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Effect of organic acid treatment on the properties of rice husk silica

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Rice husk, an agro waste material, contains about 20% ash which can be retrieved as amorphous, chemically reactive silica. This silica finds wide applications as filler, catalyst/catalyst support, adsorbent and a source for synthesizing high performance silicon and its compounds. Various metal ions and unburned carbon influence the purity and color of the ash. Controlled burning of the husk after removing these ions can produce white silica of high purity. The present paper deals with the investigation carried out on two rice husk samples of different origin, one from the state of Andhra Pradesh (APRH) in the central part of India and the other from Kerala (KRH) the southern most part of the country. Leaching the husk with acetic and oxalic acids was attempted for the first time and the improvement in properties of the ash was studied. The husk samples were also treated with hydrochloric and nitric acids of different concentrations for comparison. The ashes produced by controlled burning of these samples before and after acid treatment, were characterized for the optical properties in addition to the chemical and physical nature. The APRH ash was found to be inferior to the KRH ash in all properties. Pretreatment of the husks with the organic acids improved the properties of ashes and the effect was comparable to that achieved by mineral acid leaching. Amorphous, reactive and high purity silica with high surface area and pore volume and good optical properties could be prepared from both the husks under specific conditions.

1. Introduction

Amorphous silica with high purity and reactivity is an excellent starting material for the synthesis of advanced materials such as carbides and nitrides of silicon, magnesium silicide, high purity elemental silicon etc. Properties like high surface area and porosity give added advantage to the silica for its use as adsorbents, catalysts and catalyst supports. Rice husk on burning gives 14–20% ash which contains 80–95% silica in the crystalline form and minor amounts of metallic elements. By controlling the burning conditions like temperature and time, amorphous silica of ultrafine size and reactivity can be produced. Pretreatment of the husk with mineral acids followed by controlled ashing gives silica with high purity.

Rice husk is a by product in rice mills and creates disposal and pollution problems. It is reported that about 30 million tons of rice husk per annum is produced in India. Therefore, an efficient utilization of RH is urgently needed. A number of papers have been published on various aspects of rice husk [1–3]. The major constituents of rice husk are cellulose, lignin and ash [3]. The chemical constituents are found to vary from sample to sample which may be due to the different geographical conditions, type of paddy, climatic variation, soil chemistry and fertilizers used in the paddy growth. The silicon atoms are concentrated in the protuberances and hairs on the outer and inner epidermis of the husk [4]. Formation of reactive silica by burning rice husk is a simple process compared to the conventional technique for its production. Thus, any process to produce this silica has the benefit of not only getting valuable material but also of reducing disposal and pollution problems of the husk.

A review article on the processing, properties and applications of reactive silica from rice husk has been recently published from our laboratory [5]. The rice husk ash is used as a good pozzolana in cement industry [6–8] and also as a support material for metal catalysts. Preparation of different value added products like SiC, porous carbon, zeolites, cordierite, etc from rice husk ash has been reported [10–17]. It has extensive uses as filler, additive, abrasive, oil adsorbent, sweeping component, suspension agent for porcelain enamels etc. It is also used for soil treatment, water purification, glazing pottery ware, in ceramics and

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Figure 1 Geographical map of India.

refractory materials, making special quality bricks etc. [18–22]. Each application requires specific properties such as reactivity for cement and concrete, chemical purity for synthesizing advanced materials, whiteness and proper particle size for filler applications and high surface area and porosity for adsorption and catalytic properties.

Generally, white color is preferred for silica in most of the filler applications. However, measurement of optical properties such as brightness, whiteness, color values etc. is essential to quantify the color of the material. Brightness, whiteness, yellowness and *Lab* color values (expressed in ISO units) constitute the important optical properties which are stringent for white pigments. Brightness represents the % of reflectance of light at a wavelength of 457 nm and the difference in reflectance values at 457 and 570 nm gives the yellowness. Hunter whiteness and yellowness indices have the advantage of single number quantities that are based on the entire visible spectrum. The whiteness formula relates better to people's visual assessment than brightness whereas yellowness indices normally do not correlate well with the visual judgment of yellowness. The *Lab* system based on the color opposites gives a better representation of the colors. The term L is a measure of lightness/darkness and varies from 100 for perfect white to 0 for absolute black. The red/green color is indicated by a. The more positive is its value, greater is the reddishness and negative value indicating greenishness. Similarly, the yellow/blue shade is represented by b, positive value for yellow and negative for blue. The rice husk ash is slightly colored due to the presence of carbon and other metallic impurities. The formation of black particles during the combustion of rice husk is studied by Krishna Rao *et al*. [23, 24]. The effect of treating the husk with dil.HCl on the formation of black particles has been recently reported by him. Sidheswaran *et al*. prepared pure white amorphous silica by pre treating the husk with HNO_3 followed by ashing and measured the whiteness using a color scanner [25]. However, no systematic study has been reported on the optical properties of rice husk ash.

