



Calcium Phosphate Composites and Silica Obtained from the Rice Hull for Biomedical use. Synthesis and Characterization

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This paper describes the development of composites of calcium phosphate and silica, wherein the silica is obtained from rice husk as a natural source. The objective was to develop calcium phosphate composites and silica that meet physical and chemical characteristics for potential applications in bone treatments as synthetic filler and assess their degradation in simulated physiological fluid. Carried out the synthesis of each of the materials and the physicochemical characterization of each composite and formed by means of analysis by X-ray diffraction (XRD) and scanning electron microscopy (SEM), degradation tests were carried out with the material. The composite was developed using metallurgy of powders of calcium phosphate and silica. The results showed that the calcium phosphate composite and silica obtained from rice hush can be used as synthetic bone filling material with the synthetic connotation variant.

1. Introduction

Rice hulls, RH for its acronym in English (Rice Husk), is one of the main agricultural products obtained from rice production in countries like China, India, Indonesia, Bangladesh, Viet Nam, Thailand, Japan, Myanmar, Philippines Brazil and others (Rojas, 2014). In rice producing countries, occurs around 20 – 25 % by weight of rice husk, which in 2007 was between 123 and 132 Mt (Xiong et al., 2009).

Rice hulls has a high silicon content, existing as hydrated silicon (Prakash, 2010) and additionally contains potassium (K), aluminum (Al), phosphorus (P), iron (Fe), manganese (Mn) and chlorine (Cl) (Forero et al., 2009). Its structure is porous, allowing moisture absorption. The chemical compositions of RH vary from one sample to another, related to the type of rice crop year, climatic variations, geographical conditions, and even the fertilizers used in growing rice (Chandrasekhar, 2003). The scale chemical analysis suggests that rice husk consist to about 22 % of silica or silicon oxide (SiO_2) (Farook et al., 2003), to about 74% of water and organic matter, and to about 4% of $\text{Al}_2\text{O}_3 + \text{CaO} + \text{MgO} + \text{Fe}_2\text{O}_3$, (Kumar et al., 2012) and to about 4 % $\text{Al}_2\text{O}_3 + \text{CaO} + \text{MgO} + \text{Fe}_2\text{O}_3$ (Prasad-Pandey, 2012). The percentage of SiO_2 varies between 15 % and 22 % and is in hydrated form (Chandrasekhar, 2003).

Silica is an element that constitutes our skeletal system, and is involved in the synthesis of collagen content in bone and connective tissue, as well as favorably involved in the reconstruction of destroyed cartilage in the case of joint disease. Silica is one of the base substances of biomaterials called bioglasses, which also contain sodium, potassium, magnesium, calcium and phosphorus. Bioglasses have been used in medical applications such as controlled drug delivery systems, implants without much charging cradle and bone cements (Lopez et al., 2013). Bioglass has performed well in terms of compatibility in vitro assays with osteoblast-like cells, resulting in the formation of surface apatites bioglass in (Oudadesse et al., 2011).

Hydroxyapatite comprises crystalline calcium phosphate ($\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$) and represents a tank body of 99 % calcium and 80 % of total phosphorus (Wang et al., 2003). The use of implants covered hydroxyapatite or tricalcium phosphate has been widely described for demonstrating an early attachment between them and the surface of the bone, about one month after insertion. It was also shown that the anatomy of the soft tissue around the implant is normal and there is no inflammation (Sato et al., 2005). Hydroxyapatite (HAp), obtained from natural sources or synthetic sources, is considered a bioactive substance that forms strong chemical

bonds with the host bone tissue, and thus is recognized as a good material for bone implants. HAp is osteoconductive, non-toxic, non-immunogenic, and its chemical composition and structure is similar to the mineral phase of human bone (Padilla et al., 2006). However, the outstanding features of HAp in terms of biocompatibility and bioactivity are seriously hampered by their poor mechanical properties, preventing their use in high load applications traditionally associated with orthopedic implants (Izquierdo-Barba, 2006). The research includes the development of composites calcium phosphate and silica, silica obtained from natural sources such as rice husks that meet biofunctionality characteristics of biocompatibility and potential applications in bone and evaluate treatments by degradation in simulated physiological fluids.

