

ADSORPTION OF VOLATILE ORGANIC COMPOUNDS ONTO POROUS CLAY HETEROSTRUCTURES BASED ON SPENT ORGANOBENTONITES

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Abstract—Model spent cetyltrimethylammonium bromide (CTMAB)-bentonite, and cetyl pyridinium chloride (CPC)-bentonite used for sorbing *p*-nitrophenol (PNP) from wastewater, as well as virgin CTMAB-bentonite and CPC-bentonite, were employed as the starting materials to prepare porous clay heterostructures (PCHs). The BET surface areas and total pore volumes of the PCHs based on these spent and virgin organobentonites (PNP-CTMAB-PCH, CTMAB-PCH, PNP-CPC-PCH and CPC-PCH) are 661.5 m²/g and 0.25 cm³/g, 690.4 m²/g and 0.27 cm³/g, 506.3 m²/g and 0.30 cm³/g, and 525.4 m²/g and 0.30 cm³/g, respectively. These values approximate those of activated carbon (AC), at 731.4 m²/g and 0.23 cm³/g, and are much larger than those of bentonite and CTMAB-bentonite, at 60.9 m²/g and 0.12 cm³/g, and 3.7 m²/g and 0.0055 m³/g, respectively. The PCHs have slightly higher adsorption capacities for benzene and CCl₄ than AC at higher relative pressures despite their comparatively lower benzene and CCl₄ adsorption capacity at lower relative pressures. The existence of PNP in organobentonites also enhances the volatile organic compounds (VOCs) adsorption capacity of PCHs at lower adsorbate concentrations, although some adsorption capacity is lost at higher concentrations. The hydrophobicity order of the adsorbents is: CTMAB-bentonite > AC > PCHs > bentonite. The micro- to mesoporous pore sizes, superior VOC adsorption properties, thermal stability to 750°C and hydrophobicity and negligible influences of PNP on PCHs make spent PNP-containing organobentonites ideal starting materials for synthesis of PCHs and especially attractive adsorbents for VOC sorption control.

Key Words—Adsorption, Organobentonite, Porous Clay Heterostructures, VOC.

INTRODUCTION

Volatile organic compounds (VOC) are often toxic or carcinogenic and can lead to many severe environmental and health problems such as depletion of the stratospheric ozone layer, smog formation or direct action on human tissues (Tancrede *et al.*, 1987). Adsorption onto hydrophobic materials is a proven and reliable technology for VOC control which has the added benefit of recovering valuable materials for reuse (Stenzel, 1993). An ideal adsorbent for VOC removal is usually expected to have the following characteristics: (1) sufficiently large and reversible adsorption capacity; (2) large accessible pore volume; (3) low catalytic activity; (4) hydrophobic surface; (5) high thermal and hydrothermal stability; and (6) an easy regeneration capability (Zhao *et al.*, 1998). Despite disadvantages such as flammability, pore clogging, hygroscopicity and problems associated with regeneration, activated carbon (AC) is frequently used as an adsorbent for VOCs due to its large adsorption capacity and accessible surface area.

Organobentonites are a class of potential sorbents for sorption of organic pollutants from water and gas or vapor (Smith and Dinagalan, 1995; Barrer, 1989; Barrer and Millington, 1967; Zhu and Su, 2002). They are synthesized by the exchange of organic cations, typically

having a quaternary ammonium structure, for inorganic ions on the internal and external mineral surfaces of bentonite (Smith *et al.*, 1991). The mineral surfaces of the resulting organobentonite are organophilic. Thus organobentonites are powerful sorbents for organic pollutants relative to conventional bentonite (Boyd *et al.*, 1988; Smith *et al.*, 1990; Traina and Onken, 1991; Smith and Jaffé, 1994). The primary limiting factors for practical applications of organobentonites are regeneration and the ultimate disposal of spent sorbents. Methods such as thermal desorption (Keyes and Silcox, 1994; Lin and Cheng, 2002) and supercritical carbon dioxide extraction (Ceollho, 2001) have been used in attempts to regenerate organobentonites or bentonite loaded with organic pollutants. Organobentonites are unlikely to endure the high temperatures necessary for these regeneration processes, however, because of the relatively low thermal stability of the quaternary ammonium surfactants used to create them. Thus, routine thermal regeneration or desorption methods are not likely to be suitable for organobentonites loaded with organics. Given that the boiling points of many organics adsorbed on organobentonites are greater than, or similar to, the decomposing temperature of the surfactants, the useful properties of organoclays are expected to be destroyed during the thermal regeneration process. It is important to study the economics and effectiveness of methods of disposal or reuse of spent organobentonites in order to avoid secondary pollution problems. The synthesis of adsorbents from spent organobentonites not only meets

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the requirement of VOC control but also would partially overcome regeneration and disposal problems associated with spent organobentonites.

The recent discovery of porous clay heterostructures (PCHs) makes it possible to synthesize new adsorbents for VOC control from organobentonites. Galarneau *et al.* (1995) showed the possibility of using intercalated quaternary ammonium cations and neutral amines as co-surfactants to direct the interlamellar hydrolysis and condensation polymerization of neutral inorganic precursors *e.g.* tetraethylorthosilicate (TEOS) within the galleries of 2:1 mica-type layered, high charge-density silicates, such as fluorohectorite, hectorite and vermiculite. Removal of the surfactant by calcination then leaves a mesoporous solid with a thermally stable pore. PCHs are interesting alternative adsorbents due to their large external surface area (400–900 m²/g), and unique combined micro- and mesoporosity (pore size in the range 1.4–2.2 nm) (Pinnavaia *et al.*, 1998). The synthesis processes of PCHs usually include the following steps: (1) synthesis of organo-clay derivatives; (2) synthesis of an amine-solvated organo-clay derivative; and (3) synthesis of PCHs by calcination or solvent extraction. Until now, clays such as fluorohectorite (Galarneau *et al.*, 1997), synthetic saponite (Ahenach *et al.*, 2000), and natural bentonite (Pichowicz and Mokaya, 2000) have been used as the layered hosts. Studies of PCHs have concentrated on the synthesis conditions (stoichiometric conditions, varieties and ratios of surfactants and co-surfactants, reaction conditions, calcination temperatures, *etc.*), structural characterization and catalysis properties (Pichowicz and Mokaya, 2000; Benjelloun *et al.*, 2002; Polverejan *et al.*, 2000). However, for research related to the adsorption capacities of PCH for VOC, more information on the thermodynamics of adsorption and PCH thermostability properties is required. The use of relatively cheap spent organobentonites as a substitute for organo-clay derivatives might promote practical applications of PCHs and help to overcome problems of disposal or reuse for organobentonites. Therefore, it is of great scientific and practical interest to synthesize PCHs from spent or virgin organobentonites and to understand the adsorption properties of PCHs for VOC control.

In this work, two of the most common organobentonites, cetyltrimethylammonium bromide (CTMAB)-bentonite and cetyl pyridinium chloride (CPC)-bentonite, were loaded with *p*-nitrophenol (PNP), a representative organic pollutant of higher boiling point, from simulated wastewater containing PNP. Both virgin organobentonites and these model spent organobentonites were used as starting materials for synthesizing PCHs. The surface area and porosity of these materials was characterized by N₂ adsorption. The adsorption capacity for VOCs of various PCHs was estimated from adsorption isotherms for benzene and carbon tetrachloride. The hydrophobicity of all adsorbents was characterized by water

adsorption while their thermal stability was characterized by thermogravimetry. The differential heats of adsorption of the various adsorbate-adsorbent systems were calculated from their respective isotherms. The VOC adsorption capacity and related properties of the PCHs were compared with bentonite, organobentonites and activated carbon (AC).

MATERIALS AND METHODS

Preparations of organobentonites

Bentonite obtained from Inner Mongolia, China, was used as the starting clay material. It has a cation exchange capacity (CEC) of 104 meq/100 g of clay. The predominant clay mineral in this bentonite is Namontmorillonite. The bentonite was ground and the fraction which can pass a 100 mesh sieve used in this study. Hexadecyltrimethylammonium bromide (HDTMAB) (referred to here as cetyltrimethyl (CTMAB)) and hexadecylpyridinium chloride (HDPC) (referred to here as cetylpyridinium chloride (CPC)), both of analytical grade, were used in organobentonite synthesis without further purification. Simulated wastewater was prepared using analytical grade *p*-nitrophenol (PNP) at a concentration of 1000 ppm. The melting point and boiling point of PNP are 113.4 and 279°C, respectively.

