



Surface modification of coconut shell based activated carbon for the improvement of hydrophobic VOC removal

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ABSTRACT

In this study, coconut shell based carbons were chemically treated by ammonia, sodium hydroxide, nitric acid, sulphuric acid, and phosphoric acid to determine suitable modification for improving adsorption ability of hydrophobic volatile organic compounds (VOCs) on granular activated carbons (GAC). The saturated adsorption capacities of *o*-xylene, a hydrophobic volatile organic compound, were measured and adsorption effects of the original and modified activated carbons were compared. Results showed that GAC modified by alkalis had better *o*-xylene adsorption capacity. Uptake amount was enhanced by 26.5% and reduced by 21.6% after modification by $\text{NH}_3\text{H}_2\text{O}$ and H_2SO_4 , respectively. Compared with the original, GAC modified by acid had less adsorption capacity. Both SEM/EDAX and BET were used to identify the structural characteristics of the tested GAC, while IR spectroscopy and Boehm's titration were applied to analysis the surface functional groups. Relationships between physicochemical characteristics of GAC and their adsorption performances demonstrated that *o*-xylene adsorption capacity was related to surface area, pore volume, and functional groups of the GAC surface. Removing surface oxygen groups, which constitute the source of surface acidity, and reducing hydrophilic carbon surface favors adsorption capacity of hydrophobic VOCs on carbons. The performances of modified GACs were also investigated in the purification of gases containing complex components (*o*-xylene and steam) in the stream.

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1. Introduction

Volatile organic compounds (VOCs) are odorous and toxic and emitted principally from industrial point sources, such as printing and coating facilities, chemical industries, and waste and wastewater treatment processes. They react with nitrogen oxides in sunlight to form ozone and photochemical oxidants, which contribute to ozone formation and photochemical smog. Legislation has already been introduced to reduce emissions due to their potential environmental and human health risks, even at very low concentrations.

Adsorption that captures target adsorbates on the surface of adsorbents is an effective and widely used technique for VOC control. Due to their developed high surface area, porous structure, and high degree of surface reactivity, activated carbons have been the most widely used adsorbent in the purification of organic compounds with intermediate molecular weights (typically about 45–130) from gases and vapors. Previous research has already investigated adsorption of monocyclic aromatic hydrocarbons, such as toluene, benzene, and xylene [1–6], 1,1-dichloroethane and chloroform [7] and other organic materials [8–14].

Adsorption can be a physical or a chemical process. When adsorbed on the carbon surface, molecules of organic pollutants are strongly captured by adsorption forces, which can be enhanced in small pores [15]. Both texture and surface chemistry of activated carbons are responsible for their adsorption capacity [4,16,17]. The pore structure of carbon can be controlled by various routes, such as activation conditions, precursor, and templates. Surface chemical functional groups are mainly derived from activation processes, heat treatment, and post chemical treatment, and can be modified through physical, chemical, and electrochemical treatments [17–20]. Among these techniques, the treatment of GACs by acids or alkalis is an economic and popular modification method. Kim et al. modified activated carbon by impregnation with various acids or bases. The results showed that activated carbon treated with 1 wt % H_3PO_4 had the greatest adsorption capacity for benzene and toluene, which is a promising hybrid system adsorbent for controlling low concentration VOC emissions [15]. Surface areas and pore volumes of activated carbons derived from peach stone shells can also be chemically modified by H_3PO_4 under standard conditions [21]. Previous research reported that the surface chemical functional groups determined by treatment methods, ammonization increases basic properties and oxidization increases acidic properties [22].

Activated carbon can be produced from carbonaceous materials including nut-shells, bark, coal, fly ash, and bone char. These

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different types of activated carbon have different physical and chemical characteristics, and the modification method used relies on the texture and characteristics of GAC. Coconut based activated carbon is harder than coal based carbon and has abundant functional groups on the surface. Yet very few reports have focused on the modification of coconut based GAC for the enhancement of hydrophobic VOC uptake. The purpose of this research was to pursue a suitable GAC modification method to improve hydrophobic VOC purification. Coconut based GACs were modified with acids and alkalis and adsorption of *o*-xylene was carried out to evaluate adsorption capacities. The physicochemical characteristics of original and modified GAC were analyzed by SEM/EDAX, IR spectroscopy, and Boehm's titration.

In addition, many gaseous streams involved in industrial processes contain VOC with steam. Water in VOC emissions influences removal of hydrophobic pollutants. However, many studies regard the abatement of VOCs in dry gas stream and seldom include the wet stream. In our previous study, an adsorption system was proposed to provide long-term stable operation of a biofilter under adverse contaminant feeding conditions. This integrated reactor system not only led to high and stable *o*-xylene removal efficiency, but also improved shock load resistance capacity. However, the relative humidity (RH) in gas from the biofilter was usually over 80%. The moisture was adsorbed by the GAC and resulted in a reduction in GAC ability of *o*-xylene adsorption. Thus, in this study, we also investigated the performance of the modified GAC worked as adsorbent in the adsorption of considered hydrophobic pollutants in wet stream.