2. Methodology

2.1 Synthesis of silica and calcium phosphates

Were selected 250 grams of rice husks, from a Santander company (Colombia), for the synthesis of silica. Aqueous precipitation method was used to obtain the calcium phosphate crystals using calcium nitrate tetrahydrate ($\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$) and ammonium phosphate ($\text{H}_2(\text{PO}_4)\text{NH}_4$) and 0,48M in 1M concentrations respectively (Montañez, 2011). The mixture was basified to pH 10, aged for 144 h and dried at 60 °C for 24 h. The calcium phosphate product calcined at 1,050 °C for 1 hour.

The sol gel method was used to obtain silica from rice hulls (SiO_2). Preparation of the silica gel was carried out by drying at 110 °C for 12 h, followed by calcination at 700 °C for 6 h (Dessai et al., 2013). The resulting material was heated to 50 - 60 °C in solution of 1M sodium hydroxide (NaOH) (Prasad-Pandey, 2012). The silica gel was prepared by continuous stirring and adding HCl 4M hydrochloric acid to pH 6,5. The mixture was aged for 12 h, filtered and washed twice. Followed by a drying step was performed at 110 °C for 24 h (Prawingwong et al., 2009) and calcination with inert gas at 850 °C.

2.2 Physicochemical characterization

The material was characterized by chemical and microscopic X-ray diffraction (XRD) and scanning electron spectroscopy (SEM-EDS). The characterization by X-ray diffraction was carried out on a powder diffractometer BRUKER D8 ADVANCE DaVinci geometry, at a voltage of 40 kV and current of 30 mA. The samples were pulverized in agate mortar and carried size of 30 microns (400 mesh). The selected specimens of each sample was mounted on a sample holder of polimetilmetacrilato (PMMA) by the technique of front filling an internal standard Corundum - Aluminum oxide, which was added to the sample in a known amount for the respective quantification.

2.3 Obtaining and degradation of calcium phosphate composite-silica

The composite was obtained powder and solid. For the composite powder, the material was calcined mixed at 850 °C and for obtaining solid composite was performed compacting powders using Carver press with pastillator Elmer at a pressure of 478802,69 Pa, followed by sintering same for one hour at 850 °C to obtain ceramic bioglass. The ceramic composite was formed considering the following weight to weight concentration. 30 – 70 % w / w; 70 – 30 % w / w calcium phosphate and silica respectively. The composite chemical was again characterized by the microscopic techniques mentioned above after sintering.

Composite degradation tests were conducted in simulated physiological medium PBS (Physiological saline body) (NaCl 8 g / L, KCl 0.20 g / L, 1.44 g $\text{Na}_2\text{HPO}_4 \cdot 2\text{H}_2\text{O}$ / L, KH_2PO_4 0.24 g / L) in a time of 7 d at 37.5 °C in a thermostatic bath.

3. Results and discussion

3.1 Synthesis and physicochemical characterization of silica and calcium phosphates

From 250 g of washed and dried rice husk, 51 g of rice husk ash was obtained in the calcination process. In the chemical treatment, silica gel began to precipitate as the pH becomes smaller until a value of 6.5. After washing and drying the aspect of rice hull ash treated in acid medium was a sandy powder with small size and uniform particle.

The chemical characterization of the extracted silica from rice husk by XRD showed that the sample was completely amorphous, finding quartz (crystalline SiO_2) in a 1 % lower rate. Shown in Figure 1, a signal of very low intensity at an angle 2θ of 21.86 °, that was not assigned to any crystalline phase with a wide band, indicating that the material is amorphous SiO_2 (Essien et al., 2012).

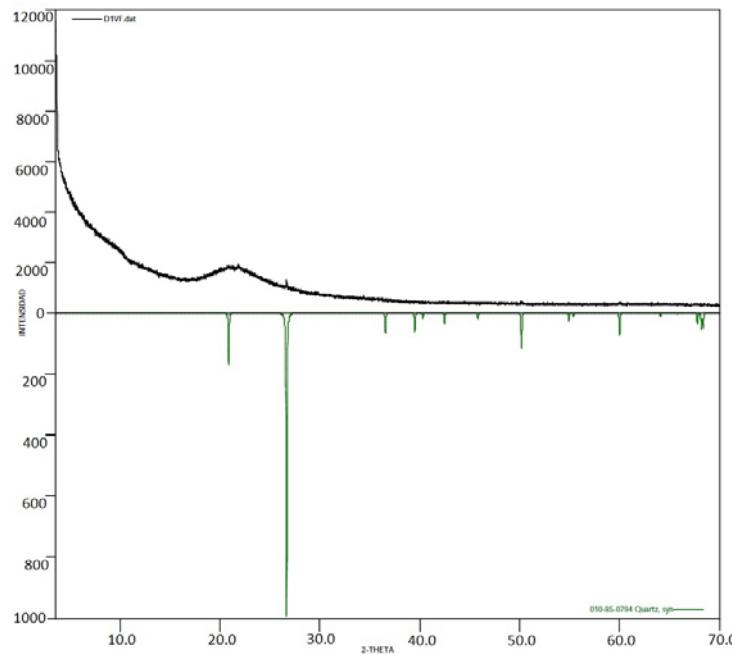
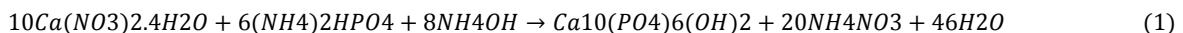


