F}^-$ | \rightarrow | $\text{CaF}_2 + 2(\text{OH})^-$ | $K_t = K_{\text{sp}}_{\text{Ca}(\text{OH})_2} / K_{\text{sp}}_{\text{CaF}_2} = 1.97 \times 10^5$ |

The global constant is 1.97×10^5 , indicating that the global reaction favors the formation of calcium fluoride, which is an insoluble salt.

The use of eggshell for removing water F is on the one hand a form of recycling a waste and, on the other hand, a form of water remediation with high potential, for its low cost and wide availability. Using this method at household level should be feasible, requiring first the separation of the waste eggshell. The aim of this work was the development of a new method for removing F from water using eggshell.

Different variables were investigated: the ratio solution volume/quantity of eggshell, the particle size of the milled eggshell, time required for calcium fluoride precipitation, need for agitation, and residue separation mechanism. Treatment after remediation was also analyzed in order to achieve adequate organoleptic water quality for consumption.

Materials and methods

F uptake was assessed using eggshell before and after the incineration process. In order to do this, eggshell was pulverized with a mixer mill (Retsch GmbH, MM200, Haan Germany) at 30 oscillations/sec for 15 min. A fraction of the milled eggshell was incinerated at 550 °C in an electric oven for 6 h. Two fractions were thus obtained: milled eggshell (ME) and incinerated eggshell (IE).

Fluoride uptake by ME y IE

Prior to the determination of the uptake parameters (maximum uptake, time needed for 50% of uptake) and the development of a methodology for the removal of F from water, 1 ml of 1.9 mg/l of sodium fluoride (NaF) solution was incubated at 20 °C with 2 mg of ME or IE for 30 min. 10 repetitions of each experiment were done. The solution was centrifuged at 2400 g for 15 min and the supernatant was obtained, in which the concentration of F was determined by direct potentiometry (see below).

ME and IE F uptake was determined by difference between the concentration of F in the initial and final solution, this was expressed in mg of F/kg of ME or IE. We found that F uptake by IE was 5.6 times higher than ME uptake, therefore all the experiments were carried out using incinerated eggshell (IE).

Sizing incinerated eggshell

Three degrees of milled eggshell prior incineration were evaluated to determine if F uptake is related to the surface of the eggshell. In order to do this, natural eggshell was placed in a mixer mill (Retsch GmbH, MM200, Haan Germany) and to determine the size of the grains of the eggshell obtained, 1.20 mg of eggshell was placed on a microscope slide,



where a picture was taken and the average size of the particles was measured with Image J 1.40 software (National Institutes of Health, Maryland, USA).

Three sizes of eggshell were generated:

1. Thick eggshell (thick IE), mixer mill frequency 30 oscillations/sec for 5 min ($441 \pm 1836 \mu\text{m}^2$ average).
2. Thin eggshell (thin IE), mixer mill frequency 30 oscillations/sec for 10 min ($313 \pm 946 \mu\text{m}^2$ average).
3. Ultra thin eggshell (ultra thin IE), mixer mill frequency 30 oscillations/sec for 15 min ($125 \pm 289 \mu\text{m}^2$ average).

The effect of the degree of pulverization and agitation on F uptake process was evaluated. IE with different degree of pulverization was placed in two tubes in the ratio of 2 mg IE/ml of 5 mg /l NaF, one tube was stirred for 30 min and the other was not stirred. The precipitate was removed and F concentration was determined in the supernatant before and after treatment with IE. F uptake was calculated by the difference between the initial and the final F concentration. The experiment was performed by duplicate for each of the eggshell sizes generated.

Determining the time of fluoride uptake by eggshell

To determine the time needed to complete the F uptake process by the IE, 2 mg IE were incubated with 1 ml of 5 mg /l NaF solution at 20 °C. Before mixing the solution with the IE and after 0.5, 1.5, 10, 15, 20 and 30 min, an aliquot of the solution was obtained, centrifuged at 2400 g for 15 min and the concentration of F was determined in the supernatant.