2. Materials and methods

2.1. Materials

2.1.1. Adsorbents

Commercially available GAC prepared from coconut shell with 60–80 mesh and 2.0% ash content was obtained from the Sinopharm Chemical Reagent Co., Ltd., in China. It is very popular in the gas phase purification due to its unique distribution of pores diameter. Before chemical treatment, GAC was purified by boiling in a water bath for 2 h and washed with deionized water to remove fine particles, and subsequently dried in an oven at 105 °C for 4 h. The acidic and alkaline solutions for preparation of GACs were made with 10 M HNO₃ (NA), 9.0 M H₂SO₄ (SA), 7.3 M H₃PO₄ (PA), 10 M NaOH (SH), and 6.6 M NH₃·H₂O (AM). The corresponding modified GACs were GAC/NA, GAC/SA, GAC/PA, GAC/SH, and GAC/AM. The GACs were soaked in each solution at 70 °C for 2 h and were then placed on a rotation vibrator at 35 °C for 24 h. The modified GACs were separated from the solution and washed repeatedly with distilled water. They were then dried in an oven at 105 °C for 4 h and transferred to a desiccator before use.

2.1.2. Adsorbate

Adsorption on activated carbon is useful for recovery of VOCs with intermediate molecular weights (typically about 45–130), as smaller compounds do not adsorb well on carbon and larger compounds cannot be removed (typically by steam stripping) during regeneration. The US Environmental Protection Agency (EPA) has listed *o*-xylene ($M_w = 106.16$) as a priority toxic pollutant, and this was chosen as the testing compound in this study.

2.2. Characterization of GAC

To better understand their variations, the original and modified carbons were characterized using a variety of analytical techniques.

2.2.1. SEM/EDAX

Surface properties of original and modified GAC were observed through a scanning electron microscope (SEM) (HITACHI S-3000N/EDAX Inc., Japan) after treatment with acids or alkalis. The distribution of elements on the surface or in the pores of carbon particles were determined by the same SEM together with energy dispersive X ray spectroscopy.

2.2.2. Texture

The surface area of the GACs were determined from the N₂ adsorption isotherms conducted in a volumetric apparatus (ASAP 2000, Micromeritics, USA). Adsorbents were degassed at 350 °C for 4 h prior to adsorption experiments. The Brunauer, Emmett, and Teller (BET) surface area was determined by applying the BET equation to the adsorption data. Total pore volume and micropore volume were measured by the Barrett-Joyner-Halenda (BJH) and the *t*-plot and Harkins–Jura methods, respectively [23]. The pore size determined by BJH method.

2.2.3. Surface chemistry characterization

2.2.3.1. Boehm's titration. Surface functional groups such as phenolic group (–OH), carbonyl group (C=O) and carboxylic group (–COOH) were determined by Boehm titration [20,23–25].

2.2.3.2. IR spectrum analysis. Fourier transform infrared spectroscopy (FTIR) was used to qualitatively evaluate the chemical structure of carbon materials. The IR spectra were collected using a Nicolet, Nexus 670 (USA) FTIR spectrometer. The GAC samples were grounded into fine powder and mixed with KBr at a weight ratio of 700:1. About 200 mg of the mixture was used for the preparation of KBr pellets. The IR spectrum was obtained over a frequency between 400 and 4000 cm^{–1}.

2.2.3.3. Zeta potential measurements. Zeta potential measurements of GAC were carried out with a Zeta Potential Analyzer (Zetasizer 2000, Malvern Co. United Kingdom). Approximately 100 mg of powder samples were ground in an agate mortar, mixed with 1 L distilled water, and settled for several minutes. The suspension with colloidal sized particles were collected to determine zeta potential after addition of 0.01 M NaCl solution and pH adjustment with 0.01 M solutions of NaOH or HCl. The pH_{PZC} was the corresponding pH value when the zeta potential was 0 mV.

2.3. Adsorption test

Adsorption of *o*-xylene was carried out at ambient temperature (22–27 °C) using a dry air flow containing 2176–2239 mg m^{–3} of the hydrocarbons, which were bubbled through a Muencks gas-washing bottle containing pure *o*-xylene and then diluted with a large dry air flow at appropriate temperature. Desired concentrations of the *o*-xylene in the influent stream were obtained by adjusting the rates of two airflows. For each experiment, the original and modified GAC (2.0 g) were placed inside quartz tubes with an inner diameter of 0.8 cm. The *o*-xylene-laden air flowed upward through the adsorption tube. All flows were controlled by flow meters at a total flow rate of 45 mL min^{–1}.

Experimental apparatus of *o*-xylene adsorption from the effluent stream of an overload biofilter (ESOB) is shown in Fig. 1. The *o*-Xylene biodegradation was carried out in the biofiltration unit, which had a single stage column of 10.0 cm diameter and working volume of 6.28 L. It was packed with porous polyurethane foam cubes for attached growth of microorganisms. The sampling ports were located at the biofiltration unit inlet and outlet in correspondence to compound concentrations prior and after treatment. Three parallel glass tube reactors were used as adsorption units. Each adsorption unit had a working volume of 0.70 L and diameter of

