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Microwave Assisted Acid Digestion of Biomorphic Ceramic Obtained from Cedar Wood Infiltrated with ZrO_2

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Abstract

This work proposes the use of experimental design for optimization of microwave-assisted digestion of biomorphic ZrO_2-ceramic. Cedar wood is used as template and it was infiltrated with ZrO_2 via sol-gel process. XPS, SEM and XRD have been used to verify the effectiveness of the synthesis. The effects of different combination of acids in the digestion of this sample have been optimized taking as response the concentration of several metallic ions measured by ICP-MS.

Keywords: Cedar Wood, Microwave Digestion, ICP-MS, Metallic Ions, Experimental Design

1. Introduction

Sol-gel processing is a new technology that is being developed more quickly for the manufacture of ceramic and glasses. In the ceramics, this method allows the uniform and fine particle formation of high purity to relatively low temperatures. These dusts can be sintered next until obtaining to a high density with their corresponding good mechanical properties. In such techniques, the fundamental characteristic is the formation of an organometallic dissolution. The phase disperses "sol" becomes a rigid "gel", which, as well, is reduced until its final composition by means of diverse heat treatments. A key advantage of the process sol-gel is that the product the forms initially by means of this procedure of liquid phase can be roasted to lower temperatures, compared with those of the conventional processes for ceramics.

The aim of this work is to optimize a microwave acid digestion procedure for the determination of metals in biomorphic ceramic samples. Microwave radiation is widely used in modern chemistry and technology as a source of energy for intensification of physicochemical processes. Microwave-assisted digestion has clear advantages over the traditional acid digestion using convective heating systems in terms of recovery, precision, short time needed (minutes) to perform decomposition of the sample, direct heating of samples and reagents (the vessels are only indirectly heated by the hot solution), minimal contamination and looses of volatile elements. It reduces the possibility of cross contamination and the consumption of reagents. The use of small amounts of reagents decreases the blank signal. The combination of different acids, such as H_2SO_4, HNO_3, HCl and HF is a very frequent method for preparing samples before their quantitative elemental analysis.

The association of factorial design [1] and microwave-assisted [2-6] digestion can contribute to accelerate the pre-treatment step, improving the accuracy of the results. On the other hand, ICP-MS is an ideal technique for determining elements, with rapid data acquisition and low detection limits. This work proposes the use of experimental design for optimization of microwave-assisted digestion of biomorphic ZrO_2-ceramic [7-13].

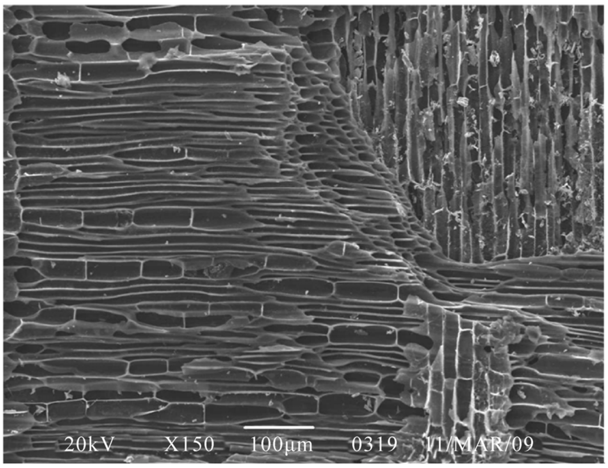
2. Experimental

2.1. Instrumentation

A Lenton Tube furnace, model LTF 16/180, was employed for the synthesis of biomorphic ceramics.

X-ray photoelectron spectroscopy (XPS) analysis was performed with a Physical Electronics 5700 instrument with a Mg Kα X-ray excitation source (hν = 1253.6 eV); binding energies (BE) were determined with respect to the position of the C1s peak at 284.5 eV. The residual pressure in the analysis chamber was maintained below 133×10^{-9} Pa during data acquisition.

Scanning electronic microscopy (SEM) JEOL, Model SM-6490LV was used to obtain the micrographs shown in **Figure 1** and semi-cuantitative analysis shown in **Table 1**.



