

## Effect of Silica Extraction on the Porous Structure and Surface Area of Activated Carbon Prepared from Rice Wastes

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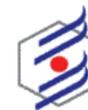
### Abstract

The present work is based on the possibility of the simultaneous extraction of silica and activated carbon as two value-added chemical products from rice wastes (straw and husk). The purpose of this work is to study the effects of silica impurities of the raw materials on the properties of the produced activated carbon. It was found that silica extraction after activation of the raw materials through the presented procedure could be beneficial for improving the porosity of the activated carbon. Chemical activation of rice wastes ash was carried out using KOH at the impregnation ratio of 0.5 under activation temperature of 800 °C for 1 h. In order to silica extraction, activation experiments were followed by an additional step: exposing the activated ash to reflux treatment in the presence of hydrochloric acid. The percentages of silica extraction from rice husk- and rice straw-based activated carbon under the certain operating conditions were 66 and 83%, respectively. In both cases, silica elimination from the activated ash increased the specific surface area of active carbons (from 521 to 947 m<sup>2</sup>/g for rice husk-based and from 499 to 1252 m<sup>2</sup>/g for rice straw-based activated carbon).

**Keywords:** Rice straw, Rice husk, Activated carbon, Silica, Chemical activation, Extraction

### Introduction

Annually about 2.4 million tons of rice are produced in Iran, mostly are grown in the northern regions including Guilan and Mazandaran provinces [1]. Lack of attention to the management of the huge amounts of rice wastes has made farmers to burn this valuable biomass in an uncontrolled manner. This phenomenon leads to many undesirable problems, such as increasing environmental pollution and consequently, cardiovascular and pulmonary diseases, in addition, the loss of useful microorganisms of soil [2]. One of the strategies for organizing carbon-rich agricultural wastes such as rice straw and rice husk is to convert them into a kind of low-cost carbonaceous adsorbent, which can compete with commercially activated carbon [3]. In 2006, Balathanigaimani et al. used a very high surface area carbonaceous adsorbent prepared from rice husk activated with KOH at 800 °C for methane storage in the Advanced Natural Gas (ANG) technology [4]. Elemental analysis of rice waste indicates the presence of silica in the composition of these materials, and so in some cases these materials are used as a source for silica extraction. In a few cases, the simultaneous extraction of silica and activated



carbon from rice husk has been reported. An et al. (2011) used the pyrolyzed rice husk for the production of silica and activated carbon. The produced activated carbon was a combined microporous/mesoporous material with the total pore volume, BET specific surface area, and iodine number of 1.22 cm<sup>3</sup>/g, 1362.62 m<sup>2</sup>/g and 1259.06 mg/g, respectively [5]. The present study specifically investigates the effect of silica extraction on the porous properties of rice wastes-based activated carbons. The procedure presented in this work has not been tested before for silica extraction from rice straws.

## **Experimental**

### **Activated carbon and silica extraction**

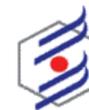
Rice straw and rice husk collected from paddy fields of Guilan province (County around Fouman). After washing and drying (and chipping into small size fibers for rice straw), the raw materials were converted into ash by burning in the presence of inert gas in a horizontal split furnace. The procedure of simultaneous extraction of silica and activated carbon involves the following main steps: (1) 10 g ash was first added into 100 ml hydrochloric acid solution (1 M) and the mixture was heated for 2 h at 75 °C, (2) the remaining solid was washed several times with hot distilled water. This process, known as acidic pretreatment, leads to silica with higher purity.

Based on the previous studies and satisfying performance of KOH as the chemical agent [6], this material was used to activate the samples in the present work. 10 g of the acid pretreated ash was impregnated with KOH solution (4 M) at a ratio of 0.5 (Equation 1), followed by oven-drying to evaporate the excess water. The solid was then collected in boats in a tube furnace and the temperature increased with the rate of 5 °C/min to reach the final value of 800 °C. The samples remained at the final temperature for 1 h under the presence of inert gas.

$$\text{Impregnation ratio} = \frac{\text{Weight of KOH powder}}{\text{Weight of rice waste ash}} \quad (1)$$