Amorphous silica of high purity, small particle size and high surface area has tremendous potential as an adsorbent and catalyst/support in fine chemical synthesis. In order to prepare amorphous silica of high purity, treatment of the husk with chemicals before and after combustion was attempted by various researchers. Mineral acid leaching of rice husk is reported by Chakraverty *et al*. [26]. They have used acids like HCl, H_2SO_4, and HNO_3 of varying concentrations. They studied the effect of various acid treatments on the removal of metallic ingredients and reported that leaching with 1N HCl is highly effective. Yalcin *et al*. have described pre and post treatments of husk using HCl, H_2SO_4 and NaOH [27]. Chemical treatment before combustion was found to be more advantageous. Even though a number of papers have been published on

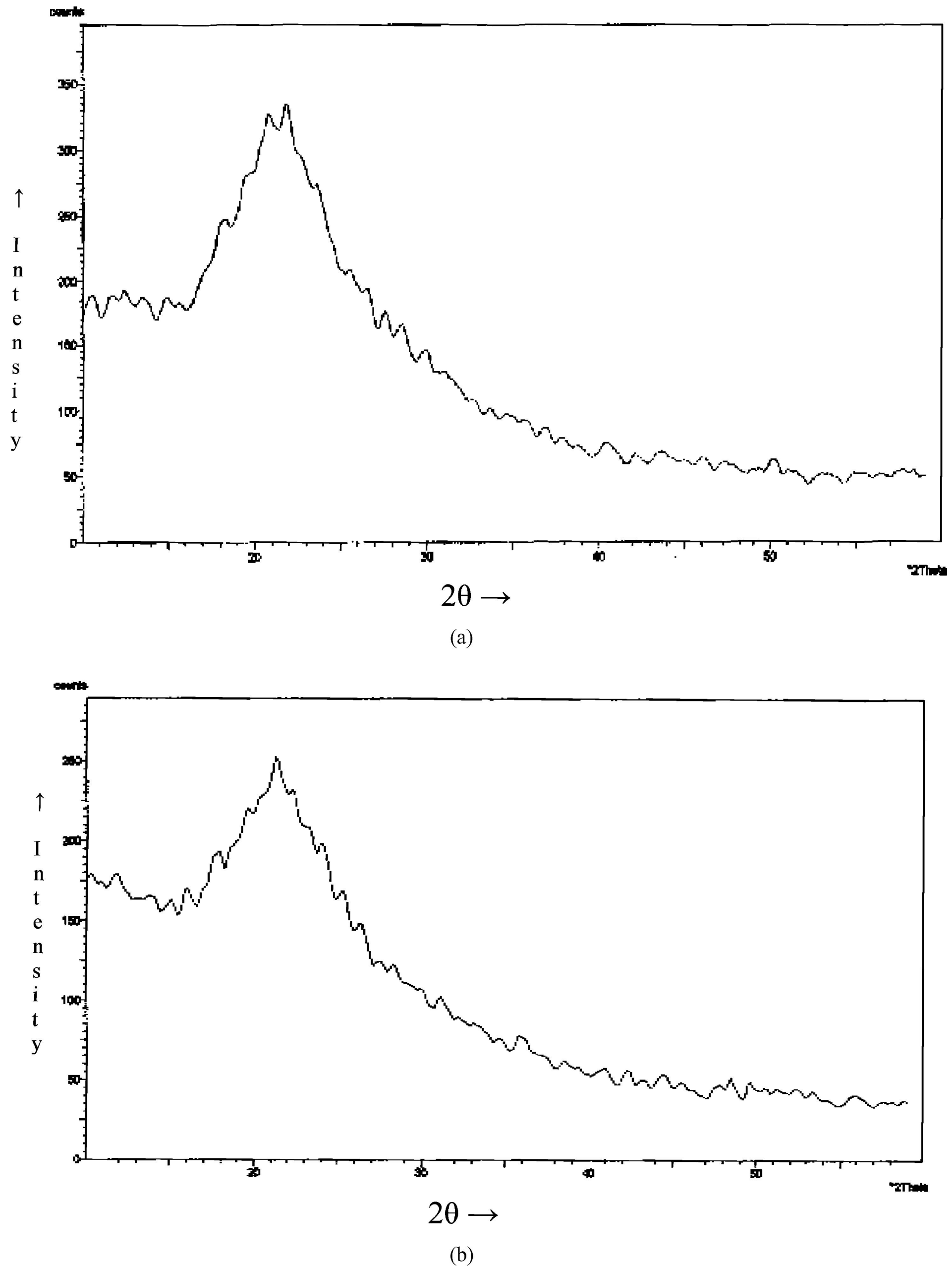


Figure 2 X-ray diffraction (XRD) patterns of (a) APRH and (b) KRH.

the leaching of rice husk with mineral acids, treatment with organic acids has not been reported so far.

The present work involves the following studies:

1. Collection of two rice husk samples from different geographical regions and their leaching with organic and mineral acids of varying concentrations
2. Thermal treatment of the husk before and after acid treatment under controlled conditions to produce the ash
3. Characterization of the ash samples for their chemical, physical and optical properties and
4. Comparative study with respect to the origin of the husks and type and concentration of the acids.

