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Effects of activated carbon properties on chlorobenzene adsorption and adsorption product analysis

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HIGHLIGHTS

- The AC microporosity much favours chlorobenzene adsorption than the AC basic groups.
- The desorption energy for chemisorbed chlorobenzene is 99.2 kJ/mol.
- Chlorobenzene adsorption decreased lactone/quinone groups with AC structure damaged.

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ABSTRACT

Activated carbon (AC) adsorption is highly effective for the removal of volatile organic compounds. The effects of AC properties on chlorobenzene adsorption were investigated in a fixed-bed reactor. The AC microporosity is more favourable for chlorobenzene adsorption than the basic groups. The interactions between chlorobenzene and AC with the adsorption products were investigated by temperature programed desorption, X-ray photoelectron spectrum, Raman and Fourier transform infrared spectrum measurements. The results show that chlorobenzene is both physically and chemically adsorbed by AC, with the chemically adsorbed chlorobenzene accounting for approximately 13.1% of the total adsorbed amount. The desorption activation energy for chemically adsorbed chlorobenzene was determined to be 99.2 kJ/mol. The chlorobenzene chemical adsorption process changes both the functional groups and the carbon crystal structure of AC. The lactone and quinone groups on AC decrease in number, and the carbon crystal structure of AC is slightly damaged after chlorobenzene adsorption.

1. Introduction

Volatile organic compounds (VOCs), which are emitted principally from industrial point sources, have been proven to cause damage to human nervous systems and to cause cancer. Current legislation strictly limits VOCs emissions [1]; therefore, effective emission reduction techniques are necessary. Activated carbon (AC) adsorption is an effective and widely used technique for the removal of various pollutants, especially for the removal of low concentration pollutants (<2 wt.%) due to its highly developed microporosity structure [2]. Many flue gases involved in industrial processes contain VOCs at very low concentrations (around 200 ppm) [3], so AC adsorption is an ideal choice for their removal. AC injection and fixed-bed adsorption are two common methods employed to remove harmful gases [4].

Activated carbon, with its large surface area and pore volume, contains useful functional groups located on the edges of the graphene layers. Both the pore structure and the surface chemical properties of AC affect the gas adsorption. Previous studies have analysed the influences of the properties of ACs on VOCs adsorption [5,6], with the general conclusion that the micropore volume and the specific surface area are the predominant properties affecting the VOCs adsorption on AC. The effects of the surface functional groups are not completely understood [6–8]. Lillo-Ródenas et al. [6] studied benzene and toluene adsorption on AC, and the results showed that the volume of the narrow micropores (size < 0.7 nm) appears to govern the VOCs adsorption and that a low content of oxygen surface groups have the best adsorption performance. Bell et al. [9] studied the adsorption of very low concentration (<50 ppm) chloroaromatic gases on AC and concluded that the surface functional groups have only a relatively small effect on the adsorption characteristics. Ghimbeu et al. [10] studied the adsorption of oxygenated hydrocarbons on AC and found that the adsorption capacities are more directly related to the chemical properties of AC where the carbon surface is involved in specific hydrophilic

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interactions with the ethanol, and the number of oxygenated surface groups increases the adsorption capacity.

To study the interactions between AC and organic adsorbates, Castillejos-López et al. [11] investigated the different desorption behaviours of phenol, aniline and nitrophenol using temperature programmed desorption (TPD) measurements. The results showed that the oxygen surface groups inhibited the phenol chemisorption due to the competition for the adsorption sites. Aniline interacts with each type of the superficial groups, and the interaction of nitrophenol with AC could produce the oxygen surface groups that decompose to form CO_2.

These diverse effects of the AC chemical properties are closely correlated to the properties of the different adsorbates. Chlorinated aromatic compounds have been shown to be the primary precursors of dioxin formation in industrial processes [12]; therefore, this study focused on chlorobenzene adsorption on various ACs. The C—Cl bond of chlorobenzene may cause the molecular diameter and polarity of this compound to affect its adsorption; so, the optimum carbon pore structure and the determination of favourable functional groups are investigated. In addition, the chlorobenzene adsorption products are investigated to analyse the interactions between the chlorobenzene and carbon functional groups.

2. Experimental

2.1. Materials and characterisation

Eight commercial AC samples with various pore structures from the Gongyi AC plant in the Henan province were selected in this study. The porous texture was characterised by N_2 adsorption at 77 K in an automatic surface area and porosity analyser (Autosorb iQ, Quantachrome). The total surface area, S_{BET}, was calculated from the N_2 adsorption isotherms using the Brunauer–Emmett–Teller (BET) equation. The total pore volume, V_T, was determined from the amount of N_2 adsorbed at $p/p_0 = 0.95$. The micropore surface area, S_{mi}, was determined using the t-plot method, and the pore size distributions were calculated using the Quenched Solid Density Functional Theory (QSDFT) split model. The micropore volume, V_{mi}, was calculated using the Horvath–Kawazoe (HK) method.