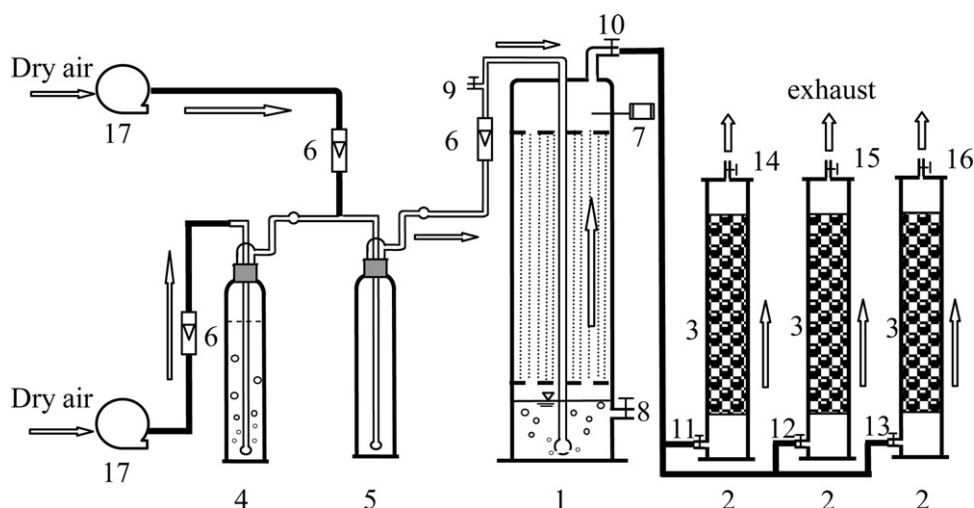


Fig. 1. Schematic diagram of *o*-xylene adsorption from the effluent stream of an overload filter (ESOB): (1) ESOB; (2) adsorption unit; (3) adsorbent; (4) Muencks gas-washing bottle containing pure *o*-xylene; (5) mix chamber; (6) flow meter; (7) Temp/RH meter; (8)–(16) sampling ports; (17) air pump.

6.0 cm. The tested GACs worked as adsorbents. Sampling ports were provided at the bottom and top of the adsorption unit to determine compound concentrations in untreated and treated gases.

The experiment was carried out continuously when the outlet concentration was equal to the inlet concentration. Inlet and outlet concentrations were analyzed by gas-chromatography (Agilent 6890 N, USA) equipped with a flame ionization detector (FID). An HP-5 column of $\varnothing 0.32 \text{ mm} \times 30 \text{ m}$ was used at 180°C with nitrogen carrier gas at a pressure of 25 psi. Serial standard *o*-xylene gases (National Institute of Metrology, PR China) were used to obtain calibration curves. Gas samples ($1000 \mu\text{L}$) were collected by a gas-tight syringe (Agilent, 5182–9604) and injected directly into the GC. Data acquisition and processing were based on an HP Chemstation Data System.

The saturated adsorption capacity of GAC was measured by the gravity method and the weight of the adsorption tube was quantitatively analyzed by a precision balance at regular intervals to investigate total uptake quantity (Q_t) of the tested GAC. Q_t (mg g^{-1}) at any contact time (t) could be determined by the following formula:

$$Q_t = \frac{W_t - W_0}{W_{\text{GAC}}}$$

Where, W_{GAC} (g) is the amount of GAC introduced in the adsorption tube and W_0 (mg) and W_t (mg) are the amounts of adsorption tube at the original and t time, respectively. Breakthrough curves for the different GAC were obtained from these data by plotting the Q_t against time.

The *o*-Xylene adsorbed on GAC were determined by collecting samples from the adsorption column and extracted three times by hexane and then analyzed by GC.

3. Results and discussion

3.1. Adsorption capacity of *o*-xylene on the GAC

The GAC adsorbents were tested for *o*-xylene adsorption capacity. A dry air stream with a known *o*-xylene concentration was continuously passed through the adsorption tube packed with prepared GAC. Gas phase *o*-xylene was transferred onto the GAC by attractive forces. Variation in *o*-xylene concentration was monitored by sampling at the tube outlet. Typically, an experiment ended when equilibrium was achieved; that is, the activated carbon was saturated with *o*-xylene. Fig. 2 dis-

plays the breakthrough curves, presented as amounts adsorbed (Q_t) versus contact time (t) for the six carbons under consideration. The sequence for uptake *o*-xylene quantities was GAC/AM (305.70 mg g^{-1}) > GAC/SH ($295.403 \text{ mg g}^{-1}$) > GAC (241.69 mg g^{-1}) > GAC/NA (220.74 mg g^{-1}) > GAC/PA (204.50 mg g^{-1}) > GAC/SA (189.46 mg g^{-1}). The uptake of *o*-xylene before and after chemical treatment exhibited high adsorption capacity over alkali-treated GAC. Compared with original GAC, the GAC modified by acids had less adsorption capacity. Uptake amount increased by 26.5% and decreased by 21.6% after modification with $\text{NH}_3\text{H}_2\text{O}$ and H_2SO_4 , respectively.

3.2. The characteristics of tested GACs

3.2.1. Texture structures of tested GACs

The specific surface areas of the prepared GAC are listed in Table 1. The large BET surfaces obtained from GAC modified by alkalis were $868 \text{ m}^2 \text{ g}^{-1}$ for GAC/AM and $846 \text{ m}^2 \text{ g}^{-1}$ for GAC/SH. They had higher BET surface areas than other samples. In contrast, the surface areas of the acid-treated GAC ranged from 441 to $608 \text{ m}^2 \text{ g}^{-1}$, which were much lower than that of original GAC ($731 \text{ m}^2 \text{ g}^{-1}$).

