MATHEMATICAL MODELING OF LEAD REMOVAL BY HYDROXYAPATITE FROM AQUEOUS SOLUTION

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Abstract *This work proposes a mathematical model for lead removal in aqueous solutions under a continuous column flow condition. Natural hydroxyapatite (HAP) obtained from bovine bone is used as adsorbent since this material is available in the region and is a very important resource for local economies. The adsorptive behavior of the material is accomplished through batch essays. Several models are calibrated, and the Langmuir model emerges as the most adequate to represent the kinetics process of the reaction, Pb^{2+}/HAP. With the adsorption model parameterized and adjusted via laboratory experiments, the flow of the lead solution through a column is modeled. To this end, the advection - dispersion - adsorption phenomenon is modeled using a non-linear elliptic partial differential equation. For the model validation, measurements of the adsorpted lead concentration are performed in laboratory and contrasted with the results of the simulation of the mathematical model. Comparison between the laboratory experimental and computational results shows that HAP could be considered a promising material for the remediation of lead in aqueous solutions. The numerical results adequately captured laboratory experimental flow measurements.*

Keywords: *Lead, Contamination, Hydroxyapatite, Adsorption, Simulation, Finite Difference*

1 INTRODUCTION

There is an important amount of literature discussing the effects of the presence of lead in the body and its consequences on life and health (Ramesh 2013). The bioaccumulation in the body (Adewunmi 1996) and inhibition of zinc and calcium proteins result in neurological and mental problems (Mohammed 1997), and anemia in both adults and children. In fact, children are more vulnerable even for significantly lower concentrations than adults (Godwin 2001), mainly due to their growth and development process. The harmful effect of lead accumulation is not limited to humans; its spectrum extends to most living organisms (Bulgariu 2012). This is why it is considered as a destructive environmental pollutant (Volesky 2001).

Several processes can be used to remove lead in wastewater; among all of them biosorption is the most studied and reported by many authors. This is due to the fact that biosorption is more effective with lower cost than operations such as precipitation, ion exchange or membrane filtration (Mohammed 2011). In the context of biosorption, hydroxyapatite has become an increasingly attractive raw material for using in bioremediation processes of wastewater contaminated with toxic metals, due to the ease of ion exchange and the formation of stable compounds. Natural hydroxyapatite is another important factor in the implementation of bioremediation systems, since it contains low cost material, reducing expenses in the process of disposal of toxic metals in solutions.

Lead removal from aqueous solutions has been generally studied using laboratory experiments using small scale devices and considering only static conditions. Unfortunately, the extrapolation to large-scale and dynamic situations is normally a very complicated task (Jellali 2016). For the predicting and capturing the process dynamics, several mathematical models have been proposed in the literature (Simunek et al. 2008). In this article we use an advection-diffusion-adsorption model where chemical and physical non-equilibrium processes are not considered. The model represents the mechanism for lead removal in aqueous solutions under continuous column flow conditions, where the natural hydroxyapatite (HAP) obtained from bovine bone is used as adsorbent for the lead capturing. For adjusting and determining the adsorption parameters of the advection-diffusion-adsorption model, the adsorption kinetic of the sorption process is previously studied using batch experiments (Jellali 2016). At a later time, the proposed model is discretized and approximated using a finite difference scheme. The column is discretized using an uniform 1D mesh grid along the longitudinal axis of the column. This allows for a grid refinement in order to satisfy both the stability condition for the numerical finite difference scheme and the accuracy necessary for comparing the results. Column tests in laboratory are also performed to contrast with the numerical results of the simulation of mathematical model.

The rest of the article is organized as follows: In §2 we present the materials with their main characteristics and the batch and column experiments. In addition, we describe the mathematical model for the advection-diffusion-adsorption phenomenon. In §3 both numerical and laboratory results area presented, commented and compared to each other. It is observed that biosorption, using natural hydroxyapatite is a promising technique under the conditions tested in this article.

