



Research Article

Spectroscopic Characterization of Eoholocene Bones Found in a Cave in Northeast Brazil

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The preservation of fossils depends on several interactions of organic and inorganic chemical processes. The hard parts, which are more suitable for fossilization, might record valuable information of biogenic processes, while the taphonomic characteristics supply information on postmortem chemical transformation. Here, X-ray fluorescence, X-ray diffraction, and infrared spectroscopy analyses were carried out in Early Eoholocene fragments of bones collected from the subsurface at Gruta do Urso Fóssil, Ubajara National Park, northeast of Ceará State in Brazil. It is suggested a lower degree of decomposition, a preservation of the original mineral composition, along with some incidence of encrustation, and the occurrence of different animal species are analyzed. These preliminary data serve as a basis for future studies involving fossil biota from the deposits of Gruta do Urso Fóssil using spectroscopic techniques.

1. Introduction

The hard parts (skeletons) which usually undergo fossilization keep valuable information of biogenic processes, and the taphonomic characteristics supply data on the post-mortem changes [1]. Geochemical investigations and physical characterizations were performed to determine the composition of a fossil provide both taphonomic and ecological data. Mineralogical composition of fossils can be adequately studied using physicochemical and mineralogical techniques such as X-ray fluorescence, X-ray diffraction, and infrared spectroscopy [2–4].

In northeastern Brazil, there are very important cenozoic continental deposits (especially caves) showing remains of organisms, valuable in the reconstruction of the

paleoenvironment. The Ubajara National Park, in northeast Ceará State (Figure 1), is a karstic region where rocks suffered corrosion processes, subsequently creating caves and valleys. This region is part of a Spelean province composed by Neoproterozoic carbonatic rocks known as Serra da Ibiapaba, originating in the Upper Neogene-Quaternary according to Auler et al. [5, 6].

Of the 14 caves of the park, the most important is the Gruta do Urso Fóssil (GUF) which lies at 03°49'58''S/40°53'34,4''W. The GUF was discovered in 1978 in Morro do Pendurado, and a fossilized skull of *Arctotherium wingei* was found [7]. At GUF, several Early Eoholocene fragments of bones and teeth from small fauna, as well as gastropod shells, have been collected and reported in the specialized literature by Hsiou et al. [8], Oliveira et al. [9–11], and Viana [1].



FIGURE 1: Map of South America, showing the Ceará state and the Ubajara town. Modified from Oliveira et al. [9].

Additionally, these authors assigned an approximate age of 8,000 years BP based on the thermoluminescence measurements of local sediments [9].

The main goal of this work is to present the qualitative, quantitative, and semiquantitative physicochemical composition of fossils from a cave in the Ubajara National Park (Ceará State), in order to obtain taphonomic information. Unidentified long bone fragments were selected and analyzed using X-ray fluorescence spectroscopy (XRF), X-ray diffraction (XRD), and infrared spectroscopy (IR).

2. Materials and Methods

This research was carried out in two stages: (1) the fieldwork for the stratigraphic analysis and collection of samples, and (2) the laboratory work to obtain data on the physicochemical and mineralogical composition of the samples, diagenetic transformation, and taphonomic analysis.

2.1. Fieldwork. A 90 cm deep excavation was carried out in the GUF's entrance chamber. A stratigraphic study was performed and divided into 8 layers of 10 cm depth, named from C1 to C8. The material of each layer was sieved *in situ* to collect mineralized organic samples, such as bones and teeth. In all, seven fragments of bones from the layers C1 to C6 and C8, were selected for X-ray diffraction, X-ray fluorescence, and infrared spectroscopy measurements. Due to the scarcity of bone samples, layer C7 was not analyzed.

2.2. Laboratorial Work. X-Ray diffraction is used to determine the atomic and molecular nature of a crystalline structure. X-ray fluorescence spectroscopy was used to analyse both major and trace chemical elements from a sample. Infrared spectroscopy was useful to identify chemical compounds and molecular compositions, including amorphous samples.

At the laboratory, the selected samples were crushed in a porcelain mortar with pestle for the following analysis.

2.2.1. X-Ray Diffraction (XRD). The X-ray diffraction patterns were obtained using a Rigaku powder diffractometer with the Bragg–Brentano geometry. The Co-K α radiation was used and operated at 40 kV and 25 mA. The XRD measurements were taken in the 2θ range of 3–45°, using step scan procedures (0.02°) at counting times of 5 s.