F uptake was expressed as mg F/g IE.min and was adjusted with an exponential function, which follows

Equation 1

$$\text{mg F/g IE * min} = C_{eq} * \left(1 - e^{-\ln \frac{2}{t_{1/2}} t} \right)$$

Where C_{eq} is the value of F uptake that remains constant as time passes, when equilibrium is reached, $t_{1/2}$ is the time required to achieve half of the value of C_{eq} (n=3).

Determination of maximum fluoride uptake by IE

Maximum F uptake was determined by the incubation at 20 °C for 30 min of several F concentration solutions: 0, 0.5, 1, 1.5, 1.9, 3, 5 and 10 mg/l with IE, in a proportion of 2 mg IE/ml solution. After this procedure, the solutions were centrifuged at 2400 g for 15 min and then F concentration was determined in the supernatant as indicated above. Each concentration was measured by quadruplicate and the entire experiment was repeated twice.

IE F uptake was calculated by the difference between F concentration before and after incubation with IE, and the results are expressed in mg F/g IE. Experimental values as a function of F concentration were adjusted by a hyperbolic function.

Equation 2

$$\text{mg F/g IE} = \frac{U_{max} * conc_{solution}}{K + conc_{solution}}$$

U_{max} is the maximum uptake of fluoride per gram of IE, its unit is mg of F/g of IE, and K is the uptake constant, which unit is mg F/l, indicating the concentration of the solution to which IE captures 50% of the maximum.

Neutralization method and elimination of precipitate

After IE treatment, water is alkaline and has a precipitate due to the formation of calcium fluoride. Therefore, the procedures performed to address both problems are described. A laboratory procedure and one that could be done domestically without special equipment were evaluated: centrifugation and aspiration of the supernatant (laboratory); and sedimentation and decantation (domestic).

In the same experiments two methodologies were evaluated for neutralizing water after remediation: by bubbling CO₂ (laboratory) and by capturing CO₂ from air (domestic).

Four tubes with 50 ml of 5 mg /l NaF solution (pre-remediation solution) with the addition of 100 mg IE were incubated at 20 °C for 30 min with constant stirring. The precipitate was removed using two different methodologies: 2 tubes were centrifuged (C) at 2400 g for 15 min and the supernatant was collected, and the other 2 tubes were allowed to settle spontaneously, and then decanted (D). The solutions C and D will be called together "post-remediation solutions". The supernatant of post-remediation solutions

were neutralized by two methods: one tube C was bubbled with compressed CO₂ (CC) and, the other tube C was exposed to air in order to capture CO₂ spontaneously (CA). Similarly, one tube D was exposed to compressed CO₂ (DC) and the other D tube was exposed to air CO₂ (DA). The CC, CA, DC and DA solutions will be called all together "post-neutralization solutions". The detailed procedure of the preceding paragraph is shown in Figure 1. Each sample was measured by duplicate and the experiment was performed 3 times. The concentration of F, which was measured by direct potentiometry, pH and electrical conductivity were determined in the pre-remediation and post-neutralization solutions.