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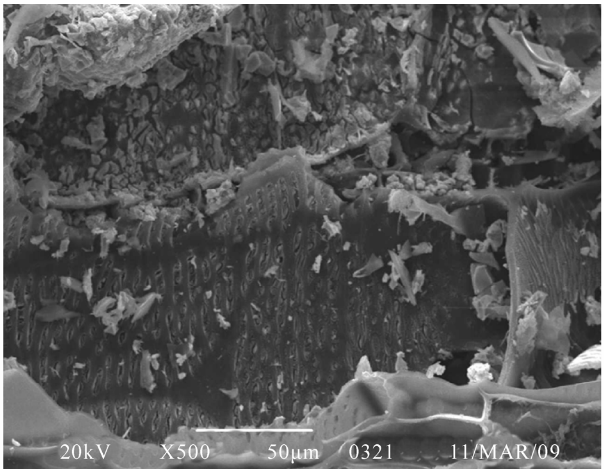

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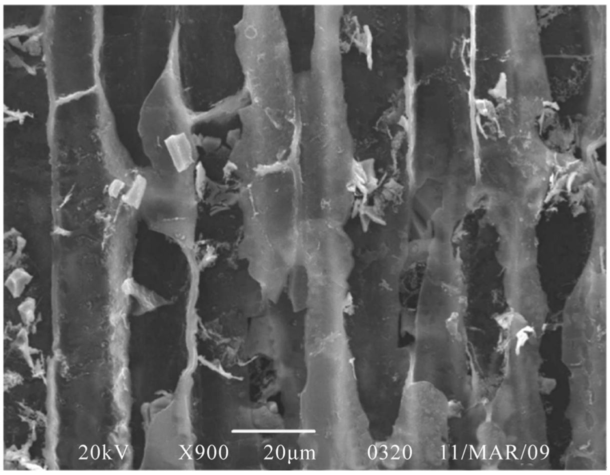

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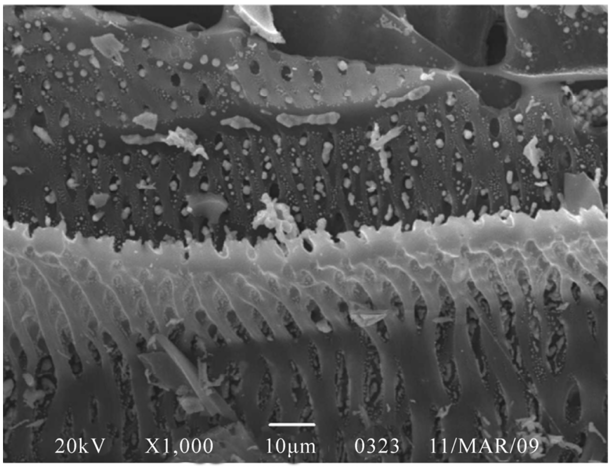

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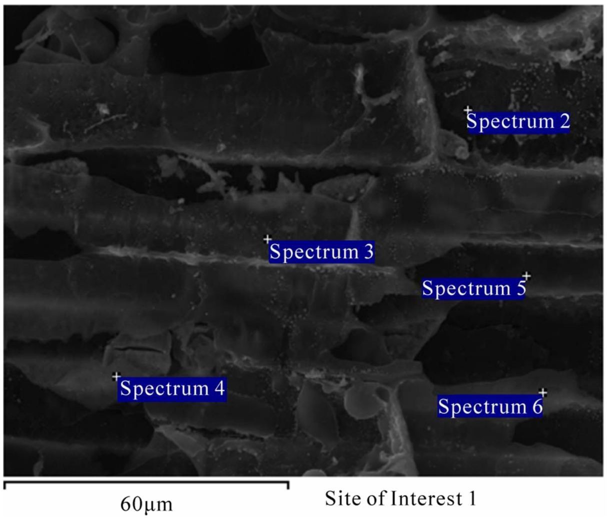


(e)

Figure 1. Micrographs of biomorphic ceramic obtained with SEM at different magnification a) ×150, scale 1:10 µm; b) ×500, scale 1:50 µm; c) ×900, scale 1:20 µm; d) ×1000, scale 1: 10 µm; e) Site of interest for results showed in Table 1.

Table 1. Semi quantitative analysis made from Figure 1(e).

Espectrum	C	O	**Ca**	Zr	**Total**
Espectrum (2)	73.98		3.71	22.31	100.00
Espectrum (3)	67.94	5.58	13.03	13.45	100.00
Espectrum (4)	87.26	4.40		8.35	100.00
Espectrum (5)	88.04	3.80		8.16	100.00
Espectrum (6)	93.81			6.19	100.00
Máx.	93.81	5.58	13.03	22.31	
Min.	67.94	3.80	3.71	6.19	

Powder patterns were collected on a X'Pert Pro MPD automated diffractometer equipped with a Ge(111) primary monochromator (strictly monochromatic CuKα_1 radiation) and an X'Celerator detector. The overall measurement time was approximately 30 min per pattern to have very good statistic over the 2 range of 10˚ - 70˚ with 0.017˚ step size. The patterns were identified using the PDF (Powder Data File).