The solid outlet was put into a flask and 15 cm<sup>3</sup> of distilled water was added per gram of solid. The resulting solution was boiled and refluxed at 90 °C for 2 h, while it was thoroughly stirring. Moreover, the reflux suspension was filtered and the residual solid (activated carbon) was washed with acid in the first step, then washing procedure was continued with distilled water. In order to extract the silica from the filtrate solution, it was put into a double-necked flask under reflux at 90 °C and stirring for 2 h. To precipitate the silica during the reflux process, the solution was titrated via a certain volume of HCl. After the reflux process, the produced silica was kept at room temperature for 3 h (aging procedure), followed by washing with hot distilled water several times to remove any activating agent. Finally, the remaining solid (silica) was dried in the oven. The operating parameters have been used in the present work were selected based on literature [6,7,8] and adjusted via the preliminary tests.

Activated carbon samples extracted from rice straw and rice husk with silica extraction are indicated by RS-SiEx-AC and RH-SiEx-AC, respectively, in the contrary, for the activated carbons obtained without silica extraction, the terms RS-AC and RH-AC are used. Silica samples from rice straw and rice husk are also named with RS-Si and RH-Si, respectively.



### Characterization

To determine the properties of the raw materials used, the carbonaceous adsorbents and the silica extracted in the present work, a series of characterization tests was applied as follows; XRF analysis was performed on the silica samples to determine their purity and the extraction percentages. To specify the effect of silica extraction on the specific surface area and porosity properties of the activated carbons from rice wastes, nitrogen adsorption/desorption analysis at 77 K was performed in the BELSORB MINI II machine. The BET, BJH and HK equations were used to find out the specific surface area, meso- and micro-porous properties, respectively. In addition, X-ray diffraction analysis (XRD, PHILIPS-PW1730) was used to determine the structure and phase of silica and activated carbon samples. To identify the functional group of the samples, the FTIR spectroscopy was carried out by the device (FTIR, Jasco-4600) in the range wavenumbers of 400-4000  $\text{cm}^{-1}$ .

### Results and discussion

The nitrogen adsorption-desorption isotherms at 77 K for the activated carbon samples are shown in Fig. 1 (a). The high initial slope of the isotherms at low relative pressures indicates the high volume of micropores in the structure of activated carbons. At slightly higher relative pressures, there is an inflection point in all isotherms where the curvature changes; this point indicates the completion of monolayer adsorption and the start of multilayer adsorption. At moderate to high relative pressures, hysteresis loop is also appeared for all isotherms, which represents the presence of mesopores in the porous structure of the adsorbents and the role of capillary condensation mechanism in nitrogen adsorption. Based on Fig. 1 (a), the specific surface area and pore volume of adsorbent samples prepared without silica extraction (RH-AC and RS-AC) were almost the same and limited; while the process of silica extraction from the activated solid led to porosity development and surface increasing. This increase was higher for the RS-based activated carbon rather than the RH-based one, might be the consequence of the higher percentage of silica extraction from rice straw (83%) compared to rice husk (66%) under the operating conditions used.

