Activated Carbon Prepared from Rice Husk: Nitric Acid Modification and BTX Adsorption

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ABSTRACT

Activated carbons (ACs) prepared from rice husk by KOH activation in inert atmosphere at 750 and 850°C were modified with nitric acid. Activation at 850°C resulted in better pore development and was confirmed by SEM, Boehm titration and BET. The modification by nitric acid could reduce the particle size while enhance the amount of hydroxyl and carbonyl groups on the surface of AC samples. Bath adsorption of benzene, toluene and *m*-xylene (BTX) as well as dynamic adsorption of *m*-xylene were measured in order to evaluate the performance of AC for removing volatile organic compounds (VOCs). The results showed that AC sample prepared at 850°C (RH-850) exhibited the best benzene adsorption capacity of 11.62 mmol g^{-1} in bath adsorption and *m*-xylene adsorption capacity of 9.140 mmol g^{-1} in dynamic adsorption at 50°C.

Introduction

Benzene, toluene and xylene (BTX) vapors, which are categorized as volatile organic compounds (VOCs), have primary and secondary hazardous impacts [1]. Eyes and throat irritation, kidney or central nervous system damage are common health problems caused by BTX. Long-term exposure to BTX at high concentration may have carcinogenic and mutagenic effects. Due to their photochemical reactivity, BTX vapors have the potential to contribute to the formation of ozone and global warming, which were particularly concerned by environmental authorities [2].

There are various VOCs control methods presently applicable, such as condensation [3], adsorption [4,5], catalytic oxidation [6,7] and thermal incineration [8]. At low-concentration level, adsorption of BTX vapors on activated carbon is the most employed method for the removal of BTX vapors. Rice husk is one of the agriculture by-products in Vietnam that does not have many applications. Nevertheless, in some regions, they even cause severe pollution due to their combustion as waste [9]. The use of rice husk as activated carbon precursor could kill two birds with one stone, removal of BTX as well as solving environmental issue.

The aim of this work is to evaluate the elimination of BTX by activated carbons prepared from rice husk. The effects of surface modification on the specific surface area, pore texture and adsorption capacity of the AC samples have been examined.

Experimental

Preparation of activated carbon

Activated carbons (ACs) were prepared from rice husk by chemical activation with KOH as a chemical activating agent followed the procedure given elsewhere [10]. In brief, the rice husks (supplied by Vinh Yen Region) were washed, dried and carbonized at 450°C in the presence of nitrogen; then the carbonized products were impregnated with KOH (weight ratio 1/4) and heated at 400°C for 20 minutes under nitrogen atmosphere to dehydrate the combination, thereafter the temperature was raised to 750 or 850°C to activate the obtained material; finally, the activated products were ground, neutralized by 0.1M HCl, washed with distilled water, dried at 120°C for 24 h and stored in a desiccator. The final samples were labeled as RH-750 and RH-850, according to activated temperature 750 and 850°C, respectively.

Surface treatment

The activated carbons RH-750 and RH-850 were modified by nitric acid to change their surface chemistry [11,12], the procedure was as followed: 8.0 g activated carbon was added to 100 mL solution of 2M nitric acid in a 250 mL Erlenmeyer flask, shake for 30 second and kept still for 24 hour. The acid modified activated carbons were then washed with distilled water until a constant pH (~ 6.0), dried at 110°C for 12 h and referred as RH-750-Nitric and RH-850-Nitric.

Characterization of activated carbons

The textural characterization of the ACs was based on the N$_2$ adsorption isotherms, determined at 77 K using a Micromeritics model TriStar 3020 analyzer. The AC samples were outgassed at 573 K for 24 h to remove any moisture or adsorbed contaminants that may have been presented on their surface. The specific surface area (S$_{BET}$) was calculated by applying the BET equation to the adsorption data [13]. The microporous surface area (S$_{mi}$) and external surface area (S$_{ex}$), as well as the microporous volume (V$_{mi}$) were evaluated by the t-plot method [14]. The mesoporous volume (V$_{me}$) was estimated by the Barrett–Joyner–Halenda (BJH) method [15]. The total pore volume (V$_{tot}$) was evaluated by summation of microporous and mesoporous volumes. The pore size distribution of AC samples is calculated using density functional theory (DFT) [16] with the assumption that the pore of the sample has slit shape.