A Panasonic (National) microwave oven, model NN-8507, and a Parr Microwave Acid Digestion Bomb, model 4782, were used for sample digestion. The bombs were cleaned before use with 10% (v/v) HNO_3 for 1 day followed by repeated rinsing with water.

The measurements of Zr, Cu, Fe, Mg and Ni elements were performed on a PerkinElmer ELAN DRCe ICP-MS quadrupole spectrometer. The samples were introduced into the ICP-MS via a RytonTM cross-flow nebulizer (PerkinElmer), Scott spray chamber (PerkinElmer) and Cetac ASX-510 autosampler. The sample transport from the autosampler to the nebulizer was established by a peristaltic pump. The operating parameters of the spectrometer are summarized in **Table 2**.

2.2. Reagents

Analytical reagent grade chemicals were used throughout. Sol was prepared from zirconium *n*-propoxide (ZNP) $Zr[O(CH_2)_2CH_3]_4$ (Merck) for infiltration into the porous biological templates. Prior to hydrolysis, ZNP was modified with acetic acid (HAc) in a molar ratio of 1:4 to reduce reactivity with H_2O.

Standard 1000 μg·mL^{-1} Zr(IV), Cu(II), Ni(II), Fe(III) and Mg(II) solutions (Fluka) were used. Standards of working strength were made by appropriate dilution as required, immediately prior to use. Water was deionised with a Milli-Q system. Concentrated acid HCl, HF, H_2SO_4 and HNO_3 (Merck) were used for digestion of the samples.

2.3. Synthesis

Based on previously described synthesis [14] in the literature, rectangular specimens of native cedar of dimensions (3.5 × 3.5 × 1) cm^3 were dried (130˚C/24 h) and later subjected to vacuum infiltration for 2 h with ZrO_2-sol. The specimens were dried at 110˚C for 1 h in air to form the gel in the wood cells after infiltration. A schematic diagram of the device used for the vacuum infiltration is shown in **Figure 2**.

The infiltration and drying process was repeated for three times. Multiple infiltrations were used to increase the content of the ZrO_2 precursor in the specimen. After the infiltration steps, the cedar samples were pyrolyzed at 800˚C for 1 h in Ar atmosphere in order to decompose cellulose, hemicellulose, and lignin into carbon. After repeated infiltration steps, the specimens were annealed up to 1200˚C during 3 h (temperature ramp 5 ˚C/min up to 1200˚C).

The infiltration/drying process was repeated up to three times to increase the ZrO_2 content in the biomorphic samples. The infiltration/annealing processing are described by the schematic diagram in **Figure 3** [13].

Table 2. ICP-MS operating parameters used for element determination.

RF power	1100 W
Nebulizer gas flow	0.92 L·min^{-1}
Plasma gas flow	15 L·min^{-1}
Auxiliary gas flow	1.2 L·min^{-1}
Nebulizer	Cross-flow
Spray chamber	Scott type
Cones	Nickel
Lens voltage	6.5 V
Analog stage voltage	−1800 V
Pulse stage voltage	850 V
Sweep/reading	20
Reading/replicate	1
Replicate	3
Scan mode	Peak hopping

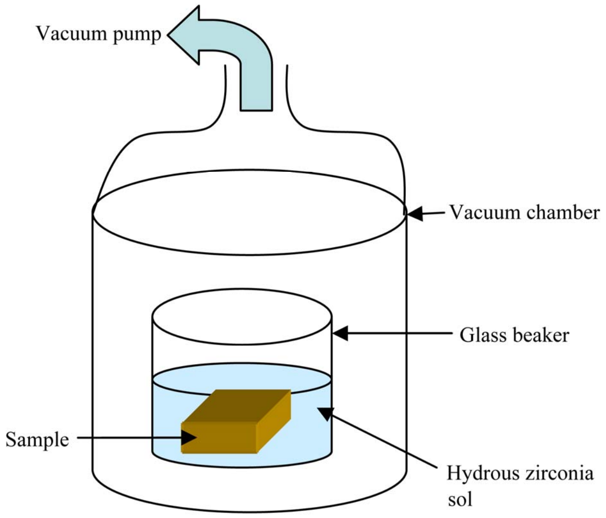


Figure 2. Schematic drawing of the experimental set-up for the vacuum infiltration process.