A total of 100 g of ground bentonite was allowed to mix with 1 L of aqueous surfactant solution containing 0.104 mol of CTMAB or CPC. The mixture was stirred at 60°C for 2 h. Then the product was separated from the solution by filtration and washed three times with distilled water to remove excess water-soluble surfactant. Subsequently, the organobentonites were air dried and then ground sufficiently to pass a 100 mesh sieve.

15 g of organobentonite were placed in a flask with 1 L of simulated wastewater consisting of a 1000 ppm aqueous PNP solution. The flask was capped and placed in a constant temperature bath at 25°C and shaken at the rate of 50 revolutions per minute for 24 h to ensure adsorption equilibrium. The mixture was then centrifuged for PNP concentration measurement. The *p*-nitrophenol concentration in the aqueous phase was determined by UV spectrophotometry (Zhu and Chen, 2000). The amount of sorbed PNP, calculated from concentration differences for CTMAB-bentonite and CPC-bentonite, was determined to be 96 mg/g and 94 mg/g, respectively. Prior to synthesis of PCHs, these model spent organobentonites loaded with PNP were air dried at room temperature and then ground with a mortar and pestle to pass a 100 mesh sieve.

Synthesis of PCHs

Analytical grade tetraethylorthosilicate (TEOS) and dodecylamine (C₁₂H₂₅NH₂) were used as the neutral inorganic precursor and co-surfactant, respectively, for PCH synthesis. The virgin or spent organobentonite was

added to dodecylamine and TEOS at a mass ratio of organobentonite derivative/dodecylamine/TEOS of 1/1/120. The mixture was allowed to react for 4 h at 50°C under continuous stirring. After reaction, the modified clay was separated by filtration (no washing), air dried overnight at room temperature and finally calcined at 550°C for 6 h. Five PCHs were thus synthesized and will be referred to hereafter as CTMAB-PCH, PNP-CTMAB-PCH, CPC-PCH and PNP-CPC-PCH, according to the starting materials used.

Adsorption measurements of benzene, CCl_4

The adsorption isotherms of benzene and CCl_4 on the various test adsorbents were determined using a dynamic method. The apparatus used is shown in Figure 1. High purity (99.999%) nitrogen gas was used to carry varying partial pressures of benzene or CCl_4 . The carrier gas pressure was reduced and stabilized by valve 1 and divided into two streams by two gas-flow gauges. Gas flows ranged up to 250 cm^3/min . The flow gauges were calibrated with a soap bubble flow meter. Gas-flow rates were adjusted using two needle valves. One of the two gas flows was conducted to the pre-saturator containing pure liquid VOC; the other diluted the VOC. Both flows passed through preheating coils immersed in a constant-temperature water bath ($25 \pm 0.5^\circ C$). An integrated adsorption unit, including secondary VOC saturator, mixing chamber and adsorption chamber, was also kept at constant temperatures ($25^\circ C$). The flow with the VOC vapor was first introduced into the secondary saturator and the outlet flow from the secondary saturator was then mixed with the dilution N_2 gas flow in the mixing chamber. By controlling the flow rates with needle valves and calibrated flow gauges, the relative partial pressure of VOC was controlled over a range from 0.03 to 0.98. The mixed gas was passed through the adsorption chamber, which consisted of a movable glass column (90×15 mm diameter), where the adsorbent was held. A small, scintered glass sieve plate supported the adsorbent.

The VOC adsorption isotherms were determined gravimetrically for each relative partial pressure of VOC. Column and adsorbent weight were obtained using an electronic analytical balance (0/1 mg sensitivity). A weighted glass fiber was inserted into the residual space of the column to prevent the adsorbent from escaping along with the gas stream. A preliminary experiment proved that adsorption of VOC by the glass fiber was negligible. The column loaded with adsorbent was then placed in the adsorption chamber and thereafter was removed for weighing every 15 min until the variation in the weight was < 2 mg. Care was taken to ensure that the column was not removed from the chamber for more than 2 min for each measurement. The VOC adsorption capacity of the adsorbent was calculated using difference in weights before and after adsorption.

Water-vapor adsorption

Because it is difficult to determine the amount of water adsorbed on the studied adsorbents using a dynamic process, the water isotherms for all adsorbents were measured by a static equilibrium method using excess water-soluble salt in contact with its saturated solution to produce a constant relative humidity or relative vapor pressure, generally accurate to $\pm 2\%$. The values of relative humidity produced by familiar inorganic salts at given temperature can be found in Marsh (1987) and Wexler and Seinfeld (1991).

In this study, 12 species of inorganic salts were selected to produce constant relative humidity (RH). Twelve portions of 0.5 g of adsorbent were placed in 12 weighted 5 cm^3 beakers. The beakers were suspended within 250 cm^3 bottles loaded with various saturated salt solutions, then covered and sealed. The bottles were placed into a constant-temperature chamber ($25 \pm 0.5^\circ C$) for 5 days to ensure adsorption equilibrium. Water adsorption capacities of each adsorbent at the various relative partial pressures were calculated from the change in mass of the sample following equilibrium.

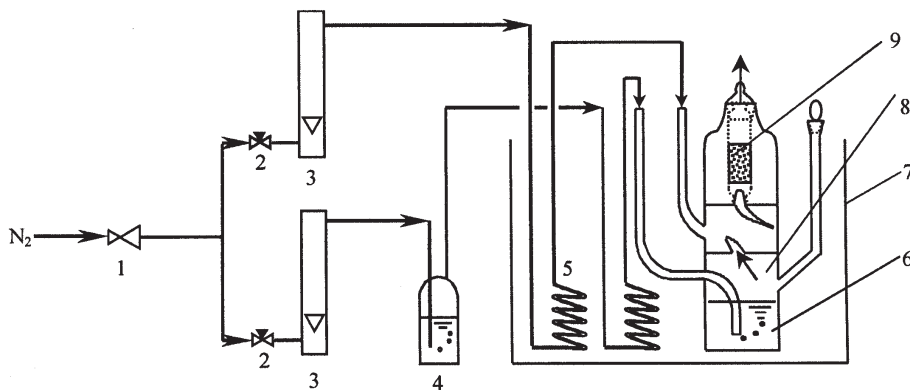


Figure 1. Flow-equilibration apparatus used to study the sorption of benzene and carbon tetrachloride. (1) Pressure-reducing valve; (2) needle valves; (3) flow gauges; (4) VOC pre-saturator; (5) preheating coil; (6) secondary VOC saturator; (7) constant-temperature water bath; (8) mixing chamber; (9) adsorption column loaded with adsorbent.

Adsorption measurements of N_2

The N_2 adsorption-desorption isotherms of bentonite, CTMAB-bentonite, CTMAB-PCH, PNP-CTMAB-PCH and AC were recorded at -196°C using an ASAP 2000 automated gas adsorption system. The adsorbents were degassed at 105°C over 16 h in a vacuum furnace prior to analysis. The surface areas were calculated using the BET equations. The pore distributions and pore volume were constructed using the adsorption branch of the N_2 isotherms based on the BJH model (Barrett *et al.*, 1951).

Thermogravimetric analysis (TGA)

The TGA analysis was performed using a DELTA SERIES TGA7. About 10 mg of adsorbent were loaded on a platinum pan and heated to 780°C at a rate of $10.0^\circ\text{C}/\text{min}$ in an air flow of $80\text{ cm}^3/\text{min}$.