The surface functional groups of AC samples were identified by Fourier transform infrared spectroscopy using a Nexus 670 FT-IR, Nicolet operating in the range of 4000 - 500 cm^{-1} and employing the KBr pellet method. The surface acidity and basicity of the samples were determined by the Boehm method [17].

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The acidic sites were estimated by adding 0.5 g of each AC samples to 50 mL beakers filled with 25 mL of 0.1M $NaHCO_3$, Na_2CO_3, NaOH, respectively. The beakers were sealed and shaken for 48 h and then filtered and titrated with 0.1 M HCl. The numbers of acidic sites were calculated under the assumption that NaOH neutralizes carboxyl, phenolic and lactonic groups; Na_2CO_3 carboxyl and lactonic groups; and $NaHCO_3$ only carboxyl groups. Similarly, the basic sites were evaluated by mixing 0.5 g of each AC samples with 25 mL of 0.1 M HCl, and the obtained solutions were titrated with 0.1 M NaOH.

Adsorption test

The adsorption capacity of the AC samples was determined as followed: 0.5 g sample was added to a weighing bottle and placed in a desiccator together with a beaker containing either benzene, toluene or *m*-xylene at 50°C (Fig.1a). After a specific period of time (30 or 60 min) the sample was weighed to evaluate the amount of organic matter adsorbed.
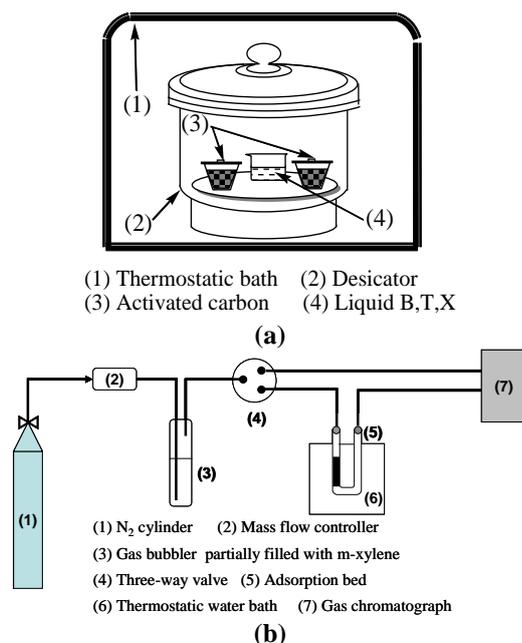

(1) Thermostatic bath (2) Desicator
(3) Activated carbon (4) Liquid B,T,X

(a)

(1) N_2 cylinder (2) Mass flow controller
(3) Gas bubbler partially filled with m-xylene
(4) Three-way valve (5) Adsorption bed
(6) Thermostatic water bath (7) Gas chromatograph

(b)

Fig 1. Schematic diagram of the experimental set up for (a) BTX adsorption (b) *m*-xylene dynamic adsorption

The dynamic adsorption of *m*-xylene was performed on the experimental set-up showed in Fig.1b. The gas flow rate was controlled by a mass flow controller. Activated carbon was placed in the adsorption bed (U-type tube) and was controlled by means of a thermostatic water bath. Both inlet and outlet gas samples were analyzed online using INTERSMAT IGC 120 FB gas chromatograph (GC) equipped with a SUPELCO 1-2233 column. The inlet stream for dynamic adsorption was prepared by purging nitrogen gas (flow rate 2 L h^{-1}) through a gas bubbler partially filled with *m*-xylene liquid at 273 K in a temperature controller bath. In this condition, *m*-xylene concentration is 2193 ppmv. The breakthrough curves for each adsorbent were acquired at 50°C. Adsorption capacity of ACs was calculated by the numerical integration of the breakthrough curve. Other parameters such as breakpoint time ($t_{5\%}$), stoichiometric time ($t_{50\%}$) and equilibrium time ($t_{95\%}$) were obtained at which the outlet *m*-xylene concentration was 5%, 50% and 95% of its inlet value, respectively. The length of unused bed (LUB) was calculated by using the following equation [18,19]:

