Novel activated cotton as eco-adsorbent for solvent vapor

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ABSTRACT

The potential of activated cotton (AC) as a low cost eco-absorbent for the recovery of organic solvent vapor was studied in this study. Its pore structure and chemical structure were characterized. Its adsorption speed, saturated adsorption volume and desorption process of solvent vapor were also evaluated. Its organic vapor adsorption process is fast enough to reach equilibrium within 10 min. It adsorbs more solvent vapor than other activated carbons due to its high microporosity. Finally, less than 200 °C is required for the complete desorption of adsorbed species.

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1. Introduction

Organic solvent is very common in different industries and can be used as solvent, fuel or raw chemical material. Methanol, ethanol and acetone are the three most widely used oxygenated organic solvents, and their global production capacities are over billions of gallons [1]. Due to their volatile nature, a large portion of their vapor escapes to the atmosphere and some may even enter the upper troposphere. Via a series of free radical photo-reactions, they have significant impacts on the ozone production rate in upper troposphere [2]. As a result, reducing their emission is very important to environment.

Currently, organic solvent vapor is oxidized to CO_2 via catalytic conversion [3,4]. Because of the increasing fuel/solvent price and the tightening of CO_2 emission limit, solvent vapor recovery with adsorbent becomes more favored. Activated carbon is one of the most suitable adsorbents for vapor recovery due to their microporous nature [5–8]. It can adsorb organic vapor from stream and desorb the vapor at elevated temperature. Its major problems are its high production cost and the requirement of high activation temperature. There is a trend to produce eco-porous adsorbent by activating low cost natural biomaterials [9–12]. Among them, it is found that cotton can be activated to be a low cost, high performance activated cotton (AC) [13–15]. It can be activated at low temperature and has excellent mechanical properties. Its fibrous structure allows fluid flowing inside while activated cotton fibers

provide micropores for adsorption. It has excellent performances in dye removal and oil adsorption. As a result, it is expected to have an excellent performance in organic vapor adsorption.

The potential of AC as a low cost eco-absorbent for the recovery of solvent vapor was studied in this investigation. AC samples with various pore structure and surface groups were fabricated with cotton, and were characterized via various methods. Their adsorption speed and adsorption capacity on the vapors from water, ethanol, methanol and acetone were evaluated. Its desorption properties were also investigated.

2. Materials and methods

2.1. Sample preparation

The AC samples were synthesized via $ZnCl_2$ activation and their pore structure was adjusted by using various activation temperatures (T_{act}) and $ZnCl_2$ solution concentrations (C_{ZnCl2}). The detailed activation procedure of AC5-95, AC6-95, AC7-95, AC6-72, AC6-115 was mentioned in our previous paper [14]. Some key parameters of their synthetic conditions and pore structure are listed in Table 1.

Surface groups were introduced on the sample AC5-95 via various post treatment methods after the activation process. Some of AC5-95 was post-oxidized with HNO_3, H_2O_2 and air. The HNO_3 treated AC (AC5-95-HNO_3) was prepared by soaking the AC5-95 in HNO_3 with concentration of 65% by mass (Merck) at 80 °C for an hour. It was dried at 80 °C for 12 h after neutralization. H_2O_2 treated AC (AC5-95-H_2O_2) was prepared by soaking the AC5-95 in H_2O_2 with concentration of 30% by mass (AnalaR Normapur,

Table 1
Parameters of different AC samples.

Sample	T_{act} (°C)	C_{ZnCl2} (g L^{-1})	Post treatment	S_{BET} (m^2 g^{-1})	V_{pore} (cm^3 g^{-1})
AC5-95	500	95	N/A	2060	1.002
AC6-95	600	95	N/A	1509	0.727
AC7-95	700	95	N/A	1486	0.717
AC6-72	600	72	N/A	826	0.401
AC6-115	600	115	N/A	1717	0.864
AC5-95-HNO$_3$	500	95	65% HNO$_3$, 80 °C	1064	0.579
AC5-95-H$_2$O$_2$	500	95	30% H$_2$O$_2$, 80 °C	1809	0.989
AC5-95-air	500	95	Air, 300 °C	2124	1.187
AC5-95d	500	95	Ar, 800 °C	1966	0.936

BDH) at 80 °C for an hour. It was dried at 80 °C for 12 h after washing with distilled water. Air oxidized AC (AC5-95-air) was prepared by heating the AC5-95 at 300 °C in air for an hour. Degassed AC (AC5-95d) was prepared by heating the AC5-95 at 800 °C in argon (Hong Kong Oxygen) for an hour to remove surface groups. The summary information is shown on Table 1.