RESULTS AND DISCUSSION

N_2 adsorption, surface areas and porosities of various adsorbents

Important pore-structure parameters such as specific surface area, pore volume and average pore size of the four bentonite-based materials (bentonite, CTMAB-bentonite, CTMAB-PCH, PNP-CTMAB-PCH, CPC-PCH and PNP-CPC-PCH) and AC were calculated by using data from N_2 adsorption-desorption isotherms. The results are summarized in Table 1. The BET surface area and total pore volume of CTMAB-bentonite are $\sim 5\%$ of that of bentonite and $\sim 0.5\%$ and 2% , respectively, of that of CTMAB-PCH and PNP-CTMAB-PCH. Surface-area parameters of the PCHs ($\sim 506.3\text{--}690.4\text{ m}^2/\text{g}$) are close to that of AC ($731.4\text{ m}^2/\text{g}$) while the pore parameters of the PCHs (average pore sizes, $\sim 24.08\text{--}31.06\text{ \AA}$) and total pore volumes ($\sim 0.25\text{--}0.30\text{ cm}^3/\text{g}$) are larger than the corresponding values of AC (12.74 \AA and $0.23\text{ cm}^3/\text{g}$, respectively). The pore and surface-area parameters of PNP-containing PCHs are comparable to the other adsorbents, although slightly smaller than their non-PNP-PCH counterparts. Thus, the influence of PNP adsorbed onto organobentonite on the formation of PCHs is finite and minimal.

According to the values of average pore size listed in Table 1, the four bentonite-based materials are mesoporous (pore diameter between 2 and 50 nm), whereas

AC is a microporous material (pore diameter $< 2\text{ nm}$). However the pore-size distributions shown in Figure 2 indicate that the pores of the PCHs are much smaller and more uniform in size than those of bentonite, CTMAB-bentonite or AC.

Furthermore, the two PCHs from CPC-bentonites have larger pore sizes (average pore diameter 31.60 \AA) and pore volumes (total pore volume $0.30\text{ cm}^3/\text{g}$) than those for CTMAB-bentonites while the PCHs from CTMAB-bentonites have slightly larger BET surface areas and greater pore-size distributions (Figure 2). This shows that the pore structures of PCHs are obviously influenced by the surfactants used in starting materials.

In forming a PCH by gallery-templated synthesis, Pinnavaia *et al.* (1998) found that the surfactants used to synthesize organo-clay derivatives can be quaternary onium ions (cations) with alkyl groups, at least one of which should have a chain length of at least six carbon atoms. Mixtures of onium ions can also be used. Certainly, the carbon chain length of the surfactant would influence the pore-structure parameters, particularly pore size. Longer alkyl chain length of surfactants produces larger pore sizes in PCHs. Although the organobentonites commonly used in water treatment are derived from tallows, typically di-dodecyltrimethyl ammonium chlorides (Xie *et al.*, 2001) which have shorter carbon chain length than those used here, the carbon atom number of the longest alkyl chains of these surfactants are usually larger than six. As a result, these organobentonites are still suitable for the starting materials of PCHs.

The N_2 adsorption-desorption isotherms of the five adsorbents showed distinct differences between bentonite, organobentonite, PCHs and AC (Figure 3). The hysteresis loops of all isotherms exhibit closure suggesting that minimal structural changes accompany the adsorption/desorption processes. Following the BDDT classification (Gregg and Sing, 1982) the isotherms of bentonite should be of type II, but only with smaller adsorbed volume, and with H_3 hysteresis characteristic of plate materials with slit-like micropores. The hysteresis evident in the bentonite isotherms is confined to relative pressure above 0.45 and adsorption is fully reversible below this relative pressure.

Table 1. Specific surface area, average pore size and pore volume of several studied adsorbents.

Adsorbent	BET surface area ($\text{m}^2\text{ g}^{-1}$)	Average pore diameter (\AA)	Total pore volume* ($\text{cm}^3\text{ g}^{-1}$)
Bentonite	60.9	77.28	0.12
CTMAB-bentonite	3.7	55.42	0.0055
CTMAB-PCH	690.4	24.08	0.27
PNP-CTMAB-PCH	661.5	24.09	0.25
CPC-PCH	525.4	31.60	0.30
PNP-CPC-PCH	506.3	31.60	0.30
AC	731.4	12.74	0.23

* BJH cumulative adsorption pore volume

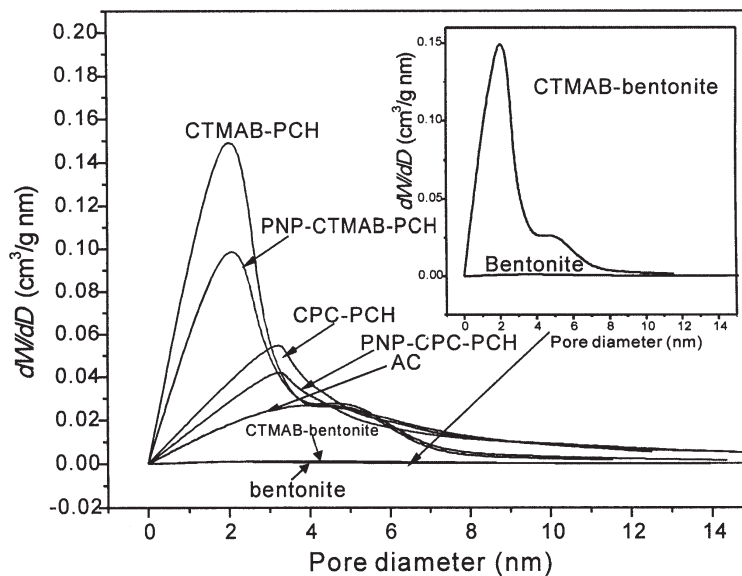


Figure 2. Pore-size distributions of various adsorbents.

Although the isotherm for CTMAB-bentonite is also type II, the sorption volume is 15 to 20 times less than that for bentonite. The adsorption isotherm at higher relative pressure is also smoother and the hysteresis is sustained to lower relative pressure than that for

bentonite. Since the hysteresis is associated with capillary condensation, this would be expected because the external surface measured for organobentonite was less than that of bentonite. Modification by excess organic salt molecules causes the slit-like micropore

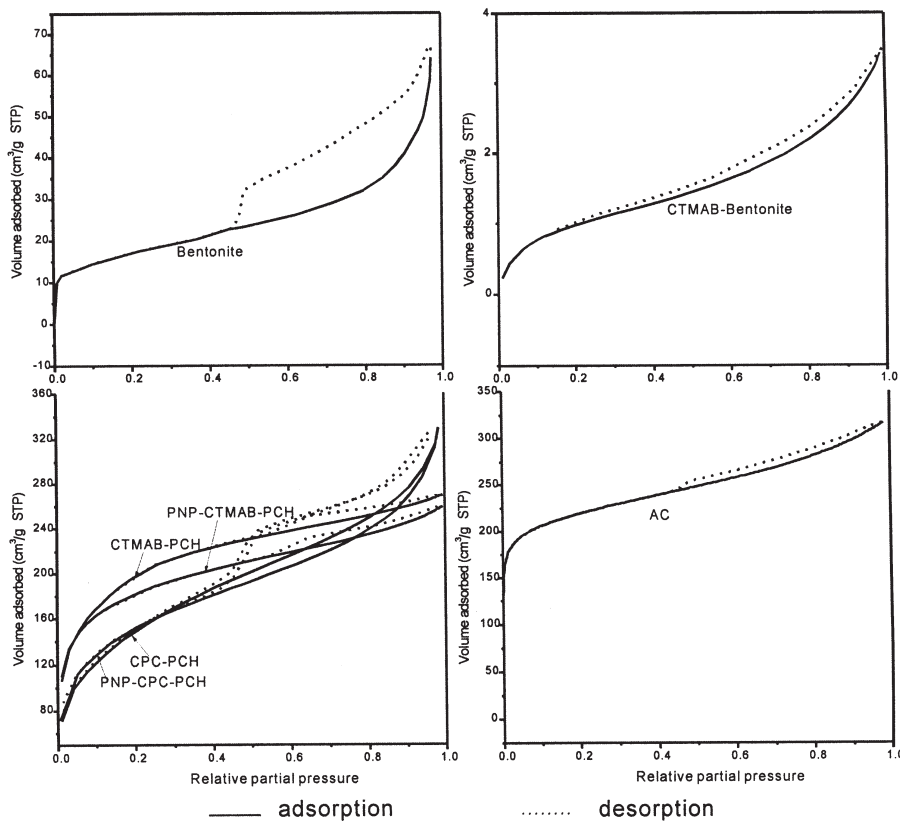


Figure 3. N₂ adsorption-desorption isotherms at -196°C.

character to disappear. Adsorption-desorption isotherms of both PNP-containing PCHs and non-PNP-PCHs are of type IV with H_3 hysteresis. The isotherms of PCHs from spent or virgin organobentonites are identical to those of the PCHs from synthetic saponites and fluorohectorite reported by Pinnavaia *et al.*, (1998), indicating that they exhibit the same porous characteristics. As shown in Figure 3, the increase in adsorbed volume at relative pressure of ≤ 0.02 is indicative of micropores while the near-linear sorption of N_2 in the region corresponds to the relative pressure range 0.02–0.2 and indicates structures in the supermicropore to small mesopore region of ~ 1.5 – 2.5 nm. Based on these characteristics, the two PCHs are unique materials with a combined micro- and mesoporosity and are therefore very promising in the field of VOC adsorption.

