# SODIUM IONS UPTAKE BY HYDROXYAPATITE FROM BOVINE BONE

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## Abstract

*The negative impact of soil salinity on agricultural yields is disturbing and significant, especially when related to agricultural plants, whose sensitivity to salinity is frequently, but not exclusively, associated with the abundance of* $Na^+$ *in the soil, which in excess becomes toxic for plants. This work aims to propose an alternative for the control of* $Na^+$ *present in waters from saline soils, by the possibility of applying bovine hydroxyapatite as a way to remedy this problematic. Hydroxyapatite powders were processed from bovine bone. The powders were characterized by X-ray diffraction analyses. Preliminary experiments were performed in batches at room temperature, adding together 5g hydroxyapatite and a dilute solution of sodium chloride. Liquid samples were analyzed by atomic absorption spectrophotometry. The results showed that the hydroxyapatite could be a promising alternative for the reduction of* $Na^+$ *concentration in waters from saline soils.*

**Keywords:** Hydroxyapatite, Sodium, Uptake, Bovine Bone

## INTRODUCTION

Sodium, an alkali metal, is found in nature in combination with other elements to form salts that are water soluble, in high concentrations is considered toxic to plants, higher values around 70 mg/l are inconvenient for irrigation since the brackish water is absorbed by leaves, which inhibits growth in most cases. In addition, the sodium embedded in soil from water, may reduce permeability and cause harmful alkaline conditions to vegetation(1).

Sodium is a mineral of vital importance, in generally, the sodium salts are considered no-toxic due to the efficiency with which the adults' kidneys excrete this mineral, however the effects on infants are severe due to the immaturity of their kidneys. A normal regime of human consumption is 3000 to 5000 mg-Na/day, the minimum amount is less than 200 mg-Na/day for children and 2000 mg-Na/day for adults, needed to maintain biological functioning. However, among individuals there is a tolerance that dependent of the genetic characteristic each one, susceptibility of the organism, hereditary conditions or physical activities.

For this reason, there is great interest in developing technologies to eliminate or reduce the salts contained in the water. Currently, the technologies used for this purpose are those that employ physical processes such as distillation, crystallization, membrane separation, and chemical processes such as ion exchange and chemical treatment(2). These technologies require a high input of energy in any form, either heat or electricity, which increases the costs and involve a high environmental impact, the consequences of the introduction of residual products in the ecosystem produces an imbalance that could be irreversible(3).

There are studies that have proposed to apply hydroxyapatite in the water treatment(4-6), and others. Such studies are directed to using hydroxyapatite as an alternative material in effluent treatment in order to eliminate or reduce contaminant ions such as lead (Pb), chromium (Cr), cadmium (Cb), zinc (Zn), cobalt (Co), copper (Cu), mercury (Hg), radioactive lanthanides, among others. However, the sodium ions adsorption by hydroxyapatite has not yet been extensively studied.

The aim of this work is to evaluate the capacity of the hydroxyapatite (Hap) of interchanging sodium ions in contact with saline solution, and to propose an alternative for the control of $Na^+$ present in waters from saline soils, by the possibility of applying bovine hydroxyapatite as a way to remedy this problematic. Hydroxyapatite powders were processed from bovine bone, and characterized by X-ray diffraction analyses. Preliminary experiments were performed in batches at room temperature, adding together 5g hydroxyapatite and a dilute solution of sodium chloride. Liquid samples were analyzed by atomic absorption spectrophotometry. The results showed that the hydroxyapatite could be a promising alternative for the reduction of $Na^+$ concentration in waters from saline soils.

## MATERIALS AND METHODS

The Hap powder samples used in this work were obtained by bovine bone according to a previous group work(7). The powder samples were characterized before and after the sorption test, by X-ray diffraction analyses. A PHILLIPS X'PERT PLUS with Cu source diffractometer, model PW4000, using 40mA and 40kV, was used to record diffractograms in the 2θ interval from $20^o$ to $60^o$ step size of $0.02^o$ and counting time of 1s. For porosity degree evaluation, total surface area was performed by porosimetry analysis (Quantachrome, Autoscan 33). The concentrations of Ca, P, K elements and others microelements were determined before and after sorption test by Atomic Absorption spectrophotometric (Shimadzu, AA-7000).

To carry out the immersion tests, rigorous cleaning of the instrumentation was performed. It was prepared a sodium chloride solution with 4300 ppm concentration, which was fractionated in eight parts of 500 ml each. One of these samples was considered as white (control) sample used to compare with the samples subjected to the immersion test. Five grams (5g) of hydroxyapatite were added into each 500 ml portion. The samples were maintained under stirring at 150 rpm and the collect times were: white sample, immediately after mixing (HAP-1), 5 (HAP-2), 10 (HAP-3), 15 (HAP-4), 20 (HAP-5), 25 (HAP-6) and 30 (HAP-7) minutes of testing. After each period, the solid was removed from the liquid, the solution was filtered and analyzed, and the solid samples were washed with distillated water and dried in an oven at $80^oC$ for 6 hours in air.

