Evaluation of the coupled reaction-adsorption of Ca²⁺ ions on ashes from sugar cane bagasse. Kinetic and thermodynamic approaches

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Evaluación de la reacción-adsorción de iones Ca²⁺ en cenizas de bagazo de caña de azúcar. Aproximaciones cinéticas y termodinámicas

Avaluació de la reacció-adsorció de ions Ca²⁺ en cendres de bagàs de canya de sucre. Aproximacions cinètiques i termodinàmiques

RESUMEN

En el presente artículo se estudia la adsorción de iones Ca²⁺ y la reacción puzolánica del Ca(OH)$_2$ con un bio-reactivo (cenizas de bagazo). Se desarrolla en la investigación una caracterización completa del bio-material que incluye análisis de XRD, análisis térmico diferencial (TDA), análisis termogravimétrico y la determinación de parámetros generales como densidad pignométrica, compresibilidad, porosidad, etc. Se propone un mecanismo de cuatro etapas para describir la reacción puzolánica, este mecanismo responde a las postulaciones de Zhulaev. A través de la reacción se constata una conversión de 85.15% de Ca²⁺ y el resto de la especie queda de forma adsorbida, esto último valida la hipótesis de ocurrencia de un mecanismo adsorción-reacción. La cinética del proceso responde a una ley de pseudo-primer orden y el mecanismo es controlado por la difusión en la película.

Palabras clave: reacción puzolánica, absorción, cinética, termodinámica

SUMMARY

The adsorption of Ca²⁺ ions and the pozzolanic reaction between ashes from sugar cane bagasse (bio-reactant) and Ca(OH)$_2$, are studied in the present paper. The characterization of the bio-reactant by means of XRD, specific surface Brunauer-Emmett-Teller (BET), thermal differential analysis (TDA), thermo-gravimetric analysis and other physical parameters such as pignometric density, porosity, compressibility, form factor and flow velocity, is developed. A four stages mechanism is proposed to describe the pozzolanic reaction according to Zhulaev postulations. Once the reaction takes place, an 85.15% of Ca²⁺ is converted and the rest remains as adsorbed specie validating a dual adsorption-reaction process. The kinetics of the adsorption process can be described by means of a pseudo-first order model and the mechanism is controlled by the film diffusion model. The thermodynamics of the adsorption process fits to the Freundlich isotherm.

Key words: Pozzolanic reaction, adsorption, kinetics, thermodynamics

RESUM

En aquest article s'estudia l'adsorció d'ions Ca²⁺ i la reacció putzolànica del Ca(OH)$_2$ amb un bio-reactiu (cendres de bagàs). En la investigació es desenvolupa una caracterització completa del bio-material que inclou anàlisi de XRD, anàlisi tèrmica diferencial (TDA), anàlisi termogravimètrica i la determinació de paràmetres generals com son densitat pignomètrica, compressibilitat, porositat, etc. Es proposa un mecanisme de quatre etapes per descriure la reacció putzolànica, aquest mecanisme respon a les postulacions de Zhulaev. A través de la reacció, es constata una conversió de 85.15% de Ca²⁺ i la resta de l'espècie queda de forma adsorbida. Això últim valida la hipòtesi d'ocurrència d'un mecanisme adsorció-reacció. La cinètica del procés respon a una llei de pseudo-primer ordre i el mecanisme és controlat per la difusió en la pel·lícula.

Paraules clau: reacció putzolànica, absorció, cinètica, termodinàmica

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1. INTRODUCTION

The sugar cane industry is one of the most important sources of food and green fuels in several developing countries. The diversification of the sugar industry, have drawn an important impact to the environment and the valorization of the wastes in this industry is an important issue, which must be raised to increase the sustainability of the derived productions [1-4]. In the present paper, the useless ashes wasted from the cogeneration boilers running on sugar cane bagasse, is used to increase not only the sustainability of the sugar industry but the safety of the environment by including a biomass derived waste into a pozzolanic reaction of the cement industry.