The resemblance between the N_2 adsorption-desorption isotherms of PNP-containing PCHs and non-PNP-PCHs proves that the PNP loaded on organobentonites has negligible influence on the synthesis of PCHs. Although the adsorption-desorption isotherms of the two PCHs obviously differ from those of bentonite and organobentonites, the type- H_3 hysteresis shows slit-like pores. In other words, even after intercalation of organic cation modifiers and calcination, the lamellar textural characteristics of base smectite still exist. The adsorption branches of isotherms of both the PCHs resemble AC indicating that they all possess microporous characteristics, but the desorption branch of the isotherm of AC is of type H_4 which is indicative of micropores rather than type H_3 of the PCHs. In addition, the adsorption-desorption isotherms shown in Figure 3 indicate that the two PCHs and AC have similar sorption volumes.

Thermogravimetric analysis

The heat-resisting temperature of an adsorbent can be determined by thermogravimetric (TG) analysis. Figure 4 shows the weight-loss curves (TG) of bentonite, CTAMB- and CPC-bentonites, CTMAB- and CPC-PCHs, PNP-CTMAB-PCH, PNP-CPC-PCH and PNP-CTMAB-bentonite together with the corresponding derivatives of the weight-loss curves. The mass lost for all eight materials between room temperature and 150°C is due to loss of water from the clay structures.

For the two organobentonite and PNP-CTMAB-bentonite samples, the major losses occur between 200 and 400°C due to the burning off of the surfactants and any adsorbed PNP. This suggests that the calcining temperature for synthesis of PCHs based on these materials should be $\geq 400^\circ\text{C}$. The thermogravimetric data also suggest that CTMAB-bentonite and CPC-bentonite are thermally stable to $\sim 200^\circ\text{C}$ when they are used as adsorbents. The largest weight losses in the region of 200 to 400°C should depend on the weights of surfactants and PNP in the materials. However, the TG curves for PNP-CTMAB-bentonite and CTMAB-bentonite are very similar, indicating that the same calcining temperature can be used to synthesize PCHs based on both spent and virgin organobentonites. Dehydroxylation reactions are responsible for the weight loss of bentonite, the two organobentonites and the PNP-CTMAB-bentonite in the temperature region of 500 to 750°C . The four different PCH materials exhibit similar resistance to temperatures above $\sim 150^\circ\text{C}$ indicated by their negligible weight losses of ~ 2 – 3% between 200 and 750°C , the maximum TGA temperature. The order of thermal stability for the adsorbents based on bentonites is: PCHs > bentonite > organobentonites. Therefore,

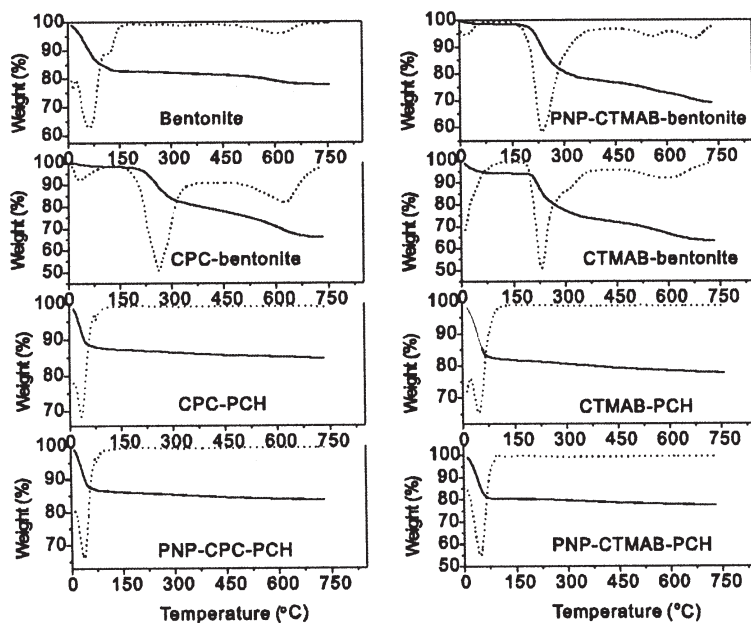


Figure 4. TG curves (solid lines) of eight materials based on bentonite and their derivatives (dotted lines).

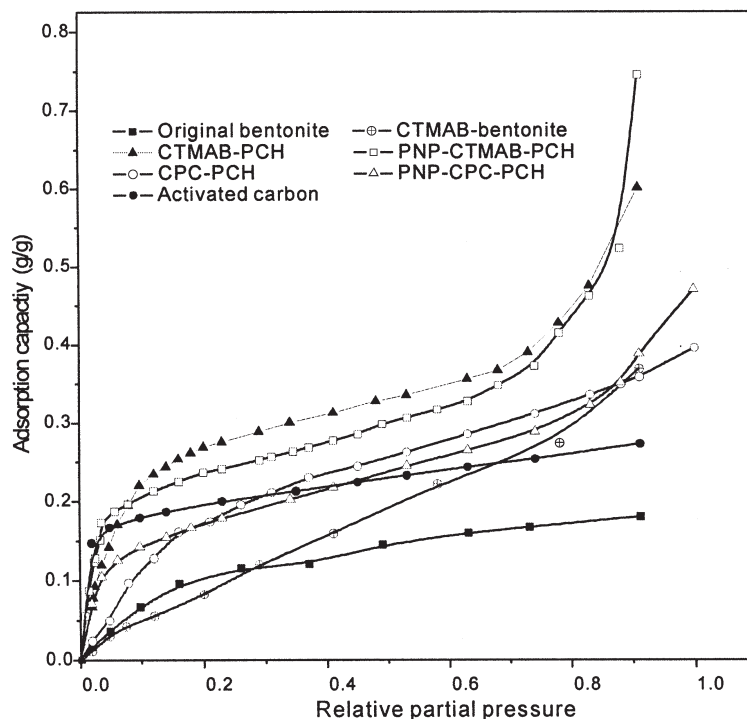


Figure 5. Benzene adsorption isotherms of various adsorbents at 25°C.

regeneration of PCHs, following sorption of VOCs should not be an issue.

