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Silica from Rice Husk Ash as an Additive for Rice Plant

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Abstract: The motivation for this study was to find a possible economic alternative for the residual Rice Husk Ash (RHA) as well as a way to mitigate the growing environmental problem in Southern Brazil (illegal deposition of exceeding rice husks and RHA). For this, an investigation was carried out into the preparation of two kinds of xerogel silicas from micronised rice husk ash and their utilisation as additives in the cultivation of rice. The effect of the parameters of silica extraction was evaluated by means of Response Surface Methodology and the maximal yields were 96 and 98%. The silicas were characterised in terms of their chemical composition, particle size distribution and surface area. High values for specific surface area, 183.73 and 232.42 $m^2\ g^{-1}$ and mean particle size of 67.93 and 28.41 μm, were found for the potassium-and sodium-based silicas, respectively. The effect of Si on rice production was studied under conditions of soil samples containing low concentrations of Si, with addition of 0, 100, 200 and 400 kg Si ha^{-1}. The Si content of the soil samples increased with the increase in the dose of both silicas, causing an increase in grain yield.

Key words: Rice husk ash, silica extraction, xerogel silica, rice cultivation additive, response surface methodology

INTRODUCTION

Brazil is the most important Latin-American rice producer and the State of Rio Grande do Sul (RS) is the country's main producer (IBGE, 2011). Rice husks in our country have begun to be regarded as an agro-industrial residue of importance and as a potential raw material for thermal and chemical processes, as well as a source of soluble silica.

However, attempts to use rice husks for industrial purposes are still facing technical difficulties, mostly due to their poor protein content, low degradability and high mineral percentage (Zhang *et al*., 2010).

For these reasons, if a suitable application could be found for residual rice husks, it could provide a challenging business opportunity, while also bringing about benefits to the environment and public health (Martins *et al*., 2007; Zakaria *et al*., 2010). At the moment, most of the rice husks remain unused which causes environmental problems, for example, emission of CO_2 and long lasting smoke from open sky combustion and methane, when they are left to degrade on the ground (Umeda and Kondoh, 2010).

For every 4 tons of rice, 1 ton of rice husks is produced. After combustion for power generation, 15-30% of this results in RHA (Mehdinia *et al*., 2011) comprising around 95% silica (Kermani *et al*., 2006). Thus, it is estimated that the availability of silica is around 380,000 ton $year^{-1}$ in the state of RS. Previous studies have shown that it is possible to obtain silica from rice husks and Rice Husk Ash (RHA) with similar yields compared to other processes (Zaky *et al*., 2008; Zhang *et al*., 2010; Lima *et al*., 2011). A simplified method of sol-gel extraction of silica at room temperature was also reported in the literature (Lima *et al*., 2011).

Zaky *et al.* (2008) have prepared silica nanoparticles from RHA by employing statistical design to optimise the parameters affecting the dissolution of silica, such as stoichiometry, time and temperature as well as achieving efficiency of 99% on the extraction. Zhang *et al.* (2010) produced amorphous silica from RHA treated with HCl solution, obtaining surface area of 287.86 $m^2\ g^{-1}$, mean particle size of 50 mm and 99.87% purity. Other works have described rice husks and RHA as excellent sources for high quality silica (Lima *et al*., 2011; Kalapathy *et al*., 1999; Witoon *et al*., 2008). However, these silicas have

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only been proposed as substitutes for commercial sources, such as nanosilicas, ceramic and cement additives.

On the other hand, silica also plays an important role in almost all living organisms. It is absorbed by the roots of plants and deposited on the outer walls of epidermal cells as a silica gel, where it acts as a physical barrier against pathogenic fungi and attacks by insects. Moreover, it reduces the loss of water through transpiration, stiffens the cell walls and keeps the leaves more erect (Nakata *et al*., 2008; Abdalla, 2011).

The rice plant responds most positively to the application of Si and the use of soluble silica as a fertiliser is largely employed (Ramos *et al*., 2008). The benefits for the culture of rice include increased growth and production, positive interactions with fertilisers, as well as higher resistance against diseases, plagues, drought and salinity (biotic and abiotic stresses) (Voleti *et al*., 2008). According to Rodrigues *et al*. (2003), an increase in the Si content of rice plants by the application of Ca silicate to the soil, as wolastonite, explained the significant reduction of the occurrence of sheath blight on the leaves.