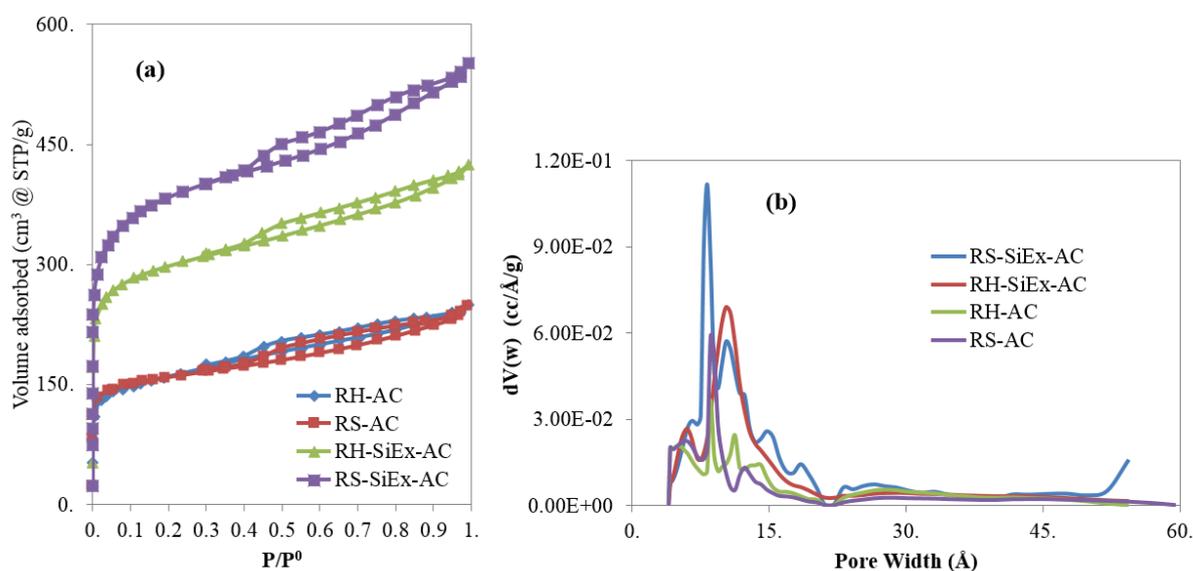
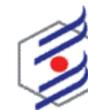


Fig. 1 (a) Nitrogen adsorption-desorption isotherms at 77 K for the produced activated carbons from rice wastes with silica extraction and without silica extraction; (b) DFT pore size distribution of the samples



The most important porous properties of the activated carbons are shown in Table 1. As it can be observed, rice straw-based activated carbons have higher surface area than the rice husk-based ones. The higher percentage of impurities and more rigid structure of RH may be the reason of its larger resistance against activation under the same operating conditions. The extraction of silica from the activated RH and RS ash resulted in a significant increase in the specific surface area, total pore volume, micro and mesopore volume of the adsorbent particles. The average pore size of the adsorbent particles was calculated with the assumption of cylindrical and parallel pores ( $d_{\text{mean}}=4V_{\text{tot}}/S_{\text{BET}}$ ); the average micro- and mesopore sizes were also calculated based on the HK and BJH (desorption branch) models. Silica extraction led to a little decrease in  $d_{\text{avg,mic}}$ ,  $d_{\text{avg,meso}}$  and  $d_{\text{mean}}$  for both samples; it means that the percentage of micropores in the total porosity of the activated carbons increased from around 61-62% for the simple ACs to about 67-69% for the silica-extracted ones. DFT pore size distribution of the samples was also calculated and is shown in Fig. 1 (b). It can be seen that the silica extracted samples are more microporous sorbents with larger pore volume for the pores smaller than 20 Å.

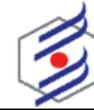
**Table 1. Specific surface area and porous properties of the activated carbons derived from rice husk and straw (with and without silica extraction)**

Sample	$S_{\text{BET}}$ (m <sup>2</sup> /g)	$V_{\text{tot}}$ (cm <sup>3</sup> /g)	$V_{\text{meso}}$ (cm <sup>3</sup> /g)	$V_{\text{mic}}$ (cm <sup>3</sup> /g)	$d_{\text{mean}}$ (Å)	$d_{\text{avg,meso}}$ (Å)	$d_{\text{avg,mic}}$ (Å)
RH-AC	521	0.3862	0.1819	0.2384	29.65	34.14	8.375
RS-AC	499.2	0.3844	0.1835	0.2390	30.80	38.23	10.33
RH-SiEx-AC	947.3	0.6564	0.2579	0.4501	27.72	34.09	6.475
RS-SiEx-AC	1252	0.8548	0.3445	0.5771	27.30	34.23	5.625

The FTIR spectra of the activated carbon samples are shown in Fig. 2 (a). The simple activated carbons especially RS-AC shows a strong peak in the region of 430-530 cm<sup>-1</sup>, which could be related to Si-O [9]. Similar peaks can also be found for the silica-extracted ACs but with lower impact. The peaks appeared at around 1074 cm<sup>-1</sup> and 1500 cm<sup>-1</sup> are respectively due to the stretching vibrations of C-O and the double bond of C=C. The mild peak at the wavenumber of 2355 cm<sup>-1</sup> indicates the presence of CO<sub>2</sub> in the samples. The peaks in the range of 3300-3800 cm<sup>-1</sup> confirm the existence of -OH containing functional groups in all the activated carbon samples.

