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Preparation and Characterization of High Purity Silica Obtained from Rice Husks

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Although SiO_2 is produced mostly from mineral sources like quartz, it has recently been obtained from lignocellulosic natural resources, such as rice husk (hull). Several methods for extracting silica (SiO_2) from rice husks are available in the literature. These methods are based essentially on heat treatment and/or extraction. This study represents a thorough account of heat treatment and acid-base extraction, to obtain silica from rice husks with a high purity and to eliminate other inorganic impurities. Rice husks, considered to be a potential silica source, were pretreated with various acids, base and water and then thermally degraded in a fixed bed reactor under an inert gas atmosphere (N_2). The materials produced in these conditions were characterized by Brauner-Emmett-Teller analysis, for surface area and pore volume, by Fourier transform infrared spectroscopy, powder X-ray diffraction, X-ray fluorescence, and scanning electron microscopy.

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1. Introduction

Silicon is a crystalline semi-metal. Though silicon, which makes up about 30% of the Earth's crust, is so ample and ubiquitous, it is not naturally found in its pure state. Silicon in nature occurs mainly in the forms of dioxides and hydrates. The only stable form of silicon at normal conditions is silicon dioxide (silica). Silica is consumed in large quantities in many industrial areas, such as construction industry, in the production of glass, and optical fibers and silicon chips for telecommunication and as additive and fining agent in food industry.

Rice husks contain over 70 percent of silica by mass, with minor amounts of metallic elements, such as calcium, potassium, sodium and magnesium and could be a viable option for the production of silica [1–4]. Commercial silica is mainly produced in multi-step processes, involving high temperature and pressure. Many researchers have been studying alternative ways to extract silica from rice husks more effectively. Silica has been prepared using different techniques, including vapor-phase reaction [5], sol-gel [6], thermal decomposition methods [7] and acidic-basic pretreatments [8]. The aim of this study was to use a simple and effective way to obtain silica from rice husks at a relatively low temperature (500 °C), in the inert N_2 atmosphere, using acid, base and hot water pretreatment.

2. Experimental

2.1. Chemicals

Analytical grade hydrochloric (37%), sulphuric (90%), nitric (90%), phosphric (85%) (acids), ammonium dihydrogen phosphate (base) were all purchased from Merck Millipore. Ultra-pure water was used in the preparation of all solutions and in the hot water pretreatment of the rice husks.

2.2. Materials and chemical pretreatment

The raw material used in experiments, which was collected from a poultry farm at the city of Balıkesir in the Northwest region of Turkey, was washed thoroughly with distilled water to remove surfactants, dust and contaminants. The material was then dried in air oven at 105 °C for 24 hrs. The washed rice husks were designated as untreated rice husks (UP). The other designations are given in Tables I and II. Prior to experiments, 0.1 M acid and base solutions were prepared. Afterwards, 20 g of dried and ground rice husks were mixed separately with 300 ml of H_2SO_4, HCl, H_3PO_4 and HNO_3 acids and 300 ml of $(NH_4)H_2PO_4$ base. The mixtures were placed in 400 ml Erlenmeyer flasks, kept at 85 °C for 5 hrs in a laboratory-scale hot-water bath with vigorous stirring. The pretreated rice husks samples were washed repeatedly with ultra-pure water to a pH of about 7 and dried at 70 °C for 24 hrs in an oven and stored at room temperature.

2.3. Rice husk ash production (thermal treatment)

Thermal treatments of rice husk at temperatures up to 400 °C under the inert N_2 atmosphere are characteristically unable to completely decompose the organic components i.e. cellulose, hemicellulose and lignin and yield black char, which contains a relatively low amount of silica. Therefore, to maximize rice husk ash (RHA) production, all thermal degradation experiments, for each pretreatment, were conducted in a fixed bed reactor at 500 °C with a nitrogen flow rate of 150 cm^3/min. The detailed description of experimental set-up and of the followed procedure can be found elsewhere [9].

