

SILICON DIOXIDE EXTRACTION FROM CASHEW NUT ASHES

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Abstract. After the cashew nuts processing, the husks rich in silicon are used as fuel in boilers where they are burned at temperatures above 1000 °C. In this study, it was investigated a form of silicon extraction from the ashes taken from the boiler using a chemical route. At first, the ashes were bathed with an aqua regia solution ($HCl + HNO_3$), then it were bathed with sulfuric acid (H_2SO_4) and taken to the oven at 600 °C for two hours. After the heating process it were made analyzes of X-Ray Diffraction (XRD) and X-Ray Fluorescence (XRF). The results of XRD indicated the presence of approximately 45% of silicon on the samples and the results of the XRF indicated that most of the element was in the form of crystalline oxide SiO_2 . It can be concluded that is possible to purify the ashes to use a waste of cashew nuts processing industry as a source of obtaining silicon dioxide in quartz format.

Keywords: silicon dioxide, cashew nuts ashes, chemical Route

1. INTRODUCTION

Silicon extraction from organic silica (SiO_2) present in rice husks has been studied since the 1970s by researchers as Kamath and Proctor (1998) and Conradt *et al* (1992) in countries with high production of this agricultural waste, such as India and China. Similar studies have also been performed in Brazil, as the developed by Junior *et al* (2010), but apart from rice husks there are other waste of the national agricultural industry that can serve as organic silicon source, such as cashew nut shells.

The state of Ceará is the major producer and exporter of cashew nuts and CNL (cashew nuts liquid), having industry specialized in planting, cultivation, and processing. The process waste, especially the nut husks, is used as fuel in boilers which operate at temperatures above 1000 °C.

This present work aim to extract silicon from the ashes of cashew nut husks by a chemical route, similar to that used in the rice husks purification, turning a waste of cashew processing industry in a useable product for the manufacture of photovoltaic panels.

1.1 Organic Silica

According to Iler (1979), in addition to mineral springs, silicon can also be found in living organisms and despite of being considered a non-essential element, there is evidence that appear in all bio-system, always in coordination with oxygen in the form of silica. The silicon dioxide in amorphous phase is found in the physiological structure of viruses, bacteria, fungi, algae, plants and animals.

In plants, the silica is absorbed through soil in the form of silicate ions and, although it not necessary for the healthy growth of most plants, appears to present side effects in their physiology. For example, Iler (1979) states that some plants use silica to build part of its support and defense structures, being present in the stem, the thorns and in the nut husks and shells, while in other increases resistance to fungal diseases, resistance to cold weather and the growth rate.

The silicon is absorbed by roots in the form of hydroxylated ions, along with water and other ions. After penetrate cell membranes, the hidroxylylated silicon ions $[Si(OH)_4]$ polymerize in micro amorphous silica particles within the

vesicles, plant cell organelles responsible for storing water to give support to the tissue. Over time, the particles fuse to form colloids that reach diameter of tens of nanometers, when no longer run through the porous membrane and remain inside permanently.

2. EXPERIMENTAL PROCEDURE

The ashes used in the procedures were provided by the Companhia Industrial de Óleos do Nordeste (CIONE) and were obtained from burning the chestnut shells along with other cashew beneficiation process waste and coal in boilers that operate at temperatures above 1000°C. XRF analyzes showed that the samples have from 1.2% to 1.9% silicon, among other elements.

The applied methodology consists in wash the samples with aqua regia and sulfuric acid solutions to remove organic compounds, after that, the compounds with low boiling point are removed by a thermal treatment at constant temperature in a furnace casting.

An aqua regia solution was prepared using 75 ml of HCl and 25 ml of HNO₃, diluted in 400 ml of water and mixed by a Fisatom thermal magnetic stirrer model 752A for 20 minutes. 25 grams of ash were added to this acid solution and left to react for 2 hours on the stirrer. After this time the solution was filtered with a Merck Millipore filter paper and the solid part was taken to dry in a KAMP oven, remaining at the temperature of 100°C for 2 hours.