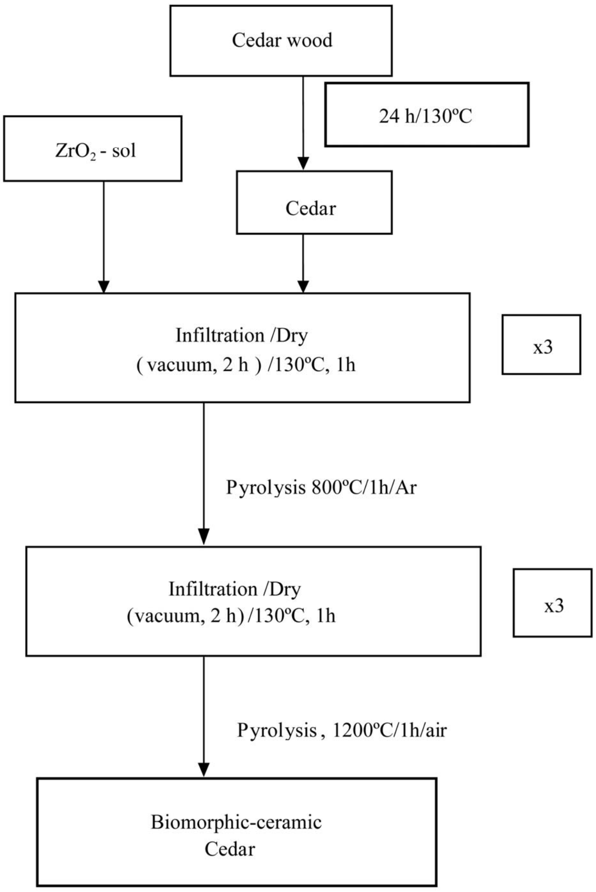


Figure 3. Flow chart for the manufacturing of biomorphic ZrO_2 cedar.

2.4. Microwave-Assisted Pressure Digestion with Acids

In a preliminary step, ten samples of 10 mg each one were weighed accurately and then different acid mixtures (combination of binary and ternary mixtures of HCl, HF, HNO_3 and H_2SO_4) were added to the digestion vessels and were treated for 2 min to maximum power. The dissolutions obtained were completely transferred into a 25 mL calibrated flasks and diluted to volume with water. Then, the optimum mixture of acids was obtained by means of the ICP-MS and taking as response variable the concentrations of several ions to select the better mixture of acids. From these data we concluded the best acid mixture was (H_2SO_4 + HF).

Later, a 5^2 multi-level factorial design with 25 runs (in duplicates) was developed in order to determine the influence of the factors and their interactions on the system. Two factors were studied: volumes of acids selected (H_2SO_4 and HF).

The sequence of the experiments carry out is shown in **Table 3**. The experimental data were processed making use of the STATGRAPHICS 5.1 plus program [15]. The significance of the effects was done by analysis of variance (ANOVA) and using *p*-value significance levels. This value represents the probability of the effect of a factor being due solely to random error. Thus, if the *p*-value is less than 5%, the effect of corresponding factor is significant. The effects and significance of the variables in the microwave-assisted digestion system were evaluated using Pareto's charts.

3. Results and Discussion

3.1. XPS Analysis

XPS has been used for the study of the surface composition of the sample. For this study the biomorphic materials were powdered and homogenized in an agate mortar. Measurements were performed on samples mounted in a cup (1 mm × 3.5 mm, i.d.) and pressed manually.

XPS spectrum obtained is shown in **Figure 4**. Consequently, the performance of the synthesis of biomorphic ceramics can be evaluated approximately from these data.

The atomic concentration calculation is expressed as a percentage in a tabular form based on the area under the peak, multiplied by the sensitivity factor for each element, and provides a ratio of a single element to the sum of the others elements present [16] (**Table 4**). The error of the method is approximately of 10%.

3.2. XRD Analysis

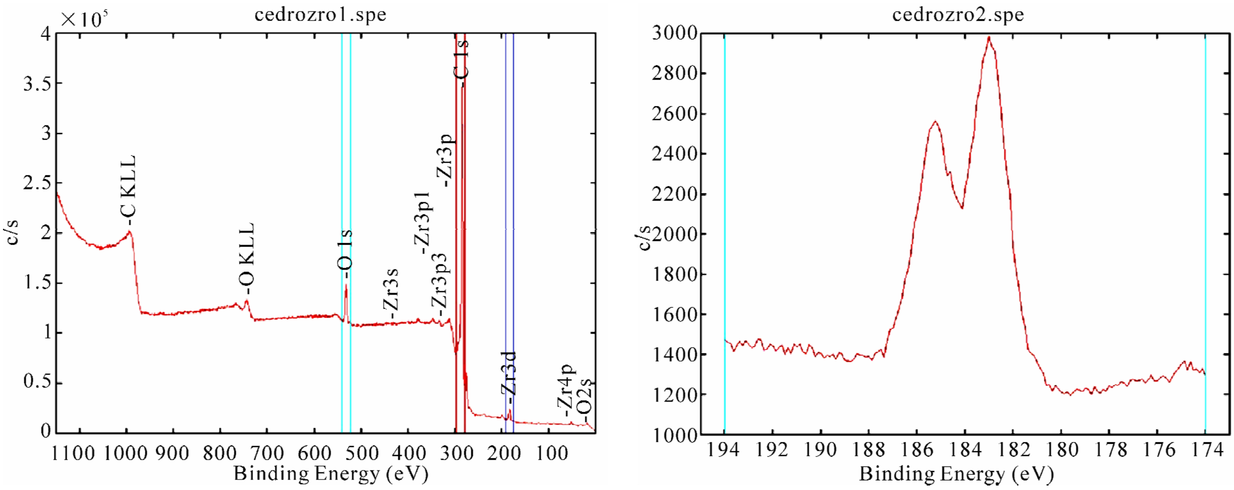
The identification is based on PDF data base. The content of amorphous phase in the sample is high as can be seen from **Figure 5**, due to the background curvature between 20˚ - 30˚ 2 theta and 40˚ - 50˚ 2 theta. From this figure we can conclude the sample is especially monoclinic ZrO_2 (PDF number 01-086-1450), although the sample shows in less proportion tetragonal phase of the same oxide (PDF number 01-080-0784).

