J. Mater. Environ. Sci. 3 (4) (2012) 760-765
ISSN : 2028-2508
CODEN: JMESCN

Characterisation of the rice production waste for the use in pharmaceutical industry

E. F. Ledesma[1], C. R. Acosta[1], M. L. Garrido[2], M. C. González[1], M. M. Bernal[1], X. R. Pileta[1], M. G. Hurtado[1, 2], P. Quintana[3], P. Bartolo [3]

[1] *Engineering and Chemical Research Center, C.P. 10600 C. Havana City, Cuba.*
[2] *Institute of Materials Science and Technology, University of Havana. Cuba. Email: liva@imre.oc.uh.cu*
[3] *CINVESTAV, IPN, Merida Unit, Department of Applied Physics, Merida, Mexico.*

Received 13 Feb 2012, 17 May Revised 2012, Accepted 17 May 2012.
* Corresponding Author: edenia@inor.ciiq.minbas.cu

Abstract
In this work we provide the technological parameters for obtaining silicon dioxide from rice husk for its possible use at the pharmaceutical industry. We also show the results obtained in the chemical and physical analysis. The Cuban rice variety (M-10) was characterised and the results were compared with similar data from the literature. Preliminary tests conducted to 2^3 full factorial design, taking as dependents variables the loss percentage, the silicon dioxide percentage and the sample coloration. The independents variables were the concentration of hydrochloric acid, the temperature and the calcination time. Optimal conditions included washing of the rice husk with hydrochloric acid 1M and calcination at 700 ºC during 1 hour. The results derived from the chemical and physical characterisation were within the established range. This work allows the use of an industrial residue, reducing the environmental pollution caused by the accumulation of solid waste.
Keywords: excipient, natural fibers, rice husk, silicon dioxide

1. Introduction
The rice husk is the biggest waste resulting from agricultural production of grains. Its final destination is one of the problems facing rice-producing countries, which so far has no definitive solution. For four tons of rice produced, one ton is shell. Several studies have estimated that each year, over 100 million tons of paddy rice in the world is generated [1].
To reduce the volume of this waste the rice husk can be burned. Although this is a good alternative from the economical and energetic point of views (it can be used as fuel for the production of Portland cement, for generating electric power, etc), it entail another problem: the fate of the ashes produced. It is estimated that the establishment of the rice husk ash is about 20% by weight of the burned skin. In México, there is a production of about 450 000 tons of rice husks which represents 20% rice hulls (90 thousand tons) [2].
It is known that the rice husk is an important silicon dioxide source. Silicon dioxide (SiO_2) is a composite of a remarkable structural complexity, presenting 12 different crystal forms. The colloidal silicon dioxide is largely used in pharmaceutical, beauty and food products. The particle size and the specific surface area can provide desirable flow characteristics, which are exploited to improve the properties of dry powder in various

processes, such as tableting. It is also used to stabilize emulsions and as a thixotropic agent, thickening and suspending gels and for semisolid preparation. In aerosols is used to promote the suspension of particles and minimize the clogging of spray nozzles. In addition, it can be used as a disintegrating agent in tablets and as a dispersant for powders or suppositories [3]. It is generally used at a concentration ranging from 0.5 to 25% of the finished product.
The aim of this work is to provide the technological parameters for obtaining silicon dioxide from rice husk for its possible use at the pharmaceutical industry. We also show the results obtained in the chemical and physical analysis.

2. Materials and methods

Rice husk sample of national production (variety M-10, 2009 wet season, harvested 15 days after flowering), was obtained from the Research Institute of Grain. Aerosil 200 was obtained from Pharma, Germany. The reagents used in the analysis were all from Riedel-de Haën with the highest degree of purity. The burning process was carried out in an oven Barnstead / Thermolyne 6000. An analytical balance Mettler Toledo AB 204, a drying oven Merck ULM-500, a mechanical stirrer Barnant 20, and an Orion 420A pH meter were also used.
The structural characterisation of the rice husk ash was performed in a brand X-ray diffractometer Bruker Advance D-8, using CuKα radiation (λ = 1.5418 nm) and graphite monochromator in the diffracted beam with a step of 0.03 °, -70 ° 2θ = 4 and t = 0.3 s, Japan. The infrared spectrophotometry was performed on a Fourier transform infrared FTIR, Brucker, model Vector 33, Japan. A scanning electron microscope and high vacuum JEOL, model JSM-5410LV, Japan was used. The specific surface area and pore volume were determined by the BET method in a team scores Sorptomatic 1800, Carlo Erba.
The results showed in the tables 1, 2, 3 and 4 are the average of three replicas.
For processing the results we used the statistical software Statgraphics 5.1 and Microcal Origin 6.0 software. Chemical analysis of the ash was conducted according to quality specifications in the pharmacopoeias USP34-NF29 [4] and BP2011 [5].

