Ultra-large Specific Surface Area Activated Carbon Synthesized from Rice Husk with High Adsorption Capacity for Methylene Blue

ZHOU Fan\textsuperscript{1,2}, BI Hui\textsuperscript{1}, HUANG Fuqiang\textsuperscript{1,2,3}

(1. State Key Laboratory of High Performance Ceramics and Superfine Microstructure, Shanghai Institute of Ceramics, Chinese Academy of Sciences, Shanghai 200050, China; 2. School of Physical Science and Technology, ShanghaiTech University, Shanghai 200031, China; 3. State Key Laboratory of Rare Earth Materials Chemistry and Applications, College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, China)

Abstract: Activated carbon with high surface area and abundant pore structure is widely used for contaminant adsorption in wastewater treatment. Rice husks (RHs) with unique composition and microstructure are often used as carbon source to prepare activated carbon. Herein, ultra-large specific surface area activated carbon was synthesized from rice husks with pre-activation and activation by supersaturated KOH solution at different temperature. With the increase of activation temperature, the specific surface area and total pore volume of activated carbon gradually increase. The activated carbon obtained at 900 °C shows the largest specific surface area of 3600 m\textsuperscript{2}/g and the maximal total pore volume of 3.164 cm\textsuperscript{3}/g, which are significantly superior to those of the commercial activated carbon (YP-80, the specific surface area of 1310 m\textsuperscript{2}/g and the total pore volume of 0.816 cm\textsuperscript{3}/g, respectively). The highest maximum adsorption capacity for methylene blue was found for the activated carbon with the largest specific surface area, namely, 983 mg/g, which is almost twice as high as that of YP-80 (525 mg/g). By adsorption kinetics fitting, the results are consistent with pseudo-second-order model which indicates that the process of adsorbing methylene blue is chemical adsorption.

Key words: rice husk; ultra-large specific surface area; activated carbon; adsorption; methylene blue

Activated carbon (AC) has been always appealing to researchers’ attention due to its excellent properties and versatility. Relying on their low-cost stocks, large specific surface area (SSA\textsubscript{BET}), abundant pore structure, high chemical stability and non-toxicity, AC has been widely applied to treat waste water containing methylene blue (MB)\textsuperscript{[1]}. The MB is commonly utilized for hair colorant, textile dyeing, coloring paper and so on\textsuperscript{[2]}. Because of carcinogenesis effect, the amount of MB in the body is large enough to cause cancer, mutation and dermatological diseases\textsuperscript{[3]}. Therefore, removing MB from waste water is significantly important.

The synthesis methods of AC include physical and chemical activation with microwave heating assisting occasionally. Various agricultural wastes are used as raw materials, such as peanut hull\textsuperscript{[4]}, tea-leaves\textsuperscript{[5]}, cotton\textsuperscript{[6]}, coconut husks\textsuperscript{[7]}. CO\textsubscript{2} and water vapor are applied as activating agents in physical activation\textsuperscript{[8-9]}. ZnCl\textsubscript{2}, KOH and H\textsubscript{3}PO\textsubscript{4} are usually utilized as activator in chemical activation\textsuperscript{[10-12]}. Bellington et al.\textsuperscript{[13]} utilized ZnCl\textsubscript{2} to activate tobacco stems with microwave heating, and the product got the SSA\textsubscript{BET} of 684.68 m\textsuperscript{2}/g and the maximum adsorption capacity of 123.45 mg/g for adsorbing MB. Viscose-based AC fibers were prepared by steam with different flows at 900 °C for the adsorption of MB and they performed the SSA\textsubscript{BET} of 1614 m\textsuperscript{2}/g and the adsorption capacity of 325.8 mg/g\textsuperscript{[9]}. Bamboo shoots were activated by KHCO\textsubscript{3} to prepare AC for removing MB from waste water, which exhibited the SSA\textsubscript{BET} of 2271 m\textsuperscript{2}/g and the maximum adsorption capacities of 458 mg/g\textsuperscript{[14]}. Obviously, the SSA\textsubscript{BET}
of AC has an essential impact on the adsorption capacity for MB. Therefore, there exists a great challenge to find a certain kind raw material or method for the preparation of AC with larger SSA$_{\text{BET}}$.