2 MATERIALS AND METHODS

The HAP powder samples used in this work were obtained from bovine bone according to a previous work (Ferreiro, et al., 2012). The hydroxyapatite was calcined at $900°C$ and sieved at 37 μm. After this treatment, the powder obtained resulted in a carbonate hydroxyapatite type B. To carry out column and batch assays, a solution of Pb^{2+} was prepared by dissolving appropriate amounts of $Pb(NO_3)_2$ (p.a., Cicarelli, Argentina) in double distilled water. Both assays were conducted at room temperature. KCl (p.a., Cicarelli, Argentina) was used for tracer experiments in column operation. To measure the conductivity of potassium chloride solutions, an electrical conductivity meter (HI 8733, Hanna Instruments) was used. The samples collected at different times of the column assay were analyzed by an atomic absorption spectrometer (iCE 3500, Thermo Scientific).

2.1 Batch experiments-isotherm modeling

Batch assays were conducted with the objective of determining the capacity of the HAP surface to remove lead ions. For performing these assays, we prepared eight samples with different masses of HAP (0.06, 0.08, 0.10, 0.12, 0.14, 0.18, 0.2 and 0.25 g) and submitted them to contact with a lead solution, of the same concentration and volume. The samples were maintained under stirring at $250\,rpm$ for $12\,hours$. After this time, the HAP samples were removed from the solution by filter syringes $0.45\,\mu m$ (Sigma-Aldrich) and washed with distilled water and dried at $80°C$ for $6\,hours$ in an oven. From the data obtained, an adsorption isotherm was plotted. The amount of adsorbed lead at equilibrium, for different masses, was calculated according to the difference of the initial and final concentration, according to Eq. 1.

$$S = \frac{(C_0 - C_e)V}{M}, \tag{1}$$

where S $(mg \cdot g^{-1})$ is the adsorbed lead amount, C_0 $(mg \cdot L^{-1})$ is the initial concentration of lead solution, C_e $(mg \cdot L^{-1})$ is the lead concentration at equilibrium, V (L) is the volume of aqueous solution and M (g) is the adsorbent mass used.

For plotting the adsorption isotherms, adsorbed lead (S) vs residual lead concentration (C_e), Langmuir and Freundlich models were applied and compared with the experimental data. Of these methods, the best method was used to estimate the lead adsorption behavior in the column assays. From the experimental results (S_{exp}) obtained and the estimated values (S_{fit}), for each model, it was possible to calculate the average percentage error (APE) by Eq. 2.

$$APE(\%) = \frac{1}{N}\sum_{i=1}^{N}\frac{\mid (S_{exp,i} - S_{fit,i}) \mid}{S_{exp,i}} \times 100, \tag{2}$$

where N is the number of samples used.

2.2 Column experiments

Adsorption studies in column operation were carried out to evaluate and determine the adsorption capacity of HAP under continuous flow conditions. In a $150\,mL$ perfusion tube of $16\,cm$ length and $3.3\,cm$ internal diameter, layers of sand with particle size greater than $177\,\mu m$ and less than $250\,\mu m$ were placed at the column boundaries and in between them the HAP layer of $5\,cm$ length. The function of sand particles was to hold the column of HAP and to fill the rest

of the space within the entire length of the cylinder. Both the sand particles as well as the HAP created a joint porous medium through which the solution had to flow. The bulk densities of both the HAP porous bed and the sand were approximately 1.26 and $1.56\, g \cdot cm^{-3}$, respectively. The flow of the solution was directed from bottom to top of the column and kept constant at $1.33\, mL \cdot min^{-1}$ with a peristaltic pump (Y Z151x; LongerPump).

Non-reactive tracer experiments were carried out to determine transport parameters that were to be used in the models. Distilled water was initially allowed to flow through the column for 24 hours. For this experiment, an inert solution of $5\, g \cdot L^{-1}$ of potassium chloride was allowed to flow filling every space in the porous media and its conductivity was measured. Then, the solution was switched to one of $15\, g \cdot L^{-1}$. The second solution was fed and the time until the conductivity stabilized was recorded. The concentration of the solution was then calculated from the conductivity values.

The probe of the conductimeter was inserted inside a recipient where the fluid coming out of the column dripped and filled it so the probe could make the readings. A measurement was made every minute, beginning with the moment that the highest concentration solution started to fill the column until the moment where the conductivity was the same as the pure solution. Using an equation elaborated by Shedlovsky (1932), conductivity values were correlated with the concentration of the solution.

Reactive experiments with lead were conducted to verify the accuracy of the proposed model. In this case, a solution of $879\, mg \cdot L^{-1}$ of lead nitrate (Pb^{2+}) at the pH of the solution (approximately 4) was pumped into the column. Samples of $4\, mL$ were taken initially every $15\, minutes$ for $18\, hours$ and later lead concentration was measured.