Sorption of benzene and CCl₄

Figures 5 and 6 show the adsorption isotherms of benzene and CCl₄ onto the seven various adsorbents at

25°C. The isotherms of benzene and CCl₄ on bentonite and AC are all of type IV. Over the range of relative partial pressures, the adsorption capacities of CCl₄ on CTMAB-bentonite are less than those of bentonite. In contrast to bentonite, the CTMAB-bentonite's benzene adsorption capacity is lower over the range of relative

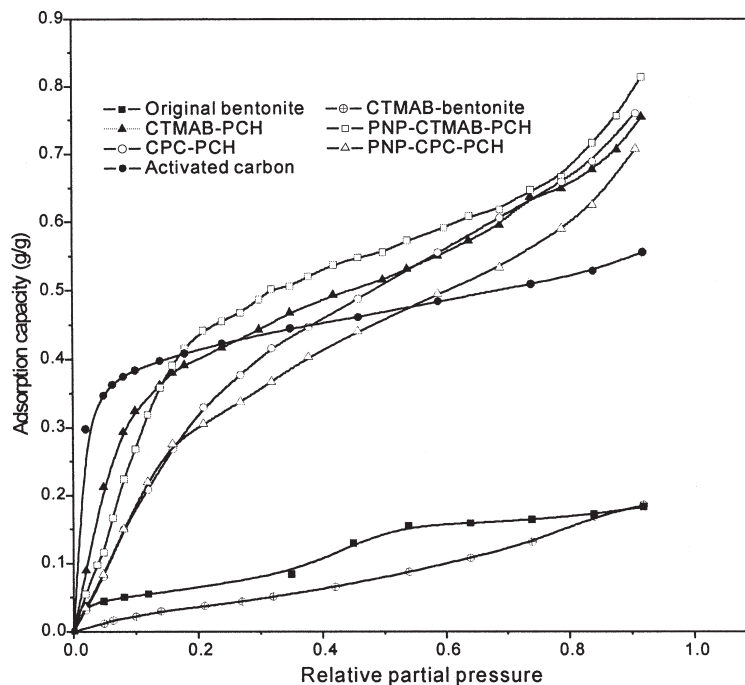


Figure 6. CCl₄ adsorption isotherms of various adsorbents at 25°C.

pressure from 0 to 0.3 and higher above 0.3. When the two VOCs were adsorbed onto CTMAB-bentonite, the interlayer CTMAB filled all the interlayer space. The long carbon chains were closely packed and steeply oriented to the surface (Barrer, 1967, 1989). As a result, the CTMAB-bentonite swelled further when it imbibed certain molecules, yielding isotherms whose shapes resemble type IV isotherms (Barrer, 1967). The extent of intercalation is different, and associated with the factors such as the properties and contents of surfactants and the CEC of the clay.

The isotherms of the two VOCs adsorbed onto the four PCHs all behave as type II isotherms. This is very common in cases of physical adsorption and is probably associated with the formation of a multi-molecular adsorption layer (Langmuir, 1918). The type II isotherms of the four PCHs reveal an appreciable amount of mesoporosity in these adsorbents, where, beyond a certain pressure, the adsorption progresses by multilayer or capillary condensation.

Figures 5 and 6 also show that the adsorption capacities of PCHs for VOCs are considerable and exceed that of AC at higher relative pressure. For example, while the relative pressure varies from 0.1 to 0.98, the benzene adsorption capacities of PCHs based on CTMAB-bentonites (with or without PNP) increased from ~0.2 g/g to 0.6 g/g, whereas those of PCHs based on CPC-bentonites (with or without PNP) increased from ~0.15 to 0.4 g/g. The adsorption isotherms of the PCHs for CCl₄ and benzene are similar, although the CCl₄ adsorption capacities are much larger and the differences between precursor surfactants are less.

The relative partial pressures where capillary condensation occurred are centered between 0.025 and 0.2 for all four PCHs and at ~0.01 for AC. As the porosities of PCHs are larger than that of AC, the VOCs adsorption capacities of PCHs are less than that of AC at lower VOC relative pressure but significantly greater than those of AC at higher relative pressure. However, the benzene adsorption capacity of PNP-CTMAB-PCH is equal to that of AC at lower relative pressure. The type II isotherm of the PCHs indicates that VOC concentration in the carrier gas must be high to fill their accessible pores. In most industrial situations, VOCs are normally present at high relative pressures. However, tailoring pore sizes by choosing different surfactant chain lengths, for example, could conceivably reduce the pore size of PCHs to enhance VOC adsorption at lower concentration (Galarneau *et al.*, 1995).

It is evident that the type of modifying surfactant influences VOC adsorption onto PCHs. PCHs based on the use of CTMAB have larger adsorption capacities over the whole relative pressure range than those based on CPC. Although both surfactants have the same alkyl chain length and can be used in the synthesis of PCHs, quaternary ammonium appears to be more suitable.

Estimation of adsorption with D-A equation

It is necessary and important to predict the breakthrough curves and isotherms under a wide range of temperatures and pressures if the adsorption technologies are to be used to control VOC pollutants in atmospheric emission effluents. Many isotherm equations corresponding to different adsorption theories have been published and reviewed (Gregg and Sing, 1982; Óscik, 1982; Langmuir, 1918). In this study, the Dubinin-Astakhov (D-A) theory (Dubinin and Astakhov, 1971) on the volume of filling micropores was chosen to describe the isotherms and then used to derive the differential heats of adsorption for all adsorbate-adsorbent systems.

The D-A equation can be written in the following form (Dubinin, 1966)

$$W = W_0 \cdot \exp [-(A/E)^n] \quad (1)$$

where $W = a \cdot v$ is the volume of condensed adsorbate (cm³/g); a is the adsorption capacity (mol/g); v is the molar volume of adsorbate at experimental temperature (cm³/mol); W_0 is the limiting adsorption volume (cm³/g); $A = RT \ln (P_0/P)$ is the adsorption potential (kJ/mol), where T , P_0/P and R are temperature, relative partial pressure and the gas constant respectively; E is the characteristic energy of adsorption (kJ/mol), and n is a temperature invariant parameter (Chen and Yang, 1994). The magnitude of E can be related to the characteristic energy E_0 of a standard adsorbate by the similarity coefficient β , *i.e.* $E = \beta E_0$. In this way, and with a set of data for a single adsorbate in a particular adsorbent, adsorption isotherms can be simulated. The most common reference adsorbate is benzene, but substances discussed in the literature with various physical properties were also considered as reference adsorbates. Typical adsorbates such as benzene, CCl₄, water and N₂ can be used as standard reference adsorbates for aromatics, chlorinated hydrocarbons, polar compounds and gaseous non-polar molecules, respectively. The value of β can be determined from the physical constants of the standard and the test adsorbates, mainly from the relation between the molecular parachors or between the molar polarizations (Reucroft *et al.*, 1971).

The isotherm data for benzene, CCl₄, water and N₂ sorbed onto all seven adsorbents were fitted with the D-A equation. Values for the equation parameters W_0 , E , β and n are listed in Table 2. The adequacy of fit was checked by calculating the correlation coefficient, R^2 . The results suggest that the experimental data for all isotherms can be reduced to Dubinin-Polanyi type potential plots, and obey this type of relationship relatively well.

According to Dubinin and Stoeckli (1980), a qualitative relationship exists between parameter E or E_0 and the dimension of the micropores and dependence of E on pore size has been the basis for calculating pore-size distribution from the D-A equation (Dubinin and

Table 2. Parameters of the D-A equations for various adsorbate-adsorbent systems.

	W_0 (cm ³ g ⁻¹)	E_0 (kJ mol ⁻¹)	E (kJ mol ⁻¹)	β	n	Number of data	R^2
Benzene							
Bentonite	0.197	5.8	5.8	1.00	1.62	10	0.9951
CTMAB-bentonite	0.438	2.6	2.6	1.00	0.92	10	0.9954
CTMAB-PCH	0.482	7.0	7.0	1.00	1.53	25	0.9586
PNP-CTMAB-PCH	0.686	4.1	4.1	1.00	0.60	28	0.9022
CPC-PCH	0.383	5.2	5.2	1.00	1.50	16	0.9914
PNP-CPC-PCH	0.460	5.0	5.0	1.00	0.68	15	0.9816
AC	0.341	18.8	18.8	1.00	0.57	11	0.9984
CCl ₄							
Bentonite	0.152	1.8	3.3	0.56	0.62	11	0.9634
CTMAB-bentonite	0.160	0.8	1.4	0.54	0.65	13	0.9967
CTMAB-PCH	0.400	6.4	6.7	0.96	1.64	21	0.9653
PNP-CTMAB-PCH	0.426	8.2	5.8	1.41	1.81	29	0.9847
CPC-PCH	0.436	4.0	4.6	0.88	1.48	15	0.9966
PNP-CPC-PCH	0.386	4.8	4.9	0.98	1.50	15	0.9915
AC	0.351	0.2	2.0	0.10	0.78	14	0.9888
Water							
Bentonite	0.318	1.8	3.2	0.55	1.14	11	0.9856
CTMAB-bentonite	0.120	0.3	0.9	0.33	0.59	10	0.9937
CTMAB-PCH	0.408	0.7	2.2	0.32	2.54	10	0.9441
PNP-CTMAB-PCH	0.413	1.3	2.3	0.56	1.23	12	0.9939
CPC-PCH	0.433	0.6	1.8	0.34	2.03	10	0.9680
PNP-CPC-PCH	0.356	0.7	1.8	0.37	2.81	10	0.9609
AC	0.300	0.2	1.9	0.10	2.33	10	0.9769
N ₂							
Bentonite	0.142	0.002	0.1	0.02	0.25	12	0.9989
CTMAB-bentonite	0.005	0.2	0.6	0.25	0.59	31	0.9890
CTMAB-PCH	0.414	1.5	3.2	0.47	1.01	31	0.9983
PNP-CTMAB-PCH	0.398	3.5	3.8	0.93	0.79	31	0.9970
CPC-PCH	0.506	0.4	1.5	0.29	0.59	31	0.9972
PNP-CPC-PCH	0.488	0.6	1.7	0.34	0.54	31	0.9937
AC	0.543	3.3	7.8	0.42	0.37	212	0.9992