$$LUB = \frac{t_{50\%} - t_{5\%}}{t_{50\%}} \times bed\,length \qquad (1)$$

Results and discussion

Characterization of activated carbon

SEM pictures of the raw and modified ACs are presented in Fig.2. It can be seen from the pictures that the ACs prepared from rice husk existed in the form of spherical shaped particles with a size of $5 \div 20$ nm that aggregated together to form pieces with different sizes. The AC prepared at 750°C (RH-750) has rather smooth surface while the one prepared at 850°C (RH-850) has more pores and caves. Particle sizes were found to be reduced after nitric acid modification, more notable in RH-750 sample. This could be explained by the carbon oxidation by nitric acid during the acid treatment.
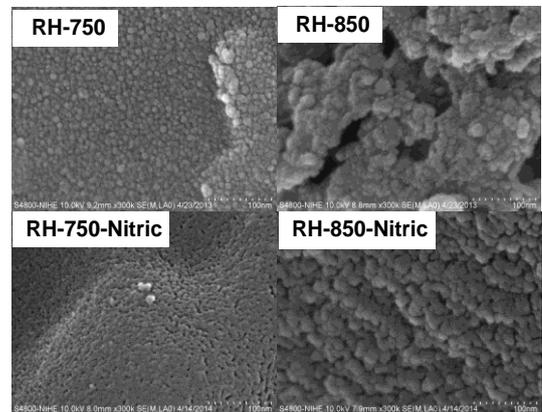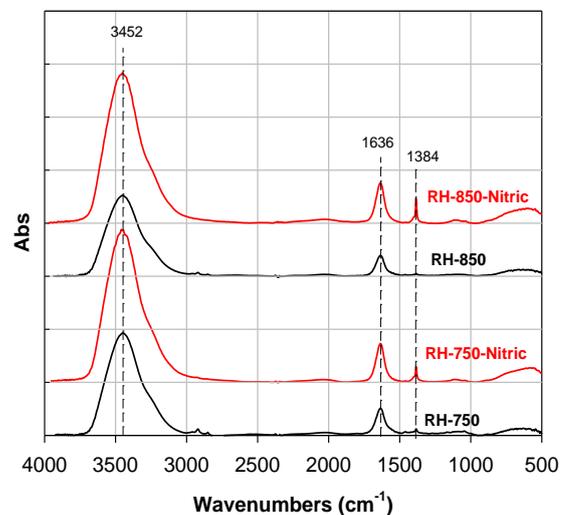

Fig 2. SEM pictures of AC samples under study

Fig 3. FTIR spectra of AC samples

FTIR spectrums of AC samples under study are illustrated in Fig.3. All the FTIR spectra have similar shapes with most of the bands located on the same wave number range. The band at 3452 cm^{-1} could be assigned to O-H stretching of hydroxyl groups or adsorbed water [20]. The band appeared at 1636 cm^{-1} corresponded to the C=O vibration of lactones, carboxyl or anhydride groups [21]. The band at 1384 cm^{-1} was attributed to C-H stretching of aliphatic carbon or due to CH_2 and CH_3 deformation. No SiO_2 characteristic absorption band (1101, 944, 789 and 470 cm^{-1} [22]) were detected, that is to say, silica was effectively removed from all the AC samples by synthetic method and appropriate treatment. It can be noticed from FTIR spectra that the intensity of the bands located at 3452 and 1636 cm^{-1} increased after nitric acid modifying. This result suggests that nitric acid modification could increase the amount of hydroxyl and carbonyl groups on the surface of AC samples.

Table 1. Results of Boehm titration

Sample	Groups (mmol g^{-1})			Total acidity (mmol g^{-1})	Total basicity (mmol g^{-1})
	Carboxylic	Lactonic	Phenolic		
RH-750	0.975	0.350	0.900	2.225	0.271
RH-850	0.650	0.075	0.675	1.400	0.450
RH-750-Nitric	1.306	0.282	0.343	1.976	0.320
RH-850-Nitric	1.411	0.161	1.028	2.600	0.180

