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Research Article

Synthesis of Carbonaceous Adsorbents for Volatile Organic Compounds Analysis in Hard Disk Drive components

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ABSTRACT

In hard disk drive manufacturing process, contaminants such as small particles or volatile organic compounds can obstruct hard disk drive reliability because these particulate contaminants and volatile out gassing could cause scratches, corrosion or read/write error of hard disk drive components. Volatile organic compounds (VOCs) or outgas are generated from the hard disk drive components during the process of applying adhesive or chemical substance to the hard disk drive component at high temperature. Such volatile organic compounds include acrylates/methacrylates, siloxanes, acetophenone, dioctyl phthalate and hydrocarbons. In order to detect and analyze outgas in hard disk drive components, an out gassing test was performed by adsorption of volatile organic compound on an adsorbent followed by desorption process. Then desorption vapor was sent to GC-MS for analysis. Since recent adsorbent used in the out gassing analysis is imported and expensive, synthesis of adsorbents with lower cost would be beneficial to the hard disk drive industry. Thus this research was focused on synthesis of adsorbents in out gassing test of hard disk drive components. The adsorbents were synthesized from 3 types of raw materials namely coconut shell, coal and coke. These raw materials were pyrolyzed at 500°C for 3 hr followed by chemical activation with either potassium hydroxide (KOH) or phosphoric acid at 800°C for 1 hr. The surface area, pore size, pore area and pore volume of synthesized adsorbents were measured by BET measurement. The adsorption capability of adsorbents was determined by performing adsorption/desorption of 2 types of volatile organic compounds (2-hydroxyethyl methacrylate and octamethylcyclotetrasiloxane) with 3 level of contents. The amount of each volatile organic adsorbate was analyzed by GC-MS. The results of synthesized adsorbent were compared with the commercial adsorbent (Carbotrap™ B and Carbotrap™ C). It was shown that adsorption capability of adsorbent prepared from coconut shell with 40 wt% KOH activation was the best among the adsorbents prepared from other raw materials. It was indicated that the maximum adsorption capability of 59.74% and 66.06% could be obtained when 0.1 g of coconut shell-adsorbent and commercial adsorbent Carbotrap™ B were used to adsorb 0.0638 mmole of 2-hydroxyethyl methacrylate, respectively. The results also showed that when octamethylcyclotetrasiloxane with loading content of 0.0017 mmole was used as adsorbate the highest adsorption capability of 50.82% and 72.52% per 0.1 g of adsorbent were obtained using coconut shell-adsorbent and commercial adsorbent Carbotrap™ B, respectively. The result from the isotherm plot confirmed that surface adsorption of coconut shell-adsorbent and commercial adsorbent was different.

Key words: Adsorbent, Carbonaceous materials, Volatile organic compounds (VOCs)

INTRODUCTION

In the hard disk drive industry, cleanliness is vital in production quality improvement. Various processes all involve usage of chemicals, resulting in chemical contamination on the hard disk drive components, such as in application of adhesives or coating which brings about contaminants such as acrylates, siloxanes, or hydrocarbons on their surfaces [1]. These materials under high temperatures release volatile organic compounds (VOCs) that may cause sticky patches on the components which in turn simply accumulate dirt and scratches, resulting in lessened read/write efficiency. Besides, hard disk drive components themselves may emit gases if they are under high temperatures. Therefore, volatile

organic compounds (VOCs) in hard disk drive components should be measured.

Analysis of volatile organic compounds (VOCs) is generally measured through adsorption and desorption process. Firstly, adsorption was carried out by heating a hard disk drive specimen, then VOCs from the specimen were released and adsorbed on an adsorbent. Desorption of VOCs from the adsorbent was performed after adsorption was completed. The desorbed VOCs content can be analyzed by the Gas Chromatography-Mass Spectrometer (GC-MS), which is a high precision tool even in the case of very low content of VOCs.

