The structural and sorptive characteristics of high-surface-area carbonaceous material (HSACM) in soils

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Abstract

The structural and sorptive characteristics of the high-surface-area carbonaceous material (HSACM) isolated from soils were investigated. The HSACM contents in soils were first identified by the organic petrology method. A novel isolation method using acid demineralization, base extraction, and ZnBr$_2$ floatation sequential steps was developed to extract the HSACM from soil. The differences in structural and sorptive characteristics with the HSACM and the intact soil were investigated using nitrogen adsorption isotherms and trichloroethylene (TCE) sorption isotherms at low concentrations (0 to about 2 mg/L) both with and without tetrachloroethylene (PCE) as the cosolute. It was found that HSACM possesses a much higher specific surface area and pore volume as well as a smaller pore size than the original soil. Moreover, the sorption of TCE to HSACM is noticeably more nonlinear and competitive than to the original soil. A small amount of highly adsorptive HSACM is largely responsible for the nonlinear soil sorption of a single solute at very low concentrations.
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1. Introduction

It is well established that soil organic matter (SOM) behaves primarily as a partition medium and that mineral matter acts as an adsorbent for the sorption of nonionic organic compounds (NOCs) [1–5]. The sorption of low-polarity NOCs from water to soils occurs usually by partition into SOM (unless the SOM content is very low) because the adsorption on mineral materials is strongly suppressed by water. In this case, the sorption isotherms of organic solutes are commonly linear over a wide range of solute concentrations. It has been recently reported, however, that the sorption isotherms of nonpolar and polar NOCs in some soils display various extents of nonlinearity at low relative solute concentrations ($C_e/S_w = 10^{-5}$ to 10^{-4}, where C_e is the equilibrium solute concentration and S_w is the solute solubility in water) even when the SOM content is significant [6–11]. These observations indicate that more than one mechanism may be responsible for the sorption of NOCs on SOM at a low relative solute concentrations.

Several hypotheses have been proposed for the nonlinear sorption at low solute concentrations in soils with a significant SOM content. The glassy–rubbery SOM model of Weber et al. [6,7] considers the soil sorption of NOCs to be a composite of a linear partition to the rubbery portion of the SOM and a nonlinear adsorption to the glassy portion of the SOM. The internal-holes model of Pignetallo et al. [8,9] views the solute nonlinear sorption to result from the NOC uptake by various SOM internal holes in conjunction with the linear partition into the SOM matrix. The problem with the glassy–rubbery model and internal-hole model to account for the nonlinear sorption behavior of NOCs on soils has been addressed [10]. Chiou et al. [10,11] suggested instead that the low-relative-concentration nonlinear sorption of nonpolar solutes on soils results from the sorption onto a small amount of high-surface-area carbonaceous materials (HSACM) similar to charcoal, soot, char, or black carbon (BC). The HSACM is a ubiquitous form of carbon comprising a range of materials from elemental to polyaromatic or graphitic carbon, which originates largely from biomass or fuel burning settling and transports eventually into soils and sediments. The sorption of NOCs to HSACM may be higher than to the HSACM-free soil

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because the HSACM possesses a high surface area. Accordingly, although the amount of HSACM in soils may be low, the adsorption of NOCs from dilute solution onto HSACM may become significant to result in a nonlinear soil sorption [11–16].

To test the nonlinear sorption effect with HSACM, it is necessary to isolate HSACM from soils for direct experimental studies. In general, the complete isolation of HSACM from soils/sediments is difficult due to the small amount of HSACM present and the lack of effective isolation techniques. Various attempts have been made to isolate HSACM from soils or to use model HSACM (e.g., soots) to measure the sample's surface and sorption characteristics [17–21]. Methods for quantifying the HSACM in soils are of interest from scientific and engineering considerations. The most common methods may be divided into four groups [22]: (1) the microscopic (organic petrology) identification, (2) the thermal/optical analysis, (3) the chemical pretreatment with subsequent HSACM detection, and (4) the chemothermal pretreatment with a subsequent HSACM detection. Karapanagioti et al. [23–26] adopted the organic petrology to isolate organic matter on a glass slide for visual observation and quantification of HSACM. The disadvantage of thermal/optical method is the uncertainty in its accuracy. Moreover, it is also difficult to apply to soils and sediments that have comparatively larger fractions of inorganic matter. The chemical oxidation employs UV-photo-oxidation, hypochlorite, or acidic chromate to remove the non-BC fraction. However, the intense oxidation processes may drastically alter the surface properties of BC and reduce the adsorptive behavior of the BC [27–32]. The chemothermal treatment procedure also produces unresolved issues such as the modification of HSACM properties during the isolation procedure [21,22]. For instance, Cornesissen [33] treated polluted lake sediments by combustion to evaluate the role of environmental BC in the sorption of phenanthrene. It was found that the BC adsorptive capacities are not comparable before and after the combustion.