One of the eight AC samples was treated according to the five procedures listed in Table 1 to obtain AC samples with various surface functional groups. The BET surface of the chosen AC sample is 783 m^2/g and its adsorption amount is moderate among the eight AC samples. After treatment, the AC–N, AC–H, and AC–A samples were washed with distilled water until the filtrate reached pH 7.0 and then dried at 383 K for 24 h.

The surface functional groups and adsorption products were analysed using a Fourier transform infrared (FTIR) spectroscope (Nicolet 6700, Thermal). The spectra were collected on a Perkin–Elmer Spectrum One spectrometer operating in the infrared region of 500–4000 cm^{-1} with a resolution of 4 cm^{-1}. The background spectrum was recorded using the atmospheric vapour correction to eliminate CO_2 and H_2O vapour during the experiment. Three scans were collected for each sample. The Boehm titration was used to quantitatively measure the oxygen groups based on the selective neutralisation by equilibrium with a series of bases and an acid [13]. The bases used were $NaHCO_3$, Na_2CO_3, NaOH, and the acid used was HCl. A 0.20 g AC sample was placed in 50 ml of each solution. The vials were sealed and shaken for 24 h at 298 K and then filtrated. A portion (10 ml) of the filtrate was transferred to a flask, and the unreacted base or acid was titrated with HCl or NaOH. The number of acidic sites was determined with the assumptions that NaOH neutralises carboxylic, lactonic, and phenolic groups, Na_2CO_3 neutralises carboxylic and lactonic groups, and $NaHCO_3$ neutralises only carboxylic groups. The number of basic sites was calculated from the amount of HCl that reacted with the carbon.

Table 1
AC treatment methods.

Sample	Treatment method
AC–O	Dried in the atmosphere at 383 K for 24 h
AC–T	Heated in N_2 at 1173 K for 2 h
AC–N	Soaked in 6 mol/L HNO_3 solution for 12 h at 293 K
AC–H	Soaked in 30 wt% H_2O_2 solution for 12 h at 293 K
AC–A	Soaked in 30 wt% ammonia solution for 12 h at 293 K

The surface chemical composition of the samples was measured by using X-ray photoelectron spectroscopy (XPS, ESCALab 250, Thermo Electron) with an Al Kα X-ray source (1486.6 eV) at a constant recording ratio of 40. The X-ray source operated at a reduced power of 150 W. The pressure in the analysis chamber was maintained at 10^{-8} Torr or lower during each measurement. To compensate for surface charge effects, all of the binding energies were referenced to the C1s hydrocarbon peak at 284.6 eV. Raman spectra were obtained with a Raman spectrometer (Labram aramis, HORIBA Jobin Yvon) using a 514.5 nm Ar line as an excitation source. Raman spectra from 0 to 4000 cm^{-1} at an approximate 0.5 cm^{-1} interval were measured for 15 s in the backscattering geometry with a filtered 64 cm single monochromator.

2.2. Chlorobenzene adsorption and desorption tests

The adsorption of chlorobenzene on the AC samples was investigated in a fixed-bed reactor. The quartz tube reactor was 8 mm in diameter and 500 mm in height with a sieve plate in the middle. Each sample (0.10 g) with particle sizes of 38–62 μm was loaded on the plate for each experiment. The reaction temperature was 393 K. The gas flow rate was 300 ml/min at standard state, and the gaseous hourly space velocity (GHSV) was approximately 72,000 h^{-1}. The simulated gas consisted of chlorobenzene vapour and a balance of N_2. The chlorobenzene vapour was generated using N_2 from a bubbling container bathed in 313.0 ± 0.1 K water, and the chlorobenzene concentration was calibrated using a gas chromatograph (7890, Agilent) at 250 ± 10 ppm. After the gas was mixed in the mixing vessel, it was injected into the reactor with the effluent gas continuously detected by a quadruple mass spectrometer (GAM200, IPI). Before each test, the mass spectrometer was purged with high purity nitrogen for 4 h. The chlorobenzene was identified using the major mass ion 112 detected by the mass spectrometer, and the total adsorption time was 3 h for chlorobenzene.

The adsorption amount of chlorobenzene on the AC was calculated by numerical integration of the experimental data based on the breakthrough curves, as shown in the following equation:

$$v = \frac{F_o M}{22.4 \times m_o} \int_o^t (C_o - C_t) dt \qquad (1)$$

where v is the adsorbent adsorption amount (mg/g), M is the mole fraction of the adsorbate (112 g/mol for chlorobenzene), F_o is the volumetric feed flow rate (ml/min), m_o is the adsorbent mass (g), C_o is the adsorbate feed concentration (ppm), and C_t is the adsorbate concentration (ppm) at time t.

The temperature programmed desorption coupled with a mass spectrometer (TPD–MS) method was used to analyse the adsorption products and the specific interactions between the AC and the adsorbate. The samples were placed in a quartz crucible of a thermogravimetric (TG) analyser (Versa Therm HM, Thermal). The desorption process was recorded in the temperature range of 303–1273 K with a fixed heating rate, and argon gas was used as