2.2.2. X-Ray Fluorescence Spectroscopy (XRF). The X-ray fluorescence spectroscopy was performed using a ZSX Mini II equipment from Rigaku, operating with a Pb tube, using a power of 40 kV \times 1.2 mA.

2.2.3. Infrared Spectroscopy. The infrared spectra were measured using the absorbance mode of transmittance measurement, and KBr pellets were used to dilute the samples. The samples were mixed with KBr powder in the proportion 1:100 from each sample (at about 5–10 mg). The pellet thickness varied from 0.5 to 0.6 mm, and they were measured in the spectral range from 400 to 4000 cm^{-1} using a Vertex 70 spectrometer from Bruker.

3. Results and Discussion

The excavation resulted in the schematic section represented below, which demonstrates the stratigraphic distribution of the fossils in all layers found of unconsolidated sediments composed of both cave carbonate and siliciclastic material carried into the cave (Figure 2). The siliciclastic material was determined by microscopic analysis (not shown here), revealing the presence of small crystalline grains.

Table 1 summarizes the XRF analyses from seven small species of bone samples collected during the excavation at GUF. From this analysis, the main chemical elements were detected: Ca and P, which are the mineral components of the bones, and trace elements such as Zn, Sr, Si, S, Mn, K, Fe, Cl, and Al. The elements K, Si, Al, Fe, and Cl are basic constituents from the soil formation [12]. The amount of Zn in bones is an indicator of meat food, and the amount of Sr and Mn is an indicator of plant food, suggesting different species of animals were found [13]. Observing Ca/P amount relationship, it is possible to infer about similar groups C1, C3, and C4 (9.3–8.2) and C5, C6, and C8 (6.2–5.5). However, C2 (7.6) can not be related with any group cited above.

The XRD diffractograms indexed hydroxyapatite ($\text{Ca}_{10}(\text{OH})_2(\text{PO}_4)_6$) as the majority phase in all samples, which were identified using the ICDD Reference code: 00-001-1008, PDF index name: calcium hydroxide phosphate. These results suggest that the biomineralization of the bones is preserved (Figures 3 and 4). Other phases of the diffractograms include crystalline calcium carbonate as calcite (CaCO_3). The elemental analysis (XRF) was not able to identify C and O because of the limitation of equipment. However, Ca and P are the majority elements identified by XRF, and the measurements are agreeing with XRD. These chemical characteristics and the incrustation observed from fossil analyses suggest that in all layers, there has been an

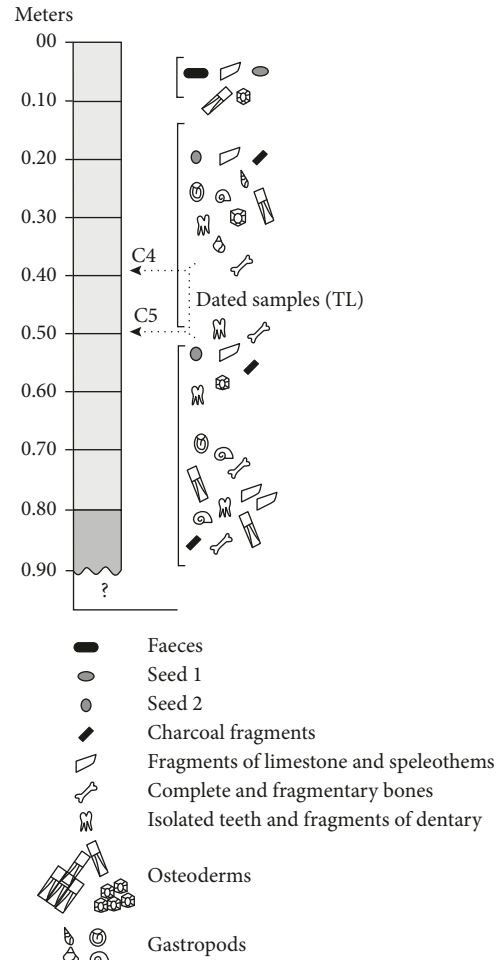


FIGURE 2: Schematic section showing the stratigraphic distribution of fossils in the GUF's entrance chamber [9].

TABLE 1: Chemical elemental percentage of the C1, C2, C3, C4, C5, C6, and C8 samples measured by XRF.