The Response Surface Methodology (RSM) is a statistic-mathematical tool based on factorial planning (Mohagir *et al*., 2009) which allows to achieve more precise results with less experiments, obtaining higher product yield, lower response time and material consumption (Charyulu and Gnanamani, 2010). It is not recommended for a large number of variables (Gummadi and Kumar, 2006). Besides this, the RSM has been much used for the optimization of the process parameters and to raise the yield of the desired products (Jaiswal *et al*., 2011).

Thus, the purpose of this study was essentially to evaluate the potential use of micronized RHA for the production of xerogel silicas and their possible use as fertilisers in rice cultivation. Tests were also carried out with non-micronised RHA, where similar results were obtained (not examined in this study).

MATERIALS AND METHODS

This study was developed from March 2009 to March 2010 at the Chemistry Department of the Federal University of Santa Maria with the collaboration of colleagues from the Institute of Agrarian Sciences of the Federal University of Uberlândia, Brazil.

Preparation of the RHA: The micronised RHA used in this investigation was supplied by a local market developer for RHA from the thermoelectric combustion of rice shells (Fig. 1). After being sent to the laboratory, the RHA was classified in a sieving system (Bertel, São Paulo, Brazil) using a 2.4 mm mesh sieve. The RHA samples were dried in a kiln (Ideal, São Paulo, Brazil) for 24 h at 110 °C; after that, they were left to cool in a desiccator and were later stored in hermetically-sealed glass flasks for subsequent use. Following this, X-ray fluorescence spectrometric analysis was conducted to determine the silica content of the micronised RHA.

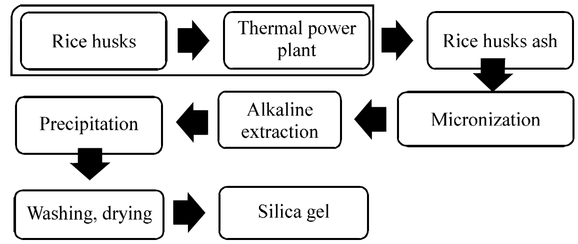

Fig. 1: Extraction of silica from rice husks ash

Silica production: The silicas were prepared with the aid of NaOH and KOH extracting solutions with the respective bicarbonates being used as catalysts, following the process (with some modifications) described by Kalapathy *et al*. (2002). Micronised RHA (20 g) was placed in a 250 mL round-bottom flask and mixed with the corresponding alkaline solution and catalyst, in concentrations predicted by the Response Surface Methodology (RSM) for sodium-based silica, using as independent variables the pH (1, 3, 5, 7 and 9), base concentration (2.0, 3.5, 5.0, 6.5 and 8.0 mol L^{-1}), catalyst concentration (0.6, 1.3, 2.0, 2.7 and 3.4 mol L^{-1}) and time (1, 2, 3, 4 and 5 h). The yield of the silica extraction was regarded as the dependent variable.

The mixture was then kept under reflux for 3 h in accordance with the DOE (design of experiment). Following this, the solution was passed through a paper filter with 2.0 μm porosity (Whatman, Springfield Mill, UK) and the filtered material was acidified to the pH predicted by the RSM with a solution of 5.5 N H_2SO_4 which formed a slightly pink silica precipitate. It was filtered again in the same way as mentioned before, now adding 20 mL of 3% H_2O_2.

The discoloured silica xerogel was dried in a kiln for 24 h; after that, it was washed with distilled water to remove the excess acid (pH~6) and put back in the kiln for a further drying period of 24 h. In the final stage, the silica xerogel was cooled in a desiccator, ground in porcelain mortar and classified at 0.24 mm mesh.

Characterization of silica xerogels: The X-ray diffractograms of the silica xerogels and the RHA were obtained with the aid of a Shimadzu Diffractometer Model XD 7A (Shimadzu, Tokyo, Japan), using CuKα radiation, acceleration voltage of 30 kV, current of 30 mA and scan angle of 2-72°.

The specific surface areas were calculated through the Brunauer, Emmet and Teller (BET) method (Brunauer *et al*., 1938), in a volumetric apparatus fitted with a turbomolecular pump (Edward, Milwaukee, OR, USA). The analysis of the pore distribution was carried out by laser diffraction technique with a Cilas 1064 L particle size analyzer (Madison, WI, USA). A Philips X-ray spectrometer PW 2400 (Philips, The Netherlands) with a 3 kW tube and rhodium target was used for fluorescence measurements.

Experiments involving the addition of silica xerogels to different types of soil: These experiments were conducted at the Institute of Agrarian Sciences, Federal University of Uberlandia, with the aim to confirm the benefits of the use of the silica xerogels as fertilisers. The experiments were carried out in a greenhouse using soil samples classified as dystrophic Red Latosol with a moderate A horizon and a medium texture (77% sand).