After drying, the ash received a second bath with 20 ml of sulfuric acid (H₂SO₄) diluted in 80 ml of water, remaining 2 hours on the stirrer to react. After a second filtration process, the ashes were placed in an 1800 EDG-S 3P oven at 600 ° C for two hours.

After each procedure step, a small portion of mass was removed and tested using a Panalytical diffractometer for polycrystalline samples, model XPert Pro MPD, in way to obtain the XRD spectrum and a Rikagu X-ray fluorescence equipment, model ZSXMini II, in ways to obtain the mass percentage of each element that composes the material. Both tests were performed in the X-Ray Laboratory from Federal University of Ceará Physics Department.

3. RESULTS AND DISCUSSION

3.1 XRF Analysis

The XRF analyzes showed that the weight percentage of silicon increases after each process step as shown in Tab. 1.

Table 1 – Silicon mass percentage in each process step

Element	Raw Material	After Chemical Treatment	After Thermal Treatment
Total Sample Mass (g):	25.00	4.35	0.89
Si (%)	1.92	10.97	53.33
Impurities (%):	98.08	89.03	46.67

The initial sample of 25g had 1.92% silicon, equivalent to 0.4793g of the material. After chemical treatment, the mass dropped to 4,35g due to the removal of impurities solubilized in acidic solutions. The percentage of silicon in the sample increased to 10.97%, which corresponds to 0.4773g of the material. After the heat treatment, the compounds with a boiling point below 600 ° C were removed and the sample weight was reduced to 0.89g. In this last step, the percentage by weight of silicon was 53.33%, which corresponds to 0.4746g of the material.

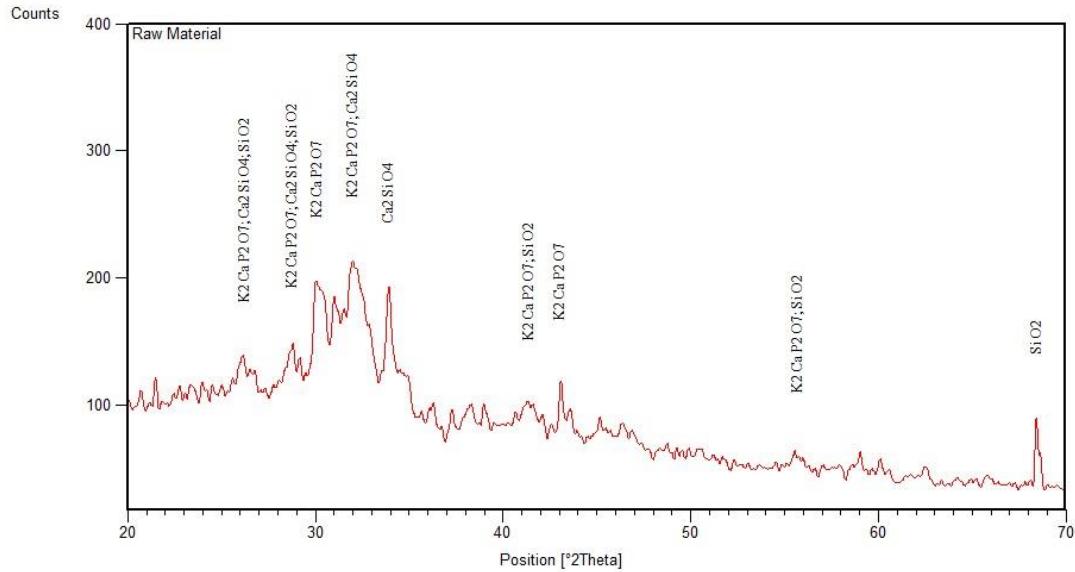
Among the impurities shown in the XRF analysis, the main compounds were potassium (K), sulfur (S), calcium (Ca) and phosphorus (P). It was noted that the K and Ca elements were largely eliminated after the chemical treatment, which was expected, once the alkali metals are soluble in acidic medium. The other elements were eliminated during the heat treatment, once they have boiling point below 450 ° C.

