Experimental Research of Activated Carbon on Adsorption of Oil Vapor

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Abstract. The adsorption properties of pillared activated carbon (PAC) on the oil vapor were studied through physical characterization and the dynamic adsorption measurement. The PAC was a typical microporous material with the well-developed interstitial structure and appropriate to be used as adsorbent for recovering of oil vapor. The influence factors of the ambient moisture, the inlet concentration, and supplying velocity on the adsorption amount of oil vapor were investigated using simulation device. During the first adsorption stage, the adsorption amount of oil vapor and the adsorption layer temperature increased remarkably with time, while the adsorbed vapor was relatively difficult to remove as using the vacuum pumping. A competitive adsorption between water and the hydrocarbon molecules reduced the adsorption performance of the PAC. When the supplying velocity increased, the adsorption amount of oil vapor on the PAC decreased for the shortening of contact time. With the increase of inlet concentration, the adsorption amount of oil vapor increased, while the adsorption time decreased.

1. Introduction
Volatile organic compounds (VOCs), usually having stronger reactivity, are known as the major contributors to the formation of photochemical smog and PM2.5, which would result in harmfully healthy and seriously environmental problems. As a typical kind of VOCs, the emission of oil vapor from gasoline during the transportation and storage will bring about the fuel’s dissipation besides of the above disadvantages [1-2]. Therefore, the recovery of oil vapor in petrochemical industries is an important item in the VOCs treatment scheme in China.

With the advantages of low energy consumption, convenient operation and low operation cost, etc., adsorption process was adopted for oil vapor recovery in exceeded 85% gasoline storage depot. The selecting of an appropriate adsorbent, undoubtedly, is crucial for efficient adsorption. An ideal adsorbent for VOCs removal is expected firstly to possess properties of high adsorption capacity, fast diffusivity and easy regeneration to ensure the cyclic adsorption-regeneration usage. Besides, such the characters as high hydrophobicity, high thermal and hydrothermal stability may promise the service life [3-5].

Activated carbon (AC) made from coal, petroleum, vegetable and polymeric precursors is the adsorbent most widely applied in adsorption process for those advantages of the hydrophobic property, the high surface area, and the chemical stability. A large amount of researchers have endeavored to investigate the influence factors and performing pattern in the adsorption of activated carbon. As the dominating adsorption mechanism of AC in the removal of VOCs is physical adsorption, investigations were mostly focused on the relation between the pore structures, surface physicochemical properties
with its performance [6-7]. Many modification methods of ACs have been applied to raise the adsorption capacity, such as the acidic and alkaline treatments, oxidation and reduction treatments as well as doping methods [8-12]. Meanwhile, the functions of ACs serving in adsorption were highly impacted by external factors such as the nature of adsorbates, the ambient temperature, humidity, and the working pressure etc. [13-15].

When activated carbons are used for oil vapor recovery, some engineering conditions may be more valuable and should also be taken into account to determine the dosage of ACs, the technological process, etc. The article presented the investigation such influence factors as the moisture, the vapor concentration, and the supplying velocity on the adsorption properties of a commercial pillared activated carbon using the simulation device.

2. Experimental

2.1. Materials and Instruments

Materials used were the Pillared activated carbon (PAC) (Norit, Nederland) and 93# gasoline (Sinopec, China).

A Methane/Non-methane Hydrocarbon Analyzer (Series 9000, Baseline-Mocon, USA) used to measure the exit concentration of vapor and a HC detector (RI-415, RIKEN KEIRI) to measure the inlet vapor. Scanning electron microscope (SEM) (S-3400, HITACHI) to obtain the structure photos of the PAC; Accelerated Surface Area and Porosimetry System (ASAP 2020, Micromeritics, USA) to characterize the porosity of the PAC; A thermostat wet box (type PR-3G, ESPEC Shanghai) to provide a certain environment of temperature and relative humidity.

The experimental device for dynamic adsorption including adsorption tank with the ratio of height to diameter 4:1, the vapor generator, a water-circulative vacuum pump, and a water bath to provide a certain temperature.

2.2. Physical Characteristics

The porosity properties of the PAC, including the specific surface area, pore volume distribution, and pore size were obtained through N2 (g) adsorption in ASAP 2020 Accelerated Surface Area and Porosimetry System at 77K in liquid N2. The surface area was calculated by the Brunauer-Emmett-Teller (BET) method [16]. Total pore volume and micropore volume were measured by the Barrett-Joyner-Halenda (BJH) method and the t-plot and Harkins-Jura methods, respectively [17-19]. The porous structure was also observed using the SEM. The surface of a specimen be examined is scanned with an electron beam, and the reflected (or back-scattered) beam of electrons is collected, then displayed at the same scanning rate on a cathode ray tube. The image on the screen represents the surface features of the specimen, which may be photographed. The magnifications were set from 200 to 50,000 times to get the great depths of field [20].