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2.4. Characterization of the produced RHAs

Quantitative chemical analysis of the RHAs obtained by acid, base and hot water pretreatment was accomplished by X-ray fluorescence (XRF, Rigaku Primus II). Mineralogical analysis was performed by X-ray diffractometry (XRD, PANanaytical X'Pert HT-XRD), with Cu K_α radiation in the 2θ range from 5° to 90°, with a step size of 0.02°, at a scanning speed of 1°/min. The surface properties of the RHAs were determined by Brunauer-Emmett-Teller (BET) analysis using Micrometrics ASAP 2020 Plus Physisorption. Inorganic functional analysis was performed by Fourier transform infrared spectroscopy (FTIR) (Perkin-Elmer Spectrum 100).

3. Results and discussion

3.1. XRF and inorganic composition

XRF was used for identifying the chemical compositions and percentage of silica, produced from rice husks by thermal degradation at 500 °C, under an inert N_2 atmosphere. Table I shows that silica (SiO_2) is the main component and the RHA contain metallic impurities in varying amounts, depending on pretreatment. It is clear that acid pretreated RHAs, especially those after hydrochloric acid pretreatment, have much higher content of silica.

3.2. FTIR and crystallinity analysis

The obtained RHAs were analyzed by FTIR, as seen in Fig. 1. The spectra of all untreated and pretreated RHAs show strong broad absorption bands at 1030 cm^{-1} and 800 cm^{-1}, corresponding to the stretching vibrations of Si–O and Si–O–Si, respectively. Similarly, the absorption peaks at 530 cm^{-1}, 725 cm^{-1} and 1417 cm^{-1} were assigned to Si–O asymmetrical bending, Si–O symmetrical bending and Si=O stretching vibrations, respectively. In addition, the peak at 3100 cm^{-1} was ascribed to Si–O–H stretching vibrations, caused by absorbed surface water [9, 10]. The crystallinity of the RHAs was calculated by comparing the ratio of intensity of the characteristic peaks at 766 cm^{-1} and 700 cm^{-1} [11].

3.3. X-Ray diffraction and amorphous form analysis

X-ray powder diffraction (XRD) analysis was used to evaluate the crystalline form of silica, which occurred in the RHAs. Figure 2 depicts the XRD patterns of the RHAs produced by the nontreating and pretreating methods. The XRD patterns of RHAs have a typical amorphous shape, that shows a broad peak centered at $2\theta = 22.3°$, related to amorphous silica. The lack of sharp and distinctive peaks reveals the absence of any crystalline form. This information is in agreement with the results calculated from the FTIR spectra (Table I).

TABLE I

Chemical composition of RHAs obtained from untreated and pretreated rice husks, after thermal degradation.

Inorganic content[a] [wt.%]	Production procedure						
	Untreated material	Base pretreatment	Acid pretreatment				Water pretreatment
		Ammonium dihydrogen phosphate ($(NH_4)H_2PO_4$)	Nitric acid (HNO_3)	Phosphoric acid (H_3PO_4)	Sulphuric acid (H_2SO_4)	Hydrochloric acid (HCl)	Hot water (H_2O)
Designation	UP	AP	NP	PP	SP	CP	WP
SiO_2	79.6	91.49	92.1	96.1	97.9	98	89.85
Al_2O_3	1.59	0.40	0.39	0.20	0.50	0.44	0.28
Fe_2O_3	0.48	0.24	0.16	0.31	-	0.16	0.3
CaO	3.18	1.61	1.50	0.58	0.17	0.18	1.61
MgO	0.49	0.39	0.13	-	-	-	0.16
Na_2O	0.47	0.86	1.39	0.14	0.11	-	0.10
K_2O	7.64	1.67	3.48	0.63	0.59	0.52	2.48
SO_3	1.85	0.22	0.21	0.21	0.42	0.24	0.10
P_2O_3	1.96	0.84	-	1.58	0.10	0.24	0.11
MnO	0.54	0.42	0.38	-	-	-	0.28
F	0.21	0.14	-	-	-	-	0.15
Others	1.99	1.72	0.26	0.25	0.21	0.22	4.58
Amorphicity[b] [%]	99.14	99.08	99.06	98.97	98.89	98.74	99.12
Crystallinity[b] [%]	0.86	0.92	0.94	1.03	1.11	1.26	0.88

[a] expressed as oxides, [b] for silica.