The results obtained by the Boehm method are presented in Table 1. It can be observed that the total amount of acidic groups is significantly higher than the amount of basic group. When activation temperature increased from 750 to 850°C, total amount of acidic groups are decreased from 2.225 to 1.400 mmol g^{-1}, while the amount of basic group increased from 0.271 to 0.450 mmol g^{-1}. This could be explained by the decomposition of the functional groups at higher temperature. Carboxylic, lactonlic (acidic groups) decomposition in temperature range 150 ÷ 650°C, much lower than that of quinone (basic group) 650 ÷ 980°C [23], hence, the acidic groups decreased at higher activation temperature. As expected, nitric acid treatment resulted in the enhancement of carboxylic group, from 0.975 to 1.306 mmol g^{-1} for RH-750 and from 0.650 to 1.411 mmol g^{-1} for RH-850. However, for RH-750-Nitric, nitric acid modification leads to the decrease of other acidic groups (lactonic and phenolic) which in turn decrease its total acidity.
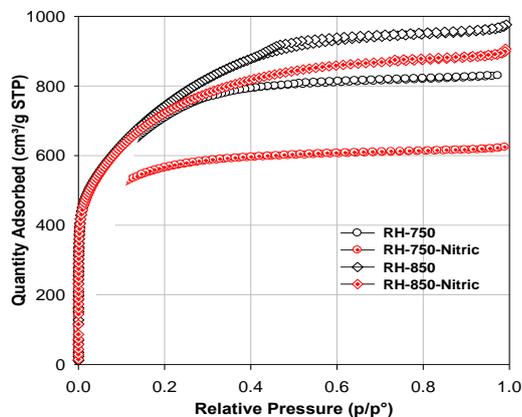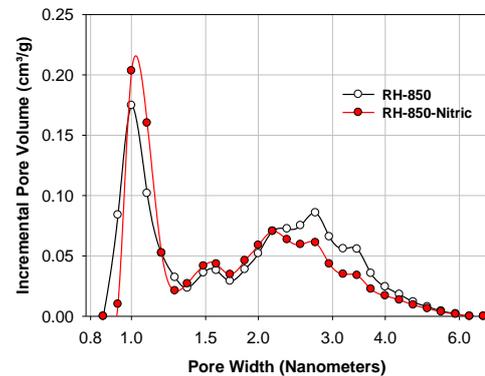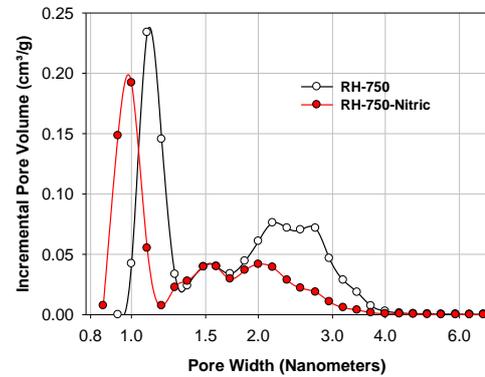

Fig 4. Adsorption/desorption isotherms of N$_2$ at 77K for AC samples

Nitrogen adsorption-desorption isotherms at 77K for all AC are shown in Fig.4. The results show that all samples have mixed type isotherm characteristics, type I at low relative pressures (p/p^0) and type IV at intermediate and high relative pressures [21]. There is a sharp adsorption uptake in low relative pressures region, which is a representative of microporous solid. However, the knee of the isotherms is quite wide with no clear plateau attained, which indicating the presence of large micropores and mesopores. It can also be seen that the AC prepared at 850 ^{o}C present the wider knee of the isotherms than the sample activated at 750 ^{o}C, therefore it has higher amount of mesopores. Nitric acid modification resulted in a slightly decrease in the adsorption content of N$_2$ at relative pressure p/p^0 > 0.2 for RH-850-Nitric, yet significantly decrease and occurred at relative pressure p/p^0 ≥ 0.01 for RH-750-Nitric sample. The change in the isotherms could result in accordingly change in specific surface area and pore texture. The overall physical properties of the ACs obtained from N$_2$ adsorption are given in Table 2. For sample activated at 750 ^{o}C, BET surface area decreased from 2584 to 2077 m^2 g^{-1} (19.6 %) and total pore volume dropped from 1.3072 to 0.9667 cm^3 g^{-1} (26.0 %). It can also be seen from Table 2 that the reduction of

the BET surface area and the pore volume is mainly contributed by micropores.

Table 2. Physical properties deduced from N$_2$ adsorption at 77 K on AC samples

Sample	S_{BET} (m^2 g^{-1})	S_{mi} (m^2 g^{-1})	S_{ex} (m^2 g^{-1})	S_{mi}/S_{BET} (%)	V_{mi} (cm^3 g^{-1})	V_{tot} (cm^3 g^{-1})	V_{mi}/V_{tot} (%)
RH-750	2584	2513	71	97.3	1.1977	1.3072	91.6
RH-750-Nitric	2077	2027	50	97.6	0.8985	0.9667	92.9
RH-850	2703	2572	131	95.2	1.3414	1.5250	88.0
RH-850-Nitric	2646	2531	115	95.7	1.2436	1.4118	88.1

