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The pH-dependent adsorption of tributyltin to charcoals and soot

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Tributyltin adsorption to black carbon increases at increasing pH but charcoal exhibits electrostatic and hydrophobic adsorption, whereas soot only adsorbs hydrophobically.

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ABSTRACT

Widespread use of tributyltin (TBT) poses a serious environmental problem. Adsorption by black carbon (BC) may strongly affect its behavior. The adsorption of TBT to well characterized soot and two charcoals with specific surface area in the range of 62–111 $m^2 g^{-1}$ have been investigated with main focus on pH effects. The charcoals but not soot possess acidic functional groups. TBT adsorption reaches maximum at pH 6–7 for charcoals, and at $pH > 6$ for soot. Soot has between 1.5 and 15 times higher adsorption density (0.09–1.77 $\mu mol\ m^{-2}$) than charcoals, but charcoals show up to 17 times higher sorption affinities than soot. TBT adsorption is successfully described by a new pH-dependent dual Langmuir model considering electrostatic and hydrophobic adsorption, and pH effects on TBT speciation and BC surface charge. It is inferred that strong sorption of the TBTOH species to BC may affect TBT toxicity.

1. Introduction

Tributyltin (TBT) is a unique organotin biocide that has been widely used for different purposes starting in the 1950s, e.g. as antifouling paints on ships, wood preservative and agriculture fungicides (e.g., Huggett et al., 1992; Hoch, 2001). However, TBT has been found to exhibit acute and chronic toxicity towards aquatic organisms and humans (Blaber, 1970; Boyer, 1988; Fent, 1996; Lau et al., 2007; Nicklin and Robson, 1988). For example, for the very sensitive mollusc *Nucella lapillus* (dog whelk), the no observed effect concentration (NOEC) is only 2 $ng\ L^{-1}$ (ECHA, 2008). Due to public concern about TBT toxicity, its use in shipyards was completely banned worldwide in 2008 (Brandli et al., 2009; IMO, 2003). Accordingly, decreasing TBT concentrations have been reported at various places, e.g. declining from 81 to 7 $\mu mol\ kg^{-1}$ in sediments, and from 1.3 to 0.2 $nmol\ L^{-1}$ in seawater (Choi et al., 2009). However, high concentrations of TBT can still be found in certain aquatic organisms (0.03–3.2 $\mu mol\ kg^{-1}$) (Sousa et al., 2009), in seawater ($\sim$5 $nmol\ L^{-1}$) (Berto et al., 2007) and in sediments ($\sim$74 $\mu mol\ kg^{-1}$) (Burton et al., 2005). The relatively high concentrations of TBT in organisms and sediments compared to water, reflect the high bioconcentration and strong adsorption of TBT (Choi et al., 2009; Burton et al., 2004), which may retard degradation of adsorbed compared to dissolved TBT (Craiq, 2002; Hoch, 2001).

Black carbon (BC) is ubiquitous and originates from incomplete combustion of biomass and fossil fuels (Goldberg, 1985; Kuhlbusch and Crutzen, 1995; Novakov, 1984; Penner et al., 1993), which has been interpreted to consist of two continua formed in different ways: (i) soot formed by condensation of volatiles at high temperature, and (ii) solid residues of char (charcoal) formed at low temperature combustion (Elmquist et al., 2006; Hedges et al., 2000; Masiello, 2004). The mode of formation affects the physicochemical characteristics of BC such as size, structure, element ratios and functionalities (Baldock and Smernik, 2002; Masiello, 2004; Preston and Schmidt, 2006). Owing to their composition, BC exhibits stronger adsorption affinity for hydrophobic organic contaminants (