Pore texture characteristics of tested GACs are compiled in Table 1. Both GAC/AM and GAC/SH increased total pore volume but did not affect mean pore diameter. Modification by acids produced a slight increase in pore size and decrease in total pore volume. These changes were due to the widening of pores, resulting in lower pore volume. In all cases, GACs modified by alkalis had a total micropore volume slightly higher than that of GACs modified by acids.

The SEM photographs of acid- or alkali-treated GAC are shown in Fig. 3. The GAC modified by $\text{NH}_3\text{H}_2\text{O}$ (GAC/AM) exhibited a rough and purified surface. Various pore sizes were observed on the surface and inside the particle. The surfaces of GAC/SH were similar, although some pores were blocked. Both the surface and pore structure of GAC treated with acids (e.g. GAC/NA, GAC/SA, and GAC/PA) were partially destroyed or enlarged, which greatly decreased BET surface area.

3.2.2. Elements and functional groups on the surface of original and modified GAC

The SEM/EDS analysis provided information on the distribution of elements in the original and modified carbons, which was necessary to understand the chemical reaction occurring in the process of modification. Table 2 shows that untreated GAC had elements

Table 1
The specific surface area and *o*-xylene uptake quantity on GAC.

Adsorbents	GAC	GAC/AM	GAC/SH	GAC/NA	GAC/SA	GAC/PA
Surface area ($\text{m}^2 \text{g}^{-1}$)	731	868	846	528	608	441
Pore size (\AA)	23.46	23.91	23.72	25.14	23.58	24.42
Volume (mL g^{-1})	0.168	0.176	0.178	0.170	0.156	0.150
Median pore diameter (nm)	5.87	5.87	5.90	6.20	5.84	6.13
pH_{PZC}	4.5	7.3	7.5	2.5	3.3	2.7
Acidic (mmol g^{-1})	0.18	0.09	0.15	0.95	0.85	0.78
Basic (mmol g^{-1})	0.37	0.33	0.56	0.08	0	0

of C, O, Mg, Al, and Cl at the surface and inside the pore of a carbon pellet. Elements of Na, N, S, and P immersed in GAC/SH, GAC/AM, GAC/NA, GAC/SA, and GAC/PA, respectively, compared with untreated GAC. Metal elements of Mg and Al in the original GAC disappeared after treatment with acids and NaOH, while their concentration decreased slightly when modified by $\text{NH}_3 \cdot \text{H}_2\text{O}$, indicating that chemical reactions occurred during the treatment

processes. All samples had an oxygen element, showing they have some oxygen-containing groups on the surface. Significantly, more oxygen was detected in the acid-modified GACs.

Distribution of elements on the carbon particle was not homogeneous. An obvious difference of newly emerging element concentration was found between the surface and inside the pore, with content much higher inside the pore than at the carbon