## RESULTS AND DISCUSSIONS

Figure 1 shows the x-ray diffractograms of Hap samples immersed at different times in sodium chloride solution and the standard diffractogram for Hap. From the diffractograms, it can be observed the change in the Hap crystal structure, evidenced by the reduction in the intensity of peaks. According to studies reported in the literature, removal of sodium in solution with Hap is given by ion exchange, where the calcium ion site is occupied by sodium ion(8). Since the sodium ion is monovalent and calcium ion is divalent, two sodium ions would be required to take the place of calcium, in a 2:1 ratio (Na/Ca). However, the addition of sodium on calcium sites is considered a relatively slow process, involving hours or requiring many steps and consuming several chemicals(9). As sodium reduction in the solution resulted in a few minutes, in this work, the phenomenon may be considered as a typical non-specific trapping of rapid precipitation and not physiologically relevant, given the reduced immersion time. The most probable reason for the specific entrapment of sodium was the similar atomic radii between sodium and calcium. The intensity reduction of peaks can be attributed to the dissolution of calcium without the occurrence of ion exchange.

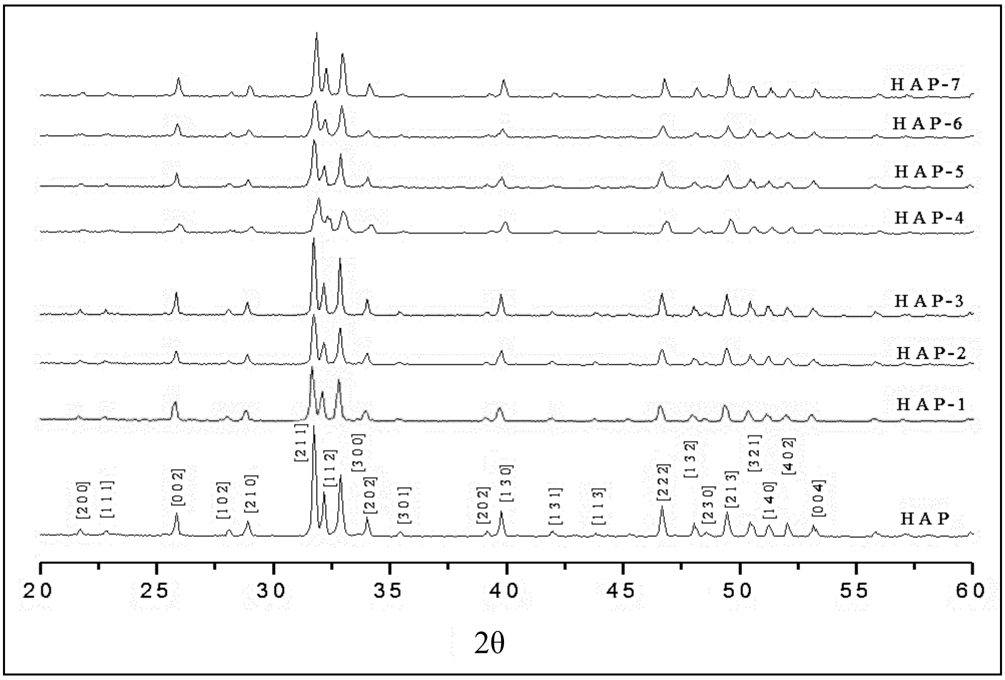

Figure 1: X-ray diffractogram of the solid samples at different immersion time.

Figure 2 shows the curve that represents the resulting average for the concentration reduction analysis of sodium ions in the sodium chloride solution as a function of time. It can be seen that after 15 min the curve reaches the maximum point, which means the maximum sodium amount removed from the solution. From this point the curve declination is also observed, indicating a reversal of the reaction. This can be explained by the fact that ion exchange has not been occurred, but a crystal precipitation of preformed sodium in Hap surface. Such phenomenon corroborates with the data recorded in Table 1, which shows the pH variation over time. It is noted that the maximum sodium removal, Figure 2, correspond to the maximum pH value and from this point the pH values decrease.