Current isolation techniques for HSACM rely often on a sequence of acid demineralization, base extraction, and chemical oxidation to remove salts/minerals, humic acid, and the refractory kerogen. It has been observed that the HSACM isolated from soils via a destructive oxidation means is not appropriate for adsorptive characterization [34]. To overcome this deficiency, we here adopted a nondestructive physical method using a $ZnBr_2$ solution to isolate the HSACM by density fractionation following the above-mentioned acid and base treatments. The activated carbon (AC) was used as a reference carbon to test the suitability of the method. The sorption isotherms of TCE with and without cosolute on original soils and on isolated HSACMs were measured at low TCE relative concentrations to evaluate the variation in soil sorption property. The surfaces and pore structures of isolated HSACMs were characterized using classical and fractal analyses using the nitrogen adsorption isotherms and the sample X-ray diffraction (XRD) patterns. The overall aim for this study is to characterize the HSACM's structural and adsorptive characteristics. The relationship between the surface/pore structure and the sorption characteristics of the HSACM is also discussed.

2. Materials and methods

2.1. HSACM content

The selected soils and reference carbon in this study included Tai-Shan soil (TS), Sha-Mao soil (SM), Florida peat (FP) and activated carbon (AC). TS soil was collected from the Tai-Shan Mountain in Taipei County (Taiwan). SM soil is an organic-rich top soil from the Sha-Mao Mountain in Taipei County, Taiwan. FP is a peat from Everglades, Florida, USA, which is also a reference peat for the International Humic Substances Society. The soil samples were air-dried and then sieved to obtain particles of less than 2.0 mm for all subsequent experiments. AC (Darco-60) was purchased from Aldrich Chemical Company. The soils were sent to University of Oklahoma (USA) to characterize the HSACM contents by the organic petrology method [25]. The organic matter concentrates for microscopic examination were prepared using hydrochloric acid (HCl) and hydrofluoric acid (HF) to remove the carbonates and the silicates, respectively. Mineral residues were separated from organic matter by centrifuging, ultrasonic vibration and flotation by zinc bromide ($ZnBr_2$). The isolated organic matter was mixed with epoxy and was mounted on a glass slide for visual observation. Microscopic investigation was conducted using a Vickers M17 research microscope. Different organic matters were identified using white and fluorescent light in transmitted and reflected light mode. The details of the testing procedures have been described at previously work of Karapanagioti et al. [25].

2.2. HSACM isolation and characterization

The HSACM is resistant to acidic or alkaline solution and has a density greater than water. According to the characteristics of HSACM, the purification procedures of HSACM were designed as follows. Firstly, 50 g soil or AC powder and 200 ml 0.5 M NaOH were added to a 250 ml Teflon bottle. Then, the bottle was sealed and shaken for 24 h. After equilibration, the solid and liquid phases were separated by centrifugation at 3500 rpm for 50 min and the supernatant was decanted. The bottle with the remaining solid was refilled with 200 ml 0.5 M NaOH and shaken for 24 h. This procedure was repeated until the solution turned clear after equilibration. After the alkali treatment, 200 ml of 0.05 M $Na_4P_2O_7$ was added to the remaining solid materials to extract polyvalent cations bound to the organic matter. After shaking for 24 h, the suspension was centrifuged at 2500 rpm for 50 min and the supernatant was decanted. Repeating this step twice, the remaining solid materials were flushed with distilled water four times to remove residual chemicals. A total 100 ml of 12 M HF and 6 M HCl solution (1:1, v/v) was then added to eliminate the mineral portion (such as silicates and carbonates) in the remaining solid material. The remaining solid material was then thoroughly washed with distilled water four times to remove residual acids. The remaining solid material was then placed into $ZnBr_2$ solution (with a density of 1.8 g/cm³) for 2 h to float the remaining mineral residues and fulvic acid and to allow the HSACM to settle down to the bottom, as the HSACM has a density of about 2.0 g/cm³. Finally, the purified HSACM
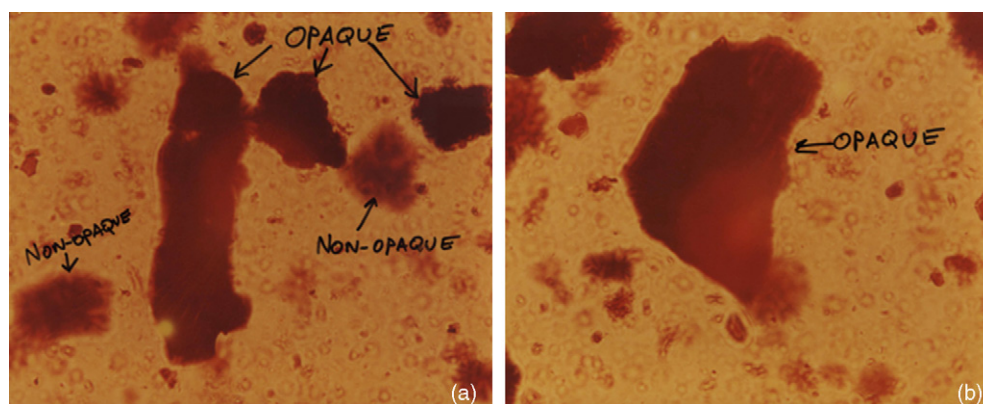
Fig. 1. The images of HSACM isolated from (a) TS and (b) SM.