As an abundant agricultural bio-waste, RHs which hollow fibers are assembled by cellulose, hemicellulose, lignin and significant amounts of SiO$_2$ of about 20wt% have great potential to prepare AC with ultra-high SSA$_{\text{BET}}$ owing to their natural structure and component$^{[15]}$. Most of SiO$_2$ and spacious carbon skeleton exist in the outer glume of RHs. The inner glume of RHs is composed of a large number of bundles of vascular tubes to transport nutrients$^{[16]}$. SiO$_2$ as a hard template can react with molten alkali in the activation process to provide some pore structure. In the subsequent activation, pores formed are further broadened in the original SiO$_2$ sites. It has also been reported that NaOH can be used as activator to prepare AC showing relatively large SSA$_{\text{BET}}$ of 1873 m$^2$/g based on RHs$^{[17]}$.

In this study, supersaturated KOH solution was adopted to prepare AC with ultra-large SSA$_{\text{BET}}$ based on the unique advantages of RHs. MB adsorption experiment on the RHAC was conducted to explore the influence of temperature on the SSA$_{\text{BET}}$ and the adsorption capacity. The SSA$_{\text{BET}}$, pore structure, and adsorption capacity of RHACs were compared with other AC materials made from other agricultural bio-waste such as tobacco stalk, viscose fibers and sawdust.

## 1 Experimental

### 1.1 Materials and synthesis

The raw RHs were bought from the Taobao network. The received RHs were washed with the deionized water to eliminate the impurities. Then, they were put into drying oven at 60 °C for 24 h. Potassium hydroxide (AR, 90%) was purchased from the Aladdin. Methylene Blue trihydrate (biotechnology grade) was bought from the Shanghai Macklin Biochemical Co., Ltd. Hydrochloric acid (AR) and hydrofluoric acid (AR) were purchased from the Shanghai Hushi Laboratorial Equipment Co., Ltd.

The raw RHs were pyrolyzed at 400 °C in the argon atmosphere for 1 h in the horizontal tubular furnace to obtain RH biochar (RHBC). RHBC (4g) and KOH solution (2 mol/L, 107 mL) were mixed and stirred for 30 min. The mixture was put into a drying oven at 100 °C for 48 h to remove water. The dry mixture was heat-treated in the horizontal tubular furnace in the argon atmosphere for 2 h at 700 °C to produce RHAC1. RHBC (4g), KOH (12g) and 25 mL deionized water are to produce RHAC2 and the preparation method is the same as that of RHAC1.

RHBC (8 g), KOH (32 g) and 50 mL deionized water were mixed and stirred for 30 min. The mixture was put into a drying oven at 100 °C for 48 h to remove water. The dry mixture was heat-treated in the horizontal tubular furnace in the argon atmosphere for 2 h at 600 °C, 700 °C, 800 °C and 900 °C at heating rate of 13 °C/min to produce RHAC600, RHAC700, RHAC800 and RHAC900, respectively. The impurities including alkali, alkali oxides and silica in products were removed by HCl and HF mixture solutions for 48 h. Finally, all of RHAC were washed with the deionized water and dried in an oven at 120 °C for 12 h.

### 1.2 Characterizations

Surface morphology was investigated by scanning electron microscope (SEM-JMS-6510). Highly resolution transmission electron microscope (HRTEM) images were conducted on JEOL 2100F. The crystalline structure was carried on Bruker D8 X-ray diffractometer with the source of Cu Kα radiation at 40 kV and 40 mA. Raman spectra was measured on a thermal dispersive spectrometer using a 10mW laser (532 nm). Nitrogen adsorption-desorption isotherm was measured on a Micromeritics Tristar 3000 system at 77 K. The SSA$_{\text{BET}}$ was obtained by the Brunauer-Emmett-Teller (BET) method and the pore size distribution was gained from Nonlocal Density Functional Theory (NLDFT).

### 1.3 Adsorption experiments and kinetic studies

MB solution with concentration of 500 mg/L was prepared for adsorption experiments in advance. The commercial AC (YP-80) was utilized as a control group. AC (100 mg) and MB solution(100 mL) were added into the beaker and magnetically stirred at room temperature (~25 °C). The sampling intervals were 2, 4, 6, 8, 10, 15, 20, 25, 30, 45, 60, 90, 120 and 180 min. After highly speed centrifugation, the supernatant was extracted for analyzing its absorbance on the UV-visible spectrometer (Hitachi U4100) equipped with an integrating sphere. All tests were conducted at a specific wavelength, namely, the maximum absorbance (664 nm) of MB at room temperature. The correlation between absorbance and the MB concentration is determined according to the Lambert-Beer's Law$^{[18]}$. Afterwards, the amount of each carbon addition dwindled gradually until the adsorption limit appeared.

