



A sustainable route for the preparation of activated carbon and silica from rice husk ash

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ABSTRACT

An environmentally friendly and economically effective process to produce silica and activated carbon from rice husk ash simultaneously has been developed in this study. An extraction yield of silica of 72–98% was obtained and the particle size was 40–50 nm. The microstructures of the as-obtained silica powders were characterized by X-ray diffraction (XRD) and infrared spectra (IR). The surface area, iodine number and capacitance value of activated carbon could achieve 570 m²/g, 1708 mg/g, 180 F/g, respectively. In the whole synthetic procedure, the wastewater and the carbon dioxide were collected and reutilized. The recovery rate of sodium carbonate was achieved 92.25%. The process is inexpensive, sustainable, environmentally friendly and suitable for large-scale production.

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1. Introduction

During the last two centuries, human activities such as the production and consumption of fossil fuels, as well as agricultural and industrial activities have caused an increase in the atmospheric concentration of greenhouse gases [1]. Fossil fuel shortage and energies environmental problems have created the urgency for the exploitation of clean renewable energies [2]. Therefore, many countries have put forward plans to reduce carbon dioxide emissions and energy consumption.

Biomass is one of the most promising energy-carrying agents and can play an important role in environmentally friendly energy utilization. Rice husk (RH) is an important kind of agricultural residues. It was reported that the annual output of RH of the world and China was about 80 and 40 million tons, respectively [3,4]. Most of RH is burned as fuel to generate energy resulting in the waste product, rice husk ash (RHA). If these RHA are not utilized, it will result in tremendous waste generation, energy loss and environmental pollution. Therefore, it is very important to find ways to utilize RHA comprehensively.

The main components of RHA are carbon and silica. Therefore, many studies were focused on RHA to produce silica [5–9]. At present, the main method to prepare silica in industry involves the reaction between sodium carbonate powder and quartz. The silica produced has many technological applications, such as thixotropic

agents, thermal insulators and composite fillers [10]. Activated carbon is a well-known material used in ever increasing quantities in environment protection, in wastewater treatment, in gas filters, electrode, etc. [11,12]. Although there were many reports on the preparation of activated carbon [13–16], reports on activated carbon prepared from RHA are few, and there is no reference on the preparation of silica and activated carbon simultaneously.

We have studied the preparation of rice husk-based porous carbons and the extraction of silica from RHA [17–19]. The silica produced was modified with long-chain alcohols and the reaction mechanism was proposed [20]. The adsorption of colored dyes by rice husk-based porous carbons [21–23] and the performance of electrical double layer capacitors with porous carbons derived from rice husk [24] were studied. These previous work involved the preparation activated carbon and silica separately, and lacked the comprehensive utilization of raw materials.

This study aims to develop a route (Fig. 1) which is different from previous studies for the preparation of activated carbon and silica simultaneously from RHA to achieve a green and sustainable production process. The specific procedure is discussed as follow.

2. Materials and methods

2.1. Materials

RHA was obtained from nearby power house Changchun city. Here, the RHA was the residue from pyrolysis of rice husk. In this process, the pollution-carrying residue (RHA) was utilized as material in our work. All chemical reagents were analytically pure from

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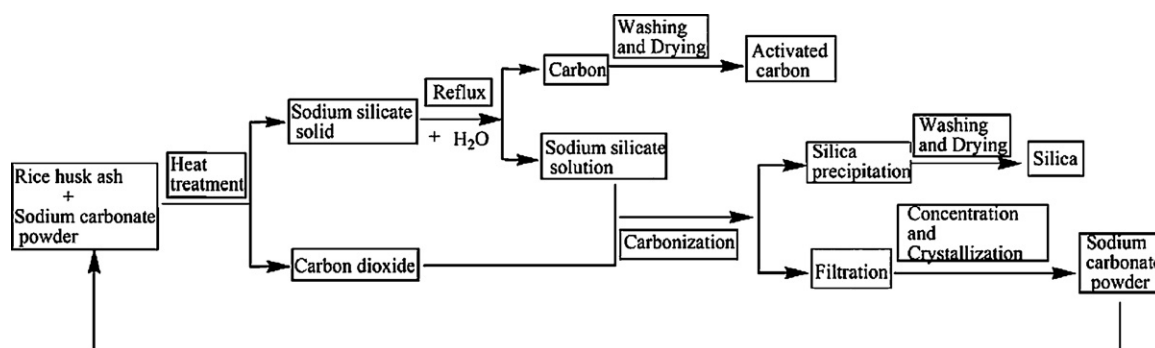