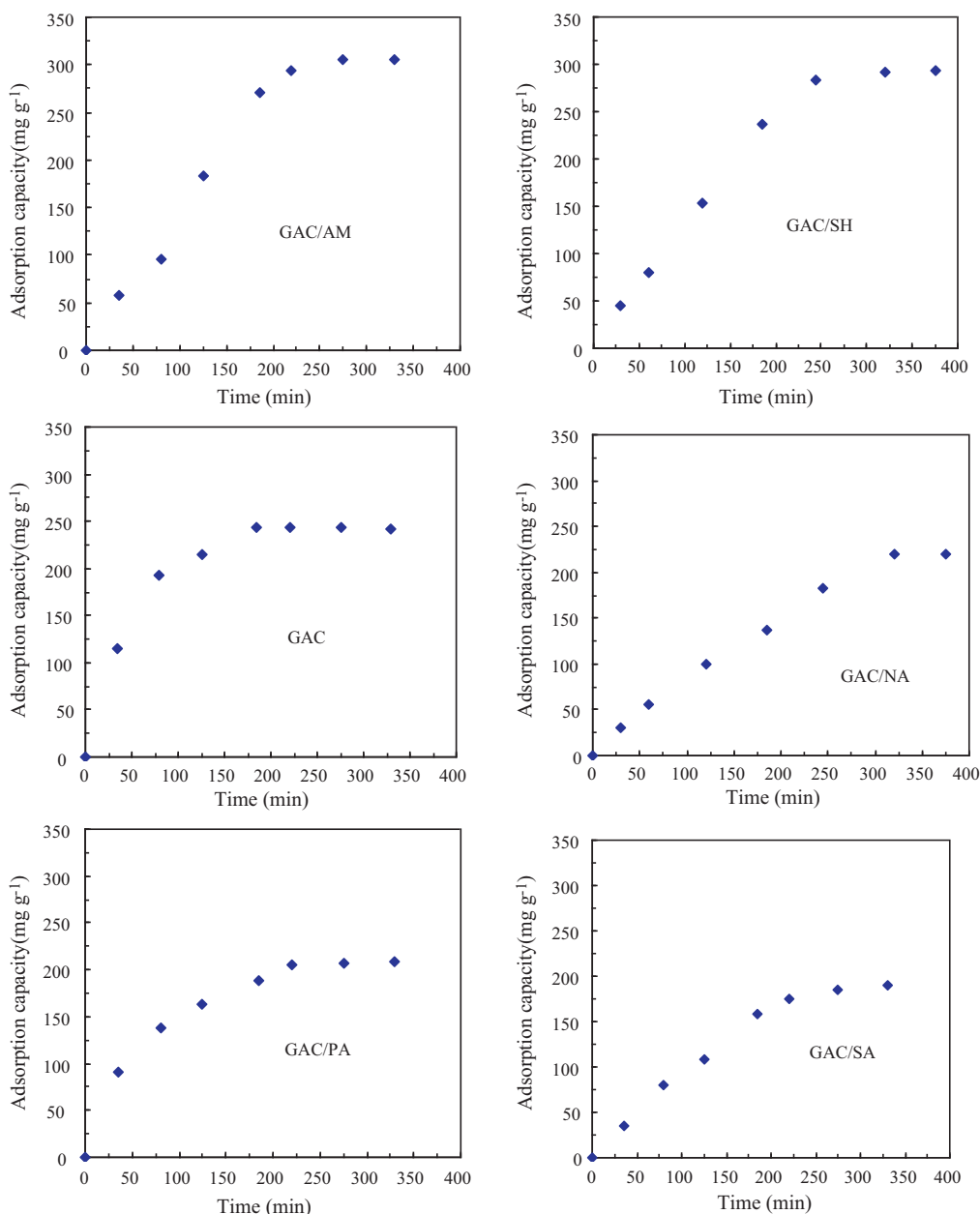


Fig. 2. Change of adsorption capacity with contact time.

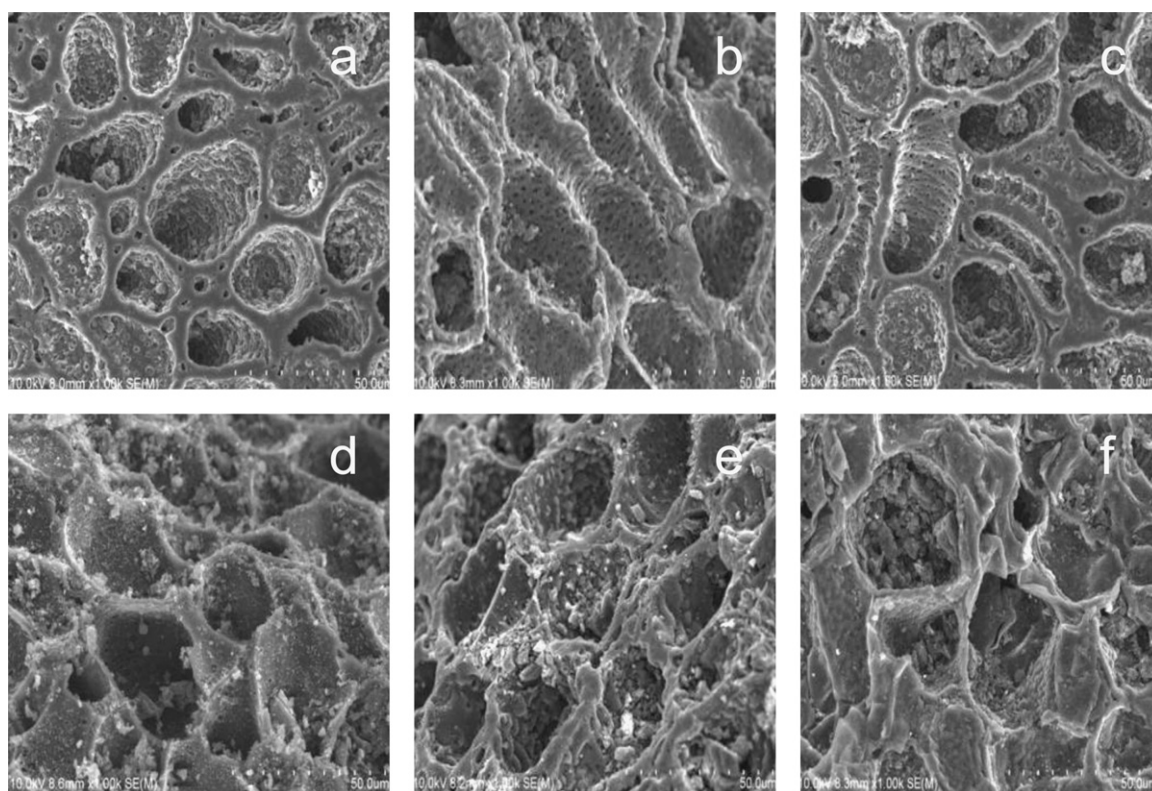


Fig. 3. SEM photographs of acid- or alkali-treated GAC: (a) GAC/AM; (b) GAC; (c) GAC/SH; (d) GAC/NA; (e) GAC/SA; (f) GAC/PA.

Table 2
Elements on the test GACs.

