Colloids and Surfaces A: Physicochem. Eng. Aspects 428 (2013) 60–64

Contents lists available at SciVerse ScienceDirect

Colloids and Surfaces A: Physicochemical and Engineering Aspects

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

Adsorption of tetrabromobisphenol A on soils: Contribution of soil components and influence of soil properties

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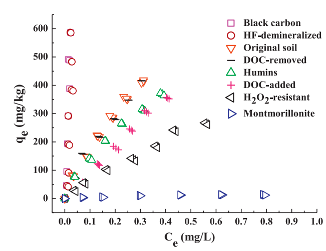
HIGHLIGHTS

- Hydrophobic and electrostatic interactions dominate TBBPA adsorption on soils.
- Organic carbon and pH are the key factors determining TBBPA adsorption on soils.
- Black carbon shows the highest adsorption capacity among all soil organic fractions.
- Minerals exhibit the lowest adsorption capacity among all soil components.

GRAPHICAL ABSTRACT



The adsorption of tetrabromobisphenol A on various soil components

ARTICLE INFO

Article history:
Received 14 November 2012
Received in revised form 7 March 2013
Accepted 22 March 2013
Available online 1 April 2013

Keywords:
Tetrabromobisphenol A
Adsorption
Soils
Soil components

ABSTRACT

The adsorption of tetrabromobisphenol A (TBBPA) on several typical Chinese soils and soil mineral and organic components were comprehensively investigated in the present study. The adsorption isotherms were well described by the Freundlich equation and the corresponding adsorption capacity constant K_f ranged from 2.46 to 357.30 L/kg and 16.52 to 136,731.98 L/kg for the original soils and the soil components, respectively. Correlation analysis between the adsorption capacity and soil properties indicates that soil pH and soil organic carbon (SOC) content were the predominant factors determining TBBPA adsorption on the soils. At constant pH of 7.0, the soils with higher SOC content exhibited stronger adsorption affinity for TBBPA, suggesting the significant importance of SOC in the adsorption. The adsorption affinity of TBBPA became weaken for a given soil with increasing pH due to the enhanced electrostatic repulsion between the anionic TBBPA species and soil surface. Humins and black carbon of SOC played a predominant role in while soil minerals contributed slightly to the adsorption of TBBPA on the soils. The results of this study will provide a better understanding of the behaviors of TBBPA in soils.

1. Introduction

Brominated flame retardants (BFRs) have been used in a variety of commercial and industrial application for the purpose of fire prevention [1,2], and have attracted great concern as a kind of typical persistent organic pollutants [3–6]. Among the BFRs, tetrabromobisphenol A (TBBPA) possesses the largest production volume, covering around 60% of the total BFR market [7]. Moreover, the use of TBBPA is currently not restricted in many countries such as USA and China etc. [8]. Because of its large production and extensive application, TBBPA has been detected in various environmental matrices including soil, water, air, dust, sewage sludge and sediment [7,8]. Furthermore, it has been demonstrated that TBBPA at environmentally relevant concentrations can cause a variety of adverse health effects such as endocrine disruption, hepatoxicity and neurotoxicity on humans [7,9]. These raise the urgent need to understand the behavior of TBBPA in the environment.

Adsorption is a key process determining transport, bioavailability and degradation of organic contaminants in soils. Soil is a complicated matrix including organic and inorganic components

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http://dx.doi.org/10.1016/j.colsurfa.2013.03.040

Table 1
Soil characteristics.

Site	Taxonomy	pH	CEC (cmol/kg)	SOC (%)	Zeta potential[a] (mV)	Surface area (m^2/g)	Clay (%)
Heilongjiang	Mollisols	7.02	38.59	5.63	−11.80	22.71	16.59
Shenyang	Alfisols	6.67	23.65	2.10	−13.0	8.34	23.05
Liaoning	Alfisols	7.30	51.63	0.68	−12.30	33.26	39.09
Beijing1	Alfisols	7.35	76.10	2.10	−8.60	11.08	18.44
Beijing2	Alfisols	7.67	74.29	1.06	−10.40	12.79	27.36
Shandong	Alfisols	7.62	123.04	0.78	−12.60	13.23	19.67
Jiangxi	Ultisols	4.12	7.27	0.70	−5.79	42.33	43.39
Guangxi	Ultisols	4.08	10.35	0.69	−2.40	24.26	44.03

[a] Zeta potential values of soils were obtained under the original pH condition.

which intimately associate with each other [10–12]. Meanwhile, soil organic carbon (SOC), a complex and heterogeneous mixture of materials, can be operationally fractionated into humic acid, fulvic acid, humins and black carbon, which exhibit different physical structures and chemical compositions [13–17]. Therefore, it is assumed that various components would play different roles in the adsorption of organic contaminants on soils. However, most studies on the contributions of different soil components to the adsorption of organic contaminants on soils mainly focused on the hydrophobic organic compounds such as polycyclic aromatic hydrocarbons [14–16], and related information on the ionic organic pollutants such as TBBPA is scarce.