Fig. 1. Schematic representation of the synthetic procedure.

Beijing Chemicals Co. Ltd. Nitrogen was of chemical grade (at a purity of 99%). In all experiments, deionized water was used. The proximate analysis of RHA used in this study, are given in Table 1.

2.2. Acid pretreatment of material

RHA and dilute hydrochloric acid were mixed into a 500 ml three-necked flask. The suspension was boiled for 2.5 h under reflux condenser, and vigorous stirring was applied during the whole reaction process. Finally, the suspension was filtered, and solid residue was washed thoroughly with distilled water and dried for 12 h at 120 °C.

2.3. High temperature heat treatment

10 g of RHA after acid pretreatment was uniform mixed with Na₂CO₃ powder in a quartz tube at a certain impregnation ratio. The quartz tube was put into a tube furnace which was heated to a designed temperature for a certain period of time. The carbon dioxide generated in heat treatment process was compressed and saved in a steel bottle, the purpose was to use in carbonization stage. The system was cooled to 100 °C within, and transferred to a covered 500 ml three-necked flask.

In this process chemical activation of RHA was performed using sodium carbonate powder, and carbon dioxide was released, then collected and utilized for the silica precipitation process. A series of impregnation ratios were used. The impregnation ratio is given by

$$\text{Impregnation ratio} = \frac{\text{Weight of rice husk ash}}{\text{Weight of Na}_2\text{CO}_3 \text{ powder}}$$

2.4. Preparation of activated carbon

A certain amount of water was added in a covered 500 ml three-necked flask and kept boiling for a certain period of time. The dispersions were filtered, and then the activated carbon was washed thoroughly with distilled water to be neutral and dried for 12 h at 120 °C.

2.5. Preparation of silica

In carbonating procedure, silica was prepared through carbon dioxide neutralization and the precipitate separation processes.

The obtained filtrate within reactor was kept at appointed temperature 70–95 °C, then the collected carbon dioxide was introduced into the reactor through a tube for 1 h. After aging 3 h at room temperature, the precipitate was filtered using a pump, and the precipitate was washed by distilled water to be neutral and then it was dried at 120 °C for 24 h to obtain silica powders. Then the filtrate was concentrated and crystallized to prepare Na₂CO₃ powders for recycle and reused as the reactant in the heat treatment process.

2.6. Characterization

Mineral composition of the RHA was determined by atomic emission measurements using ICP emission spectroscopy (Perkin-Elmer Optima 3300 DV). The specific surface area and pore size of activated carbons were measured by using the Brunauer–Emmett–Teller (BET) method with an automated chemisorption/physisorption surface area and pore size analyzer (Quantacrome AUTOSORB-1C). The amorphous state of silica powder and the recovery of sodium carbonate was performed on an X-ray diffractometer (XRD, SHIMADZU-6000), using Cu K α ($k=1.54056$) radiation. Fourier transform infrared spectroscopy (FTIR) experiment was carried out on a Bruker IFS 66 vs⁻¹ spectrometer employing the KBr pellet method. The particles size and morphology characterization of silica was measured by Transmission electron microscopy (TEM, Hitachi H-800). The electrochemical tests were performed using a Parstat 2273 electrochemical workstation.