At present adsorbents are widely used in various industries, for example, in treatment of dyes, in adsorbing heavy metals in effluents, and in adsorbing

organic materials in air pollutants. Hard disk drive industry usually uses graphite carbon black adsorbents such as Carbotrap and Tenax [2] to detect volatile organic compounds from the components. However, these adsorbents are imported and so expensive. Various carbonaceous materials such as coconut shell, coal, coke, saw dust, rubber wood, or used tires are used as raw material to synthesize adsorbents. Since these raw materials compose of high carbon content thus adsorbent with high density and regular pore structure could be obtained. It is reported that the adsorption efficiency of adsorbent can be enhanced by either physical or chemical activation [3]. Hence, we were interested in synthesis of alternative adsorbents to substitute the imported ones for analyzing VOCs in hard disk drive components.

Materials and Method

Six adsorbents were synthesized from 3 different raw materials, namely coconut shell, coal and coke. Phosphoric acid and potassium hydroxide were used as chemical activation. Two volatile organic compounds (VOCs) namely 2-hydroxyethyl methacrylate (HEMA) with initial loadings of 0.0038, 0.0319, and 0.0638 mmole and octamethylcyclotetrasiloxane with initial loadings of 0.0017, 0.0135, and 0.0270 mmole were selected as adsorbates. Adsorption of these adsorbates on synthesized adsorbents was compared with commercial adsorbents (Carbotrap™ B and Carbotrap™ C). The experiment was divided into 3 parts. 1. synthesis of adsorbents, 2. adsorbents characterization and 3. determination of VOCs adsorption capacity of each adsorbent.

2.1 Synthesis of carbonaceous adsorbents:

2.1.1 Raw material preparation:

Coconut shells, coal and coke were pyrolyzed in an electric kiln at 500°C for 3 hr under nitrogen

atmosphere with nitrogen flow rate of 150ml/min. Then the pyrolyzed materials were ground to 20-40 mesh (420-840 microns).

2.1.2 Chemical activation:

2.1.2.1 Phosphoric acid activation:

Pyrolyzed adsorbents were heated at 800°C for 1 hr in nitrogen atmosphere, with nitrogen flow rate of 150 ml/min. Then the burned materials were immersed in 3 molar phosphoric acid at the ratio of 1:5 by weight in a sealed glass jar for 3 hr. Next, the materials were washed with boiled distilled water until pH was neutral, dried, and ground with a Ball mill and sieved through 20-40 wire mesh. The obtained materials were kept in a desiccator to protect against moisture.

2.1.2.2 Potassium hydroxide activation:

Pyrolyzed adsorbents were immersed in 40wt% potassium hydroxide solution at a ratio of 1:5 by weight in a sealed container for 24 hr. Then they were burned at 800°C for 1 hr under nitrogen atmosphere with nitrogen flow rate of 150 ml/min. Next, the materials were washed with boiled distilled water until pH was neutral, dried and ground in a Ball mill. They are then sieved through 20-40 wire mesh and retained in a desiccator to prevent moisture.

Conditions of producing adsorbents from 3 different raw materials are summarized in Table 1.

2.2 Adsorbent characterization:

Commercial adsorbents (Carbotrap™ B and Carbotrap™ C) and the 6 synthesized adsorbents were characterized for their surface areas, pore size and pore volume using the Brunauer-Emmett-Teller technique (BET) by the Micromeritics ASAP 2010.

Table 1: Summary of conditions for adsorbent production from 3 different raw materials.

Sample names	Raw materials	Pyrolysis conditions	Activation reagent	Burning conditions of chemical activation
A302	Coconut shell	500°C, 3 hr	Phosphoric acid	800°C, 1 hr
A402	Coconut shell	500°C, 3 hr	Potassium hydroxide	800°C, 1 hr
N302	Coal	500°C, 3 hr	Phosphoric acid	800°C, 1 hr
N402	Coal	500°C, 3 hr	Potassium hydroxide	800°C, 1 hr
C302	Coke	500°C, 3 hr	Phosphoric acid	800°C, 1 hr
C402	Coke	500°C, 3 hr	Potassium hydroxide	800°C, 1 hr

2.3 Testing adsorption capacity of VOCs:

2.3.1 Adsorption process:

Volatile organic compounds (VOCs), namely 2-hydroxyethyl methacrylate (HEMA) with initial loadings of 0.0038, 0.0319, and 0.0638 mmole and

octamethylcyclotetrasiloxane at initial loadings of 0.0017, 0.0135, and 0.0270 mmole were adsorbed on 0.1 g of each particular adsorbent (either synthesized or commercial adsorbent). The experimental set up of adsorption process is shown in Figure 1.