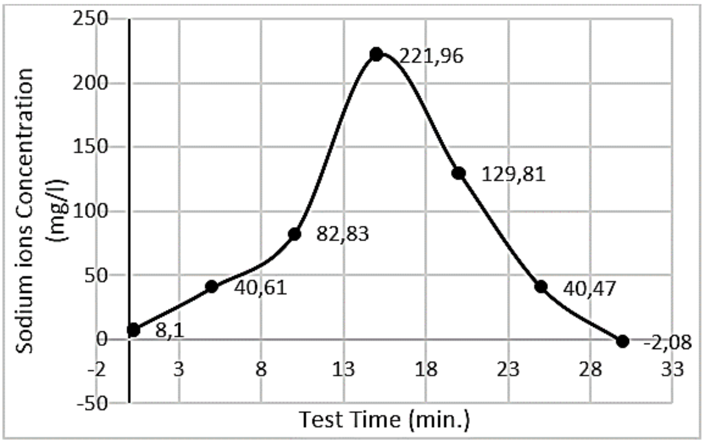

Figure 2: Variation of sodium ion concentration in NaCl solution over time.

Table 1: pH variation in the sodium chloride solution over time.

| Time (min) | w.s.* | Mixing** | 5 | 10 | 15 | 20 | 25 | 30 |
|---|---|---|---|---|---|---|---|---|
| pH | 5.93 | 10.33 | 10.62 | 10.75 | 10.86 | 10.74 | 10.68 | 10.60 |

* White (control) sample or standard solution.

** immediately after mixing (Hap + sodium chloride solution)

In Table 1, it is observed that the starting solution of sodium chloride (w.s.) presented an acidic character and the addition of Hap induced a rapid increase in pH of the solution, which remained almost constant. This behavior may be related to the rapid dissolution of calcium and successive calcium hydride formation, as shown in Table 2 for calcium concentration in the solution. Moreover, the turbidity of solution increased with Hap addition.

Table 2: Calcium ion concentration in the sodium chloride solution.

| Time (min) | w.s.* | mixing | 15 | 30 |
|---|---|---|---|---|
| $Ca^{++}$ | 0 | 9.20 | 9.60 | 9.20 |

* white (control) sample o standard solution.

** immediately after mixing (Hap + sodium solution)

## CONCLUSION

According to the observations, it is concluded that at room temperature the sodium removal by hydroxyapatite can be considered minimal, as shown by the results obtained for the sodium concentration analysis in solution. Moreover, the immersion time was not enough to reach a complete ion exchange between sodium and calcium, as indicated in the literature(8), considering that this reaction is slow and consumes several chemicals. For elucidate such behavior, tests at different temperatures are required to verify their influence on the ion exchange process. The results also indicated that the reaction can be considered reversible because of the reduced test time, since it did not reach the equilibrium or stability. Then, assays with extended times are necessary in order to assess this instability as phenomenon that precedes the ion exchange with subsequent formation of a stable compound.

## References

[1] HUDAK, P. Water hardness and sodium trends in Texas aquifers. Environm. Monit. and Assessment, vol. 68, n. 2, p. 177-185, 2001.

[2] RAMILO, L. B.; SOLER, S. M. G.; COPPARI, N. R., 2003. Tecnologías del Proceso para desalinización del agua. Revista CNEA, jan-jun, p. 22-27, 2003.

[3] ZHANG, J.; FLOWERS, J.; WANG, S., Mechanisms of sodium uptake by roots of higher plants. Plant Soil, vol. 326, p. 45-60, 2010.

[4] FERREIRO, O.; YUBERO, F.; BALESTRA, R. VARELLA, M. MONTEIRO, M., Bovine boné processing for biofilter application. Mater. Scie. Forum., vols. 727-728, p. 727-730, 2012.

[5] Valenzuela, L.; Ramírez-Hernández, J.; Sol, J. A.; Reyes, J. A., Alternativas para la eliminación domestica de flúor en el agua de consume humano. Información Tecnológica, vol. 22, no. 2, p. 23-32, 2011.

[6] de Oca, F. G. G. M.; Guzmán, F. M., Adsorción de Nd, Pm, Gd, Tb, Dy, Ho, Yb y Lu en hidroxiapatita en medio tartrato de sodio. In: XXV Congreso Nacional de Química, Palacio de Minería, Ciudad de México, 2006. Memorias Sección Química Nuclear, ciudad de México, 2006. Available in: http://www.quimicanuclear.org/memorias_congreso2006.htm. Access: February 10, 2012.

[7] Ferreiro, O. Estudio de la capacidade de retención de plomo por la hidroxiapatita obtenida a partir de hueso bovino. 2012. 79p. Monografia – Faculta de Ciencias Químicas, UNA, San Lorenzo, Paraguay.

[8] AOKI, H. Medical applications of hydroxyapatite: bone mineral, drug delivery system, cancer and HIV, IVH and CAPD, dental implant. Yshiyaku EuroAmerica, Inc., 1994. p. 1-12.

[9] ADZILA, S.; SOPYAN, I.; SINGH, R.; PUSPARINI, E.; HAMDI, M., Mechanochemical synthesis of sodium doped hydroxyapatite powder. Indian Jour. Of Chem., vol. 52A, p. 739-743, 2013.