3. Results and discussion

A series of products had been prepared from RHA as precursor with Na₂CO₃. The sodium silicate was obtained through Na₂CO₃ reacted with RHA initially, and then was removed during dissolution process to form pores. The effects of different preparation conditions on the yield of the silica and the pore volume of activated carbon were also studied.

3.1. Effects of heat treatment conditions on the yields of silica and pore volume of activated carbon

Heat treatment condition plays an important role on the yield of silica. Moreover, silica extraction ratio directly affects the adsorption capacity of activated carbon. In order to depict the degree of

Table 1
Chemical composition of RHA.

Element	Si	C	K ₂ O	CaO	Na ₂ O	MgO	Al ₂ O ₃	ZnO	Fe ₂ O ₃	CuO	MnO ₂
Wt.%	65	32	0.81	0.42	0.29	0.13	0.16	0.12	0.15	0.00025	0.64

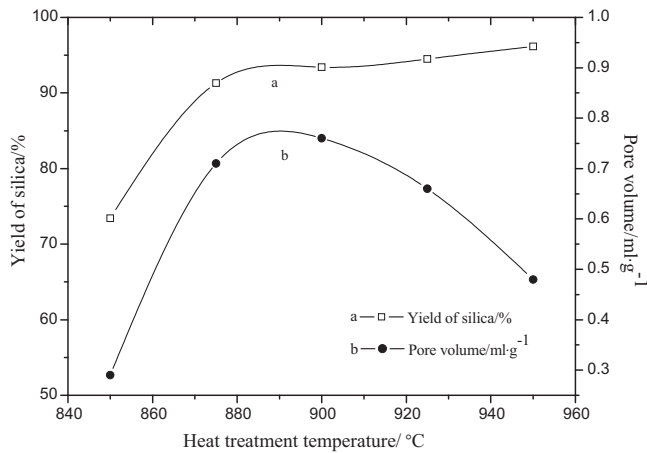


Fig. 2. Effect of heat treatment temperature on the yield of silica and the pore volume of activated carbon.

activation reaction, the yield of silica is defined as the percent of M_s/M_r , in which M_s is the mass of silica product and M_r is the mass of the silica in RHA.

3.1.1. Heat treatment temperature

Fig. 2 depicts the influence of heat treatment temperature (850–950 °C) on the yield (a) of silica and the pore volume (b) of activated carbon. Other factors (heat treatment time, ratio of RHA to Na_2CO_3 solid, dissolve water volume and dissolve time) were fixed at 1 h, 1:1.75, 350 ml and 1 h. The yield of silica increased with the heat treatment temperature increased. When heat treatment temperature ranged from 875 °C to 950 °C, the yield of silica reached the maximum value (96.17%). The curve of pore volume increased with heat treatment temperature increasing and reached the maximum value (0.76 ml/g) at 900 °C. The pore volume increased dramatically from 850 °C to 875 °C. The reason is that the decomposition temperature of sodium carbonate is 850 °C. When the temperature exceeded this critical temperature, the sodium carbonate decomposed rapidly and promoted the activation process. When heat treatment temperature ranged from 875 °C to 900 °C, the pore volume of activated carbon increased and reached the maximum value (0.76 ml/g). With the temperature increased above 900 °C, the pore volume decreased. Since progressive heat treatment temperature increased the sodium carbonate decomposition rate, it will result in increasing carbon “burn off”. These results suggested that to obtain the optimal value of the yield and the pore volume, the temperature should be around 900 °C.

3.1.2. Heat treatment time

When the other factors (heat treatment temperature, ratio of RHA to Na_2CO_3 solid, dissolve water volume and dissolve time) were fixed (900 °C, 1:1.75, 350 ml and 1 h). The effect of heat treatment time (30–75 min) on the yield of silica and the pore volume of activated carbon is shown in Fig. 3. When the time ranged from 45 min to 75 min, the yield of silica increased slowly and reached the maximum value (94.92%). So heat treatment time had little effect on the yield of silica.

