Journal of Hazardous Materials 244–245 (2013) 268–275

Contents lists available at SciVerse ScienceDirect

Journal of Hazardous Materials

journal homepage: www.elsevier.com/locate/jhazmat

Impact of organic matter properties on sorption domains of phenanthrene on chemically modified geosorbents and synthesized charcoals

Lei Wang[a], Ying Xin[a], Zunlong Zhou[a,b], Xiaoyang Xu[a,c], Hongwen Sun[a,*]

[a] MOE Key Laboratory of Pollution Processes and Environmental Criteria/Tianjin Key Laboratory of Environmental Remediation and Pollution Control, Nankai University, Tianjin 300071, China
[b] Ocean and Fishery Bureau of Zhejiang Province, Hangzhou 310007, China
[c] Institute of Policy and Management, the Chinese Academy of Sciences, Beijing 100190, China

HIGHLIGHTS

- Two geosorbents with 4 modified forms and 3 synthesized charcoals were prepared.
- Nonpolarity and aromaticity enhance phenanthrene sorption at low concentration.
- Isotherms were fitted to Dual-Mode model and corrected by Dual-Langmuir model.
- Reciprocal of polarity index (PI^{-1}) was better than $-PI$ to express the nonpolarity.
- Corrected Langmuir domains significantly related to products of aromaticity and PI^{-1}.

ARTICLE INFO

Article history:
Received 5 July 2012
Received in revised form 5 October 2012
Accepted 18 November 2012
Available online 26 November 2012

Keywords:
Sorption domain
Chemically modified geosorbent
Synthesized charcoal
Dual-Mode model
Dual-Langmuir model

ABSTRACT

To study the impact of organic matter (OM) properties on different sorption domain of hydrophobic organic contaminants, phenanthrene sorption on chemically modified geosorbents and synthesized charcoals (SCs) was investigated and explored using Dual-Mode model (DMM). Sorption of phenanthrene on two geosorbents, peat and lignite, and their modified forms by hydrolysis, oxidation, and oximation, as well as on three SCs with different pyrolytic degrees changed were significantly affected by the aromaticity (A) and polarity index (PI) of OM. Positive correlation between OM normalized parameter of Langmuir sorption capacity of DMM (S_{DM}/f_{OM}) and $A \times PI^{-1}$ was observed. To distinguish the deviation of DMM, S_{DM} was corrected by assigning the Langmuir affinity parameter (b_{DM}) of DMM to the high energy Langmuir affinity parameter (b_H) in Dual-Langmuir model (DLM). More significant correlation was observed between $A \times PI^{-1}$ and corrected S_{DM}, which confirms that the nonpolarity and aromaticity of sorbent OM contribute much to the hydrophobic organic contaminants sorption with high energy. Besides, the partition coefficient of linear domain of DMM normalized by OM (K_P/f_{OM}) was positively related to PI^{-1} rather than negatively related to PI, suggesting that PI^{-1} is more suitable than $-PI$ to evaluate the nonpolarity of sorbent OM.

1. Introduction

Sorption of hydrophobic organic contaminants (HOCs) on soil and sedimentary organic matter (SOM) is an important environmental process because it significantly affects the fate and bioavailability of HOCs in the environment. SOM is a continuum of organic molecules of different structures and properties, which creates its highly heterogeneous nature. The physicochemical properties of SOMs, such as elemental and chemical compositions, distribution of molecular weight, and polarity, vary greatly among different SOMs, depending on many factors, including SOM precursors, age, and depth in the Earth's crust [1–5], which in turn determine the sorption behavior of HOCs on them. As reported in multiple studies, different sorption mechanisms, i.e. partition (dissolution), and adsorption/pore-filling, might occur when a HOC was sorbed to SOM sorbents [6–10]. According to different sorption mechanisms, Xing and Pignatello [7] proposed a Dual-Mode model (DMM) to describe the sorption of HOC on rubbery and glassy domains of SOM, respectively. By DMM, HOC sorption is divided to two items of domains, partition and non-partition:

$$q_e = q_p + q_{np} = K_P \times C_e + \sum_{i=1}^{n} \frac{S_{i,DM}}{(1/b_{i,DM}) + C_e} \times C_e \qquad (1)$$

---

* Corresponding author at: 94 Weijin Road, #325 Mengminwei Building, Tianjin 300071, China. Tel.: +86 22 2350 4821; fax: +86 22 2350 9241.
E-mail address: sunhongwen@nankai.edu.cn (H. Sun).

0304-3894/$ – see front matter © 2012 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.jhazmat.2012.11.041

where q_e and C_e are the sorbed and dissolved concentrations of HOC; q_p and q_{np} are the partition domain and non-partition domain of sorbed HOC; $S_{i,DM}$ and $b_{i,DM}$ are the Langmuir adsorption capacity and affinity parameters for each unique site; and K_P is the partition coefficient for the linear sorption domain. Though it is widely recognized that sorption of HOCs on SOM can be divided into different domains according to Eq. (1), direct evidence of the relationship between OM properties and sorption domains of HOC is still insufficient [11]. Besides, conflicts still exist on the contribution of SOM moieties or properties on HOC sorption [12,13]. For example, positive correlations between HOC sorption and the aromatic carbon content of SOMs have been reported in some studies [14–17]; whereas SOM aliphaticity was also found to post a positive correlation with HOC sorption by others [18–20].

The major objective of this study was to examine the correlation between the OM properties of sorbent and different sorption domains of HOC. To do so, two geosorbents with different humification degree, i.e. peat and lignite, as well as their hydrolyzed/oxidized/oximated forms, were used as model geosorbents. Synthesized charcoals generated from pine sawdust with three different pyrolytic degrees were also selected as model sorbents. Sorption of phenanthrene from aqueous solution to these sorbents was measured, and the isotherms were fitted to DMM and corrected by Dual-Langmuir model (DLM). Correlation between sorption model coefficients and OM property parameters of the sorbents was analyzed.