3.3. Sample Dissolution

Factorial design approach is an useful tool to establish and improve analytical procedures. Although it seems more complex than the univariate procedure from the operative point of view, it is advantageous because it makes use of fewer experiments and provides important information on interactions among the studied variables [17,18]. A multi-level full factorial 5^2 with 25 runs was carried out in order to determine the main factors of the microwave-assisted biomorphous ZrO_2-ceramic diges-

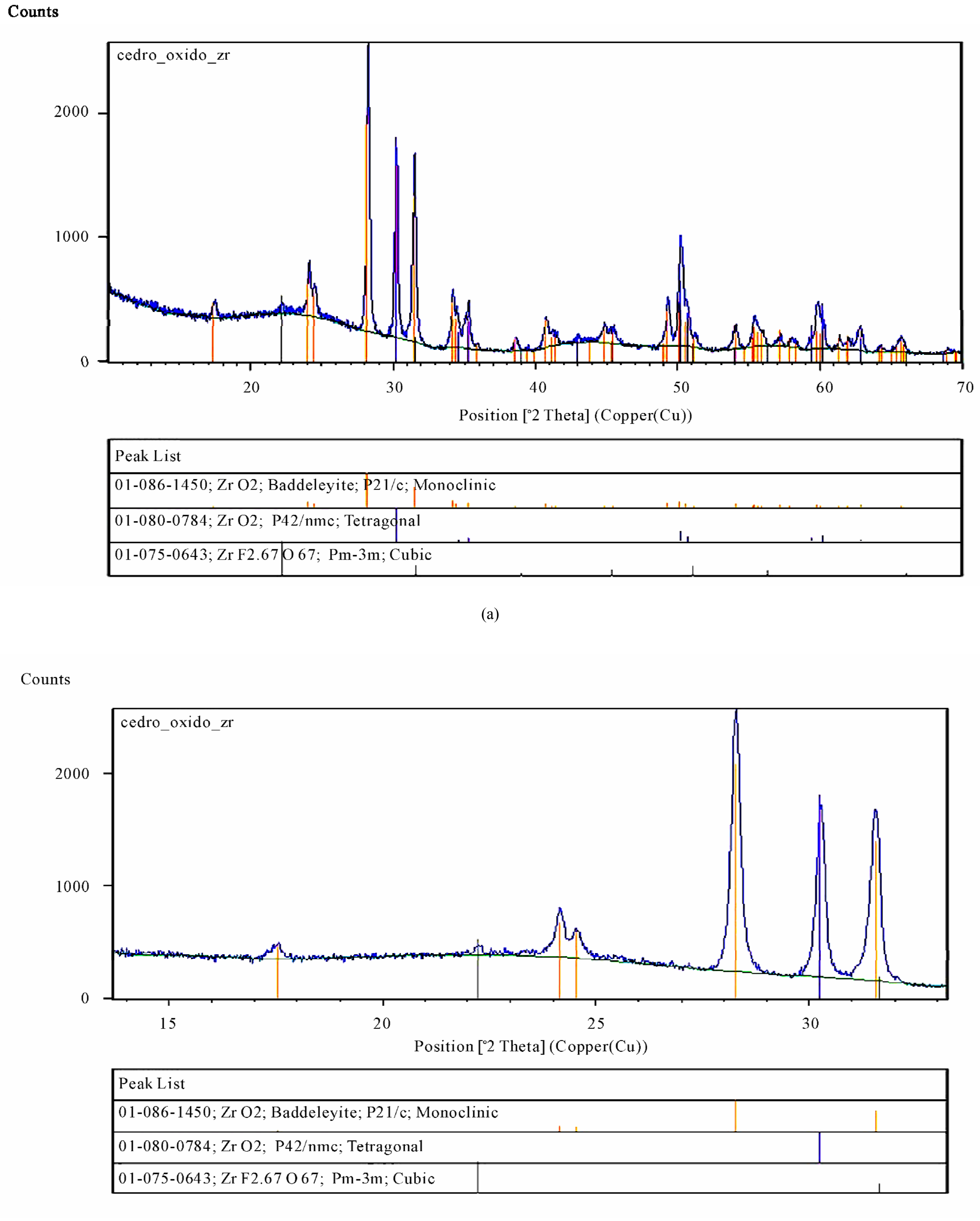
Table 3. Design matrix and the results for Zr, Cu, Fe, Mg and Ni concentration.