The experiment was started from dropping 20 µL of a particular volatile organic compound on the

glass sheet in a Teflon chamber. Then the Teflon chamber was placed in the air oven and connected with the inlet and outlet gas tube through the wall of the oven. The other end of the outlet gas tube was connected to the glass column containing 0.1 g of adsorbent while the other end of the glass column was connected to the bottle containing 20 ml of

acetonitrile solvent. This solvent would trap any unadsorbed molecule of VOC that passing through the adsorbent glass column. The nitrogen gas was fed into the Teflon chamber with the flow rate of 10-15 ml/min. The air oven was set to the temperature of 85°C for 3 hr to heat the Teflon chamber and VOC vapor was generated during heating.

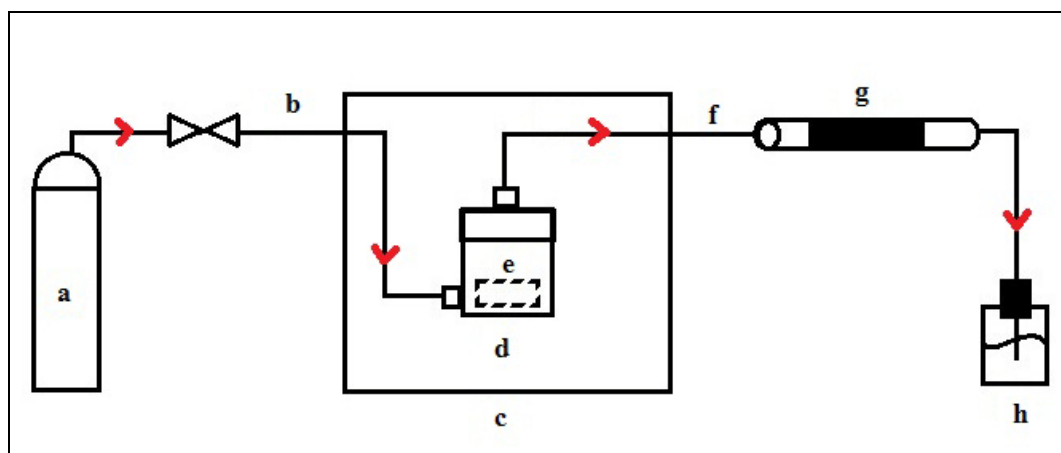


Fig. 1: Experimental set up of adsorption process (a) Nitrogen tank with 99.99% purity (b) Inlet nitrogen gas tube (c) Air oven (d) Teflon chamber (e) 2.5x3.0 cm glass sheet (f) Outlet gas tube (g) Adsorbent glass column (h) Acetonitrile solvent bottle.

2.3.2 Desorption process:

Desorption by acetonitrile solvent were used to extract the adsorbate compound on the adsorbent in each case. The adsorbent from the adsorption process was loaded into a 15 ml test tube in which 2 ml of acetonitrile was added. The tube was sealed and shaken for 5 min at room temperature. This was left for desorption to take place for about 1 hr and centrifuged at 5000 rpm, 4°C for 15 min. The clear solvent was further analyzed for the amount of VOCs with GC-MS [4].

2.3.3 Analysis of VOCs adsorbed by adsorbents:

The extracted solvents obtained from the acetonitrile solvent desorption process were

analyzed to measure the amount of volatile organic compounds using gas chromatography mass spectrometer (GCMS-QP2610, Shimadzu, Japan). The capillary column used was HP-5MS with a length of 30 m, internal diameter of 0.25 mm, and lined with a 0.25µm film thickness of Rtx-5MS.

Results and Discussion

3.1 Adsorbent characterization:

The surface area, pore size and pore volume of all synthesized and commercial adsorbents were determined using BET technique and results are shown in Table 2.

Table 2: Surface area analysis of each adsorbent based on BET technique.

