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SILICA SOL OBTAINED FROM RICE HUSK ASH

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Abstract. Rice husk ash was used to produce sodium silicate with $\text{SiO}_2/\text{Na}_2\text{O}=3$. The investigation of NaOH concentration and temperature on the silica conversion showed that NaOH has positive influence. $\text{SiO}_2/\text{Na}_2\text{O} \sim 3$ was produced with 0.8 mol/l of NaOH and 403/453 K. These solutions were used to produce silica sol with diameter of $\sim 5\text{nm}$.

Keywords: rice husk ash, sodium silicate, silica sol, nanoparticle

1. Introduction

Critical economic and environmental situations of the current days encourage companies and researchers to develop and improve technologies intended to reduce or minimize industrial wastes. As a consequence, much effort has been expended in different areas, including the agricultural production.

Rice is the second largest produced cereal in the world. Its production is geographically concentrated in Asia with more than 90 percent of world output. The United States and Brazil are the most important non-Asian producers and Italy ranks first in Europe. The rice world production was approx 400 million tons of milled rice in 2003 [1]. In most varieties rice is composed by approximately 20 % of rice hull, which contains a fibrous materials and silica; however the amount of each component depends on the climate and geographic location of rice crop. Therefore, due to its high percentage in the grain composition, the hull is considered a by-product in the mills and creates disposal and pollution problems [2-3].

Burning rice hull as a fuel substitute in order to generate energy is a useful solution which is used by many industries; however it results in a new waste, named rice husk ash (RHA). This residual ash obtained from the combustion can contain over 60 % of silica and some

amount of metallic impurities. Depending on the burning process, RHA can contain silica in the amorphous form; therefore, this residue can be considered as a new economically viable raw material to produce silica or to be used as silica resource [4].

Silica has been used in many applications, including production of nanomaterials. Tailored materials composed of nanoparticles have potential for application in numerous technological fields. The expression nanodispersed silica covers the entire variety of silica forms including sols, gels, suspensions, and pastes. Silica sol or colloidal silica refers to a stable dispersion of colloidal silica particles in water medium. It is used in many applications, such as in refractory materials, binder for inorganic paint, stiffener for hard coating reagents, abrasive particles, adsorbents, and catalyst [5-6]. Various raw materials can be used in the manufacturing of monodispersed sols but the two main ones are tetralkyl orthosilicates and sodium silicate solution. This latter has the advantage over the first one because it is less expensive and uses water as the solvent [7-8].

Sodium silicate solutions (commercially called sodium water-glass) are complex mixtures of silicate anions and polymer silicate particles especially when silica module ($\text{SiO}_2 : \text{Na}_2\text{O}$ molar ratio) is >2 [9]. The manufacture process of sodium silicates is generally considered expensive due to the energy required to reach high temperatures during the calcination stages, in addition to producing considerable air pollution by emission of dust, nitrogen and sulphur oxides. Although this calcination process is widely used in industrial scale, there is another process based on the reaction of silica with aqueous sodium hydroxide (NaOH) in autoclave. This latter one has an advantage when compared with the conventional calcinations process as it requires less energy [10].

The initial purpose of this study was the production of a sodium silicate solution with silica module of approximately 3 ($M \approx 3$; where $M = \text{SiO}_2/\text{Na}_2\text{O}$ molar ratio) using RHA as the silica resource and then, use it to obtained

silica sol via Ion-Exchange Method. In order to develop the study, the following sequence was performed: (i) characterize the RHA; (ii) investigate the influences of NaOH molar concentration and temperature on the silica conversion to sodium silicate production and (iii) utilize it to produce a silica sol.

2. Experimental

2.1. Materials

The RHA sample was supplied by Empresa Brasileira de Pesquisa Agropecuária (Embrapa). It was milled to homogenize the particle sizes; as a consequence the mean particles size was reduced from 0.64 to 0.15mm. Due to economic reasons, no purification process was performed in order to increase silica content.

Sodium and Potassium Hydroxides (purity > 99 %) from local supplier were used as received. The cation exchange resin Amberlite-120 was supplied by Vetec Química Fina, Brazil.

2.2. Experimental Production of Sodium Silicate with $M \approx 3$

Silica can be extracted from RHA since it is soluble under alkaline condition. The reaction products are sodium silicate solution (Eq. 1) and solid impurities predominantly constituted of non-reacted silica and water non-soluble material. The experimental procedure is described in Fig. 1.