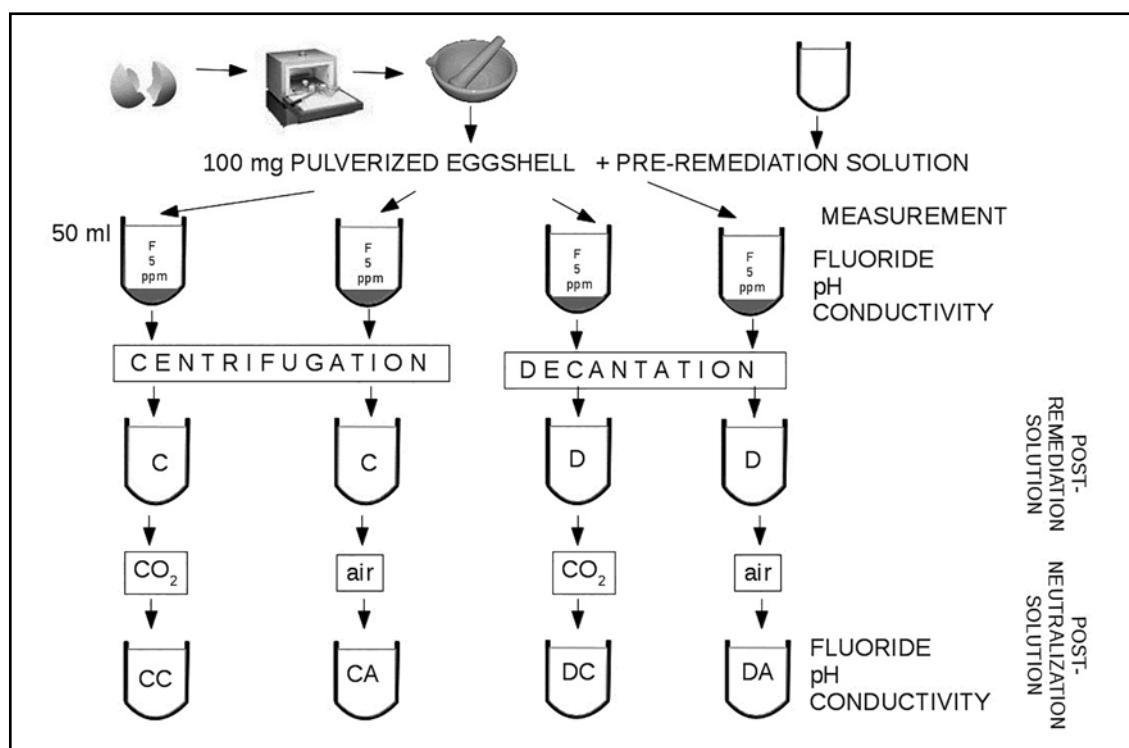


Figure 1. Detailed experimental design. See text for details

Determining the quality of the water obtained

Since the treatment is performed with the main component of the incinerated eggshell,

calcium, its concentration in the water obtained after neutralization was determined using an atomic absorption spectrophotometer Arolab MK II. The samples were diluted with distilled



water by setting the concentration of 2% SrCl₂ to remove anions which may interfere with the determination. A calibration curve was used with calcium concentrations of 0-100 mg/ml and the flame used was obtained by mixing acetylene-air ratio 1.5-1.

The organoleptic characteristics of post-neutralization obtained water were also analyzed, evaluating: color, taste (using the threshold flavor test, FTT test) and odor (using the threshold odor test, TOT test).¹³ This evaluation was conducted by blinded volunteers from the Bone Biology Laboratory.

Determination of the fluoride concentration, pH and electrical conductivity

F concentration in the solutions was determined by direct potentiometry¹⁴ using a specific ion electrode 94-09 ORION and a reference electrode Ag/AgCl connected to a digital converter. The determination is based on the linear relationship between mV developed by the electrodes and the logarithm of the concentration of F in the samples or standards used. Standard solutions of NaF 19-0.019 mg/l¹⁵ were measured. The samples and standard solutions were added a 10% solution of acetic acid/sodium acetate 2 mol/l, to adjust the pH to 5.5 and to homogenize the ionic strength of the solutions. The determination was performed by duplicate and was subjected to quality control. If the coefficient of variation exceeded 10%, the determinations were repeated. A "quality control" solution of known concentration was processed simultaneously and standard deviation units (UDS) were calculated. The measurements were repeated if the UDS were outside the range [-2,2].

The pH was determined using a pH meter Hanna 9017.

The electrical conductivity of the solutions, which estimates the total ionic concentration, was measured using a Hanna 98304. Conductivity measurements were expressed in mS/cm.