Adsorbent type	BET total surface area (m ² /g)	Micropore area (m ² /g)	Total pore volume (cm ³ /g)	Micropore volume (cm ³ /g)	Average pore diameter (Å)
Carbotrap B	116.01	5.25	1.063	0.00308	366.65
Carbotrap C	9.38	0.38	0.049	0.00010	210.87
A302	4.26	4.13	0.010	0.00220	90.21
A402	431.86	380.04	0.209	0.18144	19.39
C302	591.54	387.92	0.330	0.20281	22.32
C402	420.48	285.21	0.236	0.14731	22.44
N302	2.37	0.22	0.005	0.00018	79.50
N402	4.72	1.39	0.005	0.00018	47.83

Table 2 shows that N302, N402, and A302 yield less surface areas and pore volumes when compared

among synthesized adsorbents. Therefore, A302, N302, and N402 should not undergo further for adsorption test.

From Table 2, although synthesized adsorbents show greater surface area than commercial adsorbents, the average pore size of commercial adsorbents is much bigger. Thus, an isotherm test for nitrogen adsorption should be studied to observe correlation between adsorbed volumes and relative pressures (P/P_0). The adsorption type of each adsorbent could be identified from adsorption isotherm. Figure 2 shows correlation between adsorbed volumes and relative pressure. In Figure 2 (a) commercial adsorbents, Carbotrap B and Carbotrap C show adsorption characteristic of BET isotherm type III. This indicated that adsorbate gas widely dispersed on the adsorbent's surface, which could result from single-layer or multi-layer adsorption. This isotherm type has more exerting force between molecules of the adsorbent, resulting in better attachment and more adsorption. This adsorption isotherm occurs in the case of weak

adsorption with nonporous solids. Attraction force between adsorbent and adsorbate is also weak and hence less adsorption. Adsorption is a single-layer at low relative pressure. When adsorption is multi-layer, attraction between adsorbed compounds results in more adsorption at high relative pressure [5], which is different from adsorption isotherm of synthesized adsorbents.

According to adsorption isotherm plot in Figure 2 (b), the synthesized adsorbents A402, C302, and C402 are classified as adsorption isotherm type I, i.e., single-layer adsorption. When the molecules of adsorbate vapor are adsorbed and completely stacked in the pores, they become saturated. Stacking is in a single-layer adsorption. Adsorption increases rapidly at low relative pressure, and at high relative pressure only little adsorption takes place. Therefore, adsorption capacity depends on the molecules sizes of adsorbate, pore sizes of adsorbents, and ratio of either surface area of micropore, mesopore or macropore to total surface area.

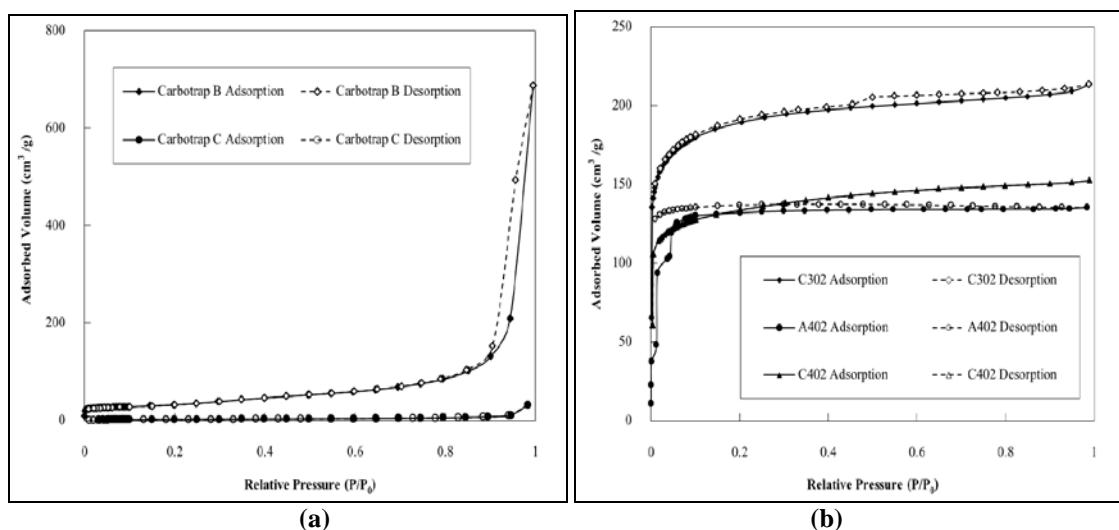


Fig. 2: Adsorption isotherm of nitrogen gas on (a) commercial adsorbents (b) synthesized adsorbents.