Experiment	Vol. H_2SO_4 (mL)	Vol. HF (mL)	[Zr] (mg/g)	[Cu] (mg/g)	[Fe] (mg/g)	[Mg] (mg/g)	[Ni] (mg/g)
1	2	4	411.8	1.9	1.8	7.6	0.7
2	5	4	672.2	3.6	2.5	9.6	1.4
3	4	4	469.7	2.1	1.6	12.3	1.2
4	5	2	417.0	3.0	2.5	9.4	1.2
5	4	5	391.4	2.7	2.7	9.4	1.3
6	3	6	626.9	2.4	1.6	13.0	1.2
7	2	5	631.0	1.6	1.7	10.0	1.3
8	3	5	555.3	1.8	2.1	8.2	1.0
9	2	3	566.8	1.5	1.0	10.1	0.7
10	6	5	531.7	4.5	2.0	7.7	2.0
11	3	3	387.8	2.0	1.6	7.7	0.8
12	3	2	518.6	2.2	1.7	34.2	1.1
13	6	4	531.6	4.0	1.4	14.0	1.7
14	5	6	766.6	3.2	2.0	14.1	1.5
15	2	6	548.2	1.4	4.0	10.3	0.8
16	5	5	692.8	3.3	1.3	13.5	1.5
17	2	2	468.0	1.2	1.5	8.9	0.6
18	6	2	685.8	4.1	1.4	12.6	1.8
19	4	3	575.9	2.2	1.4	10.0	1.0
20	4	2	536.5	2.3	1.2	8.3	1.0
21	6	3	502.7	3.5	1.5	11.8	1.6
22	3	4	619.8	1.8	1.3	10.0	0.9
23	6	6	588.4	3.0	2.2	12.6	1.5
24	5	3	558.0	2.4	1.6	12.3	1.2
25	4	6	831.4	2.1	1.8	15.4	1.1



(a) (b)

Figure 4. XPS spectrum for biomorphic ceramic from cedar wood a) survey b) $Zr3d_{5/2}$ (183.8 eV).



(a)

(b)

Figure 5. XRD spectrum for biomorphic ceramic from cedar wood (a) between 10º - 70º 2 theta (b) Amplification between 15º - 35˚ 2 theta.

tion. The results of the ANOVA carried out on the data given in **Table 3** are shown in **Table 5**.

The two-order effect combined Pareto charts (P = 95%) were obtained for the two factors considered (**Figure 6**). After the analysis of the results, it was observed that the studied variables have no significant effects for Mg however significant effects were demonstrated for HF volume in the case of Zr, Fe and Ni and H_2SO_4 volume in the case of Cu and Ni.

3.4. Comparison of Samples

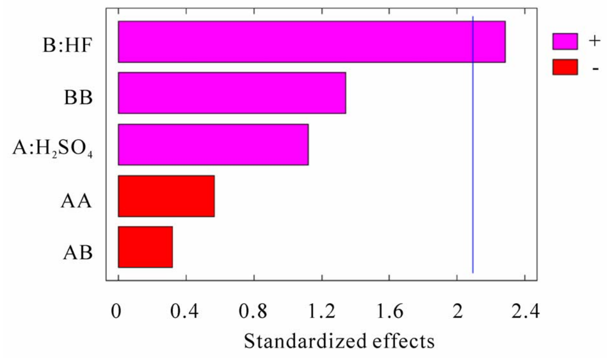
Also, we have made the comparison of the content of ions in samples of biomorphic ceramics of cedar and oak, and of cedar and pine. To carry out this comparison have employed a statistical procedure designed for to compare two sets of data, in our case concentrations of a certain

Table 4. Analysis of biomorphic ceramic by XPS.