Figure 1: X-ray diffraction Silica extracted from rice husk

In Figure 2, the scanning electron microscopy shows elemental analysis by energy dispersive spectroscopy X-ray (EDS) for the extracted silica rice husks after the degradation test, shows an atomic composition of 4.45 %, 33.95 % and 61.60 % for the elements carbon, silicon and oxygen respectively, confirming the presence of silica. The morphology of the material exhibits a porous structure, with different sizes and aggregates of grain due to the process of compacting and sintering of the sample and the degradation for 7 d. However, it is observed that the grain size is less than 1×10^{-5} m.

Calcium phosphate was synthesized by aqueous precipitation method and was obtained by Eq (1), with a Ca / P ratio = 1.67.



Characterization by XRD calcium phosphate crystal showed a total of 88.9 % and 11.1 % amorphous according to the Table 1. In Figure 3, the XRD spectrum signals observed with calcium phosphate, hydroxyapatite and whitlockite and tricalcium phosphate.

After synthesis of the silica and calcium phosphates, held composite formation. Compacting the separate materials and the formation of composites, calcium phosphates were found to be denser in the compaction process to 478802,69 Pa pressure. When the composites are sintered, they harden as a result of chemical bonding in grain boundaries of each compacted powder.

Table 1: XRD quantification of calcium phosphates

Phase	Name	Quantitative (Standard Deviation)
$Ca_3(PO_4)_2$	Tricalcium phosphate	38.1 % (0.2)
$Ca_{10}(PO_4)_6(OH)_2$	Hydroxyapatite	15.7 % (0.1)
$Ca_2P_2O_7$	Calcium phosphate	35.1 % (0.2)
Total crystalline		88.9 %