Element (Wt%)	GAC		GAC/SH		GAC/AM		GAC/NA		GAC/SA		GC/PA	
	Surface	Pore	Surface	Pore	Surface	Pore	Surface	Pore	Surface	Pore	Surface	Pore
C	96.49	96.63	956.96	96.75	96.63	94.70	95.26	97.64	94.56	93.44	95.03	95.16
O	3.43	2.83	2.46	1.75	1.12	1.13	4.17	1.13	5.02	3.60	4.26	2.83
Mg	0.03	0.09	–	–	0.09	–	–	–	–	–	–	–
Al	0.03	0.13	–	–	0.13	–	–	–	–	–	–	–
Cl	0.02	0.32	–	–	–	–	–	–	–	–	–	–
Na	–	–	1.58	1.50	–	–	–	–	–	–	–	–
N	–	–	–	–	0.31	0.79	0.57	1.23	–	–	–	–
S	–	–	–	–	–	–	–	–	0.42	2.96	–	–
P	–	–	–	–	–	–	–	–	–	–	0.71	2.01
Total	100	100	100	100	100	100	100	100	100	100	100	100

pellet surface. This indicated that chemical modification based on the reaction between carbon and acids or alkalis took place mostly in the carbon pores.

Surface functional groups such as phenolic group ($-\text{OH}$), carbonyl group ($\text{C}=\text{O}$), and carboxylic group ($-\text{COOH}$) were determined by Boehm titration. The results of these surface functional groups for various activated carbon samples are shown in Fig. 4. For original GAC, the total oxygen containing functional group was 0.18 mmol g^{-1} with 72.2% (0.13 mmol g^{-1}) phenolic group and 27.8% (0.05 mmol g^{-1}) lactone groups. No carboxylic group was found in the original GAC. When modified by acids, total concentration of oxygen containing functional groups increased dramatically from 0.18 mmol g^{-1} to between 0.82 and 0.97 mmol g^{-1} , dependent on acid used. The increase was consistent with SEM/EDAX results. As far as individual oxygen containing functional groups were concerned, the phenolic group increased from 0.13 mmol g^{-1} to between 0.19 and 0.37 mmol g^{-1} , the carbonyl group increased from 0.05 mmol g^{-1} to between 0.09 and 0.15 mmol g^{-1} and the carboxylic group increased from 0 to between 0.51 and 0.58 mmol g^{-1} . The major increase took place in the carboxylic

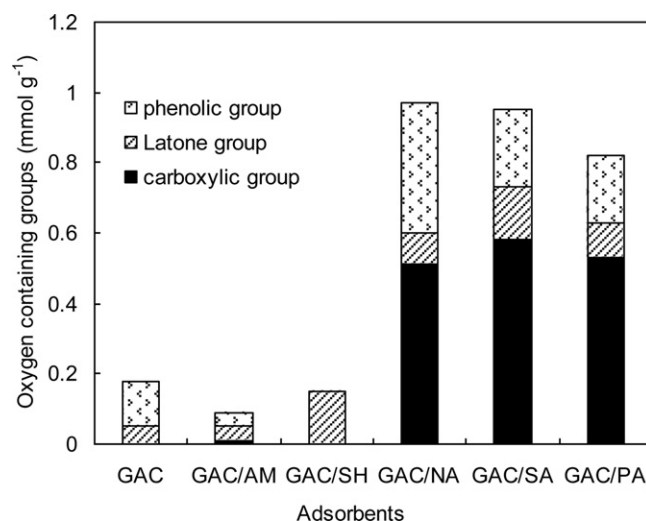


Fig. 4. Surface functional groups of various GAC (mmol g^{-1}).

group, which contributed to the strong oxidation property of treated acids. Alkali-treated GAC decreased total concentration of the oxygen containing functional groups from 0.18 mmol g⁻¹ to 0.15 and 0.09 mmol g⁻¹ for GAC/SH and GAC/AM, respectively. The decrease in oxygen containing functional groups occurred mostly on the phenolic group.

The FTIR spectra for the tested carbons were recorded to obtain better insight on the functional groups available on the carbon surface. As shown in Table 3, all samples exhibited bands at 2920 and 2845 cm⁻¹, which were due to asymmetrical and symmetrical stretching of CH₂. The absorption bands of the carbonyl group (1640 cm⁻¹) and the phenolic group (1118 cm⁻¹) were observed in GAC, GAC/SH, GAC/SA, and GAC/PA. While GAC/AM and GAC/NA showed stretching of C=O in cyclic amides at 1684 cm⁻¹ as a result of chemical modification by NH₃·H₂O and HNO₃. Only GAC/SH, GAC/NA, and GAC/PA had the -COOH absorption band, which appeared at 1380–1390 cm⁻¹.

3.2.3. Surface acidity and basicity

The zeta potential of all samples as a function of pH (pH_{PZC}) and their total surface acidity obtained by the Boehm method are shown in Table 1. The GAC had a pH_{PZC} of 4.5 when zeta potential was 0 mV. The value shifted below 3.5 when treated with acids and over 7.5 when treated by alkalis. Surface acidity of carbons gained from Behm's method was complementary with the pH_{PZC}. Both decreased with the increasing of the amount of oxygen-containing surface groups. Previous research indicates that the existence of surface functional groups such as carboxyl, carbonyl, and phenol constitutes the source of surface acidity. The opposite is observed for alkali treatment. While, oxidation of carbon with acids mainly increased the concentration of hydroxyl and carbonyl surface groups oxidation, ammonization introduced nitrogen-containing groups, such as, C=N, amino, cyclic amides, nitrile groups, and pyrrole-like structure, which generally provide basic properties. Surface chemistry of carbon materials is determined by the acidity and basicity of their surface.