The silica xerogels were weighed and mixed with the soil together with basic fertilisers which consisted of 0.3 g kg^{-1} urea, 0.5 g kg^{-1} Triple Superphosphate (Shanghai Shilei Ltd., Shanghai, China; 54% P_2O_5; small% S; Ca>10%), 0.35 g kg^{-1} KCl and 0.1 g kg^{-1} formulated micronutrients (with 9% Zn, 1.8% B, 2% Mn; 8% Cu; 0.1% Mo; 3% Fe). Half of the N and K was supplied in the sowing season and the other half 20 days later. The soil was placed in 8 kg plastic containers and remained in incubation for 20 days until the rice-sowing season.

The reactivity of the silicon sources was measured by adding to the soil increasing amounts of a standard silicate-Recmix Siligran-(12% Si; Fertion, Rio Branco do Sul, PR, Brazil) in granulated form and in powder; sodium xerogel silica and potassium xerogel silica (0, 100, 200 and 400 kg Si ha^{-1}) in random blocks with four repetitions. Ouro Minas rice was sown and cultivated in an average cycle, lasting for a period of 94 days from sprouting to blooming. It displayed the following characteristics: Fine long grain rice (needle-shaped); a yield of between 55 and 65% of whole grains; resistant to lodging and higher resistance to blast.

Statistical analysis: A Design of Experiments (DOE) was employed to reduce the number of experiments and to describe the effects on the variables investigated (Bas and Boyaci, 2007). Thus, the chosen model used was RSM with four independent variables at five levels for the extraction of silica from the RHA with lye. The results were submitted to an Analysis of Variance (ANOVA) to determinate the variables or interactions between them, that would be more significant. Checking the most suitable model for the designs was carried out with the aid of Statistics 6 Software.

RESULTS AND DISCUSSION

Characterization of silica xerogels: The diffractrograms of the silica xerogels can be observed in Fig. 2. The diffractrograms of the sodium-based and potassium-based silica samples show peaks in the range of 12.5° which confirmed the presence of amorphous regions. In the case of the potassium-based silica, a peak of 29° was confirmed with regard to $K_6Si_3O_9$ (trisilicate of hexapotassium) or tridymite, a crystalline form of silica (Real *et al*., 1996; Leu and Chou, 2011).

The specific surface areas and the mesopore volumes of the prepared silicas are provided in Table 1.

As can be observed, the high values for the surface area of the sodium and potassium-based silicas correspond to the values found in the literature (Liou, 2004, Zhang *et al*., 2010). Figure 3 shows the nitrogen adsorption-desorption isotherms. The lower part of the

Table 1: Specific surface area, mesopore volume and diameter and mean particle diameter of silicas and micronized rice husks ash

		Silicas			
Properties	RHA	Sodium	Potassium	Liou*	Zhang**
Surface area (m^2 g^{-1})	20.1	232.4	183.7	235.0	287.9
Pore volume (cm^3 g^{-1})	0.03	0.05	0.50	-	-
Mean pore diameter (um)	4	4	4	-	-
Mean particle diameter (μm)	20.75	28.41	67.93	-	-

*Liou (2004), **Zhang *et al*. (2010)