As a typical ionic compound, TBBPA shows a low solubility in water (0.72 mg/L) and a relatively high hydrophobicity with $\log K_{OW}$ of 4.5–5.0 [18]. Therefore, it is expected that there will be a significant hydrophobic interaction between TBBPA and soils. Furthermore, TBBPA exists in three different species, i.e., molecular form (TBBPA) in acidic conditions and two dissociated forms ($TBBPA^-$ and $TBBPA^{2-}$) in alkaline conditions. Different TBBPA species are expected to show different adsorption behavior under different soil conditions, and it is particularly assumed that pH may have a significant influence on the adsorption of TBBPA on soils. Although the adsorption of TBBPA on soils has been evaluated by Sun et al. [19] as the only published investigation to date, the influence of soil properties on its adsorption remains unclear since only two soils were included as the adsorbents in the study.

The objective of this study was therefore to comprehensively investigate the adsorption behavior of TBBPA on different soils. Eight Chinese soils with contrasting physicochemical characteristics and various soil components including fractionated SOC of a selected soil were used as the adsorbents to examine the effects of soil physicochemical properties and soil components on the adsorption of TBBPA on soils. The main factors controlling TBBPA adsorption and the importance of various soil components on the adsorption were discussed. The results of this study are expected to help better understand the fate of TBBPA in the environment.

2. Materials and methods

2.1. Chemicals, soil samples, soil characterization and fractionation

TBBPA (>97% purity) was purchased from Sigma-Aldrich Corporation, and dissolved in HPLC-grade methanol. Eight soils used were collected from the 5–25 cm depth zone of agricultural fields in six provinces in China. After air-drying, the soils were ground and passed through a 1-mm sieve. SOC was analyzed by the method of oxidation by a saturated solution of potassium dichromate with oil bath heating. Soil texture was determined by a laser particle analyzer (Malvern Mastersizer 2000). Soil pH was measured in 0.01 M $CaCl_2$ at a soil solution ratio of 1:5 (w:v). Dissolved organic carbon (DOC) was determined by a TOC analyzer (Phoenix 8000, Tekmar-Dohrmann Co., USA). Cation exchange capacity (CEC) was determined by the $BaCl_2$–H_2SO_4 method. Zeta potential was analyzed by a Zetasizer Nano instrument (Malvern 2003). Surface area and average pore size of soil components were measured by a Quadrasorb SI-MP surface area analyzer (Quantachrome Corporation, USA). The BET equation was used to calculate the surface area, and porosity was determined from the total pore volume with the relative pressure $p/p_0 = 0.99$. Information on soil characteristics is provided in Table 1. No significant statistical difference in the soil pore size among the soils was observed and therefore the data were not provided and also neglected in the further analysis.

The Heilongjiang soil was chosen to obtain various soil components using the procedures listed in Table 2. All components obtained were rinsed with de-ionized water and freeze-dried before use.

2.2. Adsorption experiments

Batch adsorption experiments were performed in this study. Each soil sample (0.2 g) or soil fraction (0.05 g) was placed into a 40-mL glass tube. 30 mL of background solution (200 mg/L NaN_3 in 0.01 M $CaCl_2$) was then added. The concentration of TBBPA used was in the range of 0.08–1.00 mg/L and the methanol concentration in the final solutions was always kept below 0.2% (v/v) to minimize cosolvent effects. The tubes were sealed with PTFE-lined caps and shaken in the dark at 110 rpm at 20 ± 2 °C for 24 h. The choice of 24 h for equilibration was based on the preliminary test. After centrifugation at 3000 rpm for 20 min, TBBPA in the supernatant solution was measured. The adsorption experiments and zero sorbent blank assays were performed in duplicate. The loss of TBBPA other than through adsorption by the sorbents was negligible. Adsorption of TBBPA was therefore calculated by mass balance. The original soils without pH adjustment were used to investigate the adsorption characteristics of TBBPA on the soils. To evaluate the contributions of different soil components to TBBPA adsorption, equilibrium pH was adjusted to 7.0 by using diluted HCl or NaOH in order to avoid the influence of TBBPA species on the adsorption.

Measurement of TBBPA was conducted by HPLC (Agilent 1200 series) equipped with a UV detector and the absorb wavelength was set as 210 nm. An Agilent eclipse XDB-C_{18} column (4.6 × 150 mm, 5 μm particle size) was used and the injection volume was 30 μL. The mobile phase was methanol:ultra pure water (85:15, v/v) containing 0.2% acetic acid with the flow rate of 1 mL/min. The retention time of TBBPA was 4.6 min.

2.3. Data analysis

Adsorption of TBBPA was described by the Freundlich equation $q_e = K_f \times C_e{}^n$, where q_e (mg/kg) and C_e (mg/L) are the respective equilibrium concentrations in the solid and aqueous phases, K_f ($mg^{1-n}\,L^n$/kg) is the Freundlich affinity coefficient, and n is the Freundlich linearity index. Correlation between soil physicochemical properties and adsorption capacity parameters was obtained