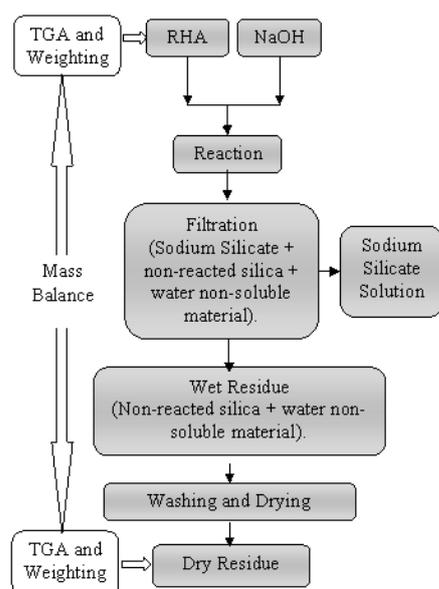
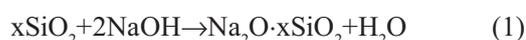


Fig. 1. Experimental procedure diagram for the production of sodium silicate solution

The reaction was carried out in a closed stainless steel vessel by volume of 1 l. The process fixed parameters were: stirring rate of 500 rpm; time reaction of 5 h; water volume of 750 ml and molar SiO_2 concentration of 1.7 (approx. 150 g of RHA). The following parameters were investigated: NaOH concentration (0.8; 1.2 and 1.6 mol/l) and temperature (373, 403 and 423 K). At the end of the reaction time, the temperature was let to reduce to room temperature and the solution was filtered through Whatman 41 filter paper to separate the sodium silicate solution. The wet residue was washed with water and dried in an oven during 24 h at 373 K. Silica conversion to silicate was calculated by mass balance taking into account RHA and dry residue (weighting and thermogravimetric analysis).

2.3. Experimental Silica Sol Production

Silica sols are dispersions of nanosized particles of SiO_2 dispersed in water. The sol particles are negatively charged due to the adsorption of hydroxide ions on their surface, which makes the system stable. The most important characteristics of the sols are the SiO_2 content and the particle size [5]. The method used in this study to produce silica sol is *via* Ion-exchange and was based on Yoshida [11] and Tsai *et al* [12] works. This method can be divided into three parts: (a) formation of active silicic acid by removal of alkali ions from a dilute silicate sodium solution; (b) formation of a dilute silica sol by nucleation from the active silicic acid and growth of discrete silica particles by polymerization and (c) increase of silica concentration in the dilute silica sol. In this study, a laboratory procedure divided in two parts was carried out in order to produce silica sols, as described below:

(a) Part 1: 100 ml of sodium silicate with silica module of about 3 obtained from RHA was passed through a column filled with the cation exchange resin Amberlite-120 to allow the sodium ions to be replaced by hydrogen ions at the exchange sites of the cation resin, giving rise to an aqueous solution of active silicic acid with pH between 2 and 3.

(b) Part 2: The nucleation, polymerization and particle growth of silica sol were performed when the active silicic acid was titrated (flow rate $10 \text{ ml} \cdot \text{min}^{-1}$) against 10 ml of a 10 % wt solution of KOH previously heated at 333 K.

Two runs were carried out and the pH and particle size distribution of silica sol obtained were measured.

2.4. Methods

Quantitative chemical analysis of RHA was carried out by X-ray fluorescence (XRF, Bruker-AXS, model S4).

X-ray diffraction pattern was performed on an Equinox 1000, INEL, using an acceleration voltage of 40 kV and current of 30 mA. The diffraction angle (2θ) was scanned from 0° to 115° .

Thermogravimetric analyses (TGA) were recorded on a TA Instrument from 298 to 1273 K using heating rate of $20^\circ/\text{min}$ under air atmosphere.

The silica sol was characterized for particle size distribution on a Malvern Zetasize Nano ZS. This apparatus has a detector placed at 446 K from the transmitted light beam and detects the size by backscattering, a patented technology known as non-invasive backscattering (NIBS). In the Malvern system, the particle size is determined *via* photon correlation spectroscopy method (PCS). This method consists of determining the velocity distribution of particle movement by measuring the dynamic fluctuations in the intensity of scattered light. The instantaneous intensity of light scattered by a colloidal material depends on the position and orientation of each scattered. The position and orientation of small colloids change because of Brownian motion which causes fluctuations of the local concentration of the particles, resulting in local inhomogeneities of the refractive index. This in turn results in the intensity of the scattered light. The linewidth of the light scattered spectrum Γ (defined as the half-width at half maximum) is proportional to the diffusion coefficient of the particles (D) (Eq. 2).

$$\Gamma = Dk^2 \therefore k = (4\pi n/\lambda)\sin(\theta/2) \quad (2)$$

where: n is the refractive index of the medium; λ – the laser wavelength, and θ is the scattering angle.