The portland cement (CPO) is one of the most important construction materials all over the world. If it is compared with other materials such as plastics, aluminum, glass, wood and steel, the energy and environmental costs are relatively lower [5]. Nevertheless, due to its high production volumes, very important energy consumption and greenhouse gasses are emitted by the technology. The previous mentioned has raised to the reduction of the process sustainability and environmental compatibility [5-6]. The mixtures of pozolanic minerals to the CPO are the most extended among the possible solutions to increase the strength and durability of the material to the environment conditions [7]. Traditionally the silica smog and ashes of high ovens are used to the CPO formulation in a reaction step defined as pozzolanic reaction [8]. Process profits, engineering and environmental benefits can be obtained if a renewable and non-polluting material is used as re-agent in the pozzolanic reaction [6-8]. During the mixture of CPO with water a series of amorphous hydrated calcium silicates are produced from the reactions denoted as Calcium-Silicate-Hydrate or C-S-H [9].

$$2\ Ca_3SiO_5 + 7\ H_2O \rightarrow 3\ CaO \cdot 2\ SiO_2 \cdot 4\ H_2O + 3\ Ca(OH)_2 + 173.6\ kJ$$

The basis for the introduction of pozzolanic materials as partial substitutes of clinker in the CPO is based upon acid-base reactions. The chemical attach of the OH- dissociated from the $Ca(OH)_2$ and the alkaline ions from the CPO hydration to the alumina-silicate networks (acid component) that are in a state of high structural disorder within the puzzolan causes a breakdown of the oxygen bridges (-O-Si-O *- Al-O-) and the release of oxyanions [(Six, Aly) Oz] n-to the solution. The solution in the pores of the cement is essentially alkaline, the reaction product is an amorphous gel in which the K^+ and Na^+ cations are dominant. However, the presence of Ca^{2+} and the low solubility of the CSH gel are feasible evidence that this is only an intermediate product. The new hydration products formed from the reaction during the hydration of the CPO, are responsible for improving the mechanical properties and durability of concrete [10].

The use of pozzolans allows enabling improvements in the durability and mechanical performance of cement, mortars and concretes. These improvements are the result of the reaction between a pozzolan material and calcium hydroxide liberated in the hydration of cement. This reaction is conditioned by the surface of the pozzolan, crystallinity and size distribution. However, not all the calcium hydroxide reacts; there is a part which is adsorbed.

Rabilero et al., [11] proposes a general mechanism to study the reaction of $Ca(OH)_2$ solution with pozzolans:

$$Ca^{2+}_{(sol)} \leftrightarrows Ca^{2+}_{(ads)} + Pozzolan \rightarrow Products$$
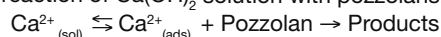
This reaction should occur in four stages:

1. Distribution of Ca^{2+} ions of the solution to the surface of the pozzolan.
2. Adsorption of Ca^{2+} ions on the surface of the pozzolan.
3. Distribution of Ca^{2+} ions through the layer of reaction products.
4. Chemical interaction between the ions Ca^{2+} and pozzolan.

As it's shown in this mechanism, the specificity of the adsorption of Ca^{2+} ions without pozzolanic reaction is not covered. The aim of this paper is to contribute to the characterization of the chemical and physical processes involved in the pozzolanic reaction of a biomaterial (bagasse ashes), by quantifying the fractions of Ca^{2+} involved in the reaction mechanism and retained by adsorption.

2. EXPERIMENTAL.

2.1 Ashes from sugar cane bagasse.
The ashes were collected from the ovens installed in the co-generation systems of different sugar cane mills in the central region of Cuba. Once collected, the ashes were washed with deionized water and dried to remove metal ions which can interfere in the reaction-adsorption mechanism.

2.2. Structure and composition characterization of ashes.
2.2.1 Scanning electron microscopy (SEM) and XRD.
The morphology of the ashes was analyzed by scanning electron microscopy (SEM) Leo 1430 VP coupled to X-ray diffraction to determine the phase components (grain size of 0.173 mm) and consulting the map library compiled by Joint Committee on Powder Diffration Standards. The X-ray was determined in a difractometer model Philips X'Pert with λCuKα1 monochromatic radiation (1.54056 Å) by applying a voltage of 40 kV and a current of 40 mA.

2.2.2 Qualitative infrared spectroscopy (FTIR) and BET.
Qualitative infrared analysis was performed on a computer brand ONE-Spectrum FT-IR Perkin-Elmer, using KBr pellet containing 1% of the sample and from the region of 4000-400 cm-1. The BET specific surface was determined in a Gemini III 2375 Surface Area Analyzer adapted to a discharge pressure of 100 mmHg/min, and equilibrium time of 60 seconds.