Chemical elements (%)	C1	C2	C3	C4	C5	C6	C8
Ca	69.45	82.20	86.67	83.80	82.03	83.17	82.13
P	8.39	10.76	9.33	10.00	13.34	13.56	14.82
Fe	0.43	0.35	0.00	0.54	0.68	0.35	0.27
S	0.12	0.09	0.19	0.14	0.42	0.67	0.31
Al	0.15	—	0.09	0.17	0.59	—	—
Cl	0.48	0.27	0.44	0.24	0.13	0.26	0.45
K	0.47	0.54	0.21	0.28	0.27	0.26	0.46
Mn	—	0.13	—	0.24	0.21	—	0.16
Si	0.36	0.46	—	0.62	1.93	1.30	1.01
Sr	2.31	4.58	2.34	2.24	0.19	0.18	0.18
Zn	0.49	0.21	—	0.41	0.10	0.12	0.10

incrustation of calcium carbonate from the dissolution and reprecipitation of the cave's carbonatic rocks.

XRD diffractograms indexed the (002) plane related to the crystalline hydroxyapatite phase. The Debye–Scherrer equation (Equation (1)) was used to calculate the crystallite size [14] (Table 2):

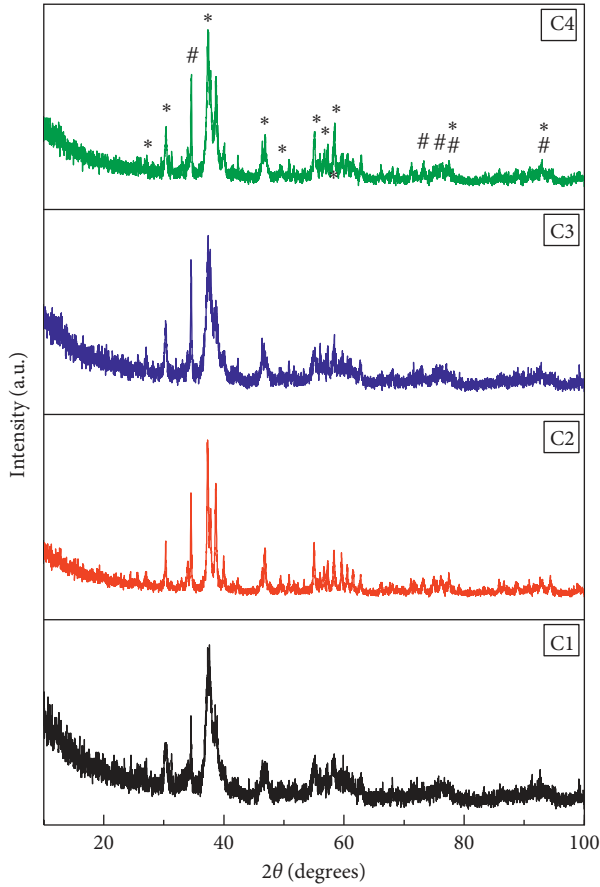


FIGURE 3: XRD diffractograms of the bone samples from the layers C1, C2, C3, and C4 analyzed, where peaks of hydroxyapatite (*) ($\text{Ca}_{10}(\text{OH})_2(\text{PO}_4)_6$) and calcite (#) (CaCO_3) are assigned.

$$\tau = \frac{k\lambda}{\beta \cos(\theta)}, \quad (1)$$

where τ is the size of crystallite (nm), k is the shape constant, $k=0.9$, corresponding to the spherical shape, λ is the Co-K α radiation wavelength (1.7928 Å), β is the full-width half maximum (FWHM) of the XRD peak plane (hkl), and θ is the diffraction angle (degrees) in accordance with Bragg's law and the (002) plane of crystalline hydroxyapatite ($\text{Ca}_{10}(\text{OH})_2(\text{PO}_4)_6$).

The results listed in Table 2 show that the sizes of crystallites were heterogeneous. Some groups presented similar crystallite sizes, C3 with C4, C2 with C5, and C6 with C8. The more crystalline samples showed larger crystallite sizes (C2 and C5).

The IR spectra (Figures 5 and 6) showed characteristic bands of hydroxyapatite [2–4]. Specifically, the bands centered at 467 and 557 cm^{-1} are associated with antisymmetric deformation of PO_4^{3-} ion, while the bands around 1020 cm^{-1} are related to the antisymmetric stretching of PO_4^{3-} . Furthermore, calcite bands at 875 cm^{-1} correspond to symmetric deformations of CO_3^{2-} , and bands at 1419 and 1460 cm^{-1} due to symmetric stretchings of CO_3^{2-} were observed [2–4]. IR results were synergistic with the XRF and

TABLE 2: Size of the crystallite obtained in accordance with to the Scherrer equation, using the (002) diffraction plane of hydroxyapatite.