3.3. The effect of surface physicochemical characteristics on adsorption capacity

The adsorption capacity of GAC relies on its surface characteristics, e.g. texture and surface physicochemical properties [26,27]. The BET surface area presented a linear relationship with the adsorption capacity of *o*-xylene for the tested carbons (Fig. 5). Higher surface area will generally result in higher adsorption capacity. For all samples, GAC/AM had the highest BET surface area (Table 1), which implied it may have better physical adsorption capacity. In addition, it had a larger pore volume than original GAC. The adsorption capacity of GAC/NA, GAC/PA, and GAC/SA decreased

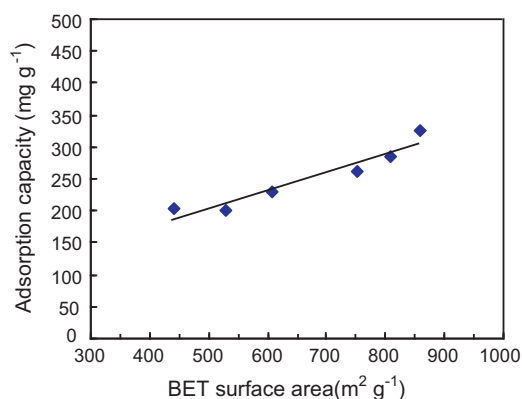


Fig. 5. BET surface area and amount of *o*-xylene adsorbed on GAC.

considerably due to its lower BET surface area, which was considered the reason for pore enlargement and surface destruction during acid treatment.

Several factors may jointly influence overall performance of the studied carbons. Besides surface area and pore size, carbon surface chemistry might contribute significantly to adsorption capacity. Oxidation by acids or alkalis removed mineral elements and emerged other atoms. A similar phenomenon has been observed in previous studies [22]. More oxygen emerged after modified by acids, indicating the addition of oxygen-containing functional groups. However, the variation of other elements had less influence on *o*-xylene adsorption ability in this study. Significantly, more oxygen was detected in all acid modified GAC compared with untreated GAC, leading to a hydrophilic surface and disadvantage to the hydrophobic VOC uptake.

Fig. 6 shows that adsorption capacities of the original and modified carbons decreased with increase in total surface oxygen containing groups. The GAC/AM containing less surface oxygen groups presented higher adsorption capacities for *o*-xylene. The amount of surface oxygen-containing groups, especially carboxylic functional groups, were enhanced after oxidation with acids and diminished after alkali treatment. This result is similar to previous reports [28]. The pH_{ZPC} and acidity values of tested samples changed accordingly.

These oxygen containing groups were mainly carboxylic acids, lactones, and phenols. Most have acid characteristics, leading to an acidic surface [19]. Many previous investigations have shown that enhancement of acidic properties results in improvement of hydrophilic of carbon surfaces [22].

The interaction between adsorbate and adsorbent is favored by the similar chemical behavior of the surface and the adsorbate.

Table 3
IR assignments of functional groups on carbon surfaces.

Surface group	Assignment	Adsorption peaks (cm ⁻¹)					
		In reference	This work				
			GAC	GAC/AM	GAC/SH	GAC/NA	GAC/SA
-OH		3435	3436	3436	3434	3448	3434
CH ₂	Asymmetrical and symmetrical stretch of CH ₂	2920	2915	2918	2925	2918	2923
		2845	2845	2843	2850	2848	2845
		2070-2040	-	-	-	2041	-
C=C=N		1629	1630	1632	1629	1634	1631
C=C	Stretch of C=C in aromatic rings	1558	-	1572	-	1568	-
C=O	Stretch of C=O	1382-1392	-	-	1384	1384	-
COOH		1157	-	-	-	1162	-
COC	Stretch	1118	1129	1115	-	-	1118
COH	OH stretch	1069	-	-	1069	-	1065
COC	Asymmetrical stretch						

Source: Adapted from [16,17,22,24].

Table 4
Adsorption capacities of GAC, GAC/AM and GAC/NA.

Adsorbent	Breakthrough time (h)	Total adsorption (mg g^{-1})	<i>o</i> -xylene adsorption (mg g^{-1})
GAC	15.1	307	214
GAC/AM	17.2	319	281
GAC/NA	12.6	325	187

o-xylene is a hydrophobic compound and is apt to be absorbed by a hydrophobic surface. Therefore, the removal of surface oxygen groups, and the reduction of the hydrophilic character of carbon surface will favor the adsorption capacity of the carbons for *o*-xylene.

Due to the abundance of carboxylic functional groups and low BET surface area, GAC/NA, GAC/SA, and GAC/PA showed less adsorption capacity than the original GAC. Compared with the acid-treated samples, the applied treatments did not significantly affect the textural parameters of GAC/AM and GAC/SH. Consequently, adsorption capacity of these two samples depended mainly on their surface chemistry.

Thus, a combination of high surface area and low surface oxygen group content is desired for GAC with high *o*-xylene adsorption capacity. This result is in agreement with previous research on aromatic hydrocarbon (BTEX) adsorption [22] and adsorption of phenanthrene in gaseous phase [29].