2.3. Dynamic Adsorption of Oil Vapor

The PACs were heated at 120°C firstly for 2 hours under vacuum. As the activated carbons with generous tiny hole were difficult to achieve adsorption equilibrium, the PACs were pretreated with the procedure named “passivation” before the dynamic adsorption. That is, the sample adsorbed the oil vapor continually until the concentration of discharged oil vapor was nearly equal to that of the upstream. The weight and the temperature changes were logged with the adsorption time. The adsorption tank were settling overnight to achieve complete adsorption. Subsequently, connecting the adsorption tank with the vacuum pump to draw out the adsorbed oil vapor, and recording the weight change of tank with desorption time.

After the procedure of “passivation”, the adsorption tank was connected to the generator of oil vapor and the outlet was connected to the Hydrocarbon Analyzer to log the change of non-methane concentration with time. As the concentration achieved a certain value, the adsorbent was weighed up to get the adsorption amount per mass. Once again, the adsorption tank was evacuated to obtain the
desorption amount. The pump was controlled to keep the vacuum gauge 0.098 MPa during the 15 minutes desorption. The above procedures were repeated for three times to calculate the average value.

3. Results and Discussion

3.1. Pore Parameters
The measurement of a nitrogen adsorption-desorption isotherms is the essential means to comprehend and predict exactly the adsorption properties of adsorbents. From the adsorption-desorption curves shown in figure 1a which is accord to the shape of a type of Langmuir adsorption, it can be deduced that the PAC was a typical microporous adsorbent. The inference was also confirmed from the pore size distribution given in figure 1b. The calculated Pore parameters in table 1 revealed the textural properties of the PAC. From the results of table 1 and figure 1b, it can be concluded that the most probable aperture of the PAC was 2.2 nm, while the contribution of external surface area (MA$_2$), not the micropore area (MA$_1$) to the total surface area (SA) was dominant. The pore structural characteristic determined the higher adsorption capacity and the better diffusion property of oil vapor which was appropriate for the PAC as adsorbent used in oil vapor recovery.

![Adsorption isotherm and pore size distribution](image)

**Figure 1.** Nitrogen adsorption isotherm and pore size distribution of PAC.

| SA (m$^2$/g) | PV (cm$^3$/g) | MA$_1$ (m$^2$/g) | MA$_2$ (m$^2$/g) | MP (cm$^3$/g) | PD (nm) |
|-------------|---------------|-------------------|-------------------|--------------|---------|
| 1273.2      | 0.7           | 154.7             | 1118.5            | 0.08         | 2.2     |

SA: surface area. PV: pore volume. MA$_1$: micropore area. MA$_2$: external surface area. MP: micropore volume and PD: pore diameter. The analysis of the sample was duplicated.

3.2. SEM Photograph
The SEM photographs of the PAC with different magnifications were given in figure 2. It can be seen that the PAC has the well-developed interstitial structure with abundant cavities, communicated with each other to form many apertures in the depth of the PAC. It is common knowledge that adsorbents with such morphologic characterization were endowed with the microporous structure to promote the adsorption affinity, as well as plenty of macro-pore and transition pores profited for gas diffusion. Based on this, the adsorbents of activated carbons are widely applied in oil vapor recovery.
Figure 2. SEM Photographs of the PAC with different magnifications: (a)×200; (b)×500; (c)×1000; (d)×5000.

3.3. Breakthrough Curve
In this experiment, the vapor generator was modified to get the entrance velocity 1 L/m and the non-methane hydrocarbon concentration 34% voL of oil vapor, respectively. The temperature of water bath was set at 20 °C. As the discharge concentration was nearly equal to 30% voL, the conclusion was drawn that the adsorbent bed was penetrated. After the operation of breakthrough, the adsorbent was regenerate using the vacuum pump. During the whole experiment course, the adsorption tank with thermometer and PAC was placed on the weightometer to record the changing of the system weight and temperature along with the adsorption/desorption times, the process records were provided in figures 3 and 4.

Figure 3. Changes of adsorption amount and temperature with adsorption time.
As shown in figure 3, the adsorption amount of oil vapor on the PAC increased quickly within original 20 minutes and tended to be stable ultimately. The temperature of the adsorbent bed increased sharply within the earlier 15 minutes and reduced through the subsequent time.