Element	Area (cts-eV/s)	Sensitivity factor	Concentration (%)	
			Atomic	Mass
C*1s*	131082	7.439	93.65	89.15
O*1s*	20606	18.619	5.88	7.46
Zr*3d*	5675	63.731	0.47	3.4

Table 5. P-value for data analysis given in Table 3 for metal ions concentration.

Design variable	P-Value (Zr)	P-Value (Cu)	P-Value (Fe)	P-Value (Mg)	P-Value (Ni)
A: Vol. H_2SO_4	0.2754	0.000	0.7339	0.8055	0.000
B: Vol. HF	0.0341	0.7507	0.0335	0.6178	0.0451
AA	0.5789	0.1545	0.7738	0.4867	0.1106
AB	0.7541	0.5671	0.1417	0.4739	0.2814
BB	0.1950	0.4585	0.2498	0.1331	0.6803



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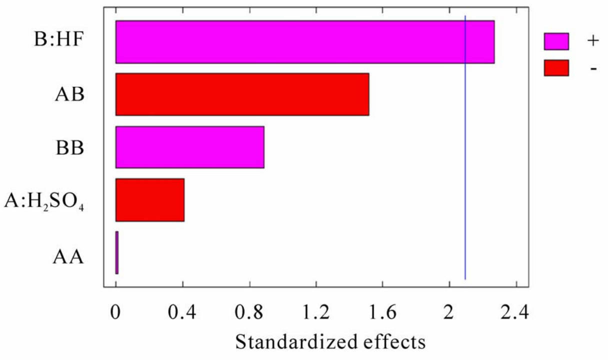

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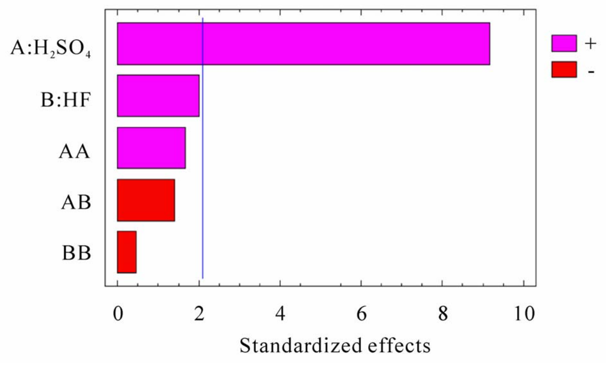

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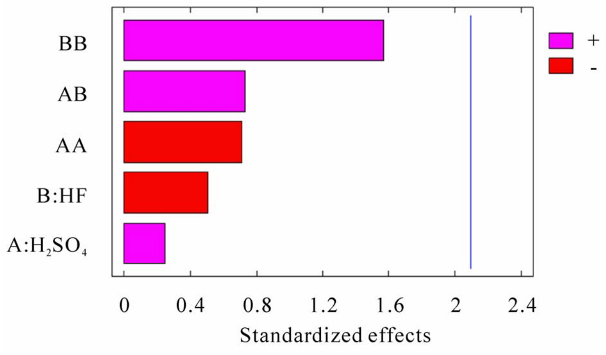