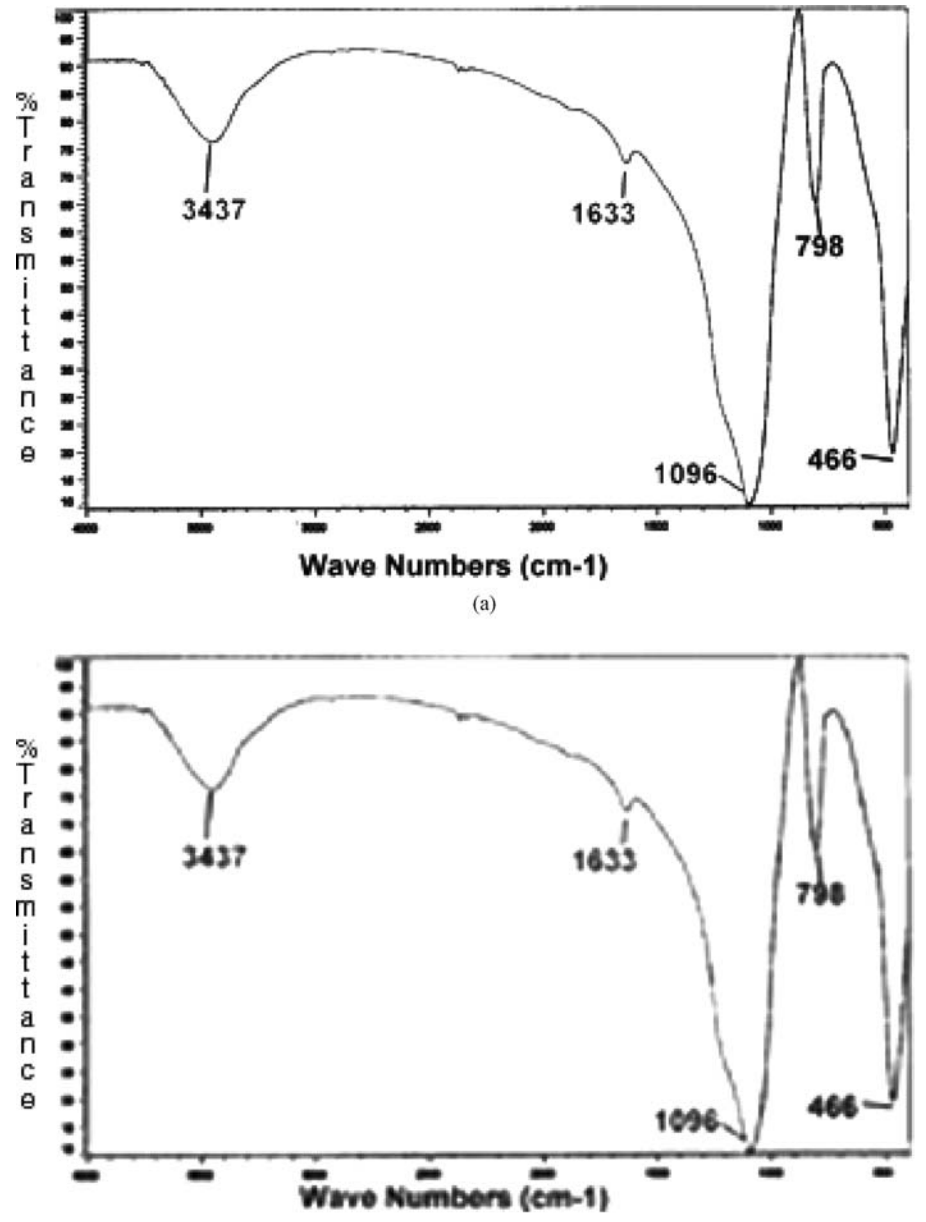
2. Experimental

2.1. Raw material

Rice husk samples for the present study have been procured from the states of Kalady (∼10°N of equator and 77° East of Greenwich), Kerala and Vijayavada (∼79° North of equator & 15° East of Greenwich), Andhra Pradesh of India. The geographical locations are given in Fig. 1. AR grade acids are used for leaching the husks.

2.2. Thermal and acid treatments

The RH samples were taken in silica crucibles and heated in a programmable furnace at a rate of 5°C per minute to 700°C and soaked for 2 h at this temperature [28]. The husk samples were separately treated with acetic, oxalic, hydrochloric and nitric acids of different concentrations. About 50 g of rice husk was added to 500 ml of the acid and boiled for nearly 90 min with frequent stirring. It was cooled and kept intact for ∼20 h. The supernatant liquid was decanted and the sample was washed thoroughly with distilled water till free from acid (pH neutral). It was dried at 110°C and



(a)

(b)

Figure 3 Infrared (IR) spectrum of (a) APRH and (b) KRH.

burned to ash in a muffle furnace under same conditions as mentioned earlier. The husks were also treated similarly with distilled water and ash was prepared.

2.3. Characterization

X-ray diffraction patterns of the ash samples were taken using a Philips X-ray diffractometer (model PW1710) with Cu K_α radiation and Ni filter. The powder sample for the XRD was prepared by putting a thin layer of powder smeared over a glass plate. The glass plate was previously coated with paraffin wax to get good adhesion. The XRD analysis was carried out at a voltage of 40 kV and 30 mA current intensity. The 2q step was 0.06 and the step time was 40 sec/step. The IR spectra were taken using KBr pellet method. About 1 mg of substance and 100–200 mg of KBr were ground together finely, dried to remove moisture and pressed to get pellets. The IR spectra were scanned in the range 400–4000 cm$^{-1.}$ A Perkin Elmer 882 IR spectrometer was used to scan the IR spectra. The morphology was examined by a scanning electron microscope, JEOL JSM 5600LV. In the Scanning Electrom Micrograph, the electron gun is operated at electron energy of 20 keV with a beam diameter of 20–25 nm. The surface of the sample is coated with a thin gold film of 10–20 nm thick by sputtering.