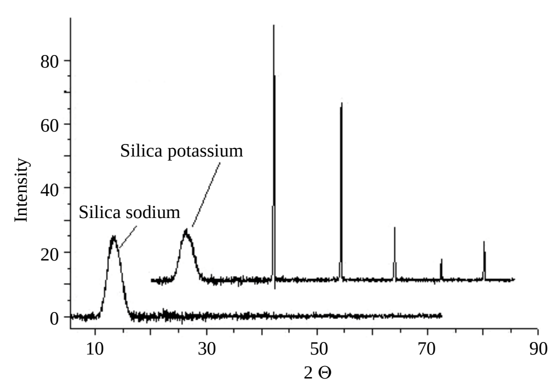

Fig. 2: Diffractograms of the sodium and potassium xerogel silicas

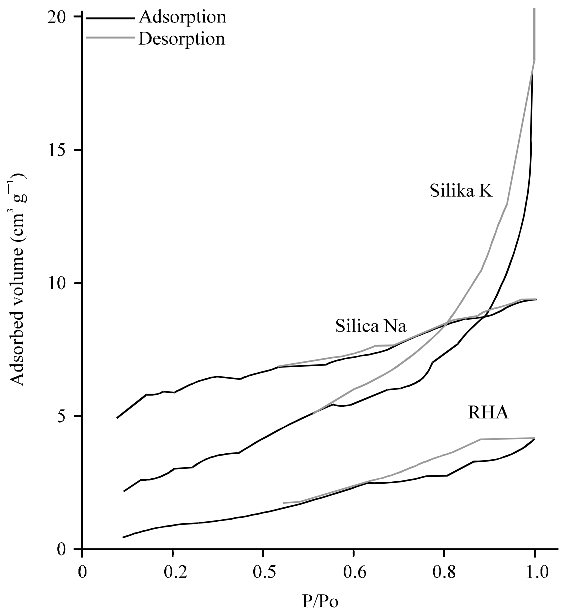

Fig. 3: Isotherms of adsorption/desorption of nitrogen

loop is traced out on adsorption and the upper portion on desorption. The isotherm loop of the sodium silica resembles type IV of the Brunauer's classification but without a significant occurrence of mesopores. It can be also seen for the potassium silica at low values of P/Po an isotherm profile similar to type III but the adsorption increases markedly at P/Po from 0.6 to 0.9 which characterizes a superimposed multi-layer. It was confirmed that the silicas obtained had mean particle diameters of 28.41 and 67.93 μm, respectively which are higher values than those recorded in the literature (Della *et al*., 2002; Liou, 2004; Zhang *et al*., 2010). However, it should be stressed that in the last case, the investigation was initiated using coarse RHA.

Table 2 shows the results of the X-ray fluorescence analysis (FRX) of the micronised RHA sample and the prepared silica xerogels. The silicas produced showed contents of 75.5 and 77.2% of SiO_2. These values can be regarded as quite satisfactory for industrial usage, considering that the raw material was coarse RHA which had not undergone any previous purification treatment. The literature records values for silicas of chemically treated raw materials with a SiO_2 content of up to 95%.

The optimization model for the parameters of silica production: As mentioned before, CCDs were employed in the experiments for sodium-based silica to evaluate the influence of the variables and determine the optimal quantitative relations.

Table 2: Oxide composition of the rice husks ash and xerogel silicas obtained by X-ray fluorescence analysis

Oxide	RHA (%)	Sodium silica (%)	Potassium silica (%)
SiO_2	91.40	75.50	77.2
Al_2O_3	0.48	0.54	0.97
TiO_2	0.00	0.01	nd
Fe_2O_3	0.02	0.00	nd
MnO	0.37	0.01	0.01
MgO	0.35	0.05	2.55
CaO	0.50	0.08	0.13
Na_2O	0.00	4.84	nd
K_2O	1.50	0.21	6.04
P_2O_5	0.18	0.00	nd
H_2O	5.63	18.80	13.7
Total	100.40	100.00	100.5

nd: Not determined

Effect of the silicas on rice cultivation: The application of increasing amounts of silica sources as an additive ensures a greater availability of Si in the soil, where it can be absorbed into the rice root system and accumulated in the leaf tissue.

As can be seen at Fig. 4, the levels of Si in the soil increased with the added amounts of both silicas in the quantity of 400 kg ha^{-1} of Si, higher than the control definition. The added amounts had an effect on the accumulation of Si in the area surrounding the plant; the best results were obtained with quantities of 200 and 400 kg ha^{-1} of Si, higher than the control definition.

A significant amount of Si accumulated in the surrounding area when standard Recmix was added together with the sodium and potassium-based silicas. In terms of the production of dry material, the best amounts were 100 and 200 kg Si ha^{-1}, higher than the control definition. In terms of grain production, the sodium and potassium-based silicas were better than the control definition (Fig. 4), which shows that increasing the amount of silica added to the soil leads to an increase in production. This effect suggests that grain production could be even higher if the amounts of Si added were higher than 400 kg ha^{-1}.

The increase in production was due to the effect of Si in controlling the severity of blast disease on the leaves (Nakata *et al*., 2008). The epidermal cells became thicker and there was a greater degree of lignification and/or silicification with a physical protective barrier being formed, enabling it to withstand attacks by fungi and insects. When the silicon sources were used, improved results were obtained with regard to the source of Siligran (Recmix) which were caused by the greater solubility of the sources of sodium-based and potassium-based silicates.