Stoehkli, 1980). Increases in E or the characteristic energy E_0 with adsorption infers smaller micropore sizes. Thus, the values of E shown in Table 2 reflect the pore-size distributions of the pores which are accessible experimentally by other methods. The values of E for each adsorbent should be different because of differences in molecular size and shape of precursor materials. The values of E for N₂ on the adsorbents follow the order: PNP-CTMAB-PCH > AC > CTMAB-PCH > CTMAB-bentonite > bentonite and are consistent with the results for N₂-BET in Table 1.

For the sorption of water, benzene and CCl₄ the values of E for organobentonite are larger than those of the bentonite, suggesting that the bentonite pores that are accessible by these adsorbates are smaller after being modified with surfactant. For the sorption of benzene and CCl₄, the values of E for all PCHs are smaller than the values for AC and larger than the values for CTMAB-bentonite. For non-polar organics, using PNP as a precursor leads to smaller values of E for PCHs with the exception of CCl₄ on CPC-PCH and PNP-CPC-PCH. Here, it leads to larger values of E for the adsorption of polar adsorbate, water and the non-polar gaseous adsorbate, N₂ on the PCHs.

Another important parameter of the D-A equation, which determines the adsorption ability of an adsorbent for a certain adsorbate, is the capacity factor W_0 . This factor is also related to the pore structure of the adsorbent and is the amount adsorbed at the saturation vapor pressure, sometimes referred to as the limiting pore volume. Thus, larger W_0 values represent higher adsorption capacity at higher adsorbate relative pressure. As shown in Table 2, all PCHs generally have larger values of W_0 than do organobentonite, bentonite and AC for all adsorbate except for N₂, suggesting that the PCHs have greater capacity for the adsorption of VOCs at higher concentrations. The values of W_0 in Table 2 show that the influence of PNP on the magnitude of W_0 seems to depend on the adsorbent.

According to the D-A equation, the values of β are indicative of affinities between an adsorbent and a certain adsorbate. The values of β in Table 2 are calculated by regarding benzene as the reference adsorbate. Comparison of β values for CCl₄ and water shows that the affinities of PCHs toward CCl₄ are larger than those for bentonite and organobentonite, and are about the same as those of AC, while the affinity of AC for water is less than any other studied adsorbent.

The exponent n in the D-A equation is related to the degree of filling at the saturated vapor pressure, P_0 . It is impossible for different adsorbates to have the same degree of pore filling on the same adsorbents. n is usually considered to be a structural parameter (Chen and Yang, 1994) and depends on the specific adsorbate-adsorbent system. According to the classification of Dubinin (1966), when $n = 2$ the D-A equation suggests that the adsorbents were of the "first structural type", *i.e.* adsorbent with micropores or super-micropores. If $n = 1$ the equation suggests an adsorbent with coarse pores where the pore dimensions are much larger than the adsorbate molecule. Based on the results in Table 2, the average values of n for benzene, CCl_4 and water on bentonite, CTMAB-bentonite, CTMAB-PCH, PNP-CTMAB-PCH, CPC-PCH, PNP-CPC-PCH and AC are 1.1267, 0.7200, 1.9033, 1.2133, 1.6700, 1.6633 and 1.2267, respectively. The <1 value for the CTMAB-bentonite indicates that this adsorbent has a surface that is nearly non-porous. The n values between 1 and 2 for bentonite, AC and all PCHs suggest that these adsorbents have mesoporous characteristics, the pore size of adsorbents are larger than the adsorbate molecule but most of the adsorbent pore sizes are not micropores and super-micropores. In addition, it should be noted that the existence of PNP in the organobentonite would lead to a reduction of the n values for these adsorbents.

Based on the potential theory, a characteristic curve, which is independent of temperature, can be obtained from the adsorption data of one isotherm curve of the tested adsorbent. The characteristic curves obtained from the adsorption data for benzene, CCl_4 , water and N_2 on the adsorbents studied are given in Figure 7. The results in Table 2 show that the adsorption characteristics of all of the studied adsorbents for the four studied adsorbates follow the D-A equation. Adsorption isotherm equations for various adsorbates-adsorbent systems at any temperature can be obtained based on the characteristic curves equation. The adsorption isotherms can be obtained by substituting the expression for

$$W = a \cdot v \quad (2)$$

where a is the adsorption capacity in mol/g and v is the volume of condensed vapor in m^3/g , and the expression for Polanyi adsorption potential

$$A = RT \ln (P_0/P) \quad (3)$$

in the equation of characteristic curve (equation 1).

Thermodynamics

According to the potential theory of adsorption, the adsorption characteristic curve is independent of temperature. It is, therefore, feasible to derive thermodynamic relations, such as heat of adsorption, from a single

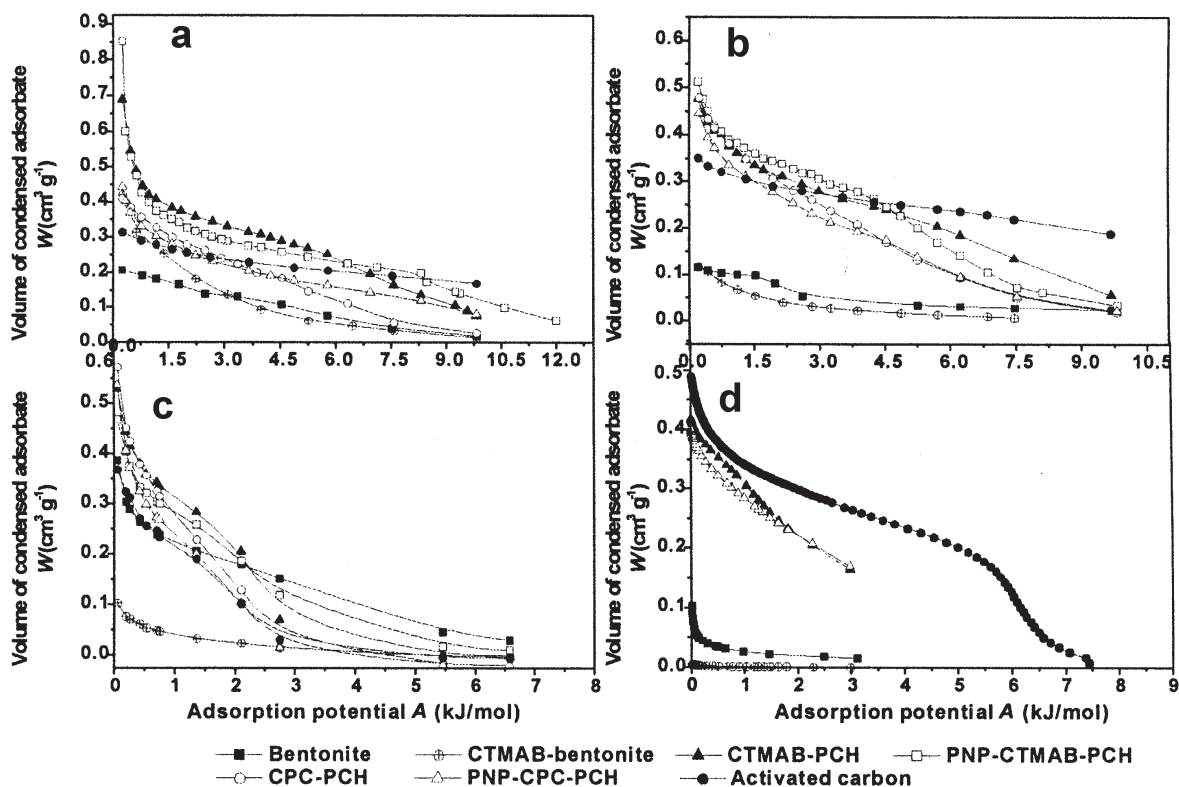


Figure 7. Characteristic curves for adsorption of (a) benzene, (b) CCl_4 , (c) water, and (d) N_2 on various adsorbents.