The ash samples prepared at different conditions were examined for their color by measuring the optical properties such as brightness, color values and whiteness using a Colour Touch^{TM} model ISO Spectrophotometer (Technidyne Corporation, USA). The sample was dried in an air oven at 110°C for one hour, cooled and pulverized for 10 s using an Anglo Pulveriser. It was then made into a pellet by applying a pressure of 55 Kg for 30 s in a Powder Press Apparatus. Then the pelletised sample was introduced into the instrument and the measurements were taken.

Standard wet chemical methods supported with instrumental techniques were adopted to determine the chemical constituents. SiO_2 was estimated gravimetrically by HF evaporation method, Na_2O and K_2O by

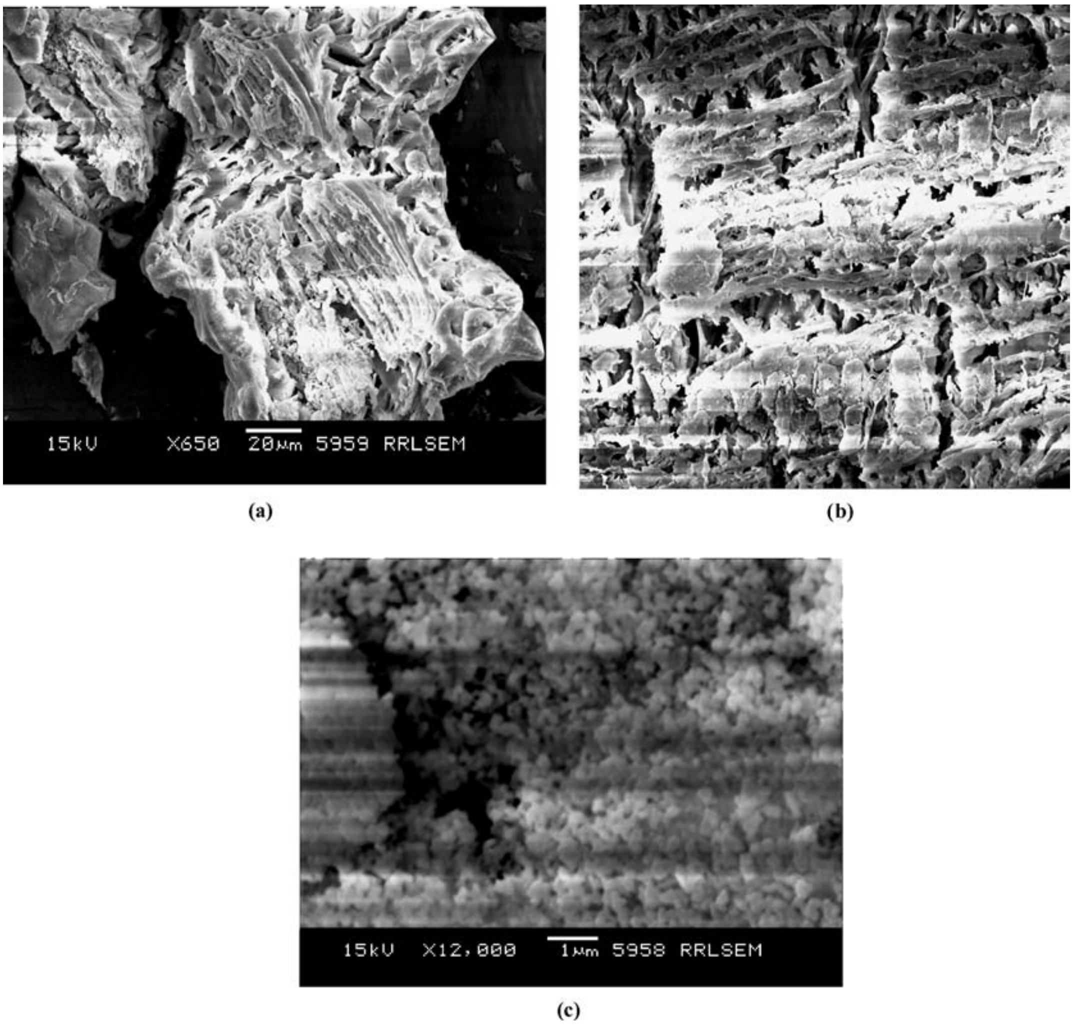


Figure 4 Scanning Electron Micrographs (SEM) of (a) APRH, (b) KRH and (c) particles in KRH.

flame photometer (Systronics 128), Fe_2O_3 by colorimetry using a UV-Visible spectrophotometer (Jenway, UK) and other trace elements by atomic absorption spectrometer (Model A Analyst 100). Carbon content in selected samples was determined using carbon sulphur analyzer (Advance research instruments Model C & S) by heating the sample to 1100°C in air and measuring the CO_2 evolved. A reference material with 1% C was used as the standard.