Adsorption of *o*-xylene from the wet effluent stream of an overload biofilter (ESOB) was also performed using the same inlet *o*-xylene concentration. As packing media filled in the ESOB contained 76% water in average, the stream was humidified when passing through the ESOB. The relative humidity (RH) of stream out of the ESOB was 91% in average. Therefore, the stream containing *o*-xylene was wet when entered into the adsorption unit which was installed followed the ESOB. The GAC/AM, GAC and GAC/NA were selected as the adsorbents and were packed into the adsorption tube. The concentration of *o*-xylene in the effluent gases of the biofiltration unit was 393–504 mg m^{-3} . The gas flow rate was 0.15 $\text{m}^3 \text{h}^{-1}$, corresponding to an empty bed residence time (EBRT) of 2.5 min for biofiltration unit and 16.8 s for the adsorption unit. The adsorption experiment was carried out at ambient temperature (27 °C) and it reached saturated adsorption when the *o*-xylene concentration in the outlet gas was equal to that in the inlet gas.

The GAC/NA reached equilibrium very quickly (~12.6 h). The GAC took 15.1 h to arrive at equilibrium, while GAC/AM took the longest time (17.2 h) (Table 4). Total amounts of adsorption obtained were 307 mg g^{-1} for GAC, 319 mg g^{-1} for GAC/AM, and 325 mg g^{-1} for GAC/NA. However, the *o*-xylene adsorbed on the

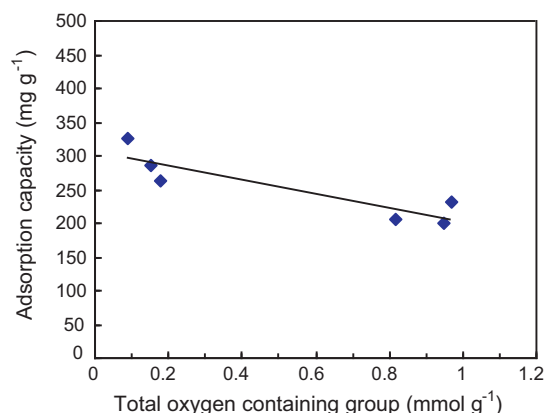


Fig. 6. Oxygen containing group and amount of *o*-xylene adsorbed on GAC.

test GACs were 214 mg g^{-1} for GAC, 281 mg g^{-1} for GAC/AM, and 187 mg g^{-1} for GAC/NA. Their breakthrough curves were similar to those obtained with dry air, although they were smaller in ESOB effluent stream than in dry air, especially for GAC/NA. Biological technologies use microorganisms to biodegrade gaseous contaminants and produce innocuous end products. This biological degradation takes place in a biofilter packed with porous solid particles on which pollutant-degrading cultures are immobilized. Packing media in biofilters often contain 60–80% water to maintain microorganism growth. The gases out of the biofilter are usually wet with over 80% of RH.

The competition between water and *o*-xylene for adsorption sites on the carbon surface led to a reduction in adsorption ability of *o*-xylene. The adsorptive capacity of GAC is determined by its porosity as well as surface chemical nature [24,30]. In this study, water adsorption increased with both porosity and surface oxygen groups, especially those with acid characteristics. The GAC/NA was hydrophilic due to its high oxygen-containing groups, and hydration resulted in blocking pore entrances towards the hydrophobic compounds. Therefore, the decrease in *o*-xylene adsorbed on GAC/NA was much greater than GAC/AM and GAC. The surface oxygen-containing groups on GAC/NA were responsible for the low uptake of *o*-xylene.

The well-developed total pore volume, high surface area, and low oxygen content of GAC/AM makes it a good adsorbent for removing *o*-xylene from ESOB and diminishing the frequency of adsorbent regeneration. From a practical point of view, to improve activated carbon performance for hydrophobic VOCs adsorption, pore volume and surface area should be as high as possible and surface oxygen-containing groups need to be reduced. To prepare this type of GAC, chemical modification by weak alkali such as ammonia is desired.

4. Conclusion

Surface modifications on coconut-based GAC were compared by treatment with alkalis and acids. High adsorption capacity was obtained for alkali-treated GAC. The sequence of uptake quantities for *o*-xylene was GAC/AM (305.70 mg g^{-1}) > GAC/SH (295.403 mg g^{-1}) > GAC (241.69 mg g^{-1}) > GAC/NA (220.74 mg g^{-1}) > GAC/PA (204.50 mg g^{-1}) > GAC/SA (189.46 mg g^{-1}). The adsorption ability of hydrophobic VOC has been further improved via chemical surface modification by ammonia.

The texture and surface chemistry of tested GACs varied dramatically after modification by alkalis and acids. The surface area and pore volume increased and total oxygen containing function groups were diminished when treated by alkalis. The opposite was observed for the acid treatment.

Variation in surface area and porosity of the adsorbents plays a key role on adsorption of hydrophobic VOC. The adsorption capacity for *o*-xylene increased with the increase in surface area, total pore volume, and surface hydrophobicity. Modification by ammonia enlarged the surface area and decreased the concentration of surface oxygen groups, which benefits GAC uptake of hydrophobic VOC. Optimized carbon adsorbents for a specific organic compound can be produced by appropriate surface modification.

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