Adsorption capacity ($q_e$) at equilibrium was calculated by the Equation (1)$^{[19]}$:
where \( q_e \) (mg/g) is the adsorption capacity of MB at equilibrium, \( C_0 \) (mg/L) is the primitive concentration of the MB solution - that is 500 mg/L, \( C_e \) (mg/L) is the equilibrium concentration of the MB solution, \( V \) (L) is the MB solution volume, \( i.e. 0.1 \) L, \( m \) (g) is the mass of added RHAC.

The pseudo-first-order models (Equation (2)) and the pseudo-second order models (Equation (3)) were utilized to fit the adsorption data for describing the adsorption equilibrium:

\[
q_t = q_e \left(1 - e^{-k_1 t}\right)
\]

\[
q_t = \frac{q_e^2 k_2 t}{1 + q_e k_2 t}
\]

where \( q_t \) (mg/g) is the adsorption capacity at time \( t \), \( q_e \) (mg/g) is the adsorption capacity of MB at equilibrium, \( k_1 \) and \( k_2 \) are the rate constant of the pseudo-first-order (min\(^{-1}\)) and the pseudo-second-order (min\(^{-1}\)), respectively, \( t \) (min) is the adsorption time.

### 2 Results and discussion

The morphologies of raw RHs, RHBC and RHACs were characterized by SEM. Obviously, there are many humps on the outer glume of raw RHs and RHBC (Fig. 1(a,b)). The surface of humps in RHs is intact. After heat-treated at 400 °C, lots of large opening pores appear on the surface of RHBC to conduce to activator-KOH enter the interior of RHBC for enhancing the process of activation\(^{11}\). The commercial AC (YP-80) shows fine granular blocks, and the visible pores are hard to find out (Fig. 1c). After activation, the abundant pore structure forms on the sample surface, which can provide adsorption sites and mass transfer channels in favor of adsorption application (Fig. 1d-1g)\(^{9}\). The inner side of RHs is activated to form spongy structure, and the outer surface of RHs forms honeycomb structure due to natural composition and structure of RHs (Fig. 1d & 1e)\(^{16}\). With the activation temperature increasing, the process of forming pores is strengthened resulting that the pore structure of RHAC900 is more abundant than that of RHAC800 (Fig.1(f, g)). The porous structure was further examined by HRTEM. The RHAC900 mainly consists of amorphous carbon and plenty of vermicular micropores, in which a few graphitized carbon layers exist.

As shown in Fig.2a, the inapparent peaks appear at around 2 \( \theta =23^o \) and 44° suggesting that RHACs and YP-80 are composed of amorphous carbon\(^{21}\). Broad peak around 2 \( \theta=22^o \) in RHBC indicates the overlapping peaks of carbon and silica, and the decrease of peak intensity suggests that SiO\(_2\) is almost completely removed (Fig.S1). Lignin and cellulose in precursors undergo a pyrolysis process at 400 °C, in which the tar is formed from highly active polymer materials and releases, leaving inert carbon skeleton and amorphous SiO\(_2\), which shows strong but wide peak at around 2 \( \theta =22^o \) (Fig.2a). In the process of activation at high temperature, the amorphous nano-SiO\(_2\) was melted in the presence of KOH and eliminated at last, weakening the intensity of peaks at around 2 \( \theta=22^o \)\(^{15}\).

Fig. 1 SEM images of (a) raw RHs, (b) RHBC, (c) YP-80, (d) RHAC600, (e) RHAC700, (f) RHAC800; SEM (g) and TEM (h) images of RHAC900

Meanwhile, a part of carbon in RHBC reacts with KOH to produce CO and CO\(_2\) gases, resulting in abundant pores formation and the increase of the degree of disorder in RHACs\(^{22}\).

Raman spectra of the RHACs and YP-80 contains D-band (1342-1352 cm\(^{-1}\)), G-band (1590-1600 cm\(^{-1}\)) (Fig. 2b). Normally, the graphitization degree of carbon increases gradually with the increase of the heat-treatment temperature\(^{23}\). However, with the activation tem-
temperature increasing, the ratio of D-band to G-band increases slightly (Table 1), resulting from that the disorder degree due to consuming carbon during activation has larger influence on the crystallinity of products than that of temperature\cite{24}.