Samples	2θ (°) Peak (002)	(2θ) FWHM	Crystallite size (nm)
C1	30.34	0.526	14
C2	30.30	0.222	40
C3	30.30	0.396	20
C4	30.36	0.357	23
C5	30.25	0.193	48
C6	30.26	0.282	30
C8	30.27	0.254	34

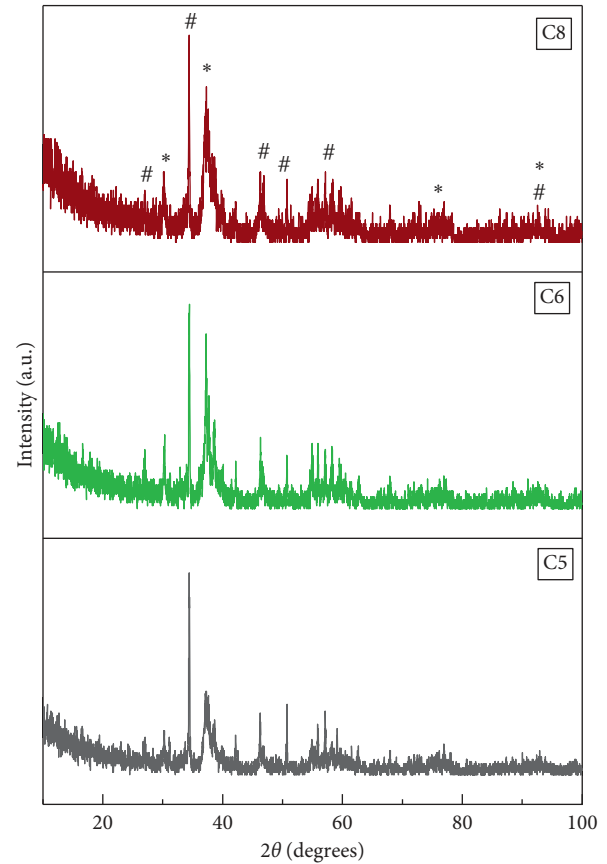


FIGURE 4: XRD diffractograms of bone samples analyzed. Results of the samples from the layers C5, C6, and C8, where peaks of hydroxyapatite (*) ($\text{Ca}_{10}(\text{OH})_2(\text{PO}_4)_6$) and calcite (#) (CaCO_3) are observed.

XRD analysis, suggesting together the presences of crystalline calcium, carbonate, and phosphate phases.

From the IR spectra, it is possible to estimate the relative amount of apatite and carbonate phases (Table 3). For this, the intensities of the two strongest peaks of both carbonate and phosphate phases were used. The base line was subtracted between 400 cm^{-1} and 1600 cm^{-1} . The relative amount of carbonate/phosphate was calculated according to the following expression:

$$\frac{\text{carbonate}}{\text{phosphate}} = \frac{AA' + BB'}{CC' + DD'}, \quad (2)$$