3. Results and discussions

When performing chemical and physical characterisation of the rice husk variety M-10, the results showed that the components, reported in Table 1, are similar to those obtained by other investigators in other countries [6].

Table 1. Characterisation of rice husk collected for agricultural use, expressed in % by weight.

$Si0_2$	**Ash**	**Organic material**	**Nitrogen**
15.20	18.58	69.85	0.47
Sulfur	**Chloride**	**Moisture 130 ºC**	**Density g/ml**
0.03	0.03	11.58	0.106

The high content of organic matter is mainly due to cellulose, hemicellulose and lignin that appear in the following range [6]:

Cellulose: 25.89-35.50%
Hemicellulose: 18.10-21.35%
Lignin: 18.20-24.60%

The preliminary experiments for the treatment of rice husk in the laboratory were made from 20 grams of sample. Calcination for two hours in a muffle at 700 º C resulted in an 85% of weight loss after the process. Runs were also conducted with a previous washing of the rice husk ash, according to recommendations made in the literature [7, 8]. The results obtained are shown in Table 2.

Table 2. Experimental results of the calcination tests.

Experience	Loss percentage	$Si0_2$ percentage	Comments
700 ºC, 2 hours, static method	85	93.16	gray fine powder
700 ºC, 2 hours, dynamic method	79	95.67	gray fine powder
700 ºC, 2 hours, before washing with NaOH 1 M	83	94.26	grizzly-white fine powder
700 ºC, 2 hours, before washing with HCl 1 M	82	95.80	grizzly-white fine powder

When carrying out a previous washing with acid or alkali, the color of the sample was white, slightly grizzly, but the percentage of loss and the silicon dioxide content did not vary significantly in any case. Thus, other parameters were considered to select the washing solution. Previous studies [7, 8] recommend acid washing to allow removal of impurities including iron, calcium, magnesium, sodium and potassium.
It is recommended to assess drugs producers the potential impact of the color obtained, as the washed samples have a color that looks more like the product to be replaced (Aerosil 200).
With the results obtained from the different experiences, a 2^3 full factorial design was used. The experimental matrix is shown in Table 3. The responses measured were the percentage of loss, the percentage of silicon dioxide and the color of the ash obtained.

Table 3. Experimental matrix to establish the optimum conditions for obtaining ash from rice husk.

Exp.	Conc. HCl 1 M	Calcination Temp. ºC	Ignition time hours	Loss percentage	$Si0_2$ percentage	Color
1	1	500	1	83.33	99.53	Dark grey
2	4	500	1	82.54	99.69	Dark grey
3	1	700	1	84.10	99.15	White
4	4	700	1	84.73	98.96	White
5	1	500	3	83.89	98.08	Clear grey
6	4	500	3	83.98	98.96	Clear grey
7	1	700	3	84.03	99.60	Grizzly-white
8	4	700	3	84.05	99.57	White
9	2.5	600	2	83.65	98.98	White
10	2.5	600	2	83.97	99.81	White
11	2.5	600	2	83.66	99.87	White

The results were statistically analyzed and concluded in order to avoid changes in the silica content over the ranges studied.
It was observed that the loss increased with increasing the calcination temperature. The interaction between

the time and the temperature was negative, meaning that an increase in the temperature together with an increase in the time may decrease the process loss.
Based on the responses obtained, it can be concluded that the minimum values for washing and calcination should be used, considering an economical criteria.
Based on the above and taking into account that in the range studied the time and the acid concentration did not have a significant influence, the optimal conditions were set to: washing the rice husk with HCl 1M and calcination at 700º C for one hour.

3.1 Chemical determinations
The rice husk ash obtained according to the conclusions of the experimental design was characterised chemically as defined in the pharmacopoeia USP34-NF29 and BP2011 for Colloidal Silicon Dioxide (Aerosil 200) showing the results in Table 4.

Table 4. Results of the characterisation of the rice husk ash and Aerosil 200.

Test	**BP**	**USP**	**Aerosil 200**	**Rice husk ash**
Identification	+	+	+	+
pH	3.5-5.5	3.5-5.5	4.72	5.5
Arsenic	—	≤ 8 ppm	< 0.5 ppb	< 0.5 ppb
Chloride	≤ 250 ppm	—	212.7 ppm	211.3 ppm
Heavy Metals	≤ 25 ppm	—	< 0.02 ppm	< 0.02 ppm
Loss on drying	—	≤ 2.5%	2.44 %	1.69 %
Loss on ignition	≤ 5.0%	≤ 2.0%	1.11 %	2.12 %
Assay (on ignited sample)	99.0-100.5%	99.0-100.5%	100.00 %	99.93 %

All quality indexes analyzed were within the permissible range for one or another pharmacopoeia, except the loss on ignition that doesn't complete the demands of the USP pharmacopoeia, for what we recommend to carry out the characterisation according to the BP pharmacopoeia. The ash obtained from rice husk, meets the chemical quality specifications established for this type of excipient [3].