sample was flushed with water until the rinsed water was neutral. The HSACM samples were then freeze–dried and stored in glass bottles until use.

The XRD patterns of the HSACM and soil samples were measured on a Siemens D-500 instrument with Cu-Kα radiation (30 mA and 40 kV). The nitrogen adsorption isotherm and desorption hysteresis were measured at 77 K with a Micromeritics ASAP-2000. One to two grams of samples were outgassed with helium for 16 h at 105 °C prior to the adsorption measurement. The morphology of the HSACM and soils were examined using a scanning electron microscope (SEM, Hitachi S-800).

2.3. Sorption measurements

Trichloroethylene (TCE) (99+%, Aldrich Chemical Co.) and tetrachloroethylene (PCE) (99+%, Riedel-de Haën Co.) were selected as the solute and the co-solute, respectively, to investigate the sorption characteristics of HSACM and AC. These two compounds were used without further purification.

The sorption capacity and selectivity of TCE with and without PCE on the studied solids were obtained by the immersion (batch) method. For the binary components sorption system, the isotherms were measured under conditions where the initial concentrations of both adsorbates were identical. The vessels were 25 ml Corex glass centrifuge tubes with an aluminum foil layered between the contents and the screw cap. About 0.01–5 g of the sorbent was added, the remaining space was filled up by Millipore water. The stock solution was prepared in acetone. The

amount of acetone in the water solution was assumed to have an insignificant effect on the distribution of the test compounds. The solid to water ratio was adjusted so that the concentration in water shows a 30–70% reduction after equilibration with the solid (soils or AC). The solutes were spiked via their stock solutions in acetone using a Hamilton microliter syringe. The preliminary experiment revealed that about 24 h was required for the sorption process to reach equilibrium with a reciprocating shaker at 25 °C. The solution and solid phase were separated by centrifugation at 8000 rpm for 25 min in a Sorvall RC-5C centrifuge. The water phase was extracted with hexane in a glass tube by agitating for 4 h on a reciprocating shaker. A portion of the hexane phase containing the extracted solute was then analyzed by a GC-ECD with DB-624 capillary column (J and W Scientific, Folsom, CA, 30 m × 0.53 mm i.d.). The measured mass recoveries were 95–100+% for TCE in most experiments. The concentrations were not adjusted for the recovery. All measurements were in duplicate and the averaged data were used. The sorption capacity of the sorbate was calculated using the relation $Q = V\Delta C/m$, where V was the volume of the liquid phase, m was the mass of the solid, and ΔC was computed from the difference between the initial and final GC-ECD readings.

3. Results and discussion

3.1. HSACM contents

Fig. 1 shows the images of the HSACM isolated from TS and SM soils by the organic petrology, and the objects marked

Table 1
Physic-chemical and structural characteristics of the examined solids

Adsorbent		Organic matter (%)	Clay content (%)	CEC (meq/100 g)	HSACM content of organic matter (%)	HSACM content of soil (%)	BET surface area (m²/g)	Total pore volume (cm³/g)	Average pore diameter (nm)	Surface fractal dimension (D)
TS	Original	1.32	10	3.4	19.2	0.25	3.87	0.014	14.2	2.57
	HSACM	–	–	–	–	–	8.66	0.019	7.5	2.68
SM	Original	18.92	8	44	51.0	9.65	5.26	0.018	24.0	2.80
	HSACM	–	–	–	–	–	48.60	0.232	10.8	2.44
FP	Original	82.56	13	147	8.0	6.60	1.14	0.007	40.1	–
	HSACM	–	–	–	–	–	30.16	0.091	10.4	2.52