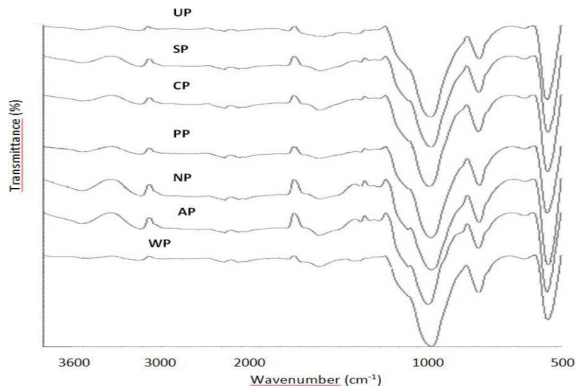

Fig. 1. FTIR spectra of RHAs.

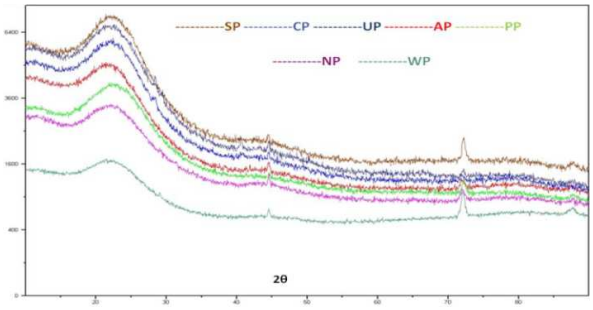

Fig. 2. XRD patterns of untreated and pretreated RHAs.

3.4. SEM analysis

Figure 3 depicts the SEM micrographs of the RHAs. The morphological structure of all RHAs has predominantly a rough and undulating surface texture. After pretreatment, marked and significant changes in morphology can be seen. Because pretreatment hydrolyzes the organic components, especially cellulose in rice husks, untreated RHA yielded a rougher surface. A similar trend is reported in the literature [8].

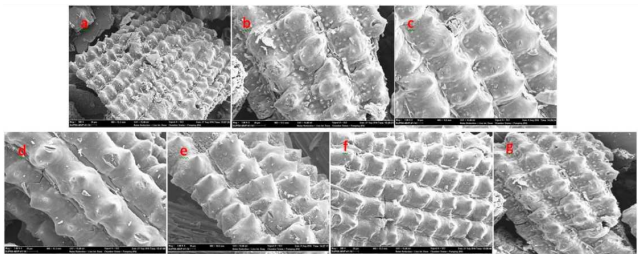

Fig. 3. SEM images of RHAs produced from (a) untreated (UP) rice husks and rice husks treated with (b) ammonium dihydrogen phosphate (AP), (c) hot water (WP), (d) hydrochloric acid (CP), (e) sulphric acid (SP), (f) nitric acid (NP) and (g) phosphoric acid (PP).

3.5. Properties of the RHAs

The pore parameters of RHAs are presented in Table II. The surface area, total pore volume and average pore width ranged from 116.92 m^2/g to 268.05 m^2/g, from 0.071 cm^3/g to 0.146 cm^3/g and from 21.03 Å to 23.734 Å, respectively. The pore properties of the RHAs were markedly influenced by pretreatment, as shown in Table II. The presence of acid, base and hot water has led to a much larger surface area and total pore volume. This increase can be ascribed to the hydrolysis of the inherent organic components into smaller substances, which could facilitate the decomposition of the raw material into the volatiles by thermal treatment.

TABLE II

Surface area and textural properties of RHAs, obtained by BET analysis.

	Designation	BET surface area [m^2/g]	Total pore volume [cm^3/g]	Average pore width [Å]
Production procedure				
Untreated	UP	119.62	0.071	23.734
Acid treatment				
Phosphoric acid	PP	268.05	0.146	21.731
Sulphuric acid	SP	253.96	0.133	21.023
Hydrochloric acid	CP	247.63	0.137	22.138
Base treatment				
Ammonium dihydrogen phosphate	AP	251.03	0.145	23.109
How water treatment				
Hot water	WP	223.42	0.131	23.542

4. Conclusions

The physicochemical pretreatment using acid, base and hot water was employed to pretreat rice husks for the production of silica. The results of elemental composition, results of surface characteristic properties and the observations of the morphological surface properties of the produced RHAs confirm that sulphuric acid pretreatment can effectively produce amorphous silica (>98%). In addition, the pretreated RHAs are porous and have high surface areas. Thus pretreated RHAs could be good candidates for adsorbents [12] for the removal of dyes and heavy metals, and adsorbents in air pollution and water purification systems [13, 14].

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