The reactivity of the ash was determined by chemical method [29]. Known amount of the sample was treated with saturated Ca $(OH)_2$ solution which reacted with the silica. The unused Ca was estimated by complexometric titrations. The drop in Ca ion concentration in the solution corresponds to the calcium, which reacted with the silica in the rice husk ash. The lime reactivity was calculated from the difference in Ca concentration before and after treatment with the ash and is expressed as mg CaO/g of the ash. The surface area and pore volume were measured by BET nitrogen adsorption method at -196°C using Micromeritics Flow Prep 060 model surface area analyzer.

2.4. Black particles in APRH

In spite of the presence of black particles, the analysis results showed a very low value of carbon in APRH ash. The sample was first treated with alkali and then with acid to remove the silica and any possible glass coating on the surface of carbon particles. The residue after filtration and washing was heated and all black particles disappeared leaving behind a white product.

3. Results and discussions

Optimization of time, temperature for getting reactive silica from KRH has been reported in our earlier publication [28]. The APRH and KRH have ash content of 17.65 and 19.25% respectively. The color of APRH ash is blackish whereas that of the KRH is light pink. Black particles were observed in the APRH ash irrespective of the temperature and time of ashing. The XRD patterns of both the ash samples (Fig. 2) confirm the amorphous nature and no peak corresponding to carbon was observed unlike reported recently [11]. The IR spectra (Fig. 3) give typical bands of O–Si–O stretching (at 1096vs and 798 s cm^{-}) and bending vibrations (at 466 vs cm^{-}). The bands at 3437 and 1633 cm^{-1} correspond to the O–H vibrations. No carbon compounds were detected and IR spectra of both ash samples were almost identical. Fig. 4a represents the SEM picture of APRH ash and 4b and c of KRH ash samples. The rice husk skeleton remains almost intact with some porosity in both samples (Figs. 4a and b). APRH ash appears to have more fused matter and less porosity (Fig. 4a). Small particles are found embedded on to the skeletal

TABLE I Chemical analysis Andhra Pradesh rice husk ash (wt% and wt ppm)

	LOI ± 0.5%	SiO_2 ± 0.01%	Na_2O ± 0.1%	K_2O ± 0.1%	Fe_2O_3 ± 0.1%	CaO ± 0.1%	MgO ± 0.1%	Zn ± 2 ppm	Mn ± 2 ppm	Cu ± 2 ppm	Cd ± 0.01 ppm
Raw ash	1.85	88.47	0.2670	2.5065	0.4065	1.8015	0.7145	32.28	56.44	16.98	0.4952
Dw	2.17	94.76	0.1446	0.5878	0.2145	1.6445	0.6065	15.31	48.87	14.87	0.3901
0.01HCl	2.51	95.35	0.0130	0.0466	0.1509	1.5478	0.3765	16.90	11.80	12.67	0.4830
0.1HCl	2.10	97.49	0.0525	0.0587	0.1491	0.9435	0.3393	22.01	3.31	10.87	0.1948
1HCl	1.93	95.49	0.1180	0.1163	0.3211	0.6617	0.3520	19.11	7.63	9.07	0.2896
0.01HNO_3	2.81	95.29	0.1303	0.2566	0.2098	1.4680	0.5773	22.62	39.65	7.35	0.3868
0.1HNO_3	3.42	95.83	0.3217	0.2654	0.1341	1.4571	0.6393	17.44	41.72	14.68	0.4832
1HNO_3	1.85	97.80	0.0790	0.0589	0.0953	0.7285	0.3665	10.95	3.62	8.31	0.2933
0.1Ac	2.36	95.58	0.0395	0.1414	0.3570	0.7501	0.3363	18.77	17.67	14.55	0.1955
1Ac	2.64	95.80	0.0778	0.2437	0.3180	0.9357	0.2772	11.36	7.70	14.90	0.2889
5Ac	2.38	95.96	0.0387	0.1269	0.2115	0.7361	0.2666	10.35	4.69	6.04	0.1916
0.1Ox	2.71	94.42	0.0393	0.0468	0.2279	0.9528	0.2259	8.74	12.26	14.11	0.4850
1 Ox	2.63	93.00	0.4043	0.2698	0.3235	1.3724	0.3883	2.34	7.01	16.46	0.4868
Sat Ox	2.14	95.47	0.1793	0.3018	0.2705	1.5560	0.5657	10.32	14.29	9.22	0.4006

LOI-Loss on Ignition, Ac-Acetic acid, Ox – Oxalic acid, Sat ox – saturated oxalic acid, Dw – Distilled water.