2.3 Model description

Advection-Dispersion model

For modeling the fluid transport throughout the column and given the geometry of the system, a cylindrical coordinates system is chosen. To this end, the center of the lower boundary is considered as the center of the coordinate system. To obtain a one dimensional approximation model, it is considered that the concentration depends only on the height. As a consequence, every angular position around the axis along the radius has similar concentration. This approximation is made observing that the movement is performed from the bottom up along the cross section area, hence for the modeling, the sideways movement due to dispersion is neglected.

To obtain a relation of the values of the lead solution concentration of a column and the time of treatment, a breakthrough curve (BTC) is obtained. This provides information about the effectiveness of column operation. For a nonreactive tracer model, only transport terms are considered resulting in the advection - diffusion equation as follows

$$\frac{\partial C}{\partial t} = D_h \frac{\partial^2 C}{\partial z^2} - \nu \frac{\partial C}{\partial z}, \tag{3}$$

where C ($g \cdot cm^{-3}$) is the solute concentration of the solution, t (s) is time, ν ($cm \cdot s^{-}1$) is the linear velocity of the solution in the z axis and D_h is the hydraulic dispersion coefficient (a combination of the diffusion and dispersion coefficients). The algorithm used for resolving equation (3) is based on an implicit centered finite difference scheme. The HAP part of the column has a size of l and is discretized in n intervals, hence the space step used in the simulation

for obtaining the numeric solution is $h = l/n$. By rescaling it is considered $l = 1$ and $h = 0.5$. On the other hand, the time step considered is $\tau = 0.25$.

Convection-Dispersion with adsorption model

In order to consider the interaction of lead solution and the porous medium, a term representing the interaction between both the lead ions and the fixed HAP particles in the column had to be introduced in Eq. 3. We model this interaction as an adsorption process. Moreover, due to the very low flow velocity used in the experiments, non-equilibrium chemical processes are not considered in the final equation. In addition, first-order degradation and zero-order production terms are neglected, since their effect on the current conditions and with respect to the reactants considered are also negligible. The resulting advection-dispersion-adsorption equation takes the form

$$\theta \frac{\partial C}{\partial t} = \theta D_h \frac{\partial^2 C}{\partial z^2} - \theta \nu \frac{\partial C}{\partial z} + \rho \frac{\partial S}{\partial t}, \tag{4}$$

where θ is the non-dimensional porous medium porosity, ρ $(g \cdot cm^{-3})$ is the porous medium bulk density and S $(mg \cdot g^{-1})$ is the adsorption of the solute by the HAP.

For completeness of Eq. 4, a relationship between the solute concentration onto the porous medium and the aqueous one is modeled using one of the following expressions.

$$S = \frac{S_m \mu C}{1 + \mu C}, \tag{5}$$

for the Langmuir model, where S_m $(mg \cdot g^{-1})$ and μ $(cm^3 \cdot mg^{-1})$ are the maximum monolayer coverage capacitie and the Langmuir isotherm constant respectively, and

$$S = K_f C^{\frac{1}{n}}, \tag{6}$$

for the Freundlich model, where K_f $((mg \cdot g^{-1})\,(cm^3 \cdot g^{-1})^n)$ is the Freundlich isotherm constant and n is the adsorption intensity.

3 Results and discussion

3.1 Batch adsorption isotherm of lead

Experimental results by batch and the curve obtained by the kinetic models for adsorption of Pb^{2+} on HAP are shown in Figure 1. The adsorption capacity (q_e) at equilibrium and the coefficient related to kinetic for second-order model are obtained from the linearized form of the following second-order model equation (Ramash et al. (2013)):

$$\frac{1}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \tag{7}$$

where k_2 is the constant rate of pseudo second-order $(g/mg.min^{-1})$, q_t in the amount of metal ions adsorbed (mg/g) at any given time t (min), and q_e is the amount of metal ions adsorbed (mg/g) at equilibrium.

Figure 2 shows the residual concentration with respect to the adsorbent mass. It is possible to observe a decrease in the residual lead concentration with an increase of the mass of HAP.