Determination of defluoridation capacity of the defluoridation medium (DC_{DM})

DC_{DM} was calculated as described by Dahi.¹⁶ Briefly, 0.5 g of incinerated eggshell (X_{DM}) were transferred into a plastic bottle with 200 ml of 5 ppm F solution (F₀). The experiment was carried out in duplicate. Bottles were shaken every 30 min and after 24 h, fluoride concentration (F_{24 h}) was measured as stated above. With F₀ and F_{24 h}, DC_{DM} was calculated with the following equation.

Equation 3

$$DC_{DM} = \frac{F_0 - F_{24\text{ h}}}{X_{DM}}$$

Evaluation of the proposed remediation method in drinking water with high fluoride concentration

Fluoride uptake by the incinerated eggshell was assessed in 3 different samples of well water collected from the city of Balcarce, Buenos Aires, Argentina. This was done to verify that the F remediation method proposed in this paper is feasible. In order to do this, eggshells were milled, incinerated, a 2 mg of eggshell was placed in contact with 1 ml of water and allowed to stand for 30 min, decanted and obtained the supernatant, which was allowed to capture atmospheric CO₂ for 6 days. F concentration, pH and electrical conductivity were measured in the remediated water obtained.

Statistical analysis

All data analysis and statistical tests were performed using the base, Agricolae and stats packages of R 2.14.1 software.¹⁷ The probability distribution of the data was analyzed using the Shapiro-Wilk test. The data were not normally distributed.

When more than two experimental groups were compared linear and two classification criteria ANOVA models were used, with

LSD post-test using the logarithms of the values. When two experimental groups were compared, Wilcoxon test was used. Nonlinear adjustments were made with the nls function of R software, using a non-linear fit minimizing the sum of squares of the deviations between the measured and estimated values by the function.

The results are shown as mean \pm SE (SE: standard error) and differences were considered significant if $p<0.05$.

Results

Fluoride uptake by ME y IE

The results of the comparison of F uptake by ME and IE can be seen in Table 1.

The results in Table 1 indicate that incinerated eggshell has a capacity of F uptake 5.6 times than natural eggshell. These favorable results for IE, determined that all subsequent studies were performed using IE.

Table 1. Fluoride uptake by ME and IE, mg F uptake/Kg eggshell (media \pm SE)

| | ME | IE |
|----------|---------------|------------------|
| F uptake | 6.6 \pm 0.8 | 37.4 \pm 1.2 * |

*indicates significant differences, Wilcoxon test $p<0.05$. Experimental conditions are detailed in materials and method.

Incinerated eggshell sizing and agitation effects on the uptake of fluoride

No significant differences in the uptake of F as a function of agitation were found, but significant differences were found in terms of thickness ($p<0.05$, two way ANOVA). The difference between initial and final F concentration in samples treated with IE ultra thin (2.37 ± 0.35) was significantly greater than with thick (1.72 ± 0.55) and thin IE (1.59 ± 0.30) (LSD test $p<0.05$). From these results, it was decided to continue the experiments without agitation and using ultra thin IE.

Time determination of fluoride uptake by IE

The milligrams of F captured by IE as a function of time were adjusted by the function proposed in materials and methods (Equation 1). Using that equation the time required to complete 50% of the uptake process was obtained (0.52 ± 0.12 min).

From these results, the incubation time used in subsequent experiments was set at 30 min, so as to ensure the completion of the F uptake process.