with the "opaque" symbol are HSACM. In general, there were five types of organic matters existing in terms of the organic petrology: (a) the coaly particulate organic matter (POM) (i.e., coal and charcoal), (b) the young POM showing fluorescence in UV/blue light (i.e., phytoclast), (c) quartz aggregates with clay matrices containing coaly POM, (d) quartz aggregates with clay matrices containing amorphous organic matter (AOM) in clay matrices, and (e) grains with AOM coatings [23]. The HSACM is clearly distinguishable from other fractions by the absence of fluorescence in blue reflected light under microscopy. The opaque particles were counted visually and found to comprise between 8% and 51% of the total grains in SOM fractions, depending on the samples. The contents of both organic matter and HSACM of the examined soils are displayed in Table 1. As shown, the HSACM content is not proportional to the organic matter content in the soil, in which the SM soil possesses the highest HSACM content.

3.2. Surface and pore structure characteristics

The HSACM surface areas of TS, SM and FP illustrated in Table 1 are 8.66, 48.6, and 30.2 m²/g, respectively. The similar results indicate the effective and appropriate isolation method.

Fig. 2 shows the nitrogen adsorption–desorption isotherms measured for the HSACM and the original soils. Some key features may be found directly from this figure. It can be seen that the monolayer capacity (or the BET surface area) of HSACM is larger than that of their corresponding parent soil (Table 1). Another key feature is that all samples show type II adsorption isotherms based on Brunauer's classification [35] in which the adsorption rises sharply at high relative pressures, where the capillary condensation in the large voids of examined samples starts. The isotherms in Fig. 2 also indicate an enormous increase in total pore volume of the HSACM (Table 1). Moreover, for HSACM, the desorption isotherms do not retrace the adsorption isotherm at high relative pressures (P/P_0), but form an obvious hysteresis loop before joining the adsorption isotherm at low P/P_0. The observed hysteresis may be the result of an intrinsic phase transition (single pore mechanism) or pore-connection effects. The structure of the pore network (its connectivity and accessibility), while irrelevant for sorption, is very critical in the desorption processes. According to the percolation theory [36], the more highly connected the network is, the easier is it for the vapor-filled pores to form a spanning cluster, which in turn induces the disappearance of the hysteresis loop. The existence of the hysteresis loop may imply a low pore connectivity. Hence, one possible explanation for the isotherms in Fig. 2 is that the pore size distribution of HSACM is wide and the pores with large sizes may be surrounded by pores of small sizes. The pore size distributions calculated from the capillary condensation model are shown in Fig. 3. As demonstrated in Fig. 3, although the pore size distributions of HSACM are wide, it is still narrower than that of the original soils, implying that the mean pore size of HSACM is smaller than that of the parent soil (see Table 1). The decrease in mean pore size of the HSACM may be ascribed to the existence of micropores in the HSACM. The micropore amounts are estimated by the *t* method [37] for HSACMs iso-
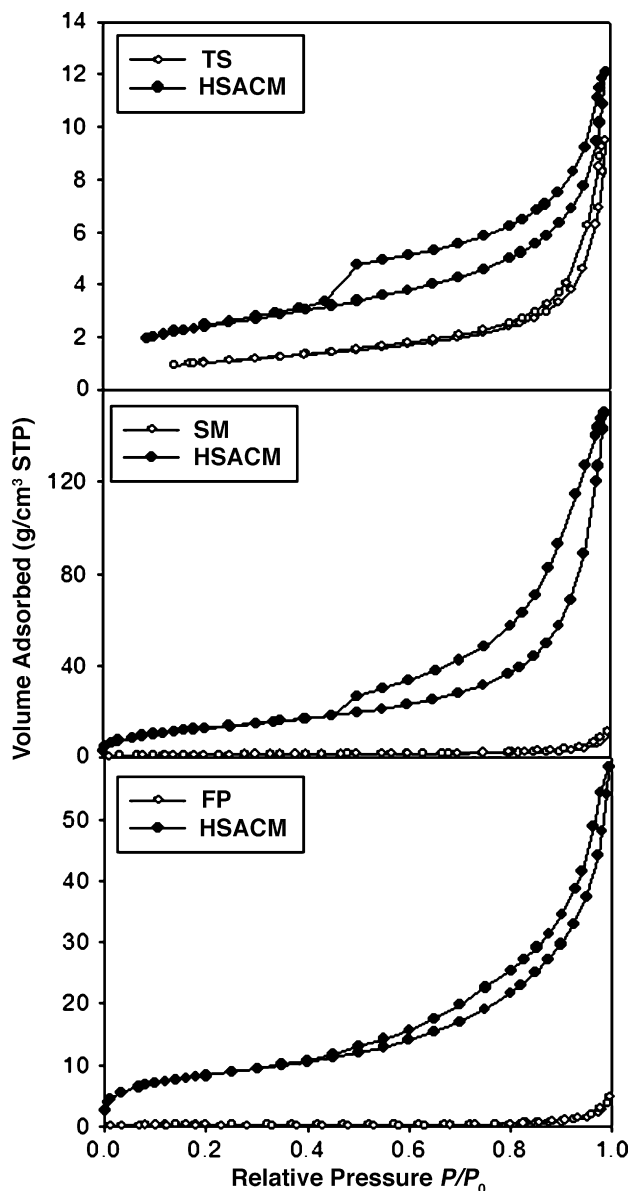