3.2 Adsorption capacity of adsorbents:

3.2.1 Adsorption capacity of adsorbent in absorbing 2-hydroxyethyl methacrylate (HEMA):

HEMA is a monomer compound in adhesives used in hard disk drive manufacturing. When this monomer receives heat, VOCs can be emitted from adhesive. The experiment was conducted to test adsorption of this compound at 3 initial loadings of 0.0038, 0.0319, and 0.0638 mmole per 0.1 g adsorbent, as shown in Figure 3. It was found that Carbotrap B could adsorb HEMA best at all loadings. Among synthesized adsorbent, A402 adsorbent was the best to adsorb HEMA at all loading. The highest adsorption capacity of A402 and Carbotrap B in adsorbing the highest initial loading of HEMA

(0.0638 mmole) was 59.74% and 66.06%, respectively. This implied that adsorption capacity of A402 for HEMA adsorption was 90.43% of adsorption capacity of Carbotrap B at the same initial loading of 0.0638 mmole. The second and third effective adsorbents are C302 and C402, respectively at 0.0638 mmole loading. Adsorption of commercial adsorbent Carbotrap C at the lowest loadings of HEMA (0.0038 mmole) could not be detected by GC-MS.

CarbotrapB adsorbs HEMA better than synthesized adsorbents because the result from the adsorption isotherm of Carbotrap B indicated a multiple layer adsorption type and the total pore volume of Carbotrap B (Table 2) is highest among all adsorbents. Therefore, Carbotrap B adsorbs HEMA at a greater amount. Compared to synthesized

adsorbents, we found that A402 adsorbs more efficiently than C302 and C402 owing to its greater ratio of micropore area to total surface areas. The adsorption isotherm of all synthesized adsorbents implied that a single-layered adsorption was occurred

on adsorbent surface. The molecules of adsorbate fill the gaps in the pores and are retained in the adsorbents.

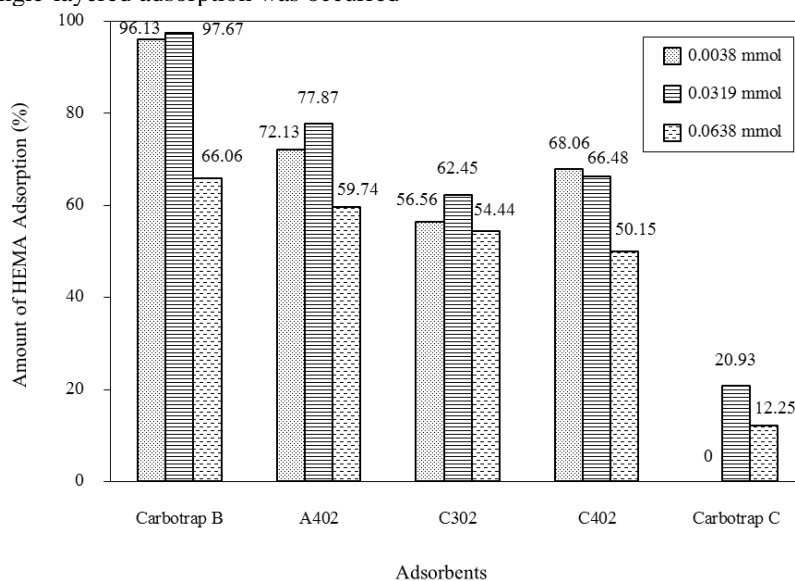


Fig. 3: Comparison amount of 2-hydroxyethyl methacrylate (HEMA) adsorption of adsorbents with various HEMA initial loadings.