Determination of maximum uptake of fluoride by IE

F uptake by IE as a function of the concentration of F in the solution was assessed. The adjustment was performed using the Equation 2, detailed in materials and methods, and the equation parameters obtained were significantly different from zero ($p<0.05$).

$$C_{\max} = 1430 \pm 28 \text{ mg F/Kg IE.}$$

$$K = 6.54 \pm 2.17 \text{ mg/l.}$$

Neutralization method determination and elimination of precipitate

No significant differences in the concentration of F of CC, CA, DC and DA samples were found (two criteria ANOVA, $p>0.05$), indicating that the precipitate separation (centrifugation/suction or sedimentation/decantation) and the neutralization process (compressed CO₂ or CO₂ in air) were equally effective in reducing the concentration of F in the solution. Similarly, no differences in pH and conductivity between CC, CA, DC and DA samples were found (two criteria ANOVA, $p>0.05$).

As a consequence of the lack of differences among CC, CA, DC and DA samples, F concentration, pH and conductivity of the tubes were analyzed together. Only the variables were compared before treatment (pre-remediation solution) and after the treatment (CC, CA, DC and DA samples or solutions post-neutralization).



A significant decrease of concentration of F after treatment was found. Table 2 shows the means of the CC, CA, DC and DA samples after treatment.

The pH of the post-neutralization solutions was significantly lower than that of the post-remediation solutions (Wilcoxon test $p<0.05$). Table 3 shows the mean and SE of the solutions after treatment with eggshell (post-remediation solution) and after neutralization (post-neutralization solution).

Electrical conductivity showed a significant decrease when the neutralization was carried out using CO_2 , and no significant differences between the two methods of neutralization (air and compressed CO_2) were found. Table 4 shows the values of electrical conductivity (mS/cm) in the post-remediation and post-neutralization solutions.

The neutralization time was 15 min when compressed CO_2 was used, 6 days when samples were neutralized with CO_2 from the air.

Table 2. F concentration, mg / l (mean \pm SE)

| | |
|-------------------------------------|-------------------|
| F concentration pre-remediation | 5.03 \pm 0.09 |
| F concentration post-neutralization | 2.76 \pm 0.03 * |

* indicates significant decrease compared to pre-remediation F concentration. Wilcoxon test $p<0.05$. Experimental conditions are detailed in materials and method.

Table 3. pH pre and post neutralization (media \pm SE)

| | |
|------------------------|-------------------|
| pH post-remediation | 11.9 \pm 0.06 |
| pH post-neutralization | 7.22 \pm 0.68 * |

* indicates significant decrease compared to post-remediation pH. Wilcoxon test, $p<0.05$. Experimental conditions are detailed in materials and method.

Table 4. Electric conductivity pre and post neutralization (media \pm SE)

| | |
|---|-------------------|
| Electric conductivity post-remediation | 2.45 \pm 1.20 |
| Electric conductivity post-neutralization | 0.25 \pm 0.07 * |

* indicates significant decrease compared to post-remediation electric conductivity. Wilcoxon test $p<0.05$. Experimental conditions are detailed in materials and method.

Defluoridation capacity of the defluoridation method

The incinerated eggshell defluoridation capacity was determined to be 0.58 mg F/ g media.¹⁶

Determination of the organoleptic characteristics of the water obtained

The organoleptic characteristics were determined by blinded operators who indicated that remediated water was: colorless, according to FTT test: no flavor was detected and according to TOT test: no odor was detected. Also, no differences were found when comparing the remediated solution with tap water of Rosario, Santa Fe, Argentina.

The calcium concentration in the post-neutralization solutions was less than 30 mg/l and this concentration did not affect the organoleptic properties of water.

Evaluation of the proposed remediation method in drinking water with high fluoride concentration

The results obtained when applying the method developed in this article are summarized in Table 5. The remediation technique was assessed in water obtained from 3 different wells.

A significant decreased in the 3 samples remediated was found, and the final F concentration was close to the WHO recommended value for F concentration in drinking water.

Table 5. F initial and final concentration (mg/l) of remediated well water (media±SE).

| | Well 1 | Well 2 | Well 3 |
|-------------------------|--------------|--------------|--------------|
| F initial concentration | 3.28±0.02 | 3.47±0.01 | 4.33±0.01 |
| F final concentration | 1.91±0.003 * | 1.66±0.004 * | 1.85±0.001 * |

* indicates significant decrease compared to pre-remediation. Wilcoxon test $p<0.05$. Experimental conditions are detailed in materials and method.