The pore volume of activated carbon affected by different heat treatment times (30–75 min) is depicted in the curve (b). As seen in the figure, when the heat treatment time increased from 30 min to 45 min, the increase in pore volume at a short time may probably be due to the longer contact time for the sodium carbonate and the RHA. When time increased from 45 min to 60 min, the pore volume of activated carbon reached the maximum value (0.92 ml/g) due to the sufficient contact time. But the decrease in pore volume at a longer time may probably be due to the

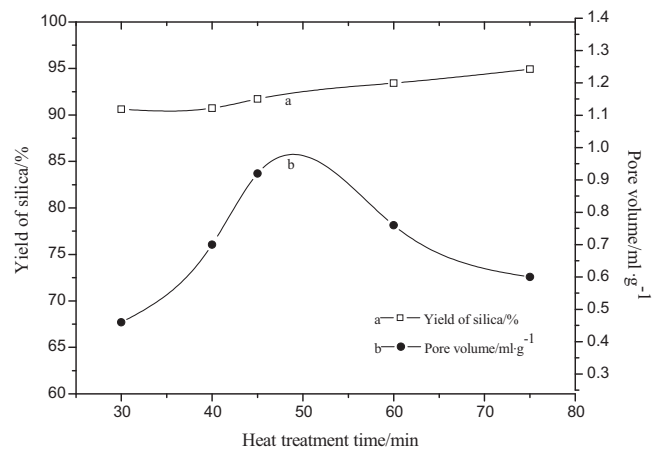


Fig. 3. Effect of heat treatment time on the yield of silica and the pore volume of activated carbon.

longer contact time for the reagent, resulting in increasing carbon “burn off”.

3.1.3. Impregnation ratio

The effect of impregnation ratio was studied using heat treatment at 900 °C for 45 min at five different impregnation ratios ranging from 1:1 to 1:3. The dissolve water volume and dissolve time was 350 ml and 1 h, respectively. Fig. 4 shows the variation of the yield of silica and the pore volume of activated carbon at different impregnation ratios. The results showed that the yield of silica increased with the increase in impregnation ratio, and reached maximum at 1:3. The pore volume increased initially, reached maximum at 1:1.75 and then decreased. The pores were created due to the evolution of sodium silicate product and catalytic oxidation of carbon surface by sodium metallic salt. At high ratio of NaCO_3 , the pores development was mostly due to the intercalation of sodium metal in the carbon structure. The pores would be destroyed under excess NaCO_3 .

3.1.4. Volume of water in reflux

The purpose of this process was to make the heat treatment solid to be dissolved into water and make sodium silicate to be separated from activated carbon. It was noteworthy that the separation conditions directly affected the pore volume and silica yields. In this step, the heat treatment conditions (heat treatment temperature, heat treatment time and impregnation ratio) were fixed (900 °C,

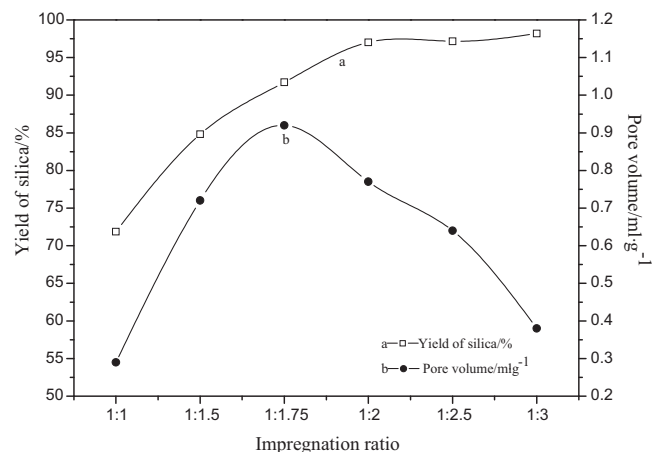


Fig. 4. Effect of impregnation ratio on the yield of silica and the pore volume of activated carbon.