With the assumption that the particles are spherical and non-interacting, the mean radius can be obtained from the Stokes-Einstein equation (Eq. 3).

$$R = k_B T / 6\pi\eta D \quad (3)$$

where k_B is the Boltzmann constant; T is absolute temperature; η is the fluid viscosity.

Information about light-scattering spectrum can be obtained from the autocorrelation function $G(\tau)$ of the light-scattering intensity (Eq. 4).

$$G(\tau) = 1 + B \cdot \exp(-\Gamma \cdot \tau) \quad (4)$$

The characteristics decay time of the correlation function is inversely proportional to the linewidth of the spectrum. Therefore, the diffusion coefficient and particle size can be determined by fitting the measured correlation function to a single exponential function [13]. By using the photon correlation spectroscopy (PCS) method, the refraction index and viscosity values, quantitative results were obtained in the form of graphs of scattered light volume as a function of the particle size. All the measurements were performed in triplicate and the particle size distribution graphs were plotted using the average of the curves obtained, with the respective error bars.

2.5. Statistical Analysis

The Software Statgraphics Centurion was used to perform statistics determination.

3. Results and Discussion

3.1. RHA Characterization

Understanding of the characteristics of each waste is fundamental to selecting, designing and implementing

waste management solutions in the industry. Figs. 2 and 3 show the statistical analysis performed with TGA data for RHA “as received” and “after milling”. In each figure, the confidence interval of weight loss as a function of temperature is presented. The comparison between Figs. 2 and 3 demonstrates that the milling process made the RHA sample more homogeneous as the confidence interval of weight loss reduced considerably, principally for temperatures above 873 K. It is also evident that weight loss was practically stabilized after 873 K. The estimation of the inorganic content present in RHA (after milling) calculated from weight loss values projected to temperatures higher than 1173 K was $72.3 \pm 0.37\%$.

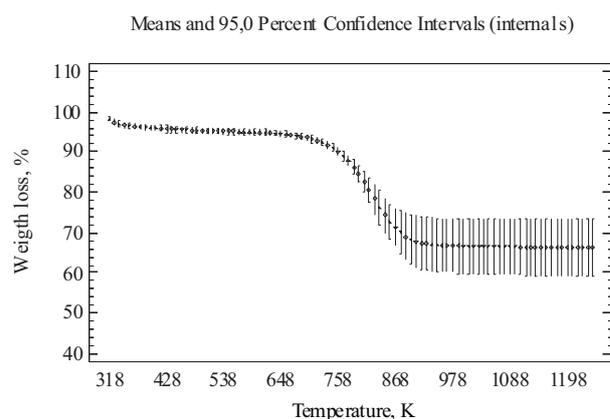


Fig. 2. TGA curve of RHA as received (five analysis)

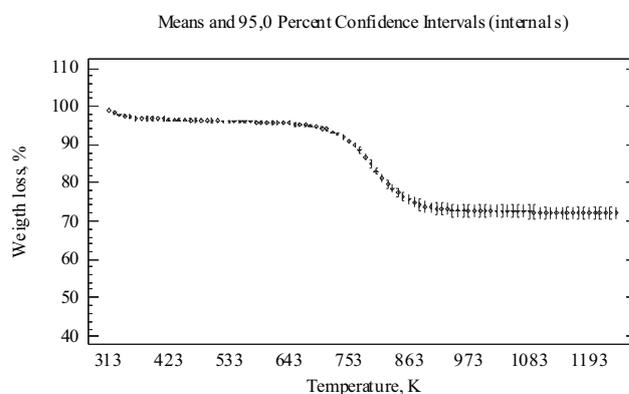


Fig. 3. TGA curve of RHA after milling (five analyses)