The SSA_{BET} of RHACs was characterized by BET test, as shown in Fig.2c. There exists two types N$_2$ adsorption-desorption isotherm curves, type-I for YP-80, RHAC600, RHAC700, RHAC800 and type-IV for RHAC900. The curves of type-I conform to Langmuir's monolayer adsorption model indicating that the pore structure is mainly composed of micropores, and the obvious hysteresis loop in the type-IV curve for RHAC900 shows that abundant mesopores exist in this material, well explaining why the total pore volume and the pore size distribution of RHAC900 are far greater than other porous materials (Table 1)\cite{25}. The SSA_{BET} and the total pore volume of RHACs are positively correlated with activation temperature, and reach the highest value of 3600 m$^2$/g and 3.164 cm$^3$/g for RHAC900 (Table 1). Supersaturated KOH solution can react with SiO$_2$ in RHBC to form K$_2$SiO$_3$ during the process of impregnation and dry, contributing to pre-activation (Fig.S2a). The formation of K$_2$SiO$_3$ makes the original vacancy of self-template SiO$_2$ exposed and drives the activator into a deeper position to promote the activation process. Accordingly, the sample RHAC2 has larger SSA_{BET} than sample RHAC1 (Fig.S2b), and the

![Fig. 2 (a) XRD patterns, (b) Raman spectra, (c) N$_2$ adsorption-desorption isotherms and (d) Pore size distribution curves of RHBC, RHACs, YP-80](image1)

![Fig.3 Effect of contact time and mass of adsorbent on the adsorption capacity](image2)
sample RHAC900 has larger SSA_{BET} compared with ACs made from other biomass materials by traditional preparation methods (Table S1). Although RHACs mainly contain micropores, there are still a small number of mesopores in these materials (Table 1). The mesopore size in RHAC600 ranges from 2 nm to 4 nm, tightly close to the range of micropore\cite{12}. With the activation temperature increasing, more carbon in RHBC reacted with molten KOH, and the pore-forming process strengthened intensely, causing the size of pores to widen\cite{15, 24}. Therefore, the mesopore size in RHAC900 enlarges from 2.5 nm to 14 nm. The SSA_{BET} and mesopore size of RHACs are superior to YP-80 (Table 1). In the range of micropore size, the peak intensities of micropore distribution curves of RHACs are stronger than those of YP-80. Although the micropore volume of YP-80 is slightly higher than those of RHAC600 and RHAC700, the micropore volume of RHAC800 and RHAC900 are higher than that of YP-80 and the total pore volume of RHACs is much larger (Table 1). The above characterization results reveal that the activation temperature has tremendous impact on the activation process and pore structure of RHACs. As the temperature increasing, the activation process becomes more violent, and more carbon will be consumed, leading to the increase of mesoporous content and size.

The temperature (~25 °C), initial concentration of MB solution (500 mg/L) and contact time (180 min) were set up to estimate the MB adsorption performance of RHACs and YP-80. As the amount of adsorbent decreasing, the adsorption limit of RHACs and YP-80 appeared one by one, as shown in Fig.3a-3d. The adsorption efficiency and capacity are associated with the SSA_{BET}, and the higher the specific surface area, the larger the adsorption capacity\cite{25}. As shown in Table 1, the maximum adsorption capacity is 983 mg/g for the RHAC900 which possesses the highest SSA_{BET} of 3600 m²/g. Nevertheless, the adsorption capacity of the RHAC800 (919 mg/g) is slightly lower than that of the RHAC700 (935 mg/g). In the case of ultra-high SSA_{BET} (>3000 m²/g), the minute difference of SSA_{BET} has no significant effect on adsorption capacity which is mainly affected by pore size and volume of materials\cite{26}. As can be seen from Fig.2d, the mesopore size range of the RHAC700 is wider than that of RHAC800 (as listed in Table 1), indicating higher adsorption capacity and faster mass transfer rate (the insets of Fig.3(c,d)).