It can be deduced that the adsorbing velocity of the PAC on oil vapor was very high at the first stage of adsorption. When the adsorption sites of activated carbon were occupied, the adsorption amount was no longer increased because of the dynamic equilibrium between adsorption and desorption. The temperature increase of the bed with adsorption time was attributed to the exothermic effect of the physical adsorption. When the adsorption equilibrium was achieved, the adsorbent bed temperature decreased for the continuous blow of the entered vapor.

The change of desorption amount of the PAC with time was given in figure 4. It can be seen that the desorbed amount was about 92 g/kg within 80 minutes, which was only 24.5% of the adsorption amount in 60 minutes. Therefore, the conclusion can be drawn that desorption of the oil vapor adsorbed by the PAC using method vacuum was difficult. The desorption difficulty of the PAC should be attributed to the stronger binding energy between the vapor molecular and the wall of the micropore endured for smaller pore diameter of the PAC [21-25].

3.4. Influence of Moisture on the Adsorption Performance of PAC
In this experiment, the dried PACs was first placed in the thermostat wet box for 24 hours under different relative humidity (RH) before loaded in the adsorption tank. The adsorption-desorption cycles were carried out and the adsorption amounts of water vapor and oil vapor were calculated and given in figure 5.
From figure 5, it can be seen that the amount of adsorbed water vapor increased with the relative humidity increase that brought about the decrease of adsorbed oil vapor in turn. There are many oxygen-containing functional groups on the surface which lead to the hygroscopicity of activated carbon. When there is moisture existed in oil vapor, the competitive adsorption between water and the hydrocarbon molecules will take place, which will eventually reduce the adsorption efficiency of oil vapor recovery system [26].

3.5. Influence of the Inlet Concentration on the Adsorption Performance

In this experiment, the vapor generator was controlled to get the inlet oil vapor with different concentration. The outlet concentration of the tank was recorded with times and given in figure 6, the calculated adsorption amounts were given in table 2.

![Figure 6. Changes of the outlet concentration with the adsorption time.](image)

| C<sub>Inlet</sub> (% voL) | Adsorption time (s) | C<sub>Outlet</sub> (% voL) | Adsorption amount (g/kg) |
|--------------------------|---------------------|-----------------------------|--------------------------|
| 34                       | 490                 | 1.01                        | 45.55                    |
| 16                       | 695                 | 1.04                        | 28.47                    |

Table 2. Adsorption amount of the PAC under different inlet concentration.

It can be seen from figure 6 that the adsorption time for the lower concentration oil vapor was longer than that for higher concentration. However, the amount adsorbed for the higher concentration of oil vapor shown in table 2 was bigger than that for the lower concentration. The difference of adsorption amount can be explained that the molecule amount collided with the adsorbent in higher concentration oil vapor will be much more than that in the lower concentration oil vapor. However, the adsorption time was decided by the velocity of the oil vapor molecules passing the adsorbent bed. The transfer velocity was relatively faster in the higher concentration of oil vapor, thus the adsorption time was shorter than that in lower concentration of oil vapor.

3.6. Influence of the Inlet Velocity on the Adsorption Amount

In this experiment, the oil vapor with the same concentration entered the adsorption bed at different velocity. As the outlet concentration reached a fixed value, the adsorption time and adsorption amount were recorded and calculated which were given in figures 7 and 8.

From figures 7 and 8, it can be seen that the inlet velocity of oil vapor influences the adsorption amount and adsorption time of the PAC evidently. That is, the adsorption amount and the adsorption
time decreased with the increase of the inlet velocity of the upstream oil vapor.

![Figure 7. Adsorption amount of oil vapor with different inlet velocity.](image)

![Figure 8. Influence of inlet velocity of the PAC on the adsorption time.](image)

It was easy to understand that the oil vapor with higher velocity was easier to penetrate through the gap between the PACs which led to the fast achievement of the goal outlet concentration of the oil vapor and a short adsorption time. The oil vapor could not be completely adsorbed to the PAC in a shorter time, the adsorption amount was smaller at a higher inlet velocity consequently.

### 4. Conclusions

The adsorption properties of pillared activated carbon (PAC) on the oil vapor were studied through physical characterization and the dynamic adsorption measurement. With the measurement of N2 adsorption-desorption and the SEM observation, the PAC was a typical microporous material with the well-developed interior structure. The adsorption amount of oil vapor on the PAC was very large during the first time, while the adsorbed vapor was difficult to remove using the vacuum method. The vapor adsorption amount deduced for the competitive adsorption of moisture. When the supplying velocity increased, the adsorption amount of oil vapor on the PAC decreased for the shortening of contact time. With the increase of inlet concentration, the adsorption amount of oil vapor increased, while the adsorption time decreased.
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