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Adsorption of volatile organic vapors by activated carbon derived from rice husk under various humidity conditions and its statistical evaluation by linear solvation energy relationships

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ABSTRACT

The adsorption of sixteen volatile organic compounds (VOCs) in the gas phase by activated carbon (AC) generated from waste rice husk was investigated under two different levels of relative humidity (RH) by inverse gas chromatography (IGC). R850 AC had the largest surface area and was characterized. Linear solvation energy relationship (LSER) was employed to understand the interactions between R850 AC and VOCs. The major functional groups on the surface of R850 AC were C=C, Si—O—Si, O—H, and C—O (H). IGC indicated that the gas/solid adsorption coefficients ($\log K_d$) for the 16 VOCs lied in the range 4.0–6.1 ($(\mathrm{g\,g^{-1}})/(\mathrm{g\,mL^{-1}})$) under medium RH (around 55%), but decreased under high RH (90%). Moreover, the $\log K_d$ value predicted from our LSER equations was highly correlated to the experimental $\log K_d$ of the R850 AC. This study demonstrates that R850 AC is a promising material for VOC removal and the established LSER equations are useful to estimate VOC adsorption.

1. Introduction

Volatile organic compounds (VOCs) are carbon-based compounds that exhibit a high vapor pressure at room temperature. Many types of VOCs are highly toxic and lethal to humans, and can be damaging to the environment. There are physical, chemical and biological treatments available to remove VOCs from air streams. A number of studies have indicated the effectiveness of VOC removal by activated carbon (AC) adsorption [1,2]. Different AC preparation methods yield products with different surface functional group compositions, leading to varied adsorption capacities to specific categories of VOCs. For instance, acid-post-treatments increase aromatic/alcoholic VOC adsorption [3] and surface oxygen-containing groups decrease *o*-xylene adsorption [4]. Thus, efficient VOC removal from air streams by AC has been demonstrated by using commercial AC in trickle-bed air bio filters [5] or green-produced AC from agricultural wastes [6].

The sustainable production of AC from agricultural waste is appropriate because a large amount of lignocellulosic biomass present in agriculture waste is applicable to AC generation [7,8]. Several agricultural wastes have been used to generate AC. Some examples include durian shell, rubber-seed shell, hazelnut shell, palm kernel shell, coconut shell, plum stones, cotton stalks, rice husk, wood, etc. These AC materials are known to exhibit high adsorption capacities for VOCs [6], and are therefore an environmental friendly material to effectively eliminate VOC in the gas phase. Among agricultural waste products, rice husk is one of the most widely available, particularly in South and Southeast Asia, where over 90% of the world's rice production is sourced back to these areas [9]. One prominent application of rice husk AC materials can be found in the field of wastewater treatments to remove different dyes, metal ions, phenols, pesticides, and chlorinated hydrocarbons, etc. [10]. However, besides wastewater treatments, only a few studies have focused on the removal of a variety of VOCs in the gas phase by rice husk AC: Hsi et al. used toluene to study the adsorption properties of various samples of rice husk AC [11]. Kumagai et al. investigated the adsorption of formaldehyde and acetaldehyde by heat-treated rice husk and found the adsorption rate is higher than commercial granular coconut-shell AC [12]. There is still a pressing need for more comprehensive studies regarding the adsorption properties of VOCs on rice husk derived AC materials.

In comparison with the conventional adsorption systems, the linear solvation energy relationship (LSER) approach has been frequently used in order to understand the more comprehensive sorption mechanism in the gas/solid system. For instance, the adsorption behavior of 22 kinds of VOCs by fullerene was described by using the LSER regression approach, suggesting that the primary adsorption behavior between VOCs and fullerene are dispersion

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interactions [13]. The LSER approach was also successfully applied to elucidate the adsorption behavior between 13 kinds of VOCs and three commercial activated carbons [14]. The adsorption behavior between complicated solid materials, such as soot [15], organobentonites [16] or other carbonaceous materials [17], and various kinds of VOCs can be qualitatively and quantitatively followed by the LSER approach. Five coefficients, included in the LSER approach, obtained from multiple regression between experimental adsorption data of the adsorbents and fundamental solvation parameters of VOCs are able to elucidate the surface properties of the adsorbents. After multiple regressions, the relative magnitude of each coefficient represents the relative levels of the five different physio-chemical interactions that contribute to the overall adsorption behavior [18].

In this study, one rice husk AC material was prepared and its adsorption capacities for 16 kinds of VOCs at two different levels of relative humidity (RH) were investigated. The AC particles were packed in a column and the adsorption experiments were conducted by inverse gas chromatography (IGC). The overall relationship between the intermolecular interactions of VOCs and the surface of AC was investigated using the LSER model. The results of the adsorption properties, behaviors and LSER equations would bring further insights and a more comprehensive understanding of VOC adsorption capacity on rice husk AC. It would also allow a basic knowledge of developing a better VOC removal technique by rice husk AC materials.