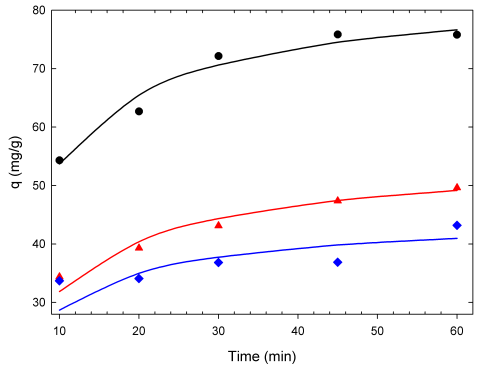


Figure 1: The Adsorption of Pb^{2+} for several initial concentrations onto HAP and fitted curves. Black, red and blue curves correspond to initial concentrations of 144, 213 and 224 mg/L, respectively.

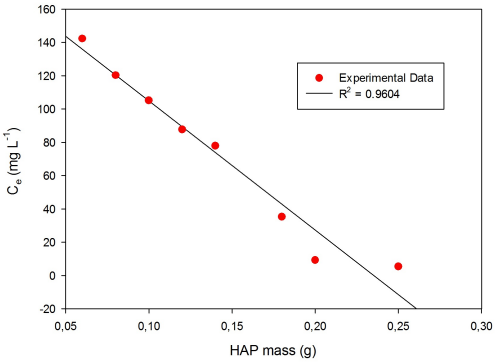


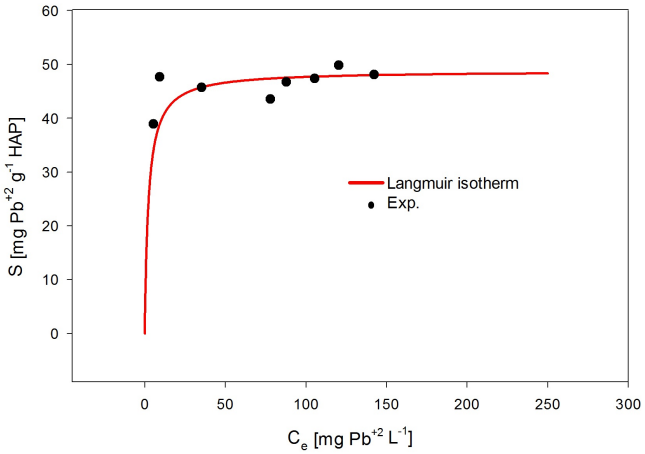
Figure 2: Relationship between residual concentration and adsorbent mass.

This decrease is approximated by linear least squares and shows that the lead removal is proportional to the mass of the adsorbent. As a consequence, in this case we linearly model the relationship between the mass and the number of active sites in the sorption process.

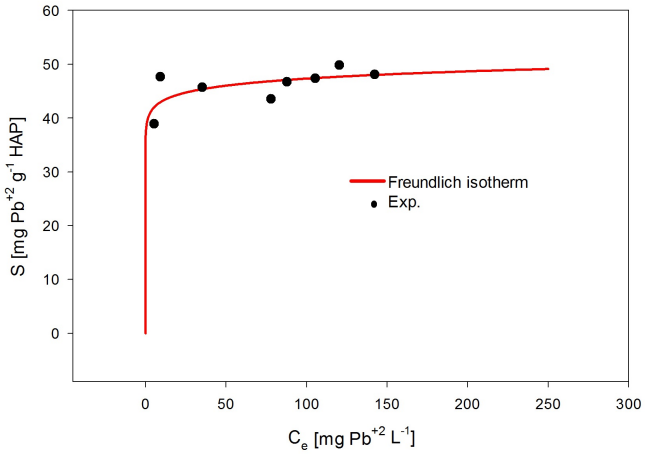
Figure 3 shows lead removal for lead adsorption and data fitting using Langmuir and Freundlich isotherm model, respectively. In Table 1 we show the coefficients of the Langmuir and Freundlich isotherm models that are used in Eqs. 5 and 6. It can be observed at Figures 3a and 3b that visually both models capture the phenomenology; however, the linear regression coefficient R^2 is larger for the Langmuir model and the APE is lower than the corresponding values of the Freundlich model. For these reasons, we choose the Langmuir model as the adsorption model to introduce in Eq. 4.

Table 1: Lead adsorption constants on HAP, Langmuir and Freundlich models.