3.2 XRD Analysis

The data obtained by X-ray diffraction were treated using Panalytical HighScore X'Pert Plus software version 2.0a. After background definition, curve smoothing and peaks identification, a screening was performed using the main compounds identified in the XRF analysis as restriction parameters.

In the Fig. 1, that shows the raw material spectrum, it is possible to observe some peaks indicating the presence of crystalline material. These compounds are mainly composed by potassium (K), phosphorus (P), calcium (Ca), and silicon (Si) in oxid form.

Figure 1 – Crystallographic spectrum of raw material



One of these oxides is the silicon dioxide (SiO_2), that according to the crystallographic record shown in Tab. 2 is in the monoclinic moganite form.

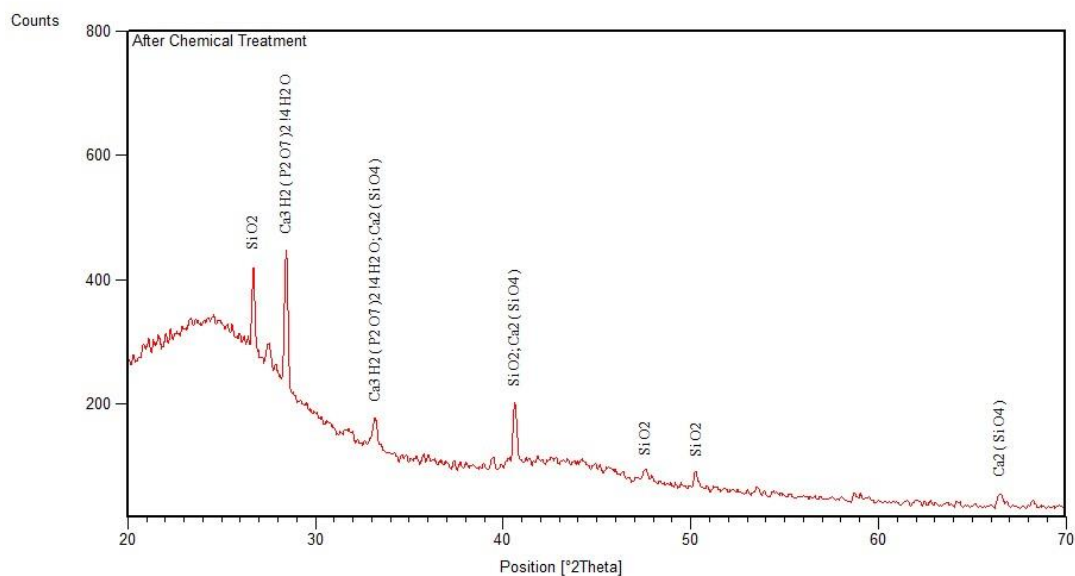
Table 2 – Crystallographic Record of silicon dioxide present in the raw material sample

Reference code	Mineral name	PDF index name	Chemical formula	Crystal system
00-038-0360	Moganite	Silicon Oxide	SiO_2	Monoclinic

The peaks were probably formed during thermal treatment that the ashes experienced within the boiler. The peak intensity were low, reaching a maximum at 200 counts, which means that the crystalline compounds were present in small amounts when compared to other process steps.

In the spectrum obtained after the acid baths, presented in Fig. 2, the peak intensity increased, indicating that the amount of crystalline material also increased. The compounds found were not the same at the raw material, because some elements, particularly the potassium (K), were diluted in the acid mixture and removed from the sample or recombined in amorphous forms, which were not detectable by XRD analysis.