2.2.3 Thermal Differential Analysis (TDA).
Thermal analysis was developed in a brand Shimadzu, model TGA-50, with a flow of N_2 at 50 mL/min in a temperature range of 25 ºC to 1000 ºC with a temperature ramp of 10 ºC/min. After the characterization tests, the determination of physical parameters such as bulk density, bulk density by imprisonment, pycnometric density, porosity, compressibility, specific surface area, pore radius, pore volume, tortuosity and flow rate was performed.

2.3. Kinetic models for adsorption and reaction.
2.3.1 Kinetics of pozzolanic reaction between $Ca(OH)_2$ and sugar cane bagasse ashes.
The kinetic study of the reaction between the sugar cane ashes and calcium hydroxide is verified at 50ºC and for 792 mg/L at different contact times (10, 20, 30, 40, 50, 60, 90, 120, 150, 180, 210 minutes). A series of calcium hydroxide solutions ranging from 781.5, 389.5, 196.4, 98.7 to 49.3 mg/L were prepared and a volume of 50mL of the

solution was contacted with 0.5g of ash from sugarcane bagasse, agitation 300 rpm, 4 hours of maximum contact time and pH of the original solution. The subsequent stages were washing and drying with lithium chloride solution 0.1 M for 6 hours at 25ºC, 300 rpm.

The initial and residual concentration of Ca^{2+} was determined in a Shimadzu atomic absorption spectrophotometer AA-670. As primary hypothesis was assumed that the reaction between Ca^{2+} ions and the ashes must occur under diffusive regime considering the Zhulaev equation [11] and the diffusion through the layer of reaction products is the limiting step.

$$\left[{}^{1}\!/_{(1-\alpha)^{1/3}} \right]^2 = \beta = K_Z t \quad (1)$$

Where:

$$\alpha = \frac{(C_o - C)}{C_0} \quad (2)$$

It was also stated that some of the Ca^{2+} ions do not react, and remain as adsorbed species. The previous mentioned was checked for all the contact times, when the ashes after reaction were dried at 80ºC and contacted with a Li^+ solution, which due to high polarizing power is capable of extracting Ca^{2+} adsorbed from pozzolanic structure.

2.3.2 Kinetic and thermodynamic modeling of Ca^{2+} adsorption on sugar cane bagasse ashes.

In order to investigate the kinetics of the adsorption process, several well-known models were used to fit the experimental data after reaction. The time dependence of the system was established by means of:

- Pseudo-first order equation (Lagergreen model).
- Pseudo-second order chemical sorption.
- Elovich model, considering that the diffusion is the rate controlling step.

The proposed kinetic models are reported in Table 1 [12-14]. Several authors have reported these models to describe the biosorption of heavy metals in different biomass derived materials such as algae [15-16], sugar cane bagasse [17-19], among others.

Table 1. *Adsorption kinetic models Ca^{2+}.*

Name	Model
Pseudo first order	$ln\,(q_e - q_t) = ln\,q_e - k_1 t$ (3)
Pseudo second order	$t/qt = 1/(k_2 q_e^2) + t/q_e$ (4)
Elovich	$q_t = \alpha + \Lambda\,ln\,t$ (5)
Intrapellet Diffusion model	$q_t = k_d t^{0.5}$ (6)
Liquid film diffusion model	$ln(1 - {}^{q_t}\!/_{q_e}) = -k_3 t$ (7)

Sorption isotherms allow studying the distribution of the solute at equilibrium with the solid phase (sorbent) and liquid (solution). The thermodynamic study is established with the application of the Langmuir adsorption isotherm (Eq. 8) and Freundlich (Eq. 9). The first considers the adsorption as a chemical phenomenon and the second takes into account the variation of binding strength as a function of the surface coverage [20].