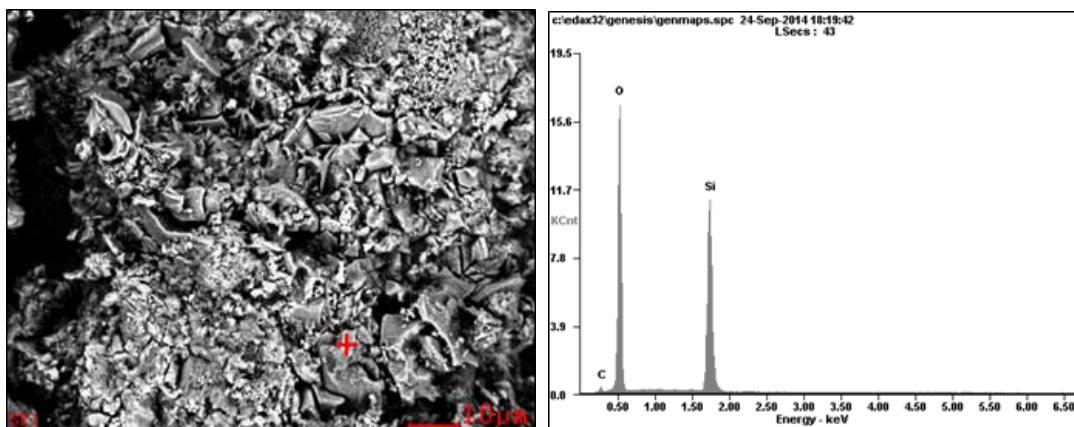


Figure 2: SEM-EDS to silica extracted from rice husk

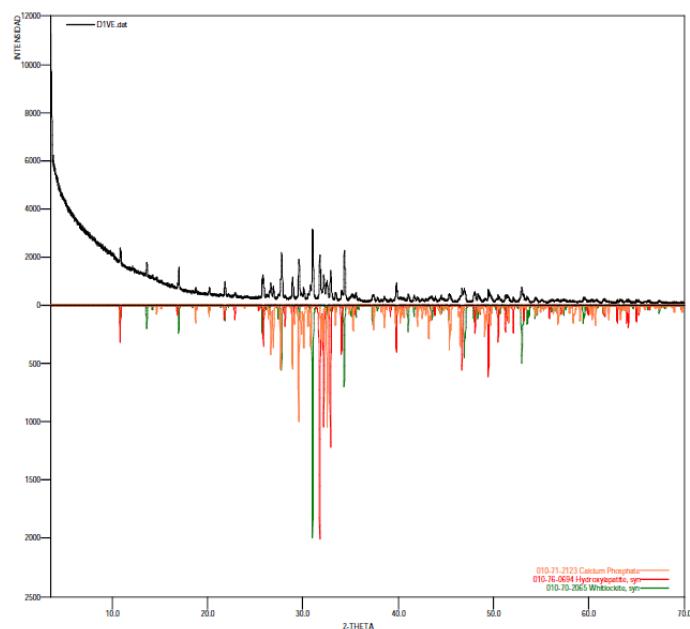


Figure 3: XRD quantification of calcium phosphates

3.2 Preparation and characterization of composite calcium phosphates - silica

Figure 4 shows the XRD spectrum of the composites shown in the compositions of 30 - 70 % w / w and 70-30 % w / w of silica and calcium phosphate respectively. Chemical characterization shows to 30 wt % silica and 70 wt % calcium phosphate shows an amount of whitlockite percentage of 23 % (0.3), 12.3 % hydroxyapatite (0.2), calcium phosphate 19.9 % (0.2) amorphous and 44.8%, while for 70 % by weight silica and 30 % by weight of calcium phosphates, whitlockite is an amount of 8.9% in percentage (0.3), 5.4% hydroxyapatite (0.3), calcium phosphate is 7.7 % (0.3) and amorphous 78.0%, showing that the proportions in which each ceramic is added to form the composite, are maintained even after compaction and sintering of the samples. In the diffraction spectra of Figure 4 shows that a wide band when the composite having a composition of 70 wt % silica is obtained, appears in 21.86 °, associated with the presence of amorphous silica, without the presence of impurities (Athinarayanan et al., 2015) and sizes of nanoscale (Weixing et al., 2012).

In Figure 5, the SEM-EDS test for composite comprising 70 % by weight of calcium phosphates and 30 wt % silica sample. A morphology is observed in non-equiaxial grains due to the sintering process, with sizes less than 1×10^{-5} m and with an atomic composition of 3.73 % carbon (C), 56.94 % oxygen (O) 0.86 % Sodium (Na), 1.03 % silicon (Si), 14.78% of phosphorus (P) and 22.66 % calcium (Ca), finding an elemental composition that makes a ceramic composite bioglass developed with wide use in biomedical use, as is known the biocompatibility of calcium phosphate (Padilla et al., 2006) and the excellent biocompatibility testing silica mesenchymal human cells (Athinarayanan et al., 2015).