Meanwhile, due to the high SSA_{BET} of 3600 m²/g, the greatly wide mesoporous size distribution from 2.5 nm to 14 nm and ultra-large total pore volume of 3.164 cm³/g, the RHAC900 has the highest adsorption capacity of 983 mg/g. Although micropore volume of RHAC900 is smaller than that of RHAC800 and close to others, the mesopore volume of RHAC900 is far larger than those of other RHACs (Table 1), resulting in fastest adsorption rate (Fig.3d)\cite{27}. On the whole, all of RHACs exhibit more outstanding adsorption performance than the commercial AC (YP-80). As seen from Table S1, the SSA_{BET} and pore volume have a crucial influence on the adsorption capacity for MB and the performance of RHAC in this study is much better other carbon reported.

Kinetic studies were conducted to further understand the adsorption mechanism in the adsorption processes for MB, and the pseudo-first-order model and the pseudo-second-order model were used to fit the adsorption data\cite{19}. For the fitting processes, the correlation coefficients ($R^2$) are determined for two models and each adsorbent, and the higher value $R^2$ is deemed as the better fitting\cite{28}.

The linear fit of the pseudo-first-order model and the values of the correlation coefficients are shown in Fig. S3(a-f). The results indicate a relatively good linear fit for RHAC600 and RHAC800, with $R^2 = 0.9352$ and $R^2 = 0.938$, respectively. Table S2 shows the values of the kinetic adsorption constants obtained from the application of the pseudo-first-order model for each RHAC. Only when the difference between $q_e$ (experimental) and $q_t$ (calculated) is the smallest possible, are the kinetic models significant\cite{28}. However, all differences between those parameters exceed 45%. Hence, the pseudo-first-order model can’t describe the adsorption

| Table 1 The ratio of $I_d$ to $I_0$, SSA_{BET}, pore volume, micropore volume and adsorption limit of RHACs and YP-80 |
|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| Carbon          | YP-80           | RHAC600         | RHAC700         | RHAC800         | RHAC900         |
| $I_d$ / $I_0$   | 0.997           | 0.992           | 1.017           | 1.025           | 1.020           |
| SSA_{BET} (m²/g) | 1310            | 2380            | 3173            | 3366            | 3600            |
| Pore volume (cm³/g) | 0.816         | 1.352           | 1.733           | 1.829           | 3.164           |
| Micropore volume (cm³/g) | 0.516          | 0.393           | 0.429           | 0.606           | 0.537           |
| Adsorption limit (mg g⁻¹) | 525           | 851             | 935             | 919             | 983             |


The linear fit of the pseudo-second-order model and the values of the correlation coefficients are shown in Fig. 4a–4f. The results indicate a perfect linear fit for RHACs and YP-80. All of the correlation coefficients ($R^2$) are extremely close to 1 suggesting that the pseudo-second-order model can precisely describe the adsorption process of MB. Meanwhile, in Table 2, all of the difference between $q_e$ (experimental) and $q_2$ (calculated) of each sample are also small enough to confirm that the adsorption process is consistent with the pseudo-second-order model.

![Fig. 4 Linear fit of the pseudo-second-order model for the adsorption of MB on (a) YP-80, (b) RHAC600, (c) RHAC700, (d) RHAC800, (e) RHAC900 and (f) corresponding correlation coefficients](image)

### Table 2 Kinetic parameters obtained of RHACs and YP-80 by the pseudo-second-order model for the adsorption of MB

| Sample      | $q_e$ (exp) / (mg g$^{-1}$) | $q_2$ (cal) / (mg g$^{-1}$) | Percentual difference ($q_e$-$q_2$)% | $k_2$ / (g mg$^{-1}$ min$^{-1}$) |
|-------------|----------------------------|----------------------------|-------------------------------------|----------------------------------|
| YP-80       | 525                        | 526.3                      | -0.25                               | 0.0090                           |
| RHAC600     | 851                        | 833.3                      | 2.08                                | 0.0006                           |
| RHAC700     | 935                        | 833.3                      | 10.88                               | 0.0018                           |
| RHAC800     | 919                        | 909.1                      | 1.08                                | 0.0007                           |
| RHAC900     | 983                        | 1000                       | -1.73                               | 0.0025                           |