Langmuir Isotherm

$$q_A = \frac{Q \cdot K' \cdot C_A}{1 + C_A \cdot K'} \quad (8)$$

Freundlich Isotherm

$$q_A = K (C_A)^{t/n} \quad (9)$$

3. RESULTS AND DISCUSSION.

3.1 SEM and chemical composition of the sugar cane bagasse ash.

The Figure 1, shows the SEM image where an irregular porous surface is exhibited with a high availability to adsorb the Ca^{2+} and to provide sites for the pozzolanic reaction between the bio-reactant and the Ca^{2+}.
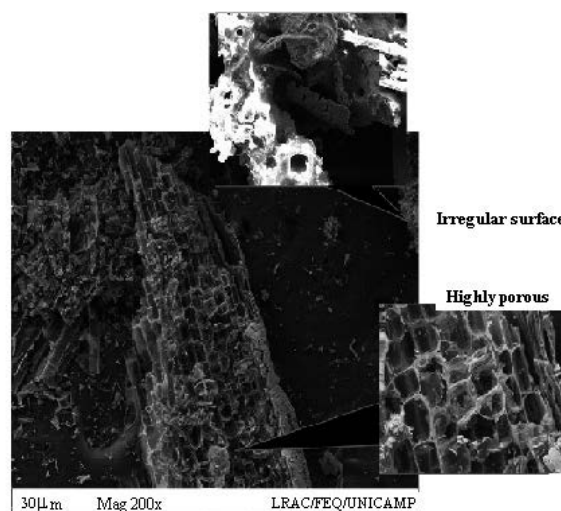

Figure 1. *SEM of the sugar cane bagasse ashes.*

Chemical analysis of the ashes (**Table 2**) showed that the main constituents are the SiO_2 and the Calcium both summing the 92.76% of the total chemical composition in the wasted ash and also giving to the product the adequate properties to be used as additive in the industry of construction materials. The hydroxyl ions are liberated when the bagasse ashes are in contact with water; these ions interact and break down the Si-O bonds in the different allotropic phases of silica. The intensity of these interactions is dependent of the structural arrangement of the previous mentioned phases. In the alumina-silicates the rupture occurs in the O bridges between the tetrahedral of Si and Al.

Table 2. *Chemical composition of ash.*

Element	%
Ca	10.2
Mg	0.4
Na	0.17
K	0.08
Al	0.05
SiO_2	82.56
Other	6.54

3.2 FTIR and XRD of the sugar cane ashes.

In the **Figure 2**, the X-ray diffraction of the original material shows the presence of cristobalite, accompanied by a potassium and calcium silicate with very low crystallinity, these is an evidence of the pozzolanic activity of the material.
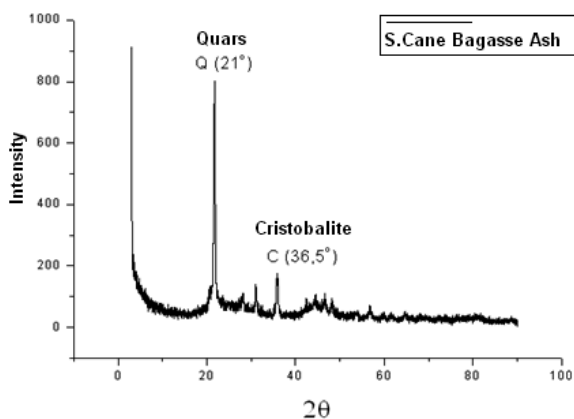
Figure 2. *XRD of sugar cane bagasse ashes used in the pozzolanic reaction.*

The high polarization of Ca^{2+} ions favors the adsorption process and allows the approach of the ions to the solid surface. The presence of carbon is visualized in the XRD due to a reflexion in the intensity between 3.0 and 3.5 Å. Qualitative infrared analysis (Figure 3) shows a band at 795 cm^{-1} which corresponds to symmetrical vibrations Si-O-Si and a band in 1089 cm^{-1} that responds to the antisymmetric vibrations of the Si-O-Si at 1630.20 cm^{-1} is observed a band at 3447.69 cm^{-1} corresponding to H_2O.
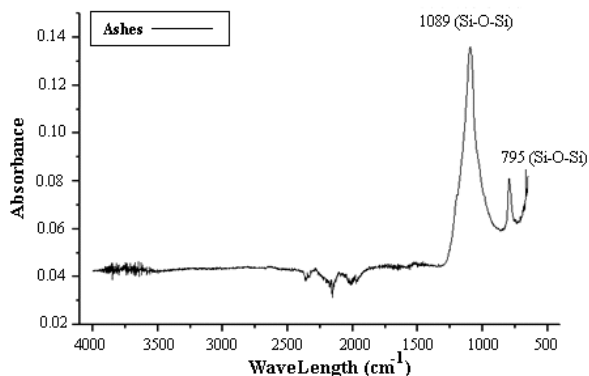