2. Materials and methods

2.1. Sorbents preparation and characterization

Peat and lignite were provided by Kaili Humic Acid Company (Yunnan, China), which were sampled from Zhaotong, Yunnan province, China. Chemical modifications of the peats and lignites included hydrolysis, oximation and oxidation. The hydrolysis and oximation treatments were performed as described by Simpson et al. with minor change [21]. In brief, hydrolysis was conducted by adding 6 mol/L of HCl to peat or lignite (5 mL per gram of geosorbens) and refluxing for 6 h. In oximation treatment, the mixture of geosorbents and pyridine containing 65.0 g of hydroxylamine hydrochloride (10 mL per gram of geosorbents) was refluxed for 24 h. Oxidation was performed by adding 5 mol/L of H_2O_2 water solution to peat or lignite (15 mL per gram of geosorbents), and the mixture was stirred for 24 h under room temperature. After each treatment, the solid residue was separated from the mixture via centrifugation at 3500 × g for 20 min, and then washed 10 times using deionized water before freeze-dried.

Synthesized charcoals (SCs) were produced by pyrolyzing pine (*Pinus massoniana* Lamb.) sawdust [22]. Air-dried and ground sawdust was put into preheated porcelain crucibles. The crucibles were covered to protect the sawdust from direct contact with air, and heated in a preheated muffle furnace at 300 °C for 0.5 h (SC-1), 400 °C for 0.5 h (SC-2), and 400 °C for 8 h (SC-3), respectively, to obtain three semi-aromatized SCs. All geosorbents and SCs were ground and sieves of 37–75 μm were collected.

The elemental contents of C, H, and N in the geosorbents and SCs were measured by an element analyzer (Elementar Vario EL, Elementar Analysensysteme, Germany). The amount of ashes was determined by mass loss after heating the sorbents at 750 °C for 4 h [14]; while O content was calculated by mass difference. Functionalities of the geosorbents and charcoals were determined by solid-state CP/MAS ^{13}C NMR at 100 MHz carbon frequency using a Varian Infinityplus-400 MHz NMR spectrometer (Varian, USA). Analytical parameters were referred in the literature [22].

2.2. Chemicals

Phenanthrene (purity > 98%) was purchased from Acros Corporation (NJ, USA). Stock solution of phenanthrene was prepared in HPLC-grade methanol. All other chemicals and solvents used were of analytical grade or better.

2.3. Sorption experiments

Sorption isotherms were obtained using a batch equilibration method. Specific amounts of the sorbents (20.0 mg of geosorbents or 2.5 mg of SCs) were weighed into 20 mL background solution in screw-capped glass vials (Agilent, USA). The background solution contained $CaCl_2$ at 0.01 mol/L to mimic the ion strength of soil solution and 200 mg/L of NaN_3 as a biocide to minimize biodegradation. Varying amounts of phenanthrene stock solution were spiked into the suspensions, with the methanol content < 0.1% (v/v) to prevent the co-solvent effect. All vials were sealed immediately using screw caps with Teflon liners. The vials were first hand-shaken for 2 min and then horizontally shaken in a shaker oscillating at 150 rpm and constant temperature of 20 ± 0.5 °C for 20 days. According to the results of our preliminary test, it needs a relatively long time for phenanthrene to reach apparent sorption equilibrium on SCs [22], although the required equilibrium time on geosorbents is much shorter. After equilibrium, the vials were centrifuged at 1500 × g for 20 min, and phenanthrene in the supernatant was analyzed by HPLC. The sorbed mass of phenanthrene was calculated by subtracting the residue mass in aqueous phase from the initial mass, since phenanthrene loss due to sorption onto the reactor walls and volatilization was less than 5%, which was assessed by running the control experiments with reference vials containing no solids.

2.4. Analysis

Aqueous phenanthrene was quantified by an SCL-10AVP HPLC system (Shimadzu, Japan) equipped with a fluorescence detector and a reverse-phase column (VP-ODS Kromasil C-18, 150 mm × 4.6 mm × 5 μm). A 20 μL sample was injected directly into the HPLC system and was eluted in a mobile phase of water/acetonitrile (20:80, v/v). The flow rate was maintained at a constant 1 mL/min. The fluorescence detection excitation/emission wavelengths for phenanthrene were 250/364 nm.

3. Results and discussion

3.1. Characterizations of modified geosorbents and SCs

3.1.1. Elemental composition

The elemental composition (C, N, H, and O) of the geosorbents and SCs are listed in Table 1. As an intermediate product of the conversion of peats to bituminous in diagenesis, lignites are more humified than peats. The C/O ratio of the lignite in the present study was 1.36%, which was higher than that of peat (1.14%); while the ash content of peat (45%) was much higher than that of lignite (3%) (Table 1). The chemical treatments (hydrolysis, oxidation, and oximation) resulted in several different alterations of geosorbents' elemental composition. Compared to the untreated geosorbents, hydrolysis treatment led to a slight increase in C content from 26.8% to 27.5% for peat and from 52.8% to 57.0% for lignite (Table 1), respectively; while the contents of O and H decreased correspondingly. Oxidation resulted in a great reduction in C content for both geosorbents, especially for peat; while their inorganic component content increased significantly. In theory, oximation treatment only altered the element composition by replacing O with N in organic components through a reaction of $RR'C{=}O + NH_2OH \rightarrow RR'C{=}NOH + H_2O$. However, oximation also