adsorption isotherm on the basis of the D-A equation (Bering and Serpinskiĭ, 1957). The net heat of adsorption is

$$q = Q - \lambda = \alpha RT^2 (\partial \ln h / \partial \ln a)_T - A \quad (4)$$

where Q is the total differential heat of adsorption in kJ/mol; λ is the heat of adsorption condensation in kJ/mol; α is the temperature coefficient of the volume of expansion of the adsorbate, h is the relative pressure and A , i.e. $-RT \ln h$, is the Polanyi's adsorption potential; $(\partial \ln h / \partial \ln a)_T$, which can be determined by use of the D-A equation expressed by equation 1. By substituting equation 1 into equation 4, the following equation for differential heat of adsorption can be obtained.

$$Q = q + \lambda = \alpha \cdot E_0 \cdot T [\ln (W_0/a \cdot v)]^{(1-n)/n} + RT \ln (P/P_0) + \lambda \quad (5)$$

The differential heat of adsorption of benzene, CCl₄, water and N₂ on various adsorbents at different adsorbate loadings was evaluated from the isotherm

data using equation 5. Figure 8 shows the dependence of the differential heat of adsorption (Q) of benzene, CCl₄, water and N₂ on the adsorbate loading. The average values of q and Q for various adsorbate-adsorbent systems are presented in Table 3 together with the data of λ for each adsorbate. As shown in Table 3, the net heat of adsorption (q) of each adsorbate on the various adsorbents is much smaller than the heat of adsorption condensation of a particular adsorbate (λ). The magnitude of the differential heat of adsorption of benzene, CCl₄, water and N₂ on all adsorbents is in the following order: water (43.82–45.73) > benzene (39.36–42.36) > CCl₄ (35.24–39.81) > N₂ (6.27–7.07), consistent with the heat of condensation: water (42.70) > benzene (34.48) > CCl₄ (31.49) > N₂ (5.70).

The magnitude of Q for bentonite is larger than that of organobentonite (CTMAB-bentonite) for the adsorption of all VOC adsorbates except N₂. Similar findings were obtained in previous studies (Zhu and Su, 2002)

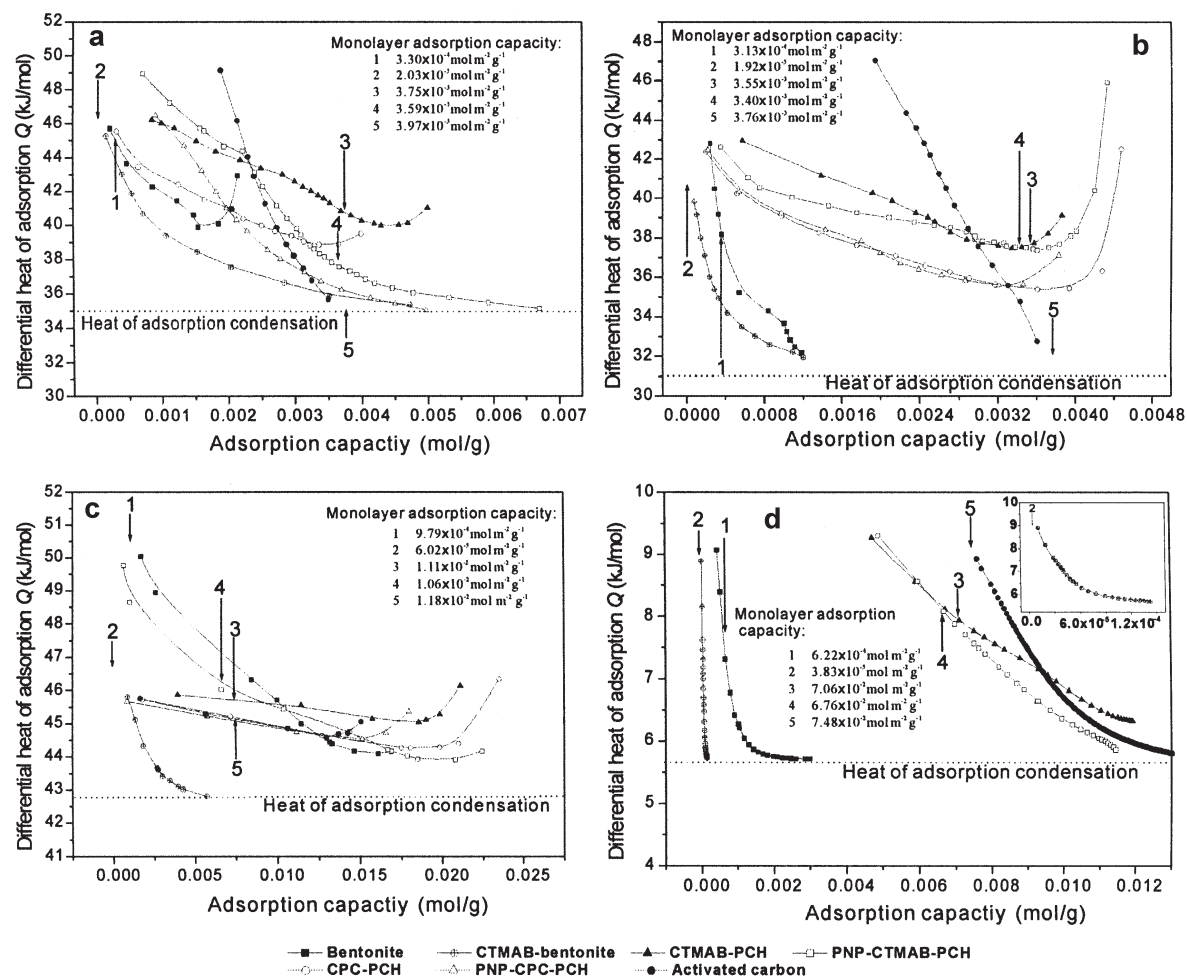


Figure 8. Differential heat of adsorption of (a) benzene, (b) CCl₄, (c) water, and (d) N₂ on various adsorbents as a function of the adsorption amount. The numbered arrows 1, 2, 3, 4 and 5 represent bentonite, CTMAB-bentonite, CTMAB-PCH, PNP-CTMAB-PCH and AC, respectively. The horizontal coordinate values of the points, which are targeted by the arrows, represent the monolayer adsorption capacities of five studied adsorbents to the various adsorbates.

Table 3. Thermodynamic data for adsorption of several representative adsorbates on various adsorbents.