TABLE II. Chemical analysis Kerala rice husk ash (wt% and wt ppm)

	LOI ± 0.5%	SiO_2 ± 0.01%	Na_2O ± 0.1%	K_2O ± 0.1%	Fe_2O_3 ± 0.1%	CaO ± 0.1%	MgO ± 0.1%	Zn ± 2 ppm	Mn ± 2 ppm	Cu ± 2 ppm	Cd ± 0.01 ppm
Raw ash	2.51	94.64	0.3926	0.5850	0.2350	1.8988	0.9645	18.20	52.24	32.17	0.4855
Dw	2.51	95.04	0.3414	0.2395	0.1894	1.6192	0.7794	6.07	32.15	20.78	0.4017
0.01HCl	3.73	95.34	0.2949	0.0879	0.0384	0.6459	0.7713	11.85	23.88	15.31	0.3639
0.1HCl	3.42	95.52	0.2340	0.0233	0.0160	0.8883	0.2711	4.73	4.25	10.92	0.3863
1HCl	3.44	95.70	0.2852	0.0463	0.0335	0.7098	0.6816	12.70	4.81	23.66	0.4799
$0.01HNO_3$	3.48	95.22	0.0943	0.0632	0.1251	0.6840	0.4133	10.67	21.24	17.66	0.4102
$0.1HNO_3$	3.54	95.48	0.1420	0.0231	0.1518	0.7629	0.6237	18.59	1.82	13.12	0.4794
$1HNO_3$	2.84	94.11	0.3063	0.0456	0.1672	0.6161	0.2006	3.60	0.38	9.28	0.4712
0.1Ac	3.33	95.00	0.2540	0.0524	0.1578	0.4461	0.4323	10.44	15.47	9.68	0.4824
1Ac	2.09	96.68	0.2087	0.0488	0.1686	0.4249	0.4095	8.74	9.12	10.99	0.4730
5Ac	2.98	95.61	0.2630	0.0486	0.0979	0.5406	0.4380	9.04	8.95	9.82	0.4763
0.1Ox	3.36	94.88	0.1277	0.0685	0.0145	1.2991	0.9426	6.63	17.78	22.90	0.4813
1 Ox	4.58	94.84	0.0257	0.0344	0.0694	0.8194	0.5922	2.29	5.14	8.19	0.3809
Sat Ox	3.51	94.91	0.0954	0.0426	0.0159	0.4460	0.9116	4.25	1.24	5.67	0.4391

LOI—Loss on Ignition, Ac—acetic acid, Ox—Oxalic acid, Sat ox—saturated oxalic acid, Dw—Distilled water.

TABLE III Estimation of carbon in rice husk ash samples

	Sample	% Carbon (± 0.1 Wt%)
1	KRH 500°C, 2 h	3.45
2	KRH 700°C, 2 h	BDL
3	APRH 700°C, 2 h	0.23

BDL—Below detectable limit.

structure of KRH ash (Fig. 4c). In APRH ash, such particles are absent which may be due to the agglomeration.

3.1. Chemical composition

The percentage of major and trace elements in the APRH and KRH ash are given in Tables I and II respectively. The APRH ash contains only 88.47% silica whereas the KRH ash has 94.64%. Minor constituents such as K_2O, Fe_2O_3 and zinc are higher in APRH and others slightly less or almost same as those in KRH. These impurities along with the black particles of carbon are attributing to the lower silica content of APRH. Table III gives the carbon content of selected samples. The KRH ash prepared at 500°C (1 h) contains visible black particles and the carbon content was found to be ∼3.5%. The black particles disappeared on heating to 700°C (1 h) and carbon in the product was below detectable limit confirming the carbonaceous nature of the impurity. On the contrary, the analysis of APRH ash prepared at 700°C gave only 0.23% carbon in spite of the visible black particles. The loss on ignition (LOI) was also less than that of KRH ash where black particles are not found. This clearly shows that carbon is retained in the APRH ash in such a form that heating to higher temperatures does not remove it. When the ash was treated with hot alkali and then with hot acid, part of the ash dissolved and the black particles remained intact. Black color of this residue disappeared completely on heating. The siliceous material is dissolving in the hot alkali and the other metallic impurities in acid leaving behind the carbonaceous residue which gets burned off on heating. Thus it can be confirmed that the black particles in APRH are those of carbon.

It is reported that porous or activated carbon can be produced by heating rice husk at a relatively lower temperature in presence of "chemical activators" such as KOH, K_2CO_3, and Na_2CO_3. In carbonization process, these chemicals function as dehydrating agents and inhibit the formation of tar [14]. The evolution of