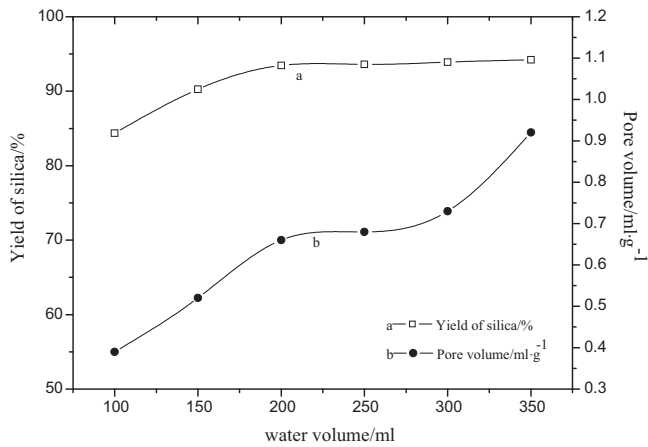


Fig. 5. Effect of water volume on the yield of silica and the pore volume of activated carbon.

45 min and 1:1.75) and the dissolution of water volume and reflux time was studied.

Five different water volumes ranging from 100 to 350 ml were studied at 100 °C for 1 h. Fig. 5 shows the variation of the yield of silica and the pore volume of activated carbon at different water volumes. The yield of silica increased with increasing water volume from 100 to 350 ml. However, the yield of silica rose slowly and presented a platform in water volume from 200 to 300 ml, and the maximum value was 94.22%. Sodium silicate as soluble alkali metal silicate material was dissolved in water. Therefore, the amount of water increased, the curve of pore volume increased, and reached the maximum value (0.92 ml/g).

Part of sodium silicate might exist in the carbon porosity, and after it is dissolved in the water, silica was separated from carbon to form pores. Even if a small change in the yield of silicon dioxide, residual sodium silicate solid would be dramatic impact on the pore volume. Therefore, the curve of pore volume and the yield showed a different trend entirely. The same situation also occurred in the study of reflux time. Details are discussed in Fig. 6.

3.1.5. Reflux time

The heat treatment conditions were fixed and the effect of reflux times was studied at 100 °C. As shown in Fig. 6, the yield of silica increased with the increasing of reflux time from 0.5 to 2.5 h. However, from the slope of curve we could find that the yield had little difference. As seen in Fig. 5, the pore volume of activated carbon slightly increased with the flux time increasing. The reason was that

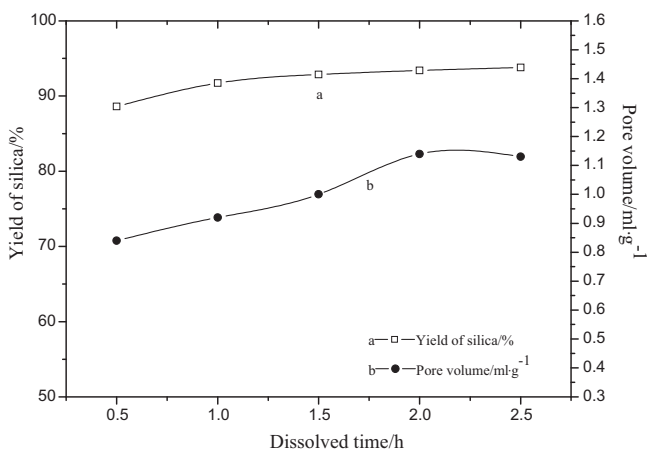


Fig. 6. Effect of reflux time on the yield of silica and the pore volume of activated carbon.