3.2 Physical studies
The specific surface area and pore volume values of 306 m^2/g throwing 0,376 cm^3/g, respectively. The value reported in the Handbook of Excipients for this type of product is between 200 and 400 m^2/g for surface area, not seeing any data on the pore volume [3].
The samples were analyzed on a Fourier transform infrared spectrophotometer. FT-IR spectra of the ash and Aerosil 200 obtained are shown in Figure 1.
The FT-IR spectra (Fig. 1) shows that there is a coincidence of the bands present in both samples, and an additional significant band at 1095 cm^{-1} for the silicate ion [9].
The analysis of the samples by X-ray (Aerosil 200 and ash) to verify that the amorphous substance obtained had similar characteristics as the marketed product. Figure 2 shows the diffractogram obtained.

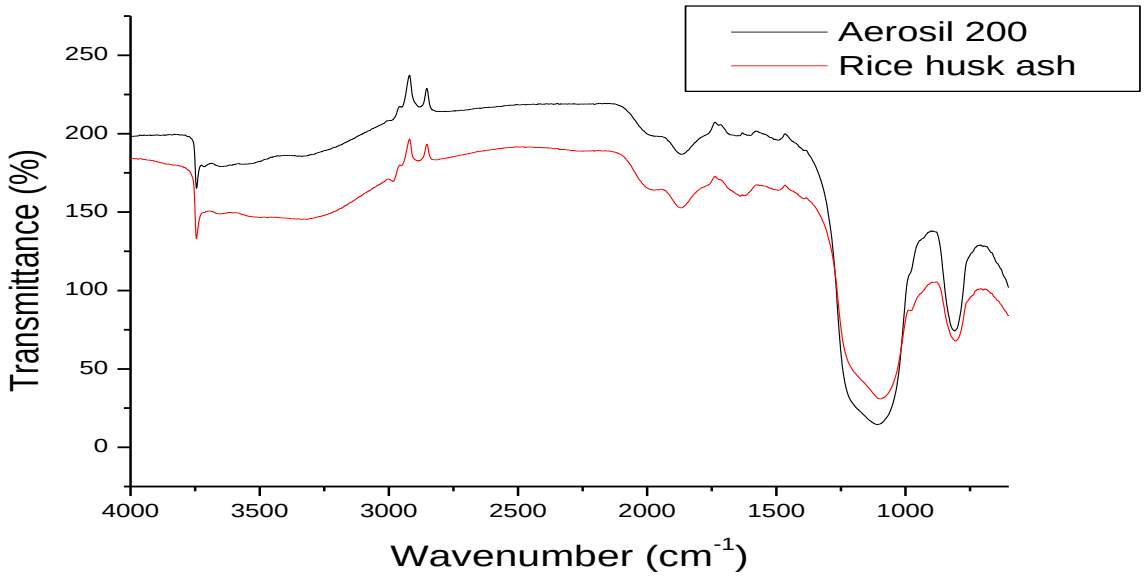

Fig. 1. FTIR spectra of the variety M-10 and Aerosil 200.