Figure 3. *FTIR spectra of the sugar cane bagasse ashes.*

3.3 Thermal Differential Analysis.

In the Figure 4 the thermal differential analysis shows a slight mass loss which is associated to a low temperature endothermic peak at 550°C. A wide peak is exhibited from 600°C to 950°C this might be related to the presence of graphite and other compounds unburned during the combustion of bagasse.
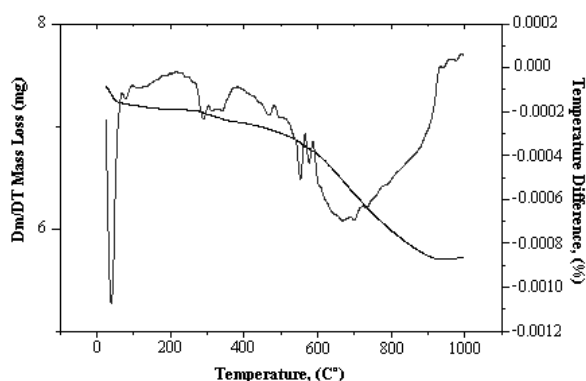

Figure 4. *TDA of the ashes.*

The results of physical characterization of the sugar cane bagasse ashes are shown in **Table 3**. It is important to note that the ashes are a waste from the ovens in cogeneration processes currently installed in the world sugar industry and it is ready for disposal. The previous mentioned makes the results presented here of a great interest to increase the added value and the sustainability of the production considering a waste as an avoided product.

Table 3. *Physical characterization of bagasse ash.*

Parameters	Value	U/M
Aparent density	0.21	g/mm^3
Aparent aprisioning density	0.26	g/mm^3
Real density	0.55	g/mm^3
Porosity	61.49	
Compresibility	18.15	%
Flow velocity	0	
Sphericity	0.45	
Specific surface	11.792	m^2/g
Pore volume	$1.23* 10^{-9}$	m^3/g
Tortuosity	1.79	-
Pore radius	$2.086*10^{-9}$	M

3.4 Kinetics coupled to adsorption of Ca^{2+} during the pozzolanic reaction.

The kinetics of the pozzolanic reaction in the ash of sugar cane bagasse was studied. As was before mentioned the equation of Zhulaev was used as hypothesis and different operational condition explored to calculate the reaction rate and the rate model parameters. Figure 5 shows the ratio between the Zhulaev rate constant with the contact time.
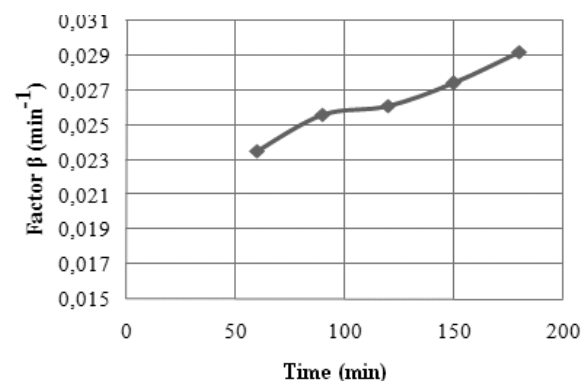

Figure 5a. *Effect of time on β. Reaction temperature = 50°C.*

Taking into account the values of α and β as shown, excluding the values of the adsorption of Ca^{2+} sets out the values of the apparent reaction rate constants for the pozzolanic reaction to the first 30 min ($\alpha = 6*10^{-4}$ min^{-1}) and for a period of 30 min to 200 min ($\beta = 4*10^{-5}$ min^{-1}).

The reaction rate model with time in minutes can be written as:

$$\left[\frac{1}{\left(1 - \left(\frac{c_o - c}{c_o}\right)\right)^{1/3}} \right]^2 = 6 \times 10^{-4} t$$

If the variation of the concentration of the Ca^{2+} adsorbed within time is taken into consideration, the parameters in Figure 5a must include a variation according to the thermodynamics (Figure 5b) and kinetics of the adsorption

process. It was determined that at the end of the reaction a 14.6% of Ca^{2+} was retained in the structure of the ashes meaning this that the remaining 86.4% was converted during the pozzolanic reaction. The previous mentioned validates the Zhulaev four step mechanism postulation and also the efficiency in using the sugar cane ashes as Portland cement additive increasing in this way the sustainability of the process and giving an added value to a waste of the sugar industry.
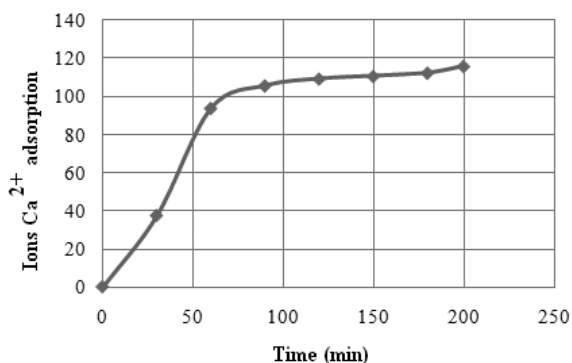