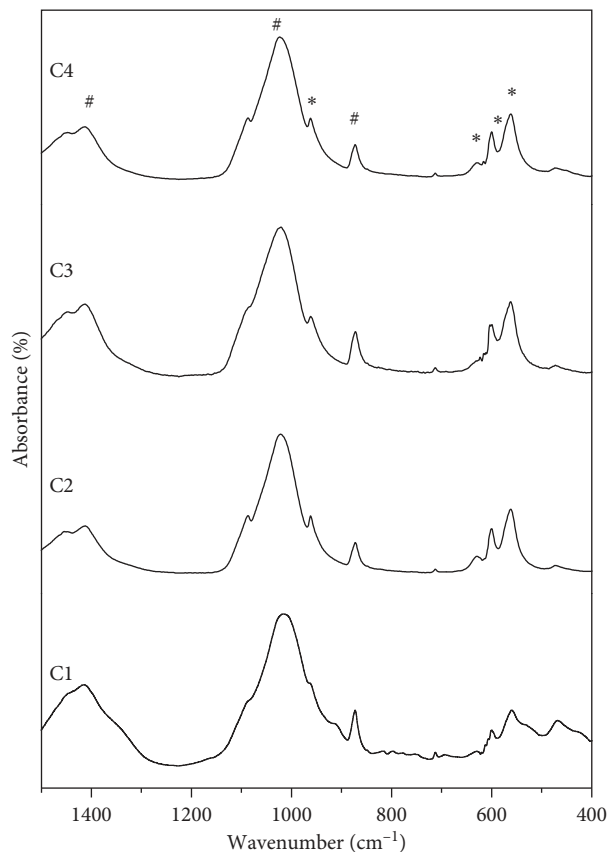


FIGURE 5: Infrared spectra of bone samples analyzed. Results of the samples from the layers C1, C2, C3, and C4, where peaks of hydroxyapatite (*) ($\text{Ca}_{10}(\text{OH})_2(\text{PO}_4)_6$) and calcite (#) (CaCO_3) are observed.

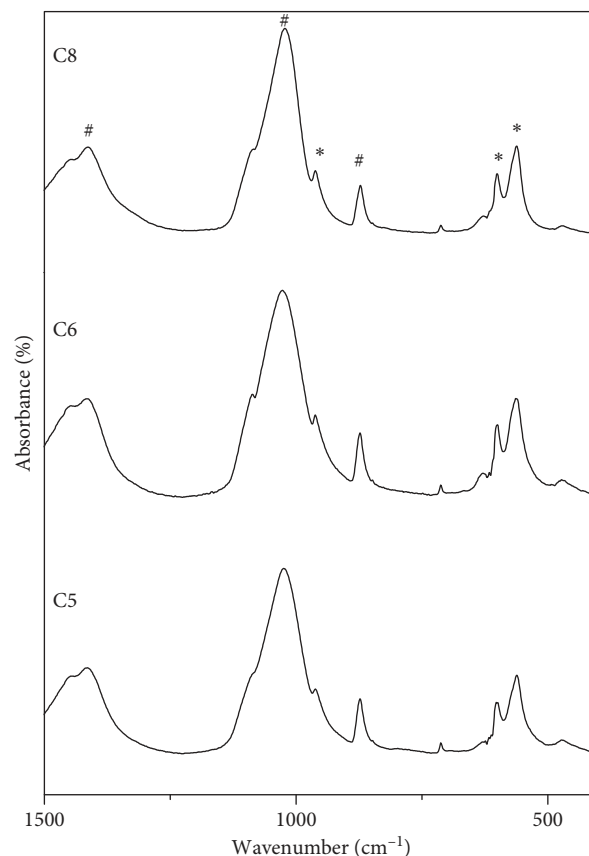


FIGURE 6: Infrared spectra of bone samples analyzed. Results of the samples from the layers C5, C6, and C8, where peaks of hydroxyapatite (*) ($\text{Ca}_{10}(\text{OH})_2(\text{PO}_4)_6$) and calcite (#) (CaCO_3) are observed.

where $[AA' + BB']$ is the intensity of the carbonate bands (1447 cm^{-1} and 1413 cm^{-1} , respectively) and $[CC' + DD']$ is the intensity of the phosphate bands (599 cm^{-1} and 561 cm^{-1} , respectively).

The IR spectra also afforded the estimation of the amount of carbonate ions (% y) in the nanohydroxyapatite (nHAp) lattice (Table 3) by calculating the ratio of intensity between the carbonate at 1420 cm^{-1} (I_c) and the phosphate at 598 cm^{-1} (I_p) bands using the following equation [5]:

$$\%y_{\text{CO}_3} = 10.134 \left(\frac{I_c}{I_p} \right) + 0.2134. \quad (3)$$

The use of XRD to address the crystallographic changes in ancient bones has often been documented [13–20]. The crystallinity Index (CI) and carbonate/phosphate ratio (C/P) are extremely useful for the determination of the mineral alteration in both diagenetic and postdiagenetic bone. Here, we interpreted the CI as a representative of common diagenetic effects. Thus, we consider that the diagenesis in general sense, e.g., a decrease in histological preservation, increased with an increase in bone porosity and mineral crystallinity. Lee-Thorp and Sponheimer [21] discussed that the relationship between crystallinity and elemental alteration is not clear. Previous studies [16, 17] have suggested that an increase in CI values is not directly correlated with

TABLE 3: Average crystallinity index ($\text{CI}_{\text{X-ray}}$) and relative carbonate/phosphate relative amount.