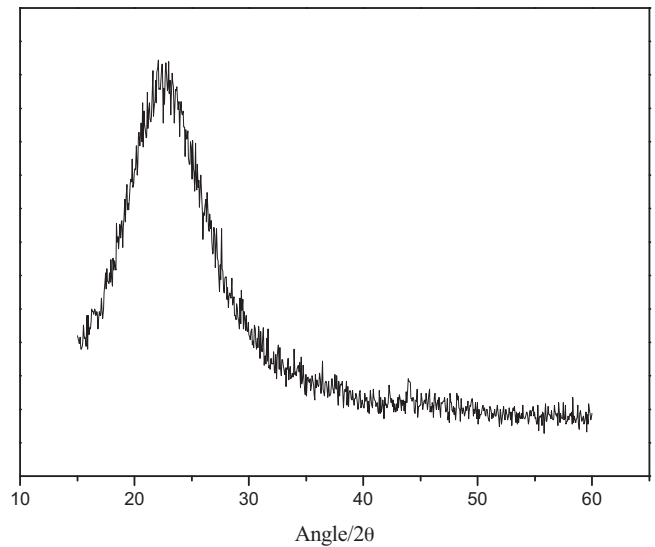


Fig. 7. XRD of silica obtained at the better condition.

in this procedure external sodium was dissolved rapidly, while the internal sodium silicate moved to the particle surface slowly and it would take a long time for that. The result illuminated that treatment time had little effect on yield of silica, which suggested that to obtain the optimal value of the yield and the pore volume, the reflux time should be around 2 h.

3.2. Characterization of silica, activated carbon and recovered sodium carbonate

With this method, we have prepared activated carbon and silica from RHA, and the optimal experimental conditions (heat treatment temperature, heat treatment time, impregnation ratio, dissolved water volume and reflux time) were determined. A series of characterization of silica and activated carbon are depicted as follow.

The X-ray spectra and characteristic absorption peak of silica have been obtained and shown in Fig. 7. The spectrum of pure silica showed a broad peak in the range of 18–30° (2θ), which was typical for amorphous solids, confirmed the absence of any ordered crystalline structure.

Infra-red spectra of the silica was recorded by FT-IR spectrometer and presented in Fig. 8, and the major chemical groups of silica are identified. The predominant absorbance peak at 1105 cm⁻¹ denoted to the Si–O–Si asymmetry stretching vibration. The band located at 797 cm⁻¹ and 472 cm⁻¹ ascribed to the Si–O symmetry stretching vibration and bending vibration, respectively. The band centered at 3363 cm⁻¹ and 951 cm⁻¹ assigned to the SiO–H asymmetry stretching vibration and bending vibration respectively. The band at 1663 cm⁻¹ belonged to H–O–H bending vibration.

Transmission electron microscopy is a major review measurement of the nano-particles size and morphology characterization. The untreated silica powder which was prepared via carbonization process was dispersed in ethanol and observed from the transmission electron microscopy (Fig. 9). From the transmission electron microscopy, it could be seen that silica particles had relatively better dispersion. No reagent was added to change the morphology of silica in the preparation process, but it could be clearly seen the tendency to form the spherical silica particles, and the silica particles in the average diameter was about 40–50 nm.

A useful indication of the pore structure of activated carbon could be obtained by visual inspection for the shape of the isotherm. The result was determined by the Barrett–Joyner–Halenda (BJH)

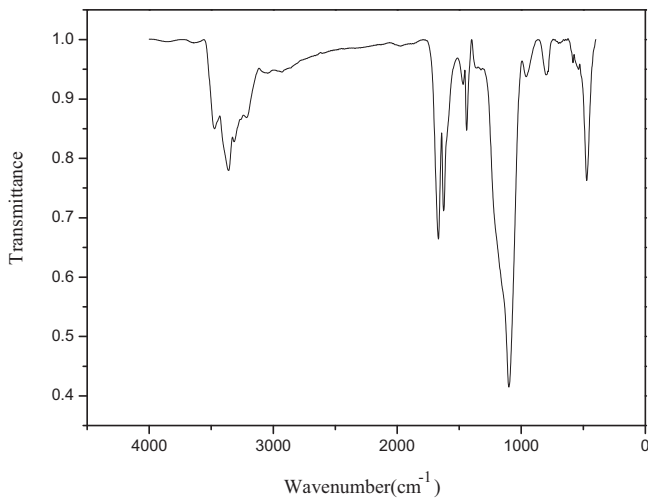


Fig. 8. FT-IR spectra of the silica.