Fig 5. Pore size distribution of AC samples

Pore size distributions (PSDs) of the AC samples were calculated using the DFT software and are illustrated in Fig.5. The obtained PSDs indicates that pore width of all the ACs in this study are less than 7 nm, therefore, Fig. 5 only shows the PSDs in the size range of 0.8-7.0 nm. It can be noticed that all the ACs has small amounts of mesopores and an appreciable amount of micropores. There are more mesopores with pore width greater than 2.0 nm in the sample activated at 850°C than in the sample with lower activation temperature. Nitric modification caused the decrease of mesopores with radii greater than 2.2 nm for RH-850-Nitric, while caused the decrease of micropores that has radii less than 1.4 nm and greater than 1.8 nm for RH-750-Nitric. These results are in accordance with the specific surface area and pore texture given previously.

Adsorption of benzene, toluene and m-xylene onto activated carbon

To determine the BTX adsorption capacity of the AC sample, the experiments were carried out at bed temperature of 50°C as shown in Fig.6. Due to their large specific surface area, BTX adsorption is quite high for all samples, adsorption capacities are in the range from 3.1 to 4.6 mmol g^{-1}. In addition, the following results could be obtained:

i) Time to reach equilibrium is increased when replaced benzene by toluene and *m*-xylene. There are two main reasons, molecule size and boiling point. Molecule size and boiling point (at 1 atm) are increase in the same sequence:

benzene (d = 0.37 nm, 353.1 K) < toluene (d = 0.59 nm, 383.6 K) < *m*-xylene (d = 0.70 nm, 412.1 K), therefore time for diffusion increase while vapor pressure of the substance decrease in that order, thus, explained the time difference in reaching equilibrium.
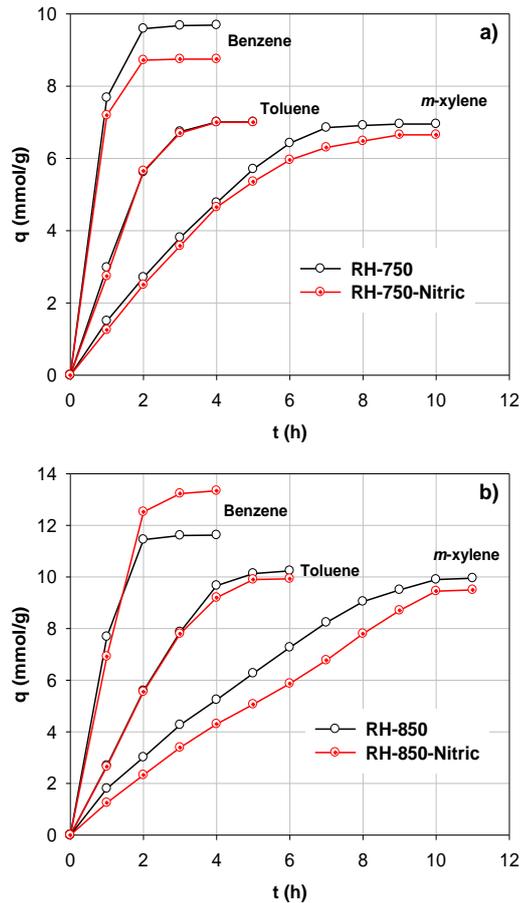

Fig 6. Adsorption of BTX at 50°C onto activated carbons prepared at (a) 750°C before and after modified by nitric acid (b) 850°C before and after modified by nitric acid

ii) Adsorption capacity (mmol g^{-1}) is decreased from benzene to *m*-xylene corresponding to molecule size of the adsorbates. As compared to RH-750, RH-850 has better adsorption ability toward BTX due to its developed specific surface area and pore volume.

iii) Adsorption capacity of RH-750 decreases after nitric acid treatment, especially for benzene adsorption. However, RH-850-Nitric has higher benzene adsorption and somewhat lower toluene/*m*-xylene adsorption compared to untreated one.