2. Materials and methods

2.1. Rice husk AC preparation

The preparation process was consisted of two steps; carbonization and activation. Rice husk (100 g) was centered in a furnace (20 cm × 20 cm × 40 cm, made in Taiwan) and purged with N_2 gas (purity of 99.995%) at a flow rate of 35 mL/min. The temperature was increased by 20 °C/min until the desired temperature was reached. This temperature was then maintained for 1 h to complete the carbonization process. For activation, CO_2 (purity of 99.5%) was purged into the furnace at a flow rate of 200 mL/min for the three selected durations. The furnace was then cooled to room temperature with N_2 gas purging. The activated rice husk AC particles were washed three times with distilled water to remove any fine ashes and then dried at 383 K. The rice husk AC particles generated at the three selected temperatures (650, 750, and 850 °C) were named R650, R750, and R850 AC, respectively.

2.2. Chemical probes

Sixteen VOCs were selected as the probe solutes. *n*-Pentane, 1,1-dichloroethylene, trichloroethylene, and 2-propanol were purchased from Acros Organics. Cyclohexane, *n*-hexane, dichloromethane, trichloromethane, methanol, ethyl acetate, and acetonitrile were obtained from J.T. Baker. Tetrachloromethane and benzene were purchased from Merck. Acetone was obtained from Mallinckrodt Baker. Diethyl ether was purchased from Riedel-de Haën. The basic chemical properties of octanol-water partition constants ($\log K_{ow}$) of these VOCs are listed in Table 1. All chemicals utilized in this study have a purity higher than 95%, and no impurity peaks were observed from our preliminary IGC analysis [19].

2.3. Characterization of rice husk AC

Dried R850 AC was characterized for its geometrical structure and surface properties, such as surface area, pore volume and surface chemical bonds. The geometrical structure and microstructures were observed with a scanning electron microscope (SEM, TOPCON, ABT-150S Thermionic Emission SEM, Japan). For surface area and pore volume, the nitrogen adsorption-desorption isotherms of the three AC particle samples were determined using a Micromeritics ASAP2100 accelerated surface area and porosimetry analyzer, operated at 77 K. The experimental procedure was described briefly as follows: The AC particles were weighed (0.2 g) and poured into a sample bottle. The sample bottle was circulated in a heating jacket, heated to 523 K and vacuumed below 3 μm Hg to remove the moisture within the AC particles. After the AC sample was completely dried, it was weighed again and placed into liquid nitrogen to keep the sample temperature at 77 K. The freezing AC sample bottle was filled with nitrogen gas to determine the surface area and pore volume. The surface area was determined by the Brunauer-Emmett-Teller method. Chemical bonds on the R850 AC surface were analyzed by X-ray photoelectron spectroscopy (XPS) (ESCALAB 250, VG Scientific, England) in the C_{1s} and O_{1s} spectra. The AC particles were carefully packed on XPS sampling templates. The XPS data was analyzed by the software universal program designed for XPS peak fitting and spectral analysis. For the surface functional group determination, the rice husk AC powder was mixed with potassium bromide with a ratio of 1:200 and then compressed to form a table. The tablet was analyzed by Fourier transformation infrared (FTIR) spectroscopy (DA8.3, Bomem, Canada).

Table 1
Octanol-water partition constant and molecular descriptors of VOCs used in this study.

Class of compounds	Compounds	$\log K_{ow}$[a]	E[b]	S[b]	A[b]	B[b]	L[b]
Alkane	*n*-Pentane	3.39	0.000	0.00	0.00	0.00	2.162
	n-Hexane	4.00	0.000	0.00	0.00	0.00	2.688
	Cyclohexane	3.44	0.305	0.10	0.00	0.00	2.964
Aromatic	Benzene	2.17	0.610	0.52	0.00	0.14	2.786
Chloroalkane	Dichloromethane	1.31	0.387	0.57	0.10	0.05	2.019
	Trichloromethane	1.95	0.425	0.49	0.15	0.02	2.480
	Tetrachloromethane	2.77	0.458	0.38	0.00	0.00	2.823
Chloroalkene	1,1-Dichloroethylene	1.79	0.362	0.34	0.00	0.05	2.110
	Trichloroethylene	2.49	0.524	0.53	0.12	0.03	2.997
Alcohol	Methanol	−0.77	0.278	0.44	0.43	0.47	0.970
	Ethanol	−0.31	0.246	0.42	0.37	0.48	1.485
	2-Propanol	0.05	0.212	0.36	0.33	0.56	1.764
Ketone	Acetone	−0.24	0.179	0.70	0.04	0.49	1.696
Nitrile	Acetonitrile	−0.34	0.237	0.90	0.07	0.32	1.739
Ether	Diethyl ether	0.89	0.041	0.25	0.00	0.45	2.015
Ester	Ethyl acetate	0.69	0.106	0.62	0.00	0.45	2.314

[a] Data were obtained from Schwarzenbach et al. [41] at 25 °C.
[b] Data obtained from Abraham [22].