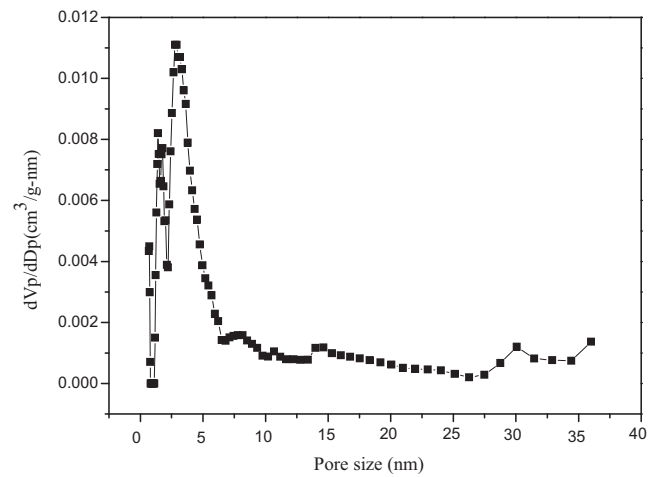


Fig. 10. Differential pore size distribution of activated carbon obtained from RHA.

method (based on the desorption branch) using adsorption isotherms of nitrogen (Quantacerome AUTOSORB-1C). The structural heterogeneity of porous material was generally characterized in term of the pore size distribution. The pore size distribution was closely related to both kinetic and equilibrium properties of porous materials used in industrial application. The pore size distribution of activated carbon at the optimal condition is given in Fig. 10. From this figure, it seemed to be a mixed-type of I+II of the BDDT classification [25], which indicated that the carbon was mainly micro and mesoporous in character with a minor presence of wider pores where capillary condensation occurred.

Fig. 11 shows the nitrogen adsorption–desorption isotherms of activated carbon at the optimal condition. At low values of PP_0^{-1} , the isotherm was similar to microporous adsorbents. Then adsorption increased markedly at PP_0^{-1} above 0.1 where pore condensation took place and the isotherm exhibited a hysteresis loop which suggested that the existence of mesopores in the carbon and the size distribution of pores became wider, and the pore size concentrated in the 1–5 nm. So adsorption capacity of activated carbon largely depended on the amount of micropores and mesopores that were presented in the activated carbon. The BET surface area of activated carbon could achieve $570 \text{ m}^2/\text{g}$ which produced the similarity results in other studies [26,27], the iodine adsorption capacity reached 1708 mg g^{-1} , and the capacitance value reached 180 F/g which can be used as the electrode.

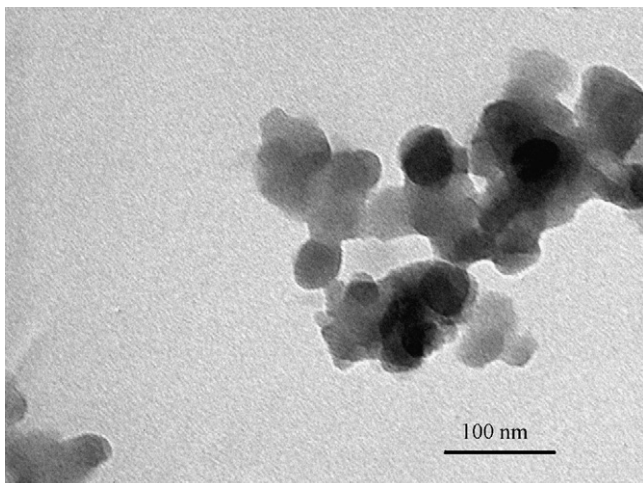


Fig. 9. TEM of the silica.