TABLE IV Optical properties of rice husk ash samples

		B,%ISO	*L*	*A*	*B*	Hw	Hy	% increase in brightness	Visual color
a. HCl treatment									
APRH	Raw ash	32.13	55.48	0.60	−1.82	36.54	−4.68		blackish
	Dw	53.36	74.32	0.51	1.79	47.63	3.44	66.08	dull-white
	0.01 N HCl	54.69	75.84	0.83	2.64	46.08	4.97	70.87	white
	0.1 N HCl	63.31	80.84	0.28	1.8	57.02	3.19	97.04	white
	1 N HCl	51.26	75.69	1.27	5.68	32.74	10.71	59.54	white
KRH	Raw ash	56.13	77.77	1.04	4.00	42.70	7.35		dull-white
	Dw	57.21	78.97	1.09	4.65	41.37	8.42	1.92	white
	0.01 N HCl	60.50	80.27	0.21	3.51	48.34	6.24	7.79	white
	0.1 N HCl	70.36	85.65	0.26	2.52	61.03	4.20	25.35	white
	1 N HCl	57.42	78.70	0.33	4.13	43.38	7.49	2.30	white
b. HNO_3 treatment									
APRH	Raw ash	32.13	55.48	0.60	−1.82	36.54	−4.68		blackish
	0.01 N HNO_3	56.43	76.68	0.49	2.20	49.18	4.09	75.63	Pinkish dull white
	0.1 N HNO_3	65.16	82.56	0.61	2.63	55.78	4.54	102.8	Pinkish dull white
	1 N HNO_3	60.61	79.96	0.70	2.96	50.40	5.29	88.64	Pinkish dull white
KRH	Raw ash	56.13	77.77	1.04	4.00	42.70	7.35		Dull white
	0.01 N HNO_3	59.83	79.93	0.53	3.63	47.30	6.49	6.59	Pinkish white
	0.1 N HNO_3	67.38	83.87	0.27	2.54	58.16	4.33	20.04	Pinkish white
	1 N HNO_3	69.90	85.43	0.21	2.60	60.27	4.35	24.53	Pinkish white
c. Acetic acid treatment									
APRH	Raw ash	32.13	55.48	0.60	−1.82	36.54	−4.68		Blackish
	0.1 N Ac	52.63	74.64	0.58	2.98	42.99	5.71	63.80	Grey white
	1 N Ac	55.72	77.29	0.82	3.75	43.18	6.93	73.42	Grey white
	5 N Ac	56.86	77.86	0.38	2.88	47.23	5.31	76.97	Grey white
KRH	Raw ash	56.13	77.77	1.04	4.00	42.70	7.35		Dull white
	0.1 N Ac	59.82	80.76	0.96	4.78	43.15	8.46	6.57	Dull white
	1 N Ac	57.71	77.86	0.19	2.76	48.37	5.07	2.82	Off white
	5 N Ac	63.03	83.04	0.98	5.12	44.66	8.81	12.29	Dull white
d. Oxalic acid treatment									
APRH	Raw ash	32.13	55.48	0.60	−1.82	36.54	−4.68		Blackish
	0.1NO*x*	61.76	81.44	0.37	4.04	47.51	7.09	92.22	Off white
	1NO*x*	54.82	76.21	0.22	3.11	44.52	5.84	70.62	Grey white
	Sat O*x*	61.83	79.45	−0.01	1.19	57.73	2.14	92.44	Off white
KRH	Raw ash	56.13	77.77	1.04	4.00	42.70	7.35		Dull white
	0.1NO*x*	59.08	78.54	−0.13	2.43	50.77	4.42	5.26	Off white
	1NO*x*	66.06	82.23	−0.17	1.39	61.09	2.42	17.69	Off white
	Sat O*x*	72.73	86.18	−0.04	1.31	67.81	2.17	29.57	Off white

Dw – distilled water; Ac – Acetic acid; Ox – Oxalic acid; Sat Ox – Saturated oxalic acid solution.

chemical morphology during carbonization and combustion of rice husk has been recently reported by Liou [12]. Out of the two rice husk samples, APRH contains a high percentage of K_2O which may act as the "activator" during the combustion. Another explanation for the presence of carbon particles is given by Krishna Rao *et al*. [11]. The K_2O in the rice husk dissociates on heating at ~620 K to form elemental potassium which causes surface melting. The carbon gets entrapped in this melt and loses direct contact with air which prevents its oxidation on further heating. Effect of mineral acid treatment, temperature and heating rate on the formation of carbon fixed particles has been studied in detail [11]. The present study also supports the fact that treatment of rice husk with organic acid and mineral acids followed by heating reduces the carbon content in the ash. The absence of black carbon particles in the KRH ash even before acid treatment may be due to the low alkali content. When the RH is treated with HCl (other acids), K^+ ions present in the husk is leached out. The K^+ ions are responsible for the fixed carbon in the ash due to surface melting. HCl is the strongest among the acids we tried. So it is found to be more effective than other acids in the removal of K^+ ions; hence the minimum carbon in the HCl treated ash [11].

The two husk samples have been treated with distilled water, organic acids such as acetic and oxalic and mineral acids like hydrochloric and nitric of different concentrations. The chemical constituents of the ash obtained from the treated APRH and KRH samples are given in Tables I and II respectively. In the case of APRH, water washing brings down most of the metallic constituents to a certain extent with a simultaneous increase in the silica content. Treatment with hydrochloric acid reduces the metal ions more effectively. A concentration of 0.1 N seems to optimum for getting maximum removal of K_2O, Fe_2O_3 and Zn whereas higher concentration is needed to remove Na, Ca, Mn, Cu and Cd. Nitric acid is less effective compared to hydrochloric acid. Both oxalic and acetic acids remove all the metallic ions to a great extent, but slightly less effective than hydrochloric acid. For Na, K and Ca, a concentration of 0.1 N seems to be the optimum whereas other metal ions need a higher concentration.

In KRH also, water washing removes most of the impurities to a certain extent. However, the silica% does not change much (like in APRH) which can be attributed to the absence of carbon particles. Hydrochloric acid treatment reduces the impurities and 0.1 N seems to be optimum for removing Na, K, Fe, Zn, Mn, Cu and Cd. Nitric and acetic acids also show similar behavior unlike in APRH. Oxalic acid brings down the Na content drastically. The Fe removal by oxalic acid is also very effective similar to hydrochloric acid and better than nitric and acetic acids. The overall effect of oxalic acid in removing the metal ions is found to be better compared to acetic acid.