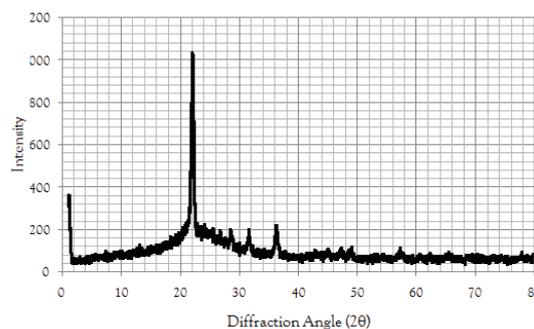


Fig. 4. X-ray diffraction of RHA sample

The chemical composition of RHA sample, obtained by XRF was 95.30 SiO₂; 1.70 K₂O; 1.70 Na₂O; 0.91 P₂O₅; 0.74 CaO; 0.61 MgO; 0.20 MnO; 0.12 SO₃; 0.10 Fe₂O₃ and 0.01 Rb₂O (% by weight). This analysis showed that inorganic content of this ash has a high amount of silica (95.33 %) and a few impurities, which are predominantly K₂O and Na₂O. On the other hand, the silica presented is not completely in the amorphous form since its diffractogram showed a sharp 2θ angle diffraction peak centered at 22, which indicates a crystalline structure (Fig. 4). The presence of crystalline or amorphous silica, or both, in RHA depends on the burning temperature achieved in the ash production. Yalcin and Sevinc [3] reported that burning temperatures higher than 973 K induced the production of crystalline structure.

3.2. Production of Sodium Silicate with M ≈ 3

The values of silica conversion to sodium silicate determined by both methodologies proposed (TGA and Weighting, Fig. 1) are presented in Table 1.

Based on the results, it is evident that no significant differences were observed comparing the two procedures. From Table 1, it is also observed that silica conversion was affected positively by NaOH concentration since silica extraction increased as NaOH concentration also increased,

even though the increments obtained were not remarkable. One possible reason for the low extraction efficiency is the presence of silica in crystalline form in this RHA sample (Fig. 4). The dissolution process of silica in aqueous solutions is mainly due to hydrolysis of Si–O–Si bonds, therefore silica configuration has strong influence on this process. As a comparison, quartz silica is the most stable form while amorphous silica is the most soluble [14].

From Table 1, no evidence can be observed that the increase in the reaction temperature would have significant influence on silica extraction. This lack of influence could also be due to the presence of crystalline silica in the RHA sample, which does not favour the extraction reaction.

Concerning the production of sodium silicate with silica module around 3, the process parameters which led to this solution were NaOH concentration of 0.8 mol·l⁻¹ and temperatures of 403 or 423 K; therefore only the solutions obtained from those reactions were selected to produce silica sol. Those solutions have density of 1.075 ± 0.001 g·cm⁻³ and SiO₂ content of 7.2 ± 0.2 wt %.

3.3. Silica Sol Production

The sodium silicate solution (MS = 3 and SiO₂ content is 7.2 ± 0.2 wt %) was eluted through a column filled with cation exchange resin to produce a silicic acid

Table 1

Effect of NaOH concentration and temperature on the silica conversion

Temperature, K	NaOH molar concentration (mol/l)		
	0.8	1.2	1.6
Silica conversion to sodium silicate by TGA method (η, %)			
373	47.6±1.0	62.4±1.0	69.4±1.0
403	52.3±1.1	63.4±1.1	-
423	54.4±1.1	61.9±1.1	-
Silica conversion to sodium silicate by weighting method (η, %)			
373	49.8±1.1	61.0±1.1	69.6±1.1
403	52.4±1.1	61.4±1.1	-
423	52.4±1.1	62.0±1.1	-
Silica module (SiO ₂ : Na ₂ O ratio – experimental)			
373	2.7±0.1	2.4±0.1	2.1±0.1
403	3.0±0.1	2.2±0.1	-
423	3.0±0.1	2.3±0.1	-
Density, g·cm ⁻³			
373	1.071±0.001	1.100±0.001	1.150±0.001
403	1.075±0.001	1.098±0.001	-
423	1.075±0.001	1.100±0.001	-
SiO ₂ content, wt %			
373	6.6±0.2	8.6±0.2	9.6±0.2
403	7.2±0.2	8.8±0.2	-
423	7.2±0.2	8.5±0.2	-

with average pH equal to 2.7 ± 0.4 . When the silicic acid was titrated to heated KOH solution, homogenous nucleation occurred producing seeds. As titration continues, either seeds growth or the formation of new seeds will occur, depending on the titration rate. If silicic acid is added slowly, seeds will grow preferentially even though new seeds may also be formed. So, titration rate has a large effect on the particle size of the silica sol [12]. As the two runs were carried out using the same titration rate ($10\text{ml}\cdot\text{min}^{-1}$), it was expected that the two produced silica sols would have similar mean particle sizes. Fig. 5 shows

the particle size distribution (vol %) and Table 2 presents the pH and the average particle size (vol %) for the colloidal silica produced in each replica.