Fig. 2. Nitrogen isotherms of all examined solids.

lated from TS, SM and FP, which gives 0.08, 0.53 and 1.99 m²/g, respectively.

Another way to characterize the surface structure of porous solids is by the fractal analysis. In this study, we estimate and compare the surface fractal dimension D of all examined solids using nitrogen isotherms with a fractal version of the Frenkel–Halsey–Hill (FHH) equations. Usually, the obtained surface fractal dimension is between 2 and 3. A surface with $D = 2$ indicates that it is regular and smooth, whereas a higher D suggests a greater wiggle and space-filling surface. At a D value close to 3, the surface is extremely irregular. Therefore, the D value may be considered as an operative measure of the surface roughness [38]. The classical FHH theory on the multilayer sorption was extended to fractal surfaces using the equation:

$$\frac{N}{N_m} \sim \left[RT \ln \left(\frac{P_0}{P} \right) \right]^{-1/m} \tag{1}$$
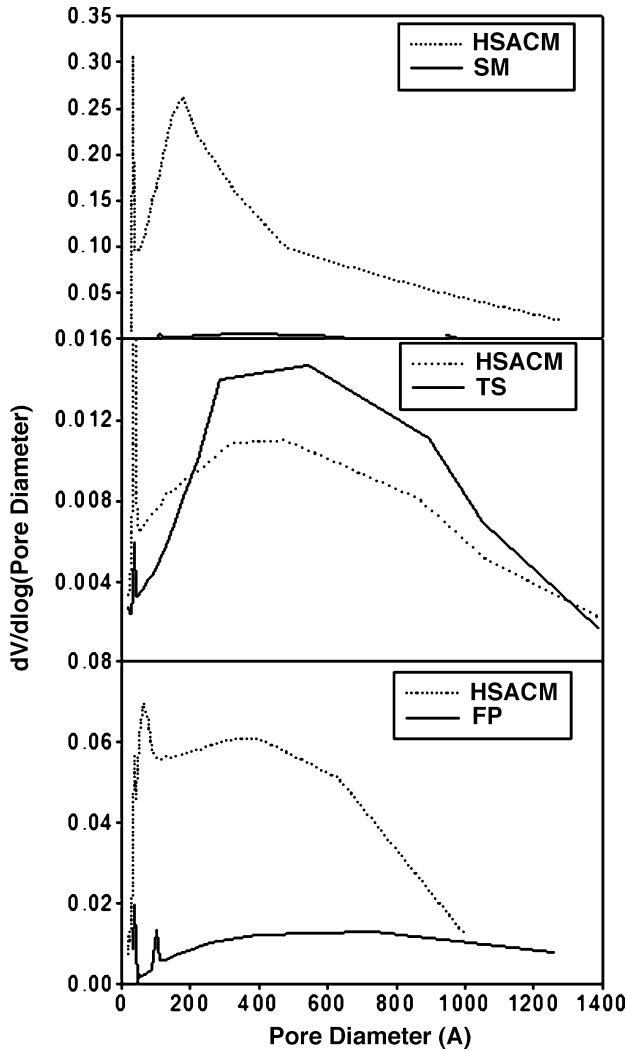
Fig. 3. Pore size distributions of all examined solids.