Figure 5b. *Isotherm of Ca^{2+}, adsorption coupled to the pozzolanic reaction.*

The sorption isotherm (Figure 5b) was performed at the same temperature as reaction 50ºC at a fixed pH. Bagasse ashes in reaction with Ca^{2+} reached a maximum sorption capacity close to 108 mgCa^{2+} g^{-1}. This finding supports the hypothesis of the coupled pozzolanic reaction-adsorption mechanism which was superimposed to the system under consideration. Experimental data were modeled using Eqs. (3)–(9), and the parameters of the thermodynamic and kinetic adsorption models are summarized in Table 4. As can be seen all the models roughly fit experimental data with discrepancies that appear either in the initial section (low residual metal concentration) or in the curvature for the intrapellet diffusion model (R^2=0.77).

According to the explored models can be stated that the expressions which better describe the system are the Langmuir isotherm with a R^2=0.97 and Freundlich R^2=0.99. The affinity constant for the Langmuir model is 0.1 Lmg^{-1} and the K value is 7.9*10^{30}. An exponential distribution of the heats of adsorption is feasible to describe the energy transfer during the adsorption process of Ca^{2+}ions.

Table 4 summarizes the results of statistical adjustment for models of adsorption of ions Ca^{2+} in the ash of sugar cane baggasse.

Table 4. *Fitting models of adsorption kinetics.*

Model	Coefficient
Pseudo first order	R^2 = 96%
Pseudo second order	R^2 = 87%
Elovich	R^2 = 87%
Intra pellet diffusion	R^2 = 77%
Liquid film diffusion	R^2 = 96%

The kinetic model fixes well the pseudo-first order equation, advocating the adsorption of ions across a single site of the adsorbent. The apparent constant of adsorption rate is 37.53 min^{-1}, while the diffusion through the liquid film kinetic is the rate controlling step, with a constant value of diffusion coefficient in the liquid film of 0.03 min^{-1}.

4. CONCLUSIONS

Two mechanisms of interaction of calcium hydroxide in the ash of sugar cane bagasse where found: Pozzolanic reaction and adsorption of Ca^{2+} ions in the structure of the proposed reactant (*sugar cane bagasse ashes*). This latter mechanism may consider the following steps:

I. Diffusion of Ca^{2+} hydrated ions of the solution to the liquid film surrounding the grain of ash.
II. Diffusion of these ions in the liquid film surrounding the grains of ash and the spaces between the grains.
III. Deformation of Ca^{2+} ions interacting with the surface of grains of ash (Pozzolanic reaction).
IV. Diffusion of Ca^{2+} ions to adsorption sites where they interact with a dot.

Stages II, III and IV should determine the speed of the adsorption process controlled by diffusion in the liquid film.

The kinetic process of Ca^{2+} can be explained by a pseudo first-order model, where the diffusivity through the liquid film is the rate controlling step.

Nomenclature

q_e	Equilibrium mass of adsorbed metal times grams of adsorbent (mg/g)
q_t	Mass of adsorbed metal times grams of adsorbent (mg/g)
t	Time (minutes)
k_1	Pseudo first order rate constant (min^{-1})
k_2	Pseudo second order rate constant (g/mg-min)
k_d	Intra-pellet diffusion rate constant (mg/g min$^{1/2}$)
k_3	Liquid film diffusion rate constant (min^{-1})
α	Initial sorption velocity (mg/g min)
Λ	Desorption constant (g/mg)
k_z	Pozolanic reaction rate constant (min^{-1})
A	Variation of Ca(OH)$_2$ concentration
C_o	Initial concentration of Ca(OH)$_2$
C	concentration Ca(OH)$_2$
Q	Maximum metal uptake to cover all the monolayer (mg of adsorbat/g de adsorbent).
K	Langmuir Constant (cm^3/mol)
C_A	Equilibrium constant for the adsorbat q_e.
κ	Constant for adsorbat-adsorbent
n	Freundlich constant
rpm	Velocity

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6. ACKNOWLEDGMENTS.