	Heat of adsorption condensation, λ (kJ mol ⁻¹)	Net heat of adsorption q (kJ K ⁻¹ mol ⁻¹)	Total differential heat of adsorption Q (kJ mol ⁻¹)
Benzene	-34.4832 (25°C)		
Bentonite		-7.4755	-41.9587
CTMAB-bentonite		-4.9370	-39.4202
CTMAB-PCH		-7.8774	-42.3606
PNP-CTMAB-PCH		-5.4824	-39.9656
CPC-PCH		-6.2631	-40.7463
PNP-CPC-PCH		-4.8847	-39.3679
AC		-6.4732	-40.9564
CCl ₄	-31.4947 (25°C)		
Bentonite		-4.3953	-35.8900
CTMAB-bentonite		-3.7436	-35.2383
CTMAB-PCH		-7.4352	-38.9300
PNP-CTMAB-PCH		-7.4781	-38.9728
CPC-PCH		-6.2830	-37.7777
PNP-CPC-PCH		-6.1187	-37.6135
AC		-8.3151	-39.8099
Water	-42.6989 (25°C)		
Bentonite		-3.0347	-45.7335
CTMAB-bentonite		-1.1218	-43.8206
CTMAB-PCH		-2.6832	-45.3821
PNP-CTMAB-PCH		-2.6772	-45.3761
CPC-PCH		-2.2074	-44.9063
PNP-CPC-PCH		-2.2812	-44.9801
AC		-2.3027	-45.0016
N ₂	-5.7040 (-196°C)		
Bentonite		-0.5654	-6.2693
CTMAB-bentonite		-0.8590	-6.5630
CTMAB-PCH		-1.3650	-7.0689
PNP-CTMAB-PCH		-1.1862	-6.8902
CPC-PCH		-0.7036	-6.4076
PNP-CPC-PCH		-0.7134	-6.4174
AC		-0.7099	-6.4139

which showed that the magnitude of Q for benzene adsorption on organobentonites increased as the amount of exchanged organic cations on the bentonite increased. These studies also showed that Q for benzene adsorption on organobentonites was larger than that of bentonite. For all adsorbate-adsorbent systems the absolute values of Q for adsorption on PCHs, based on virgin or spent CTMAB-bentonite, are larger than those of the PCHs based on virgin or spent CPC-bentonite.

The presence of PNP has little influence on Q for benzene-PCH adsorption systems. The data presented in Figure 8 indicate that the heat of adsorption, Q , for all adsorbate-adsorbent systems initially decreases as adsorbate loading increases. The values of Q for some systems (benzene adsorption onto AC, CTMAB-bentonite, PNP-CPC-PCH, PNP-CTMAB-PCH; CCl₄ adsorption onto bentonite, CTMAB-bentonite, PNP-CPC-PCH and water adsorption onto CTMAB-bentonite) continue to decrease with increased adsorbate loading until they reach the value corresponding to the heat of condensation, λ . The values of the other systems all increase after a certain adsorption capacity is reached.

In Figure 8, the horizontal coordinate values of the points, which are targeted by the arrows, represent the monolayer adsorption capacities of five studied adsorbents to the various adsorbates. The numbered arrows, 1, 2, 3, 4 and 5 represent bentonite, CTMAB-bentonite, CTMAB-PCH, PNP-CTMAB-PCH and AC, respectively. It can be observed that all the turning points of the curves are consistent with the capacity at which monolayer coverage occurs, suggesting that initial decreases in Q for all curves may be due to surface heterogeneity. The continuous decrease in Q with further adsorption capacity is expected if the dominant interactions between the adsorbed molecules and the adsorbates are repulsive after formation of the first monolayer.

Increases in Q observed for several systems might arise from the capillary filling of macropores, as indicated by their type II isotherms. According to the adsorbate classification of Kiselev (Ošcik, 1982), benzene and water, classified in groups B and D, respectively, can interact with the adsorbent surface by both non-specific and specific interactions. In contrast, CCl₄ only interacts non-specifically with the adsorbent

surface. The trends observed for Q for adsorption of benzene, water and CCl_4 on the four PCHs reveal steep increases at higher adsorbate loadings for CCl_4 , moderate increases for water and benzene, and continuous decreases for benzene on PNP-CTMAB-PCH and PNP-CPC-PCH. These results indicate that the net heat of adsorption at higher adsorbate loadings is associated not only with pore structures but also with the type of interaction between adsorbate and adsorbent. Furthermore, the dominance of non-specific interactions may be important in capillary condensation.

In the case of AC, Q decreases gradually throughout the whole range of loadings for most adsorbates, eventually approaching the value corresponding to λ . The only exception is that of Q for water on AC which increases slightly at higher adsorbate loadings. This could be due to the considerable micropore volume of AC which is large enough to allow filling by adsorbate at the same adsorbate concentrations.

Water-vapor adsorption

VOC streams generally have a relative humidity of ~50%. As a result, water can compete for adsorption sites on an adsorbent and lead to reduction in VOC adsorption capacity. Thus, it is important to study the water adsorption capacity of adsorbents.

Figure 9 shows the water-vapor isotherms for the adsorbents that were studied. As expected, CTMAB-bentonite is very hydrophobic and has very little water loading. The adsorption isotherm for CTMAB-bentonite is nearly of type IV, without any indication of pore filling or capillary condensation. This indicates that there is only a weak interaction between water and the adsorbent surface. In this case, only external pores and surfaces appear to be active in adsorbing water. In contrast, the water isotherms for all other adsorbents are all of type II. At lower relative pressures (<0.4) the

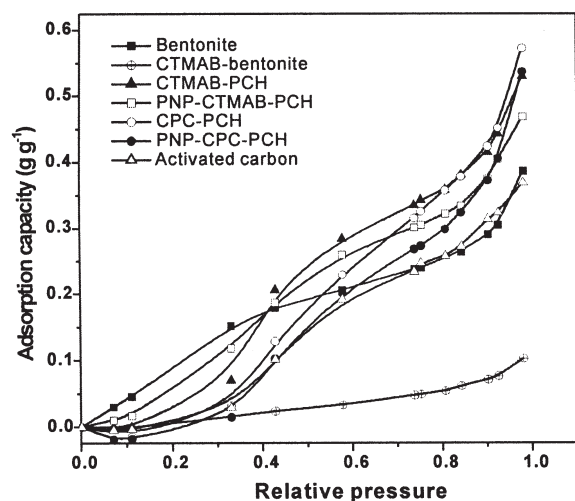


Figure 9. Water adsorption isotherms of various adsorbents at 25°C.

amount of water adsorbed on untreated bentonite is greater than that for any of the other adsorbents. Above relative pressures in the range of 0.4 to 0.75, this relationship changes so that the amount of adsorbed water becomes less than that for all of the PCHs and AC. The water adsorption amounts of all the PCHs are slightly higher than that of AC through nearly the whole range of relative pressure.

The water adsorption behavior of a solid is associated both with its pore-structure charge and its pore structure. Hydrophilic surfaces are usually highly charged leading to strong adsorption of polar molecules, such as water, at low vapor pressure. However, the water adsorption amount at higher relative pressures is mainly related to pore-structure parameters such as porosity. As a result, the higher water adsorption capability of PCHs at higher relative pressures, when compared to bentonite, should be ascribed to the porosity of the PCHs rather than any increase in hydrophilicity. According to the water-sorption capacities at lower relative pressure, the surface hydrophilicity of all adsorbents can be put in the following order: CTMAB-bentonite > AC > PCHs > bentonite. The similarity between the water-adsorption amounts and the water volumes per unit surface areas of various PCHs suggest that the hydrophilicity differences of various PCHs are negligible and that these differences are mainly the result of differences in pore structure.

CONCLUSIONS

This study demonstrates the possibility of using spent organobentonites as starting materials to prepare PCHs for VOC control. The BET surface areas and total pore volumes of PCHs based on spent and virgin organobentonites are much larger than those of the base bentonite and CTMAB-bentonite. Sorption of benzene and CCl_4 show that VOC adsorption abilities of PCHs are stronger than those of virgin bentonite and organobentonites. Even compared to a common VOC adsorbent, AC, PCHs have slightly higher adsorption capacities at higher relative pressures although comparatively lower benzene and CCl_4 sorption capacities at lower relative pressures. Further, the existence of PNP in organobentonites enhances the VOC adsorption capacity of PCHs at lower adsorbate concentrations although some adsorption capacity is lost at higher adsorbate concentrations. The hydrophobicities of PCHs were proved by water sorption to be superior to bentonite but slightly inferior to their parent organobentonites and AC. PCHs are the VOC adsorbents that can be regenerated by common thermal regeneration methods because of their thermal stability to 750°C.

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