	Langmuir		Freundlich
$S_m\ (mg \cdot g^{-1})$	88.921	$K_f(mgg^{-1}(cm^3g^{-1})^n)$	93.692
$\mu\,(cm^3 \cdot mg^{-1})$	$1.556 \cdot 10^3$	n	40.864
R^2	0.997	R^2	0.829
$APE(\%)$	3.789	$APE(\%)$	4.357



(a) Langmuir



(b) Freundlich

Figure 3: Experimental lead removal for lead adsorption and data fitting using in (a) Langmuir's model and in (b) Freundlich's isotherm model.

3.2 Column experiments

For modeling the column essay, we consider a uniform flow in the porous medium at physical equilibrium which does not involve regions of immobile water (Simunek, 2008). For determining the hydraulic dispersion coefficient D_h a non-reactive trace experiment is performed and the BTC is adjusted to the simulation. This allows to find the hydraulic dispersion coefficient D_h of Eq. 4 as $0.697\,(cm^2 \cdot min^{-1})$.

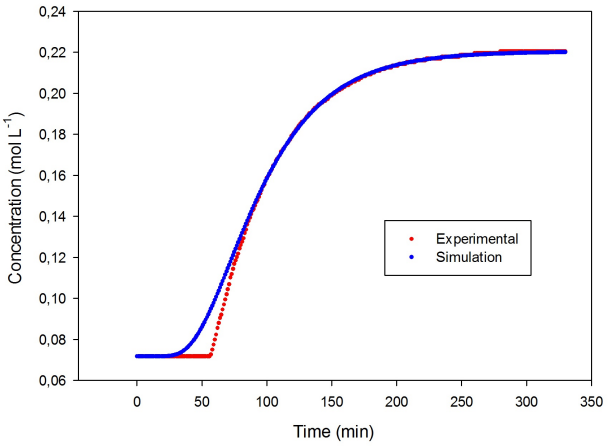


Figure 4: Experimental and fitted breakthrough curve (BTC) for the tracer: experimental and simulation in red and blue dot points, respectively.

Figure 4 shows experimental and simulation results. The latter was obtained by solving Eq. 3 based on the approximation of the velocity ν by a specific value at time t and space z. Observe the high visual agreement between the experimental data and simulation result meaning that the value of the hydraulic dispersion coefficient D_h obtained is visually precise.

Table 2: Used parameters in both forward and inverse simulations.

Parameters	Simulated	Fitted simulation
$D_h\ (cm^2 \cdot min^{-1})$	0.697	0.30
$v(cm \cdot min^{-1})$	0.240	0.35
$S_m(mg \cdot g^{-1})$	88.920	56.70
$\mu(cm^3 \cdot mg^{-1})$	$1.556 \cdot 10^3$	10.00

For solving Eq. 4, Table 2 shows the value considered for the hydraulic dispersion coefficient D_h, the velocity v, the adsorption parameters S_m and μ (see simulated column). For the resolution of Eq. 4 (numerical simulation) an initial lead concentration was $0.879\,(mg \cdot mL^{-1})$.

Figure 5 shows the numerical solution of Eq. 4 in contrast with experimental data obtained via direct measurement of the concentration. Two situations were explored (see Figure 5): 1- the curve obtained by numerical simulation (blue curve) using the values of Table 2 (simulated column) where all values were extracted directly from the experimental data of the previous sections; and 2- the curve obtained by numerical simulation (red curve) using the values of

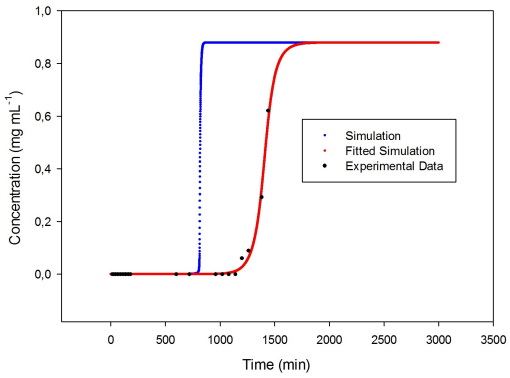


Figure 5: Experimental data and fitted simulation curves.

Table 2 (fitted simulation column) where all values were chosen (fitted) to match the numerical results with the experimental data (points at Figure 5). Observe that the fitted curve almost perfectly reproduced the experimental data, where the break point ocurrs at $977,75\,(min)$, with a concentration of $1\,ppb$ $(0.001\,mg/L)$.