The results of kinetic fitting indicate that the possible chemisorption of MB on the surface of RHAC may be realized by forming chemical complexes with functional groups[29]. All products only contain C and O leading to pretty low ash content (Table S3 & S4, Fig.S4) and oxygen-containing functional groups on the surface. The broad band at 3456 cm$^{-1}$ is due to the O-H stretching mode of hydroxyl groups (from carboxyl, phenols or alcohols) and adsorbed water. The band at 1597 cm$^{-1}$ is attributed to C-O stretching vibration from ketones, aldehydes, lactones or carboxyl groups. The peak at 1357 cm$^{-1}$ is assigned to C-O stretching and O-H bending modes of alcoholic, phenolic and carboxylic groups. After adsorption for MB, the intensity of band has decreased and the frequency of several groups has changed, which indicates that the chemisorption has occurred between MB and RHAC (Fig.S5). Therefore, the results of kinetic fitting are consistent with the FTIR characterization. This adsorption mechanism can promote the clear adsorption of the adsorbent surface without allowing its reuse[28].

### 3 Conclusion

As considering that RHs possess intrinsic advantages of structure and compositions, AC with ultra-large specific surface area from RHs are successfully synthesized through pre-activation and activation by supersaturated KOH solution. All of these activated carbon materials have hierarchical pore structure, larger specific surface area and larger pore volume compared with the commercial carbon (YP-80) and carbon materials based on other agricultural bio-waste. The RHAC with largest SSA$_{BET}$ of 3600 m$^2$/g is prepared at 900 ºC and performs the adsorption capacity of 983 mg/g, which is almost twice as high as that of YP-80. Due to hierarchical pore structure in favor of adsorbing and transporting
MB, the adsorption capacity of RHACs is superior to that of YP-80. The fitting results of the adsorption of MB on the RHs conforms the pseudo-second-order model indicating a chemisorption process. This study provides a feasible method for the reuse of RHs waste and large-scale preparation of AC with large specific surface area for water treatment.

Supporting materials
Supporting materials related to this article can be found at https://doi.org/10.15541/jim20200632.

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用稻壳制备亚甲基蓝高吸附容量的超高比表面积活性炭

周帆\(^1,2\), 毕辉\(^1\), 黄富强\(^{1,2,3}\)

(1. 中国科学院上海硅酸盐研究所，高性能陶瓷和超微结构国家重点实验室，上海 200050; 2. 上海科技大学物理科学与技术学院，上海 200050; 3. 北京大学化学与分子工程学院，稀土材料化学及应用国家重点实验室，北京，100871)

摘 要: 活性炭因具有高比表面积和丰富的孔结构被广泛应用于吸附水处理中的污染物。稻壳具有独特的组成和微观结构，是制备活性炭的优质碳源。以稻壳为原料，利用过饱和\(\text{KOH}\)溶液的预活化和活化双重作用，在不同温度下制备出超高比表面积活性炭。随着活化温度的升高，活性炭的比表面积和总孔容逐渐增大。900℃下制得的活性炭具有超高比表面积，达到 3600 m\(^2\)/g，总孔容为 3.164 cm\(^3\)/g，明显优于商用活性炭（YP-80，比表面积为1310 m\(^2\)/g，总孔容为 0.816 cm\(^3\)/g）。具有最高比表面积的稻壳活性炭对亚甲基蓝的最大吸附量达到 983 mg/g，几乎是 YP-80（525 mg/g）的两倍。通过吸附动力学拟合，吸附亚甲基蓝的过程与拟二级模型一致，表明该过程为化学吸附。

关 键 词: 稻壳; 超高比表面积; 活性炭; 吸附; 亚甲基蓝;

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Supporting Materials:

Ultra-large Specific Surface Area Activated Carbon Synthesized from Rice Husk with High Capacity Adsorption for Methylene Blue

ZHOU Fan¹,², BI Hui¹, HUANG Fuqiang¹,²,³

(¹. State Key Laboratory of High Performance Ceramics and Superfine Microstructure, Shanghai Institute of Ceramics, Chinese Academy of Sciences, Shanghai 200050, China; ². School of Physical Science and Technology, ShanghaiTech University, Shanghai 200031, China; ³. State Key Laboratory of Rare Earth Materials Chemistry and Applications, College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, China)