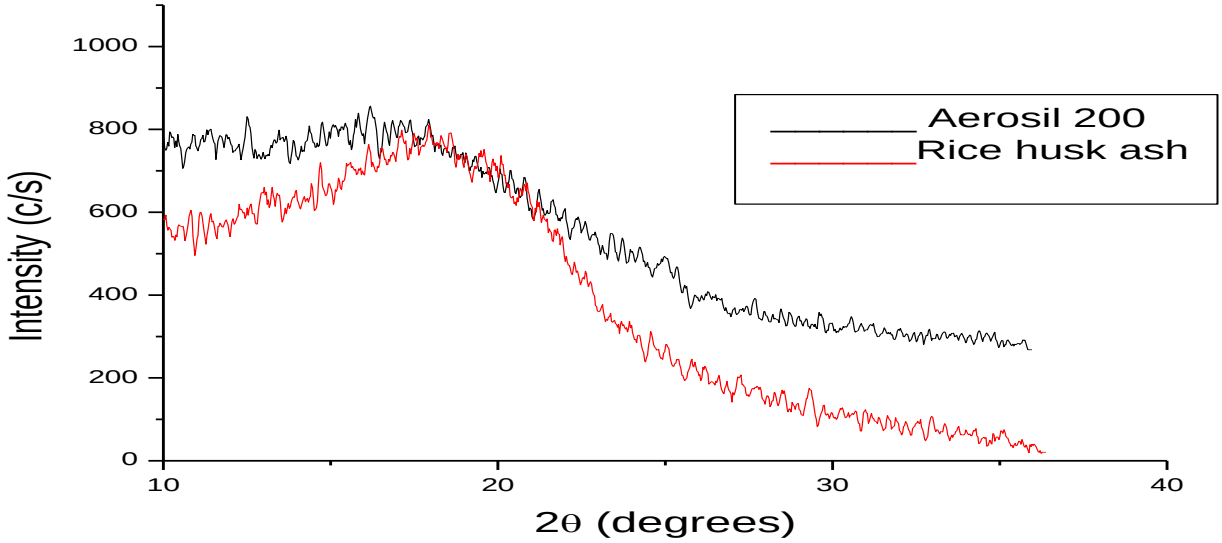

Fig. 2. XRD spectra of the variety M-10 and Aerosil 200.

Figure 3 shows the electron microscopy performed on samples of Aerosil 200 (a) and rice husk ash without grinding (b). The ash particles obtained have rugged features and irregular shape with a size much greater than that of Aerosil 200, so it is necessary to crush the ash of rice husk to achieve a particle size similar to that of Aerosil 200, which are in the form of agglomerates and a tendency to sphericity.

(a) (b)

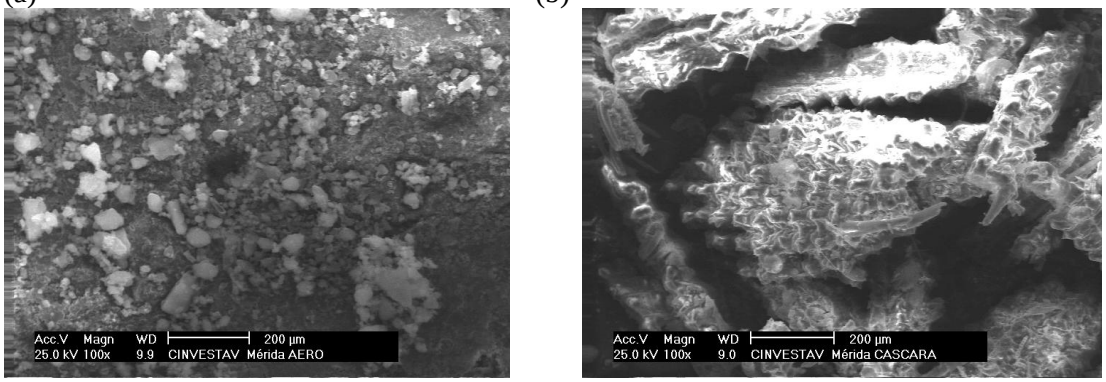

Fig. 3. SEM of Aerosil 200 (a) and rice husk ash (b).

4. Conclusions

It is possible to obtain silica from rice husk with previous washing with hydrochloric acid.
The best results are obtained with the following operating parameters:

- Concentration of washing HCl: 1M
- Calcination temperature: 700º C
- Calcination time: 1 hour

It has been shown that the product (rice husk ash) and Aerosil 200 have similar physical and chemical characteristics, which allow the use of a rice production waste in the pharmaceutical industry, reducing the environmental pollution caused by the accumulation of solid waste.

Recommendations

Submit samples of the product to pharmaceutical companies in order to assess their properties and behavior in drug formulations as an excipient.

References

1. Santos, S., Reyes, M., Gonzalez, E. 15th Science and Technique Forum, (2002).
2. Salgado, R. On line, 2008 http://www.imre.oc.uh.cu.
3. Rowe, R., Sheskey, P., Quinn, M. Handbook of Pharmaceutical Excipients, 6th Edition, APhA, (2009).
4. British Pharmacopoeia CD-ROOM, (2011).
5. United States Pharmacopoeia–National Formulary and its Supplements USP34–NF29, (2011).
6. Valverde, A., Sarria, B., Monteagudo, J. Scientia et Technica, 37 (2007) 255-260.
7. Patel, M., Karera, A., Prasanna, P. J. Mater. Sci. 22 (1987) 2457-2464.
8. Swatsitang, E., Srijaranai, S., Arayarat, P. 14th International Conference Photovoltaic Science and Engineering, (2004).
9. Coates, J. Encyclopedia of Analytical Chemistry, Meyers R.A., (2000).