2.2. Characterization

The surface morphology and Energy-dispersive X-ray spectroscopy (EDX) of the samples were characterized with Scanning electron microscope (SEM, Quanta 400) and High-resolution transmission electron microscope (HRTEM, FEI TecnaiF20). Samples were torn into small pieces before placing in SEM while they were further grinded with mortar and ultra-sonic machine before HRTEM observation. BET specific surface area (S_{BET}) and pore volume (V_{pore}) were obtained by using a Micromeritics ASAP 2020 physisorption analyzer. Non Localized Density Functional Theory (NLDFT) pore size (d_{pore}) distribution curves were calculated with the model isotherms of porous carbon provided by Lastoskie et al. [16]. The porosity results were compared with the d_{pore} distribution curve calculated from Small-angle X-ray scattering (SAXS, RU-300, Rigaku, Cu-K$_\alpha$ radiation) spectra with the spherical model. The functional groups on the surface of the AC were identified via Fourier transform infrared spectroscopy (FTIR, Thermo Nicolet 670 Nexus Euro).

2.3. Adsorption and desorption tests

The vapor adsorption kinetics tests were conducted by measuring the mass of AC versus time in the saturated vapor stream with a Thermogravimetric analyser (TGA, Perkin Elmer TGA 6) at room temperature. The sample was first degassed at 250 °C in vacuum

for an hour and about 7 mg sample was rapidly transferred to TGA after degassing. The stream was generated by heating the solvent in a vapor saturator, and was carried by N$_2$ gas in 100 mL min^{-1}. It passed a condenser at room temperature before entering into the TGA.

The saturated adsorption capacity (V_{ads}) of the AC was obtained by measuring the increase in the mass of AC after placing it in a chamber with the saturated solvent vapor for three days at room temperature. The sample and equipment were first degassed at 250 °C in vacuum for an hour. About 0.2 g sample was weighed soon after degassing and was then rapidly transferred into the chamber containing the specific vapor in saturated pressure. The final sample weight was measured soon after the 3 days test. V_{ads} was calculated as following:

$$V_{ads} = \frac{m_f - m_i}{\rho m_i} \quad (1)$$

where m_i and m_f are masses of AC samples before and after the adsorption test respectively, and ρ is the density of solvent at room temperature.

The thermal desorption of vapor-adsorbed samples was evaluated via temperature programmed desorption (TPD) with TGA soon after the V_{ads} measurement [17,18]. About 7 mg vapor-adsorbed sample was loaded into the TGA sample holder rapidly after taking out from the chamber. It was heated from 30 °C to 300 °C in N$_2$ at 10 °C min^{-1}.

3. Results and discussions

Photos of AC sample before and after activation are shown in Fig. 1. It retains the morphology of cotton ball but it becomes smaller and turns black in color. It is strong enough to be manipulated by hand or metal tweezers without breaking into smaller pieces, similar to the AC sample of Bi et al. [13]. No obvious formation of undesirable flakes occurs in relatively static environments of our adsorption and desorption tests. To further study the micro-morphology and elemental composition of AC samples, the SEM images of the AC samples and the corresponding EDX results are shown in Fig. 2a–e and Table 2. It is observed that all AC samples have retained the fibrous structure of cotton and their width is about 10–15 μm. They are fragmented because they were intentionally torn into small pieces from the bulk samples before the SEM examinations. The EDX results of AC5-95 reveals that it contains about 97% of carbon and 2.4% of oxygen. This implies that it is almost carbonized and may contain some carbon–oxygen surface groups. No obvious change in the fiber morphology is observed after various post-treatments. AC has an obvious increase in the oxygen content after post oxidation treatments. The increase is larger than the uncertainty of EDX results, which is about 2% [19]. It implies that
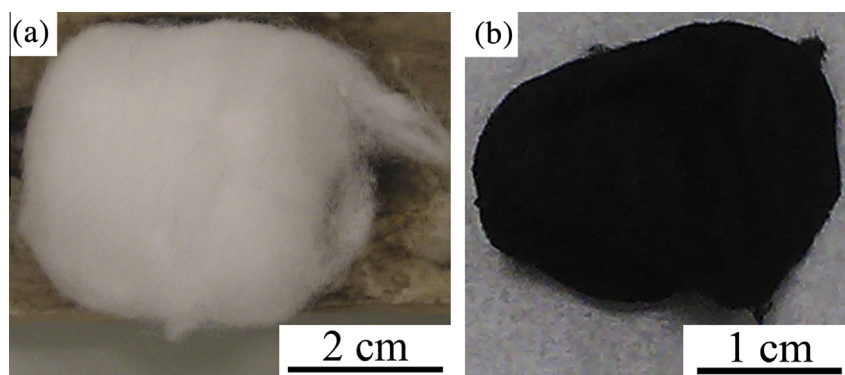

Fig. 1. Photos of (a) raw cotton and (b) AC sample.