The FTIR analysis results for the silica samples extracted from rice husk and rice straw are also shown in Fig. 2 (b). Extreme peaks were found near the wavenumbers of 430-520 cm<sup>-1</sup> and 1090 cm<sup>-1</sup> that are related to the bending and asymmetric forms of the SiO<sub>2</sub> group. The peak region of 1517 cm<sup>-1</sup> represents the dual bond of C=C in the samples. The presence of CO<sub>2</sub> in these samples was also confirmed by the small peak at 2353 cm<sup>-1</sup>. The peaks in the range of 3300-3800 cm<sup>-1</sup> indicate the presence of OH groups in silica samples [9].

The XRD patterns of the activated carbon and silica samples are shown in Fig. 3. The diffraction appeared at  $2\theta=22.5^\circ$  for the activated carbon samples (Fig. 3 (a)) is related to the presence of silica in their structures and because of the lower content of silica in the RH-SiEx-AC and RS-SiEx-AC samples, the diffraction intensity in these samples is smaller than the two other ones [10]. The diffraction at  $2\theta=44^\circ$  also represents a form of graphite in the



activated carbons samples. Fig. 3 (b) shows the XRD patterns of the silica produced from rice husk and rice straw, with an obvious diffraction at  $2\theta=22.5^\circ$ . Based on the patterns, an amorphous structure for the activated carbon and silica samples was detected [5, 6].