Discussion

The obtained results demonstrate that eggshell has the ability to capture F and consequently is an appropriate resource for the remediation of water with high concentration of F. The incineration process improves F uptake compared to F uptake by the eggshell without treatment. Because eggshell is primarily composed by calcium carbonate¹², when it is incinerated generates calcium oxide, which is more soluble. However, the incineration treatment generates an alkaline supernatant that requires subsequent neutralization.

The time required to complete 50% of F uptake process is about 0.5 min, which makes it very suitable for this type of application process. The speed of the process might allow the application to continuous remediation systems.

In our study, the maximum F uptake achieved was 1430 mg F/Kg IE. The F uptake capacity of this technique is higher than other low-costs techniques, which use, for instance, agricultural (coconut shell, rice husk, etc.)¹⁸ or industrial wastes. In addition, most of the latter must be modified for enhancing F removal. According to the WHO the best available methodology for F removal is activated alumina, which is not a waste and has the disadvantage that is expensive and that the concentration of aluminum in the processed water should be measured because of its toxicity.¹¹

The obtained results demonstrate that neutralization of post-remediation water with

eggshell using CO₂ is feasible. The same values of pH and conductivity using CO₂ from the air or from compressed CO₂ are achieved, indicating that the neutralization method can easily be done at household level. The only difference between the two methods is the time required to reach a near neutrality pH.

The incinerated eggshell defluoridation capacity was: 0.58 mg F/g media, which is similar to bone char, with the advantage that this new method does not have poor taste, bad smell, and unpleasant discoloration as it was reported with bone char method.

The advantage of the method described in this article is that is an eco-friendly F remediation technique that can be applied by most people, because of its low cost and accessibility to the main component: eggshell, which is a waste generated domestically. Consumption of eggshell differs between countries, but there are not large differences in consumption per capita. In our country an average consumption of 200 eggs/person/year is estimated.¹⁹ In other countries such as Hungary, Spain, France, USA, Russia, Denmark, Japan, Paraguay, Mexico, Netherlands, China, egg consumption is higher: 250-350 eggs/person/year.²⁰ Whereas the population of Argentina is 40 million and considering that the average weight of the eggshell is 5 g, is estimated a generation of 40,000 tons per year of this waste in Argentina.²⁰ Therefore, with the amount of eggshell produced in Argentina about 6×10^{10} mg F could be captured. Whereas with 5 mg



/l F water (with high risk of fluorosis), and the need to eliminate F up to 1 mg/l, the eggshell available would be adequate to completely eliminate F from 1.5×10^{10} liters of water. If a person consumes for food purposes 4,000 liters of water per year, then 3,750,000 people per year could consume remediated water. Leaving remediated water for 6 days in contact with air generates water ready for consumption. The bacteriological quality of the water obtained is currently under investigation.

In summary, the method for domestic remediation of water with high concentration of F will comprise the following steps:

1. Mill two eggshells.
2. Incinerate the milled eggshells.
3. Place the incinerated eggshells in 5 liters of water.
4. Leave for 30 min.
5. Precipitate and recover the supernatant.
6. Leave at room temperature covered with a piece of cloth.
7. After 6 days, decant again if any precipitate is visible and recover the supernatant.

8. Use the remediated water for cooking or drinking after boiling it.

Conclusions

It was developed a methodology for the remediation of fluoridated waters. The advantage of this method is that is an eco-friendly technique that can be applied by most people, because of its low cost and accessibility to the main component: eggshell, which is a waste generated domestically.

Acknowledgements

This work was funded by Secretaría de Estado Ciencia Tecnología e Innovación (SECTel) of Santa Fe province, Argentina and Fundación Alberto J. Roemmers of Argentina, both of them without commercial interests. We thank Hilda Moreno, Matías Terjes and María Belén Vescovo for technical assistance.