Fig. 4. Log–log plot of N/N_m vs. ln P_0/P showing the linear range where fractal behavior is observed.

where N/N_m represents the fraction of surface coverage and P and P_0 are the equilibrium and saturation pressures of the adsorbate, respectively. Two types of fractal isotherm equations are thus proposed [39]. If the van der Waals attractions between the solid and adsorbed film is the dominant factor, the D values can be estimated as

$$D = 3\left[1 - \frac{1}{m}\right] \tag{2}$$

On the other hand, if the liquid/gas surface tension (capillary force) is more important, the D value is calculated with

$$D = 3 - \frac{1}{m} \tag{3}$$

The evaluation of D from Eqs. (2) and (3) for nitrogen isotherms for all the examined solids is shown in Fig. 4 and the results are presented in Table 1. Because all desorption isotherms suggest an obvious capillary condensation in the mesopore range, Eq. (3) is used to estimate D. The D value of FP was not determinable due to its very low nitrogen sorption capacity. As shown in Fig. 4, the appearance of straight-lined sections in slope m from the
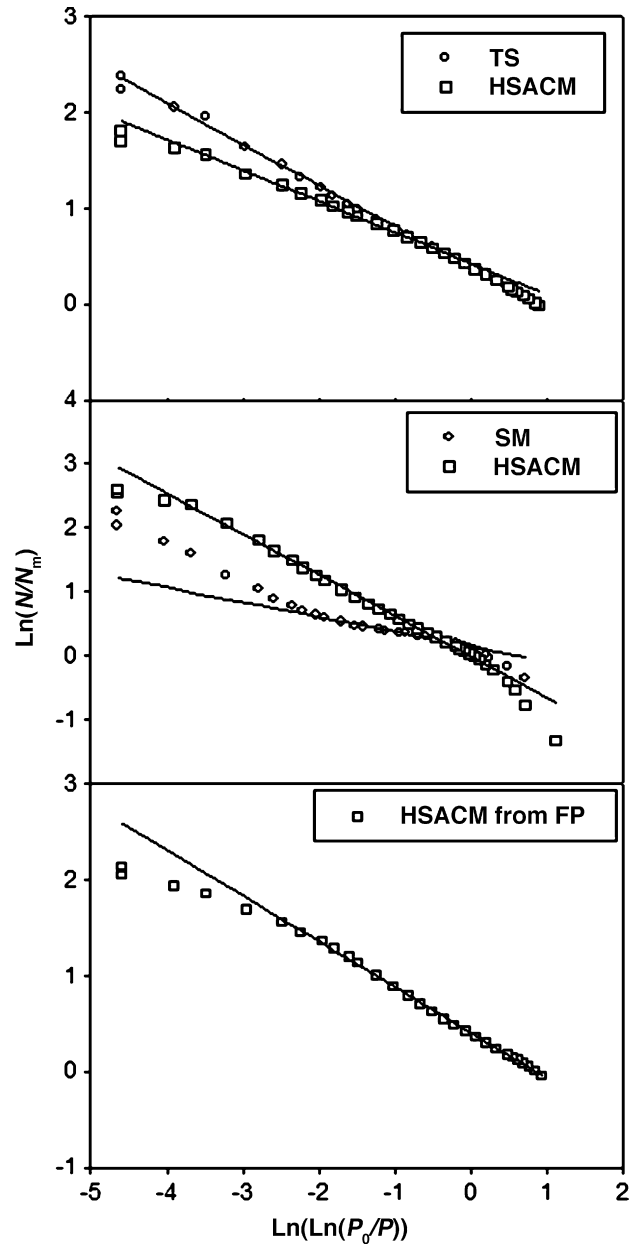
log–log plots suggests the existence of fractal surface structure within the corresponding scale range. The implication of the above fractal analyses is that the surfaces of HSACM and soils (except FP) are indeed irregular, and may be described by the fractal geometry over a limited range of length scale. Although the surface roughness can be well characterized by the D values, the change in BET surface area of the HSACM when HSACM is isolated is difficult to conclude from only the D value (i.e., the surface roughness) because the D values of HSACM may be larger or smaller than that of the parent soil.

The XRD patterns associated with the HSACM isolation are demonstrated in Fig. 5. As expected, a severe modification of the XRD patterns for HSACM is found. When the diffraction patterns are compared, it is clear that the mineral species are nearly absent in the HSACM. This implies that the soil mineral fraction
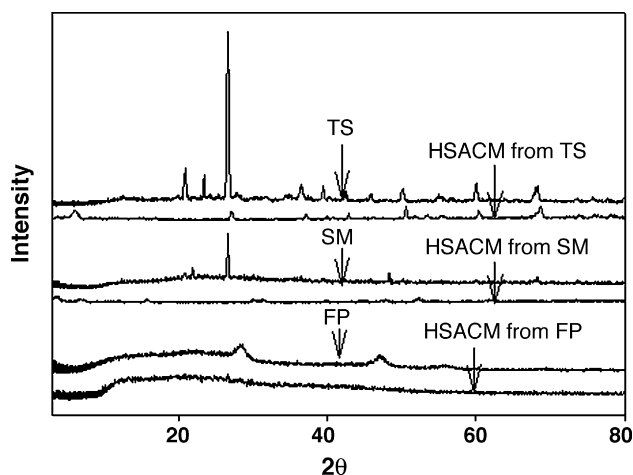
Fig. 5. XRD patterns of all examined solids.

where C_e is the equilibrium solute concentration in water (mg/L), q_e is the corresponding sorbed concentration in the solid (mg/g), and K_F is the capacity-related parameter $((mg/g)/(mg/L)^n)$ and n is the isotherm linearity index.