Table 2

Particle size and pH of silica sols

Run	pH	Particle average size	
		Diameter, nm	Vol %
1	11.0	4.7	100
2	10.5	5.6	~100

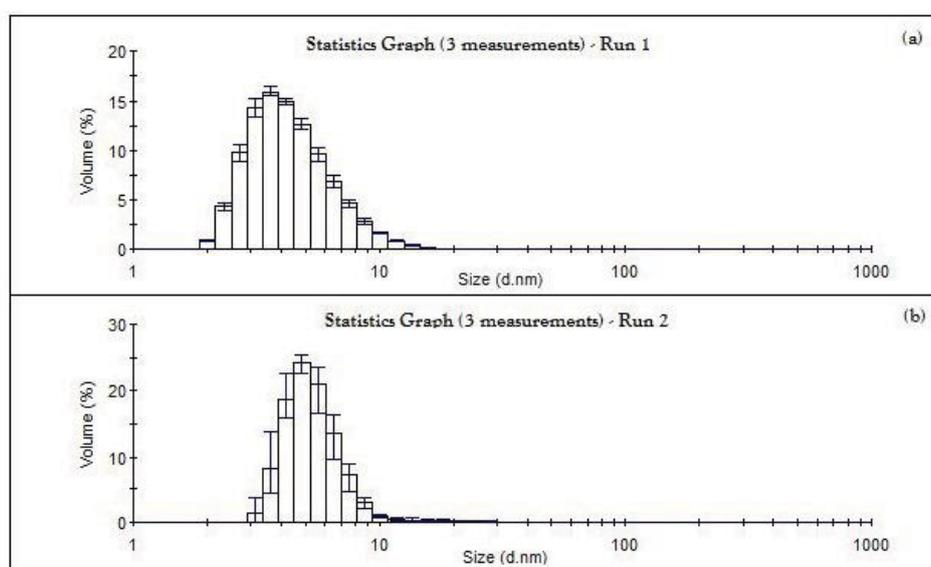


Fig. 5. Particle size distribution (vol %) of silica sols determined by dynamic light scattering – Statistics graphics of 3 measurements of silica sol run1 (a) and silica sol run 2 (b)

From these results, it was possible to verify that Run 1 and 2 showed a particle size distribution of SiO_2 in the range from 2 to 20 nm and 3 to 30 nm, respectively, although the percent volume of particle size above 10 nm was very low in both curves. Thus, silica sols containing particles with average diameter of about 5 nm can be produced using the procedure proposed. These colloidal dispersions were clear solutions due to the small sizes of the particles and remained stable throughout the time taken for writing this paper (one month).

4. Conclusions

In this study, rice husk ash (RHA), an industrial waste, was used as raw material to produce a sodium silicate solution. In order to obtain a solution with silica module about 3, the process conditions chosen were NaOH concentration of $0.8\text{ mol}\cdot\text{l}^{-1}$ and temperatures of 403 and 423 K, even though these parameters were not yet satisfactory to allow remarkable silica conversions. A

possible reason for the low efficiencies in extracting silica from RHA was the presence of silica in a crystalline form in the RHA waste. The sodium silicate solution produced from RHA was used to produce silica sols with average size diameter (vol %) about 5 nm. Consequently, this study also demonstrated that RHA can be used as silica source for products with high aggregate value.

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ОДЕРЖАННЯ КРЕМНІЄВОГО ЗОЛЮ ІЗ ЗОЛИ РИСОВОЇ ЛУЗГИ

Анотація. Одержано силікат натрію з співвідношенням $SiO_2/Na_2O = 3$ із золи рисової лузги. Вивчено вплив концентрації $NaOH$ та температури на перетворення кремнію та показано, що $NaOH$ позитивно впливає на утворення силікату натрію. $SiO_2/Na_2O = 3$ був одержаний при 403–423 К, виходячи із концентрації $NaOH$ 0.8 моль/л. Запропоновані розчини використані для отримання кремнієвого золю з діаметром частинок ~ 5 нм.

Ключові слова: зола рисової лузги, силікат натрію, кремнієвий золь, наночастинки.