3.2. Optical properties

Table IVa–d gives the optical properties of the ash formed before and after the treatment of the two husk samples. The brightness of APRH ash is much lower than KRH ash. The *L* value is quite low indicating the blackish color of the ash which can be attributed to the carbon content in the sample. Water washing of husk improves the brightness and *L* value of the ash significantly. This is because of the removal of K_2O and subsequent reduction in carbon content. The color values a, b and HY are found to be less significant compared to the *L* value. During acid treatment, considerable improvement is achieved with acid concentrations 0.1 N HCl and HNO_3, 5N acetic acid and saturated oxalic acid. The maximum brightness achieved for APRH ash is 65.16 by 0.1 N HNO_3 treatment which is more than double of the ash obtained without any treatment.

The brightness improvement in KRH ash with respect to concentration of the leaching acid is considerable for 0.1N HCl and HNO_3, 5N acetic acid and saturated oxalic acid out of which the maximum value is achieved with saturated oxalic acid leaching.

3.3. Reactivity

The chemical reactivity of rice husk silica is determined by treating with slaked lime, $Ca(OH)_2$ solution and hence termed as lime reactivity [29]. The amount of Ca which reacts with silica is directly related to the reactivity and it has been established that at higher temperatures and soaking times, crystobalite (crystalline form of silica) is formed which has very low lime reactivity [29]. Fig. 5 shows the values for the two ash samples and acid treated products. The lime reactivity of APRH ash is much lower than that of KRH ash. Reactivity of the silica/ash can vary due to sintering effects or phase transitions. The minor constituents in husk act as inhibitors when subjected to ashing at higher temperatures [29]. The presence of higher amounts of alkalis in APRH may be attributing to this phenomenon. However, acid treatment followed by ashing gives samples with much higher values of reactivity. Among the acids, HNO_3 is found to be the best at 0.1 N concentration. HCl and oxalic acids of same normality also give nearer values. The KRH ash has good reactivity and acid treatment improves the values further. Maximum improvement is achieved by treatment with 0.1 N HNO_3 with close values of samples obtained after treatment with 0.1 N HCl, 1 N acetic acid and 0.1 N oxalic acid.

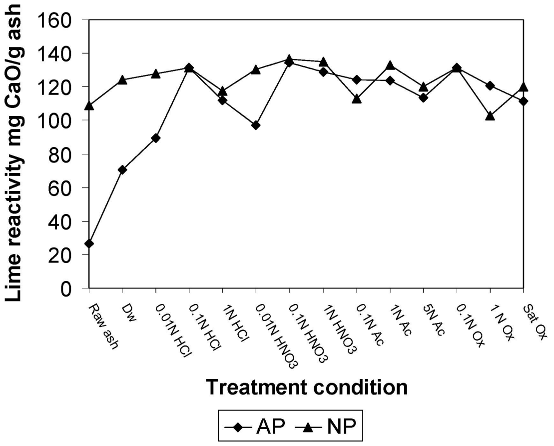


Figure 5 Lime reactivities of the rice husk ashes.

TABLE V Surface area and Pore Volume of selected rice husk ash samples

Ash samples	Surface area (m^2/g)	Pore volume (cc/g)	Sample	Surface area (m^2/g)	Pore volume (cc/g)
APRH	8.87	0.0043	KRH	149.75	0.0540
APRH 0.1 N HCl	220.54	0.0988	KRH 0.1HCl	259.50	0.1181
APRH 0.1 N HNO_3	216.62	0.0986	KRH 0.1HNO_3	216.62	0.0980
APRH 1 N Ac	193.43	0.0901	KRH 1NAc	215.34	0.1031
APRH 0.1 N Ox	166.99	0.0787	KRH 0.1NOx	270.50	0.0904

Ac – Acetic acid; Ox – Oxalic acid.

3.4. Surface area and pore volume

The important characteristics of adsorbents are surface area and pore volume. Adsorption has been considered as an important method of separation and involves the preferential partitioning of substances from the gaseous or liquid phase onto the surface of a solid substrate. Activated carbon, zeolites, silica etc are some of the common adsorbents. Selected ash samples were analyzed for these properties and the values are given in Table V. The reactivity of silica is directly related to the amorphous nature and surface area. The APRH ash has very low values and acid treatment is found to increase these properties drastically. HCl treatment gives maximum improvement. The KRH ash has much higher values and after acid treatment, achieves values similar to those of acid treated APRH ash. However, oxalic acid treatment gave sample with highest surface area. The pore volume also has a similar trend. APRH ash has a very low value compared to KRH ash. A 20 fold increase in pore volume is observed for APRH on acid treatment whereas only a 2 fold increase is found for KRH.

4. Conclusions

1. Thermal treatment of rice husk samples from Andhra Pradesh and Kerala states under controlled conditions gave 17.65 and 19.25% ash respectively and the chemical compositions were found to be different.
2. The husks on leaching with acetic and oxalic acids of different concentrations followed by thermal treatment resulted in products with improved properties like purity, reactivity, brightness, surface area and pore volume.
3. The leaching with mineral acids like HCl and HNO_3 of different concentrations followed by thermal treatment and measurement of properties showed that the organic acid treatment is almost equally effective in improving the silica properties.
4. The properties indicate that the product silica can be used as adsorbents and filler material

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