Activated carbon (AC) was selected as a reference carbonaceous material to assess whether the sorption characteristics have been altered by the isolation procedure. The TCE adsorption capacities with AC before and after the isolation method are 94.92 and 95.17 mg/kg, respectively, at TCE equilibrium concentration of 0.1 mg/L. There was no significant change in AC adsorption capacity with the isolation procedure. This suggests that the same isolation method (using the zinc bromide flotation instead of an oxidation method to isolate HSACM) will not likely alter the adsorption capacity of the isolated HSACM. With the oxidation method, the surface property of HSACM will be significantly altered [34]. A non-destructive method will be used in the future investigation of HSACM.

Fig. 7 shows the measured isotherms of TCE from water solution with and without PCE on all examined soils. Some important features are evident from this figure. Firstly, all isotherms exhibit noticeably nonlinear sorption with a concave-downward shape at low adsorbate concentrations, as characterized by the Freundlich n exponents of 0.7–0.9. Xiao et al. reported that the Freundlich n values of black carbons range from 0.663 to 0.734 [15], consistent with the results in our present work. As expected, the SM soil shows the most obvious nonlinear sorption of the three soils because it possesses the highest HSACM content. This result also indicates that sorption on a small amount of
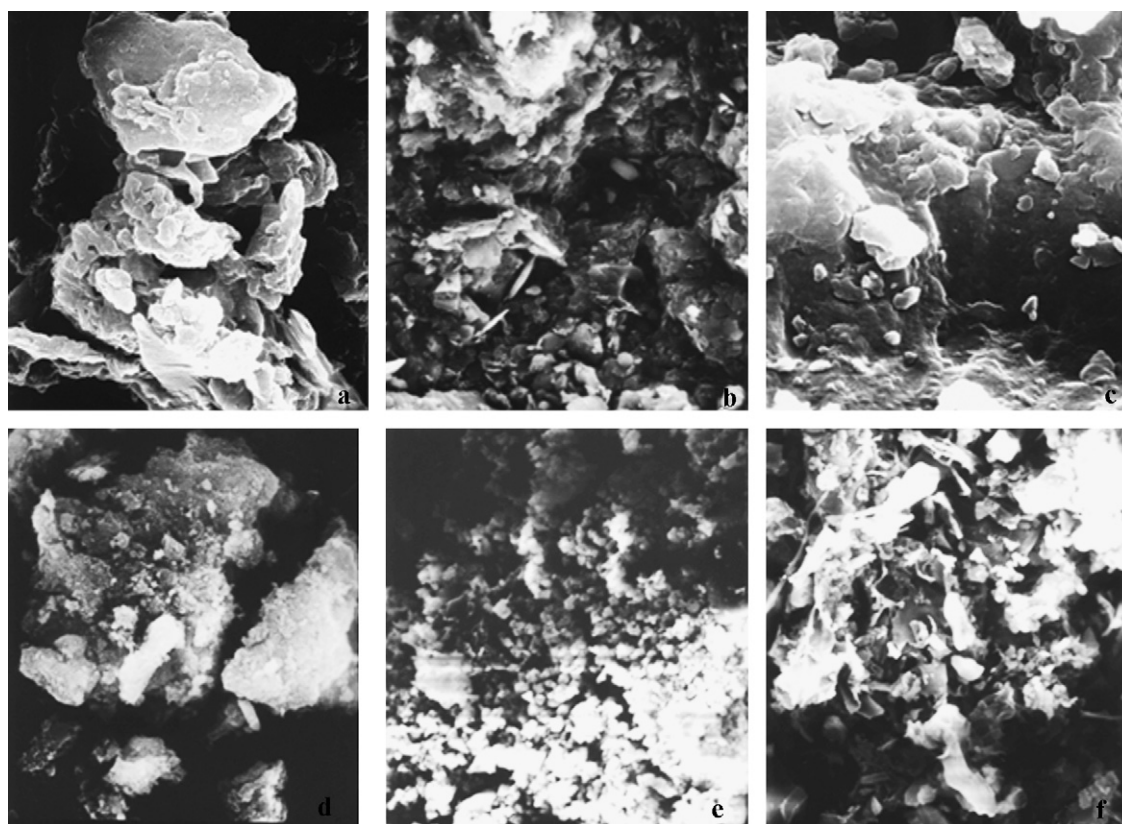
is indeed eliminated by the acid mineralization procedure. The results obtained from the scanning electron microscopy (SEM) also points to the fact that the morphology of HSACMs is clearly different from that of soils, as presented in Fig. 6.