The values corresponding to the Langmuir isothermal constants are important in the behavior of the curve. Other authors also reported discrepancies between the adsorption values obtained from batch experiments with those found experimentally by column (Hanna 2010, Jellali 2016). The reasons that can be considered are that either the solution failed to reach all the points within the system, due to the preferential flow, or that the velocity is relatively high; under these conditions terms of non-equilibrium reactions must also be included to better model the behavior by column.

4 Conclusion

In this article, we propose a mathematical model that predicts the removal of lead in aqueous solutions under continuous column flow conditions. Results show that the model with adjusted coefficients adequately and qualitatively reproduce the experimental data. This corroborates that the hydroxyapatite lead removal process is based on ion exchange and can be modeled as advection-diffusion adsorption. At this point, the authors believe that the model can still be improved, including unstructured physical and chemical processes, for better model accuracy in the saturation region.

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REFERENCES

Adewunmi, C. O., Becker, W., Kuehnast, O., Oluwole, F., & Drfler, G. 1996. Accumulation of copper, lead and cadmium in freshwater snails in southwestern Nigeria. *Science of the total environment*, vol. 193, n. 1, pp. 69-73.

Bulgariu, D., & Bulgariu, L. 2013. Sorption of Pb (II) onto a mixture of algae waste biomass and anion exchanger resin in a packed-bed column. *Bioresource technology*, vol. 129, pp. 374-380.

Ferreiro, O., Yubero, F., Balestra, R. M., Varella, M., & Monteiro, M. 2012. Bovine bone processing for biofilter application. *Materials Science Forum*, vol. 727, pp. 727-730. Trans Tech Publications.

Godwin, H. A. 2001. The biological chemistry of lead. Current opinion in chemical biology, vol. 5, n. 2, pp. 223-227.

Hanna, K., Rusch, B., Lassabatere, L., Hofmann, A., & Humbert, B. 2010. Reactive transport of gentisic acid in a hematite-coated sand column: experimental study and modeling. *Geochimica et Cosmochimica Acta*, vol. 74, n. 12, pp. 3351-3366.

Jellali, S., Diamantopoulos, E., Haddad, K., Anane, M., Durner, W., & Mlayah, A. 2016. Lead removal from aqueous solutions by raw sawdust and magnesium pretreated biochar: Experimental investigations and numerical modelling. *Journal of environmental management*, vol. 180, pp, 439-449.

Lu, H., Zhang, W., Yang, Y., Huang, X., Wang, S., & Qiu, R. 2012. Relative distribution of Pb^{2+} sorption mechanisms by sludge-derived biochar. *Water research*, vol. 46, n. 3, pp. 854-862.

Mohammad, A., & PA, M. N. 1997. Physico-chemical adsorption treatments for minimization of heavy metal contents in water and wastewaters. *Journal of scientific & industrial research*, vol. 56, n. 9, pp. 523-539.

Mohammed, F. M., Roberts, E. P. L., Hill, A., Campen, A. K., & Brown, N. W. 2011. Continuous water treatment by adsorption and electrochemical regeneration. *Water research*, vol. 45, n. 10), pp. 3065-3074.

Ooi, C. Y., Hamdi, M., & Ramesh, S. 2007. Properties of hydroxyapatite produced by annealing of bovine bone. *Ceramics international*, vol. 33, n. 7, pp. 1171-1177.

Ramesh, S. T., Rameshbabu, N., Gandhimathi, R., Kumar, M. S., & Nidheesh, P. V. 2013. Adsorptive removal of Pb(II) from aqueous solution using nano-sized hydroxyapatite. *Applied Water Science*, vol. 3, n. 1, pp. 105-113.

imunek, J., & Van Genuchten, M. T. 2008. Modeling nonequilibrium flow and transport processes using HYDRUS. *Vadose Zone Journal*, vol. 7, n. 2, pp. 782-797.

Suzuki, T., Hatsushika, T., & Hayakawa, Y. 1981). Synthetic hydroxyapatites employed as inorganic cation-exchangers. *Journal of the Chemical Society, Faraday Transactions 1: Physical Chemistry in Condensed Phases*, vol. 77, n. 5, pp. 1059-1062.