Fig. S1 XRD patterns of the product calcined from RHs and RHBC

Fig. S2 (a) XRD patterns of dried RHBC mixture impregnated with two different concentrations of KOH solution; (b) Nitrogen adsorption desorption curve of two RHAC with different concentrations of KOH solution
Table S1 Comparison of activator, SSA_{BET}, total pore volume and $q_m$ (the maximum adsorption of MB) between RHACs and other AC prepared from biomass

| Biomass                  | Activator                  | Pore volume /cm$^3$ g$^{-1}$ | SSA$_{BET}$/m$^2$ g$^{-1}$ | $q_m$/mg g$^{-1}$ |
|-------------------------|----------------------------|------------------------------|----------------------------|-------------------|
| Tobacco stalks$^{[1]}$   | ZnCl$_2$+Microwave         | 0.45                         | 684.68                     | 123.45            |
| Dipterocarpus alatus$^{[2]}$ | ZnCl$_2$/500 °C           | 0.473                        | 843                        | 269.3             |
| Sugar beet pulp$^{[3]}$ | H$_2$PO$_4$/450 °C        | 0.445                        | 1029.3                     | 250.0             |
| Palm kernel shell$^{[4]}$ | ZnCl$_2$/550 °C           | 0.571                        | 1058                       | 225.3             |
| Rice by-products$^{[5]}$ | H$_2$PO$_4$/450 °C        | 0.612/0.607                  | 814/1000                   | 246.9/213.7       |
| Viscose fibers$^{[6]}$  | Steam/900 °C              | 0.54/0.76                    | 1284/1614                  | 256.1/325.8       |
| Cotton$^{[7]}$          | H$_2$PO$_4$+Microwave      | 0.98                         | 1370                       | 476.2             |
| Cashew nut shell$^{[8]}$ | ZnCl$_2$/400 °C           | 0.973                        | 1478                       | 476               |
| Arundo donax$^{[9]}$    | ZnCl$_2$/400 °C           | 1.113                        | 1784                       | 416.7             |
| Sawdust$^{[10]}$        | KOH/1000 °C               | 1.27                         | 2254                       | 303.03            |
| Bamboo shoots$^{[11]}$  | KHCO$_3$/700 °C/800 °C    | 0.73/1.25                    | 1476/2271                  | 458               |
| Bagasse/Cluster stalks$^{[12]}$ | KOH/1300 °C            | 0.82/1.4                     | 1861/2662                  | 714.3/925.9       |
| This work               | KOH/800 °C/900 °C         | 1.829/3.164                  | 3366/3600                  | 919/983           |

Fig.S3 Linear fit of the pseudo-first-order model for five carbons: (a) YP-80, (b) RHAC600, (c) RHAC700, (d) RHAC800, (e) RHAC900 and (f) correlation coefficients

Table S2 Kinetic parameters obtained by the pseudo-first-order model for RHACs and YP-80 for the adsorption of MB

| Sample   | $q_e$ (exp.) /mg g$^{-1}$ | $q_1$ (cal.) /mg g$^{-1}$ | Percentual difference ($q_e$-$q_1$) /% | $k_1$/min$^{-1}$ |
|----------|--------------------------|---------------------------|----------------------------------------|------------------|
| YP-80    | 525                      | 19.8                      | 96.23                                  | 0.0192           |
| RHAC600  | 851                      | 438.8                     | 48.44                                  | 0.0614           |
Table S3 The element analysis of RHBC RHAC600, RHAC700, RHAC800 and RHAC900 by EDS/wt%

|          | RHBC  | RHAC600 | RHAC700 | RHAC800 | RHAC900 |
|----------|-------|---------|---------|---------|---------|
| C        | 19.48 | 95.18   | 97.21   | 94.16   | 95.63   |
| O        | 35.59 | 4.82    | 2.79    | 3.15    | 2.28    |
| Si       | 40.73 | 0       | 0       | 0       | 0       |
| Ca       | 0.1   | 0       | 0       | 0       | 0       |

Table S4 Mass and ash content of RH RHBC RHAC600, RHAC700, RHAC800 and RHAC900 before and after calcination

|          | RH   | RHBC  | RHAC600 | RHAC700 | RHAC800 | RHAC900 |
|----------|------|-------|---------|---------|---------|---------|
| Before/mg| 2502.0 | 1002.4 | 148.1   | 76.3    | 88.7    | 53.9    |
| After/mg | 375.0  | 330.0  | 0       | 0       | 0       | 0       |
| Ash content/% | 14.99 | 32.92  | —       | —       | —       | —       |

Fig.S4 Photos of RH RHBC RHAC600, RHAC700, RHAC800 and RHAC900 before and after calcination

Fig.S5 FTIR spectra of RHAC before and after MB adsorption
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