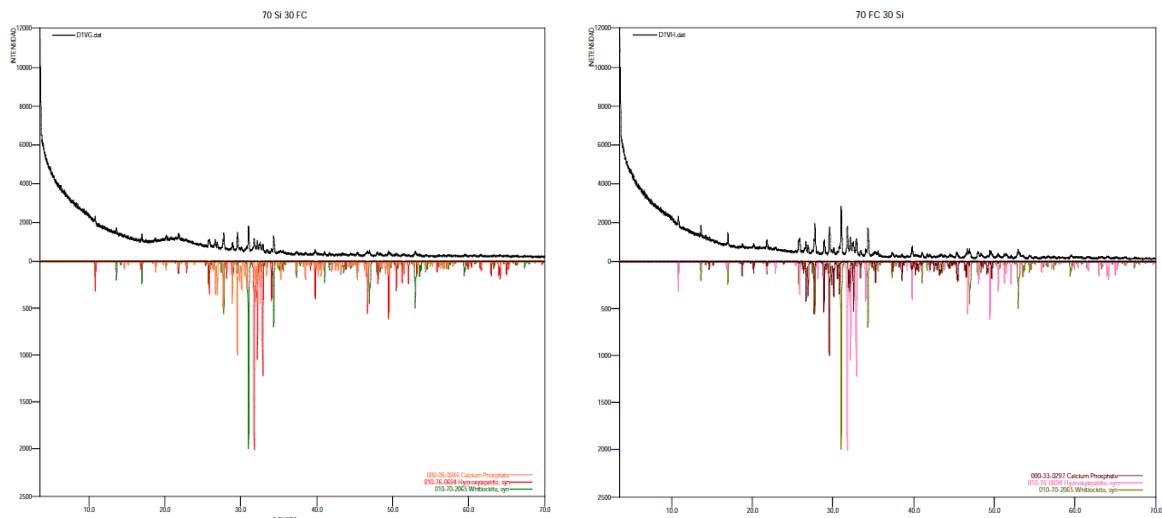


Figure 4: X-ray diffraction a) 70-30% w / w silica-calcium phosphate b) 30-70% w / w silica-calcium phosphates.

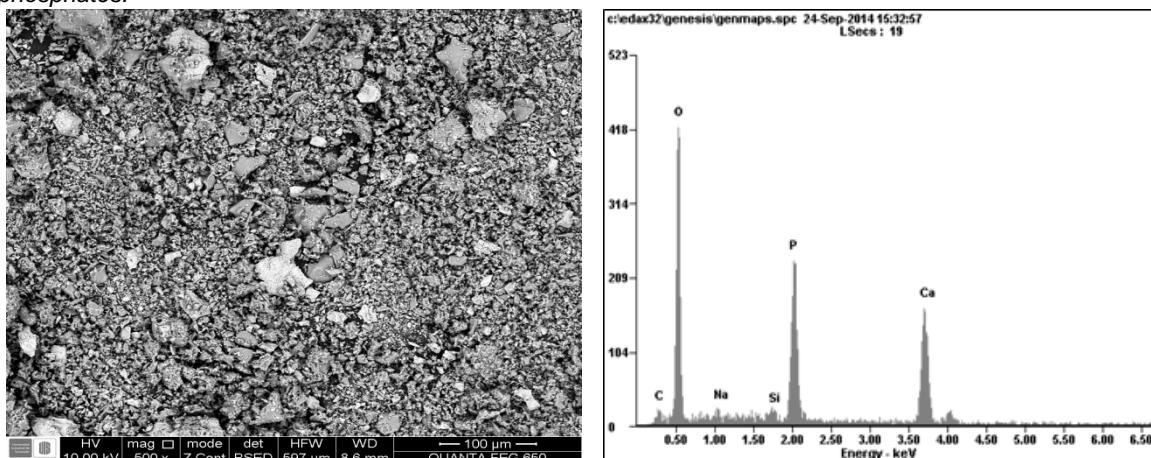


Figure 5: SEM-EDS for composite 70-30% w / w calcium phosphate-silica respectively.

In the degradation of the different samples, the sample containing silica was 100 % greater weight loss as a result of degradation in PBS simulated physiological fluid. It was observed under microscope silica samples were obtained from the scale samples porosity greater than 100 % and 70 % calcium phosphate. This higher porosity silica attributed to increased fluid absorbed and in turn not being so thick, had a higher degradation obtaining high percentages of degradation compared to the samples containing higher percentage of calcium phosphate. Table 2 shows the initial and final weights of each of the composites formed samples and calcium phosphate 100 % and 100 % silica sample. Each assay was done in duplicate. It was shown that the composite with the lowest percentage of degradation is formed on sintering with 70 % calcium phosphate – 30 % silica, due to the porosity and absorbing capacity of the silica, works best when it is added to the calcium phosphate 30 % in terms of degradability in the simulated body fluid.

Table 2: Degradation results of composites in PBS for 7 days by weight loss

CP	Si-O	Initial weight (g)	Final weight (g)	Percentage of degradation (%)
100	0	0.9577	0.9526	0.53
0	100	0.3289	0.3246	1.31
70	30	0.4734	0.4725	0.19
50	50	0.3210	0.3171	1.21
30	70	0.3158	0.3143	0.47

4. Conclusions

Composites of calcium phosphates and silica were successfully synthesized amorphous silica particles with diameters smaller than 1×10^{-5} m, from rice hulls by the sol gel method and acid treatment, and by the calcium

phosphate precipitation method of aqueous. It was found by X-ray diffraction. The process of compacting powders to 478802,69 Pa and sintering pressure used for preparing composites, to find a stronger structure with equiaxed grains not among the calcium phosphates and silica extracted from rice hulls but with a composition elemental makes bioglass ceramic material with applications in biomedical use. According to the percentage of degradation, degraded composites that were 70 % less FC – 30 % Si and 30 % FC – 70 % Si respectively.

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