Samples	$\text{CI}_{\text{X-ray}}$ (average)	Carbonate/phosphate (%)
C1	0.25	32.87
C2	0.87	11.42
C3	0.47	16.50
C4	0.68	12.47
C5	0.82	18.39
C6	0.79	14.87
C8	0.78	14.85

the age of the bones, i.e., CI does not increase with increasing age. Furthermore, the CI range is not uniform between different chemical environments. Puc at et al. [19], compared various CIs using Raman and FT-IR spectroscopy and X-ray diffractometry.

Early diagenetic factors (e.g., microbial attacks and hydrolysis) are associated with an increase of bone porosity [22, 23]. According to Smith et al. [22], the increase of bone porosity can coincide with a decrease in CI values. The porosity may increase the interaction between bone and soil water, thereby causing a loss of organic content. Thus, exogenous minerals may be deposited within bone at any time postmortem. According to Table 3, the samples C2, C5, C6,

and C8 present a small range of CI values. Although samples C3 and C6 exhibited slightly different values, the only significantly different value was that of C1 (0.25). The C1 sample results suggest the presence of calcite as an exogenous mineral, which is expected once the fossil is placed in a karst environment. In C1, there is a clear correlation between the increase of C/P ratio with decreasing CI (Table 3). These results support the literature; for example, Astibia et al. [24] reported that the degree of crystallinity increased during fossilization.

The sample fossils from GUF are the same age; therefore, the most important parameter responsible for the observed range of CI and C/P ratio values are local taphonomical conditions. The bone from C1 layer, at the top of the section, is most susceptible to interaction with pore-water and microorganisms accelerating the rate of dissolution, which facilitate exogenous and secondary minerals precipitation inside of the fossil. Indeed, the fact that the CI analyses do not differ significantly (barring sample C1) is not surprising because all samples come from the same locality. Therefore, this relative homogeneity can be explained by the fact that the remains have been deposited as individual bone fragments in the cave bottom. Person et al. [16] suggested that cave deposits offer the most favorable conditions for the preservation of original crystallinity. These facts suggest that the local conditions were key postdiagenesis parameters for the changes in the CI and C/P ratio.

4. Conclusions

It has described here a bone assembly excavated from an Eoholocene deposit in northeast Brazil. The excavation at the GUF entrance cave allowed distinguishing eight layers composed of nonconsolidated sediments and very fossiliferous, especially with bones of small to medium size individuals, whose estimated age is approximately 8,200 years BP.

The biostratigraphic characteristics observed in the field and in laboratory include the disarticulation and fragmentation of carcasses. The low concentrations of Fe and S indicated by the XRF analyses also demonstrated a very low degree of decomposition of the bones. The fossil diagenesis is represented by the following characteristics: (i) preservation of the biomineralization and (ii) a high incidence of in-crustation (both analyzed by XRD and IR).

The Crystallinity and C/P ratio seem to be related to the local taphonomical conditions. The C1 sample clearly shows a correlation between the increase in C/P ratio and the decrease of crystallinity indices; however, there are no great disparities among the other samples, which suggests that the bones remained in a closed system for long time, and it was not possible to confirm the number of different species.

Data Availability

The data used to support the findings of this study are available from the corresponding author upon request.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

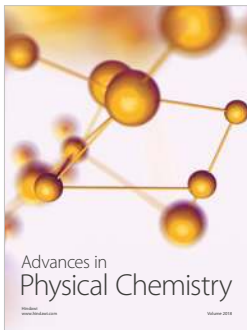
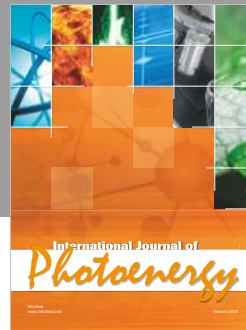
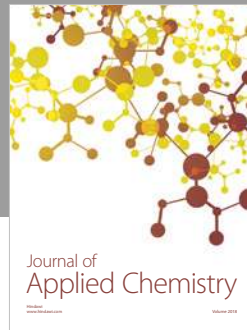
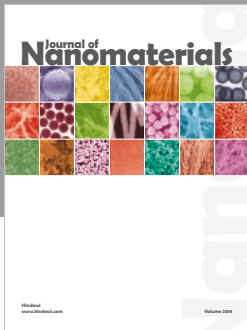
Acknowledgments

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