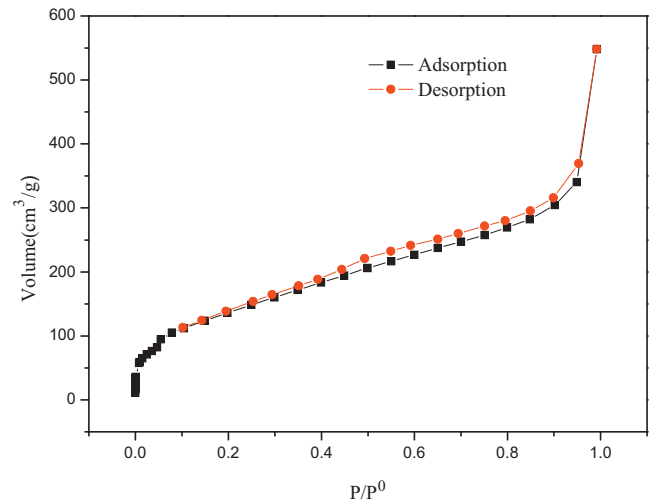


Fig. 11. Nitrogen adsorption–desorption isotherms measured on synthetic activated carbons.

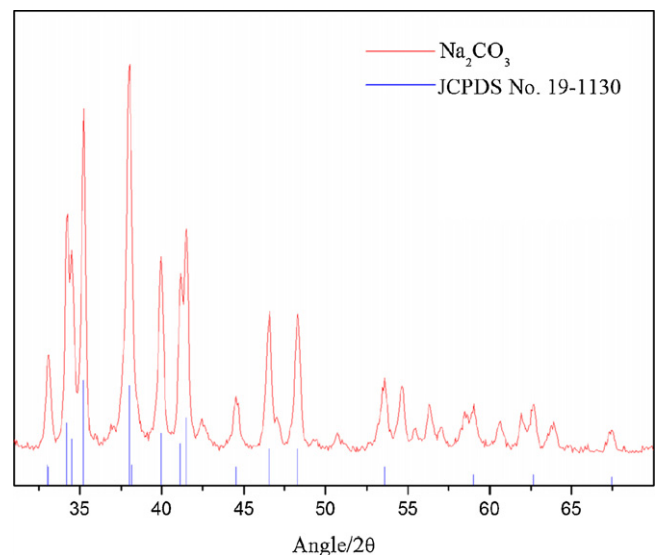


Fig. 12. XRD of sodium carbonate obtained from the filtrate of carbonation reaction.

3.3. Recycling of sodium carbonate

The X-ray spectra and characteristic absorption peak of the recovery of sodium carbonate and comparison with the standard sodium carbonate is shown in Fig. 12. All diffraction peaks were quite similar to the pure sodium carbonate and the diffraction data were in good agreement with JCPDS files no. 19-1130. No characteristic peaks of impurities, such as NaHCO_3 and other unreacted compounds were observed. Thus, the results showed that the as-prepared product was pure sodium carbonate. The recovery of sodium carbonate which had been confirmed in the experiment could be used as the initial reactant.

In our work, the yield of silica is 72–98% and activated carbon is 20–50%. The recovery rate of sodium carbonate has reached 92.25%. Based on above results, the mass of silica and Na_2CO_3 achieve balance. The loss of carbon element is because of “burn off” by Na_2CO_3 and a small quantity of air.

4. Conclusions

In view of the composition in RHA, we have successfully found a route which could prepare silica and activated carbon from the RHA at the same time, and established green sustainable production process. The results reveal the method is feasible. Operational simplicity, low cost of the material, high yield of silica, short reaction time, applicability to large-scale reactions and environment friendly are the key features of this methodology. Based on this route, we achieved the goal in developing clean and eco-friendly synthesis processes meeting such environmental restrictions within a sustainable chemistry approach. If this route comes true in industrials, it will generate positive influence to energy sustainable use and create a great social value.

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