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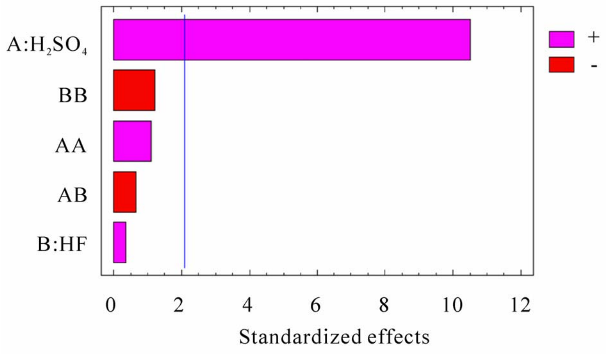
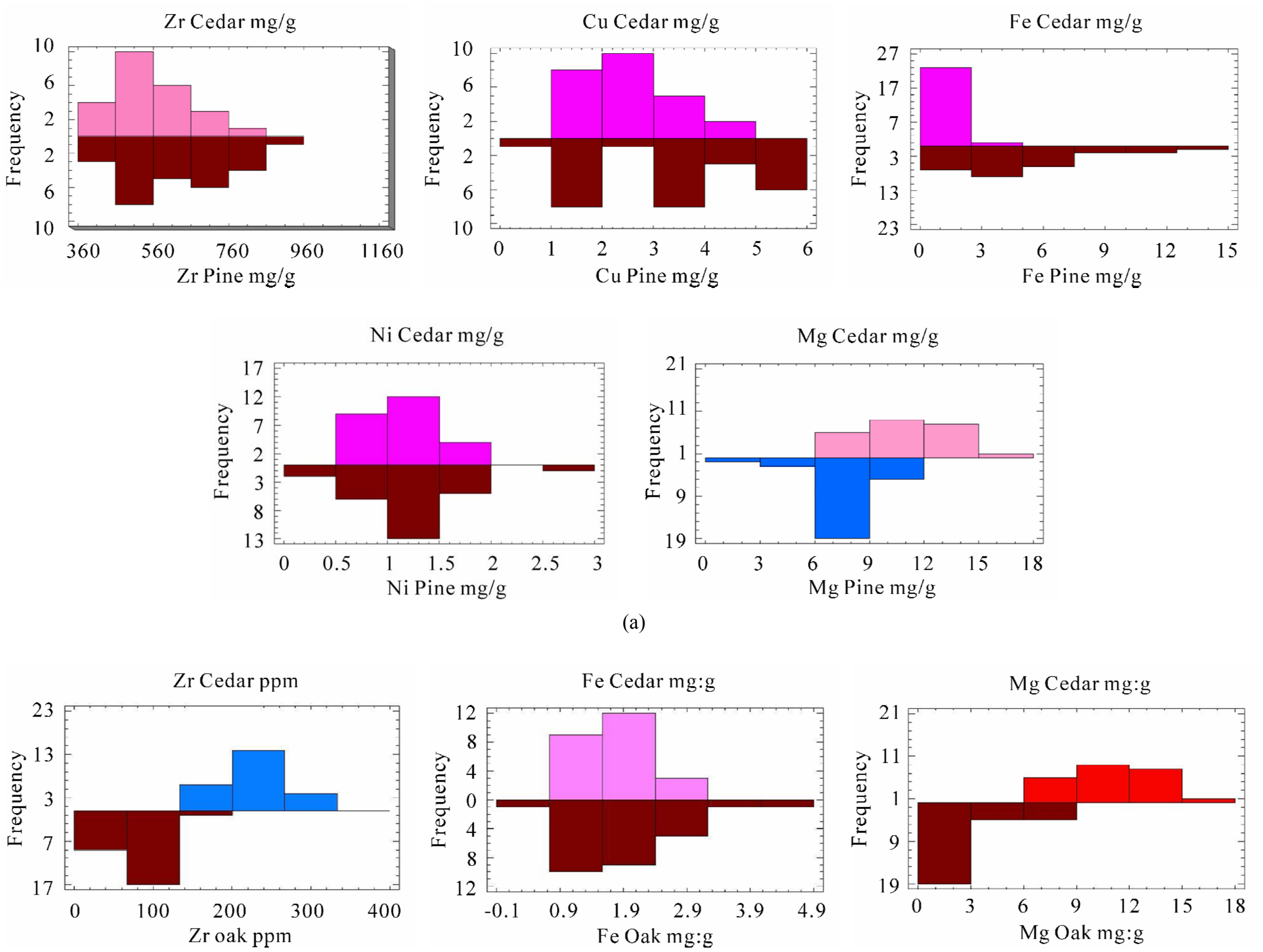


(e)

Figure 6. Pareto's charts for a) Zr; b) Fe; c) Ni; d) Mg; e) Cu.



(a)

(b)

Figure 7. Comparison of ion contents from different biomorphic ceramic samples a) cedar-pine b) cedar-oak.

ion in two biomorphic materials synthesised in the same conditions whose only difference is the employed wood as precursor (cedar, oak and pine) and the infiltrant agent (zirconium oxichloride for the oak and zirconium *n*-propoxide for the cedar and pine).

The above-mentioned procedure calculates statistical data and it gives several charts for every shows. In addition executes several tests to determine if there are statistically significant differences between two samples.

Below the F test is made to compare the variances of the two samples. Additionally intervals or confidence limits are established for every standard deviation as well as for the reason of the variances. In addition are compared also the content of ions specific to the wood as are: Mg, Fe, Ni and Cu. The results obtained are shown in **Figure 7**.

4. Conclusions

Different acid mixtures were tested for the samples digestion processes (HCl, HNO_3, H_2SO_4, HF). Of all of them the mixture (H_2SO_4 + HF) was selected in order to obtain maximum concentration of the ions.

Differences on Zr contents in two ceramics (cedar and oak) can be due because synthesis have been made from different templates and different reagents to obtain ZrO_2 sol-gel (zirconium oxichloride and zirconium *n*-propoxide), also the experimental design for the digestion process of these samples were different.

Similar Zr content were obtained from different templates (cedar and pine) when the infiltration agent (zirconium *n*-propoxide) is the same for the two samples.

5. Acknowledgements

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