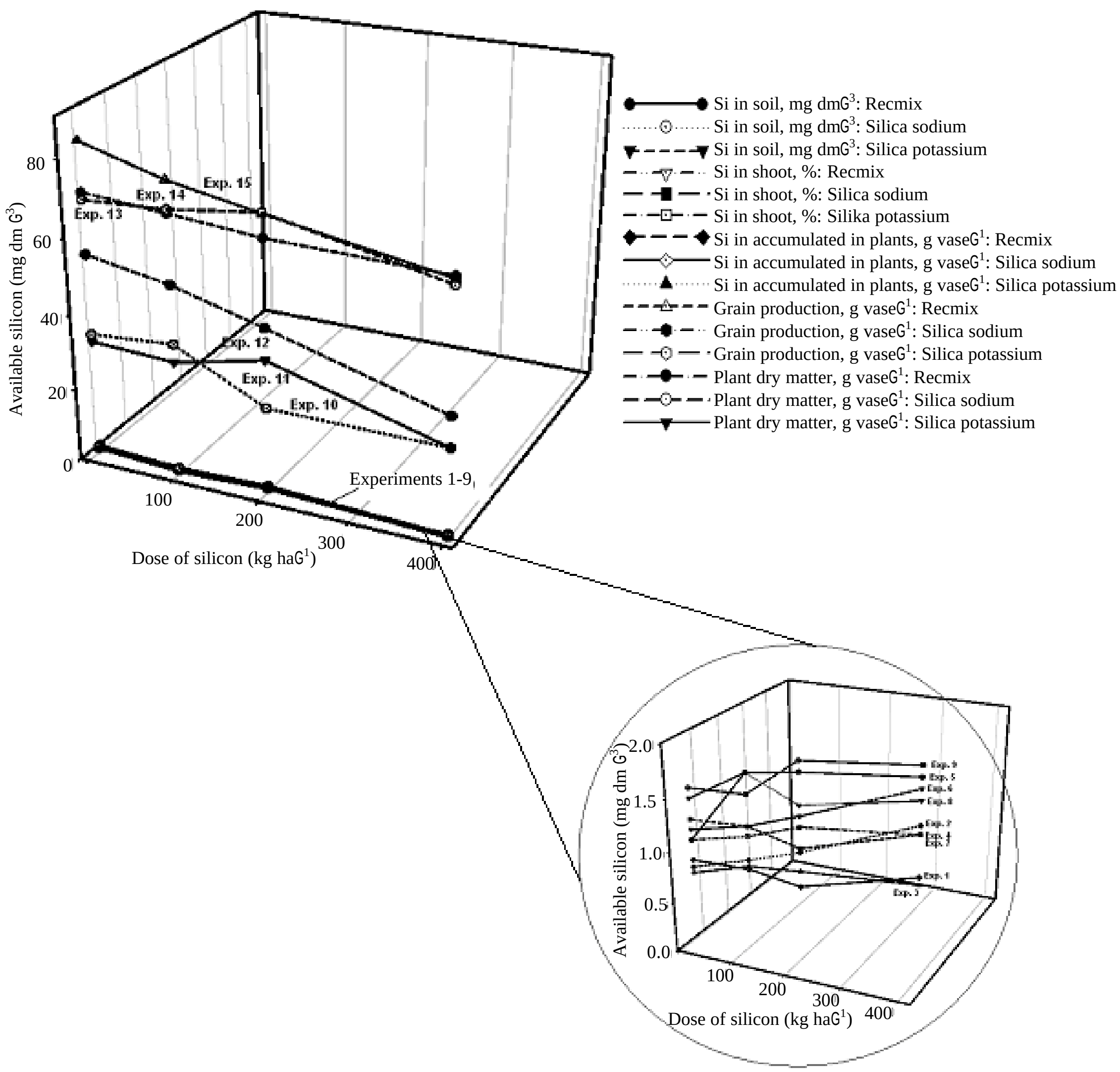

Fig. 4: Available silicon in soil (mg dm^{-3}) as a function of the dosage (kg ha^{-1})

CONCLUSION

The chemical conversion of micronised RHA with the purpose to produce xerogel silicas was shown to be a possible way of making use of this inconvenient agricultural residue by generating products of some added value which can feed back into the business chain. The xerogel silicas, moreover, showed high values for the specific surface area and favourable mean particle size for these purposes. The tests of the xerogel silicas for the cultivation of rice indicated that these sources of silicon provided increments in the soil Si content and as a consequence, increasing the grain yield and dry matter production in the rice plant leaves. Therefore, the costs of agrochemicals for the control of plagues and diseases in the cultivation of rice can be reduced, by using a low-cost, renewable and most abundant product.

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