The adsorption of BTX onto carbon-based materials were reported to be depended on various conflict factors: specific surface and pore volume, π-π interactions between the aromatic rings and those of carbon substrate or donor-acceptor interactions between the surface carbonyl groups (electron donors) and the aromatic rings (acceptors). Nevertheless, basic groups of AC materials could also act as electron donors, therefore, the amount of BTX uptake may be correlated with the total number of both carbonyl and basic groups [24]. For all aforementioned reasons, with an remarkably increasing in total amount of carbonyl and basic groups from 1.100 to 1.591 mmol g^{-1} and a slightly decreasing specific surface area, RH-850-Nitric showed an significantly enhance in benzene adsorption (11.62 to 13.34 mmol g^{-1}). Moreover, while having high number of carbonyl and basic groups, its specific surface area reduced exceedingly, as a result, benzene adsorption onto RH-750-Nitric declines from 9.69 to 8.75 mmol g^{-1}.
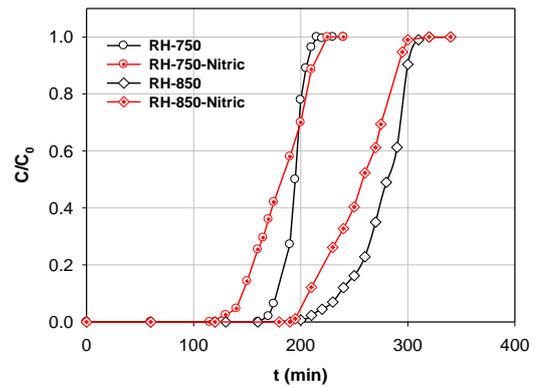

Fig 7. *m*-xylene breakthrough curves at 2193 ppmv for AC samples under study at 50 °C

Table 3. Breakthrough adsorption characteristics of different ACs samples at 50 °C

Sample	$t_{5\%}$ (min)	$t_{50\%}$ (min)	$t_{95\%}$ (min)	$t_{95\%}$-$t_{5\%}$ (min)	LUB (cm)	q (mmol g^{-1})
RH-750	173.5	194.9	208.8	35.3	0.08	6.264
RH-750-Nitric	140.8	183.4	218.2	77.4	0.16	6.078
RH-850	221.2	281.4	305.7	84.5	0.15	9.140
RH-850-Nitric	200.0	259.3	295.1	95.1	0.16	8.439

The dynamic adsorption of *m*-xylene on all AC samples at 2193 ppmv was studied using the previously mentioned conditions. The breakthrough curve during adsorption by *m*-xylene at 50°C is described in Fig.7 and listed in Table 3, respectively. All the breakthrough has typical S-shaped curve corresponding to three stages: completely adsorbed, partially adsorbed and saturation adsorbed. The breakthrough time ($t_{5\%}$), stoichiometric ($t_{50\%}$), and equilibrium time ($t_{95\%}$), as well as the interval time from the breakpoint until saturation ($t_{95\%}$ - $t_{5\%}$) for the adsorption of *m*-xylene onto activated carbon prepared at 850°C (RH-850) are higher than those of RH-750. This leads to the *m*-xylene adsorption capacity of RH-850 (9.140 mmol g^{-1}) is greater than that of RH-750 (6.264 mmol g^{-1}). Nitric acid modification reduces $t_{5\%}$, $t_{50\%}$ and $t_{95\%}$ of AC samples (except for $t_{95\%}$ of RH-750, which is slightly increased), therefore hindered the adsorption capacity of activated carbon. *m*-xylene adsorption capacity sunk from 6.264 to 6.078 mmol g^{-1} and from 9.140 to 8.439 mmol g^{-1} for RH-750 and RH-850, respectively. The length of unused bed of RH-750 (0.08 cm) is shorter than that of RH-850 (0.16 cm). However after modification by nitric acid, the LUB of RH-750 and RH-850 have the same figure. The result obtained from dynamic adsorption of *m*-xylene is in agreement with the bath adsorption study.

Conclusion

Activated carbons from rice husk were obtained by means of chemical activation. The as-prepared samples are microporous materials with developed BET surface area (more than 2500 m^{2}g^{-1}). Nitric acid modification reduces particle size and creates more functional groups on the surface of AC samples. BTX adsorption capacity of all AC samples decrease from benzene to toluene and *m*-xylene correlated to molecule size and boiling point of adsorbates. Nitric acid modification of AC sample prepared at 850°C (RH-850-Nitric) enhanced the adsorption capacity for benzene whereas reduced its toluene and *m*-xylene uptake. With adsorption capacity of *m*-xylene in the dynamic adsorption in the range from 6.078 to 9.104 mmol g^{-1}, activated carbon prepared from rice husk shows a potential in removing VOCs. Further improvements in order to achieve higher VOCs adsorption capacity are in progress.

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