Conflicts of interest: The authors report no conflict of interest.

Recibido: julio 2015.

Aceptado: octubre 2015.

References

1. World Health Organization. Guidelines for drinking water quality. 2th ed, Ginebra, Vol. 1, p. 43-45, 1995.
2. Ramadan A, Hilmi Y. The influence of climate on the determination of the upper permissible fluoride level in potable water in Sudan. *Fluoride* 2014; 47:170-80.
3. Sun D, Gao Y, Zhao L, Wang C, Wang W. Analysis on the monitoring results of drinking water borne endemic fluorosis in china (2009-2011). *Fluoride* 2012; 45:204.
4. Dahi E. Prospects for low-fluoride water in fluorotic areas in Tanzania. *Fluoride* 2012; 45:158.
5. Lupo M, Fina BL, Aguirre MC, Armendariz M, Rigalli A. Determination of water fluoride concentration and the influence of the geographic coordinate system and time. *Water Air and Soil Pollut* 2012; 223:5221-25.
6. Blanes PS, Buchhamer EE, Giménez MC. Natural contamination with arsenic and other trace elements in groundwater of the Central-West region of Chaco, Argentina. *J Environ Sci Health A Tox Hazard Subst Environ Eng* 2011; 46:1197-206.
7. Paoloni JD, Fiorentino CE, Sequeira ME. Fluoride contamination of aquifers in the southeast subhumid pampa, Argentina. *Environ Toxicol* 2003; 18:317-20.
8. de la Sota M, Puche RC, Rigalli A, Fernandez LM, Benassati S. Modificaciones en la masa ósea y en la homeostasis de la glucosa en

- residentes de la zona de Bahía Blanca con alta ingesta espontánea de flúor. *Medicina* 1997; 57:417-20.
9. Lupo M, Buzalaf MAR, Rigalli A. Effect of fluoridated water on plasma insulin levels and glucose homeostasis in rats with renal deficiency. *Biol Trace Elem Res* 2011; 140:198-207.
 10. The ISFR Communications Congress. *Fluoride* 2012; 45:3.
 11. Bhatnagar A, Kumar E, Sillanpää M. Fluoride removal from water by adsorption-A review. *Chem Engineer Journal* 2011; 171:811-40.
 12. Brun LR, Lupo M, Delorenzi DA, Di Loreto VE, Rigalli A. Chicken eggshell as suitable calcium source at home. *Int J Food Sci Nutr* 2013; 64:740-3.
 13. American Public Health Association/American Water Works Association/Water Pollution Control Federation. Standard methods for the examination of water and wastewater. 14th edition, Washington, DC, 1976, p. 117-21.
 14. Rigalli A, Alloatti R, Puche RC. Measurement of total and diffusible serum fluoride. *J Clin Lab Anal* 1999; 13:151-7.
 15. Rigalli A, Pera LI, Di Loreto VE, Brun LR. Determinación de la concentración de flúor en muestras biológicas; 1° Edition: Universidad Nacional de Rosario, Rosario, Santa Fe Argentina, 2007.
 16. Dahi E. A simple procedure for the routine determination of the standard defluoridation capacity of media. *Fluoride* 2015; 48:22-8.
 17. R Development Core Team (2011). R: A language and environment for statistical computing. R Foundation for Statistical Computing, Vienna, Austria. ISBN 3-900051-07-0, URL <http://www.R-project.org/>.
 18. Mohan D, Singh KP, Singh VK. Waste water treatment using low cost activated carbons derived from agricultural byproducts-A case study. *J Hazard Mater* 2008; 152:1045-53.
 19. Argentina Chamber of Poultry Producers. <http://www.capia.com.ar/>
 20. WATT Executive Guide to World Poultry Trends. <http://www.wattagnet.com/>