Figure 2 – Crystallographic spectrum after chemical treatment



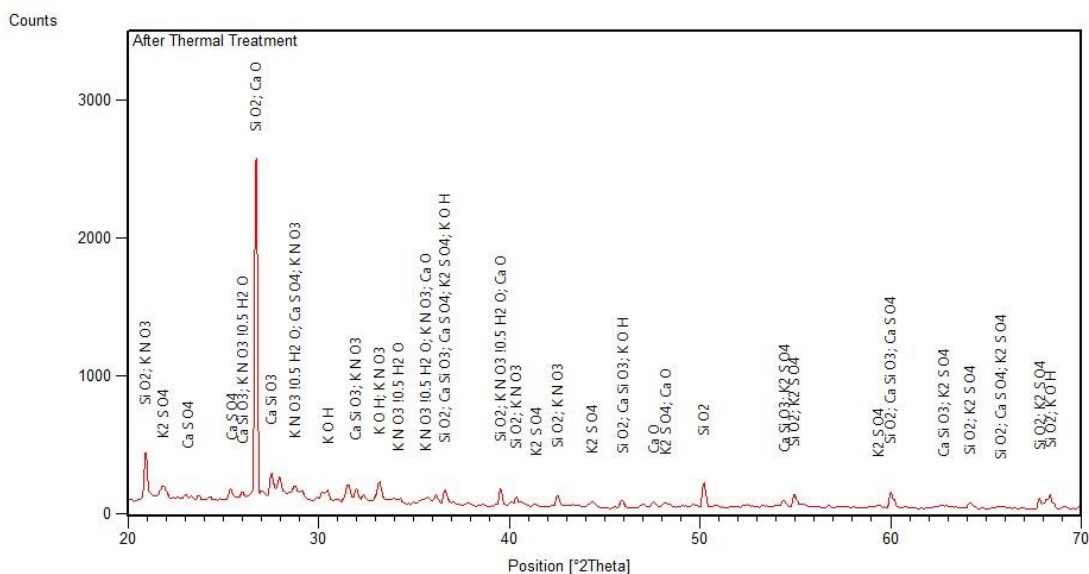
The SiO₂ crystallographic record, presented in Tab. 3, shows that the crystalline structure has changed it form from monoclinic moganite to hexagonal quartz.

Table 3 – Crystallographic Record of silicon dioxide present in the sample after chemical treatment

Reference code	Mineral name	PDF index name	Chemical formula	Crystal system
01-085-0795	Quartz	Silicon Oxide	SiO ₂	Hexagonal

The spectrum obtained after the thermal treatment, presented in Fig. 3, shows a larger the number of peaks and very high intensity compared with the previous analysis, indicating that the sample has practically no more elements in the amorphous phase.

Figure 3 - Crystallographic spectrum after thermal treatment



Some elements that not appear in the previous analysis, as potassium (K) and sulfur (S), now appear combined with other elements, also the amount of silicon dioxide peaks (SiO₂) is much higher than before. Crystallographic record of this compound, shown in Tab. 4, indicates that after heat treatment, the same hexagonal quartz structure was maintained.

Table 4 – Crystallographic Record of silicon dioxide present in the sample after thermal treatment

Reference code:	Mineral name:	PDF index name:	Chemical formula:	Crystal system:
01-085-0796	Quartz	Silicon Oxide	SiO ₂	Hexagonal

4. CONCLUSION

Comparing the raw material data with the final data it was observed that the percentage by weight of silicon considerably increased as well as its crystal structure changed from monoclinic moganite to hexagonal quartz.

At the beginning of process, 25g of ash were analyzed and the final sample had only 0.89 g, what means a 96.44% mass reduction. This loss is due to the presence of highly soluble materials in acidic solution and materials with a low boiling point, originated from other energy sources used in the boilers among with ashes.

The final sample showed 46.67% of impurities that can be removed by further treatment or avoided if ashes used were obtained only from the husk burning. In this case the silicon percentage would be possibly larger and the treatment could be more efficient.

5. ACKNOWLEDGEMENTS

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