3.3. Sorption characteristics

The Freundlich equation was used for quantifying the equilibrium sorption of solutes by soils, which takes the form:

$$q_e = K_F C_e^n \qquad (4)$$

Fig. 6. SEM images ($\times$4000) of all examined solids: (a) SM; (b) TS; (c) FP; (d) HSACM from SM; (e) HSACM from TS; (f) HSACM from FP.
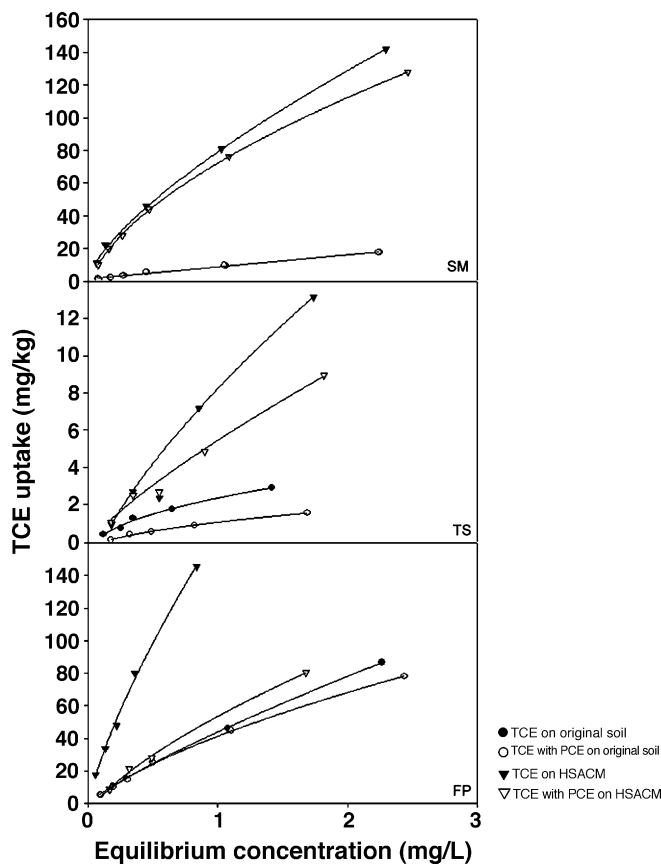
Fig. 7. Sorption isotherms of TCE from water solutions with and without the coexistence of PCE.

strongly adsorptive HSACM is indeed largely responsible for the nonlinear soil sorption of a solute at very low relative concentrations in the absence of (or at very low concentrations of) other coexisting solutes. On the other hand, although the FP contains 6.60% HSACM in the soil, it displays the least nonlinear sorption behavior. This disparity may be ascribed to the fact that FP is high in SOM (83%), where the marked partition with SOM reduces the adsorptive contribution of the HSACM. In contrast, although the HSACM content of TS is very low (0.25%), the nonlinear effect is still distinct due to the low SOM content (1.3%), i.e., the low partition contribution.

The other key feature in Fig. 7 is that the sorption capacity of TCE becomes smaller in the binary components system, giving clear evidence for the existence of competition adsorption behavior. Finally, the adsorption capacity of a HSACM is proportional to its surface area.

4. Conclusions

This study presented a novel non-destructive method for isolation of HSACM and examined the structure and adsorption characteristics of HSACM. As revealed by the classical analysis of the nitrogen adsorption isotherms, the HSACM possesses a larger specific surface area and pore volume as well as a smaller pore size than the corresponding parent soils. Moreover, the fractal analysis indicates that the surfaces of HSACM are indeed irregular, and might be described by fractal geometry in a limited range of the length scale. The sorption isotherms of TCE with soils and isolated HSACMs in single and binary solute systems were then measured to identify the sorption characteristics. It is found that TCE on HSACM exhibited a nonlinear sorption isotherm and a noticeable competitive effect. These results confirmed the hypothesis that at very low relative solute concentrations, the sorption of single solutes on a small amount of strongly adsorptive HSACM was largely responsible for the nonlinear sorption of nonionic organic solutes on soils.

Acknowledgments

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