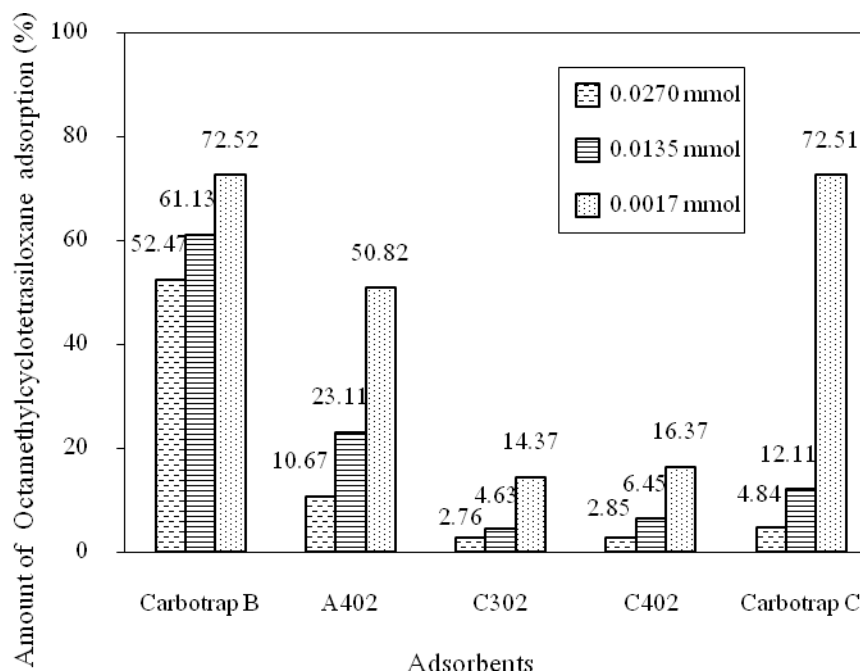


Fig. 4: Comparison amount of octamethylcyclotetrasiloxane adsorption of adsorbents with various octamethylcyclotetrasiloxane initial loadings.

3.2.2 Adsorption capacity of adsorbent in absorbing octamethylcyclotetrasiloxane:

Octamethylcyclotetrasiloxane is an intermediate compound of a silicone polymer coating agent. In hard disk drive manufacturing, slider coating is necessary. If this compound receives heat or its temperature becomes higher, volatile organic

compounds are emitted, possibly leaving patches on hard disk drives surface, a good place for dust to accumulate and scratches to appear, all of which affect hard disk drive effectiveness. Our experiment was conducted to test the three initial loadings of adsorption of this compound, i.e., at 0.0017, 0.0135, and 0.0270 mmole per 0.1 g adsorbent. The results are shown in Figure 4. A402, a synthesized

adsorbent, is still most efficient as an adsorbent when compared to all synthesized adsorbents. Its adsorption capacity is 70.07% of commercial adsorbent Carbotrap B at the lowest initial loading of 0.0017 mmol. The latter is capable to adsorb this compound at the highest of 72.52%. The next adsorption capacity at all initial loadings of synthesized adsorbents was found in C402 and C302, respectively. From figure 4, Carbotrap C can adsorb less octamethylcyclotetrasiloxane than Carbotrap B, possibly due to its lower surface area.

4. Conclusion:

4.1 BET analysis reveals a great difference between commercial and synthesized adsorbents in terms of pore sizes, pore area and surface area. The adsorption isotherm of commercial adsorbents is multiple layer surface adsorption, whereas synthesized adsorbents show a single-layered surface adsorption.

4.2 Among the synthesized adsorbent, A402 (produced from coconut shell and activated with potassium hydroxide) is the best adsorbent to adsorb HEMA and octamethylcyclotetrasiloxane. At the highest initial loading of 0.0638 mmole HEMA, adsorption capacity of A402 is 90.43% of commercial adsorbent Carbotrap B.

4.3 The adsorption capacity of A402 is 70.07% of commercial adsorbent Carbotrap B in absorbing the lowest initial loading of 0.0017 mmol octamethylcyclotetrasiloxane.

4.4 Adsorbent A402 is more suitable for absorbing HEMA than octamethylcyclotetrasiloxane.

4.5 It is possible to use A402 adsorbent to substitute commercial adsorbent Carbotrap B for HEMA contaminant analysis of hard disk drive component.

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