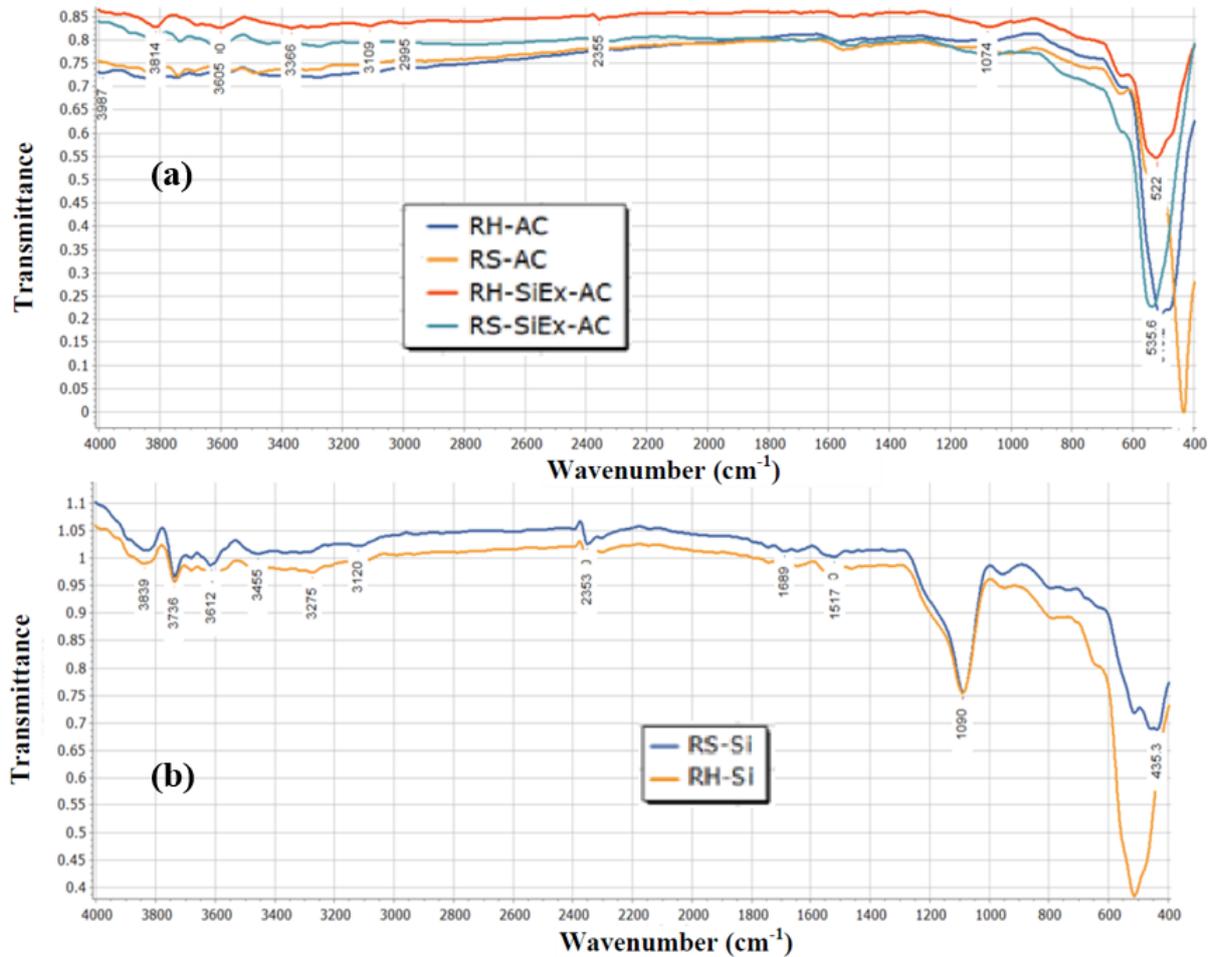


Fig. 2 FT-IR spectra of (a) activated carbons and (b) silica samples extracted from rice husk and rice straw

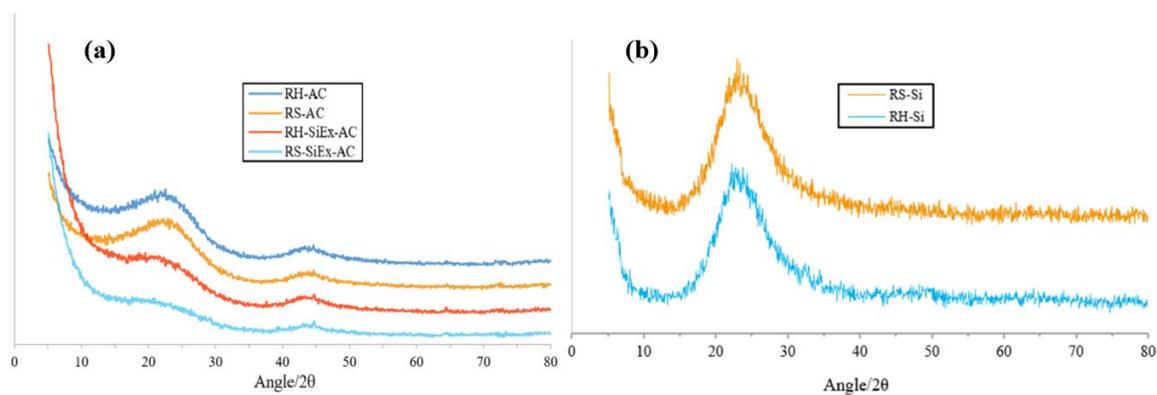
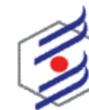


Fig. 3 XRD patterns of (a) activated carbons and (b) silica samples extracted from rice husk and rice straw



### **Conclusions**

The present study approved the negative effect of silica impurities in the structure of rice wastes on the porous properties of the activated carbons produced from. The KOH activation-silica extraction method applied in the present work under the determined operating conditions led to two kinds of valuable products: high surface area activated carbons ( $S_{\text{BET}}$ : around 1000 m<sup>2</sup>/g) and amorphous silica powders (purity: around 90%). Chemical activation was performed using KOH at 800 °C for 1 h and silica was extracted via a simple procedure by reflux of the filtrate in the presence of hydrochloric acid at 90 °C. The procedure led to better results in the case of rice straw, means that the percentage of silica extraction was higher in this case (83 %) than rice husk (66%). The larger silica content of rice husk and its more rigid structure may be the reason of larger resistance against activation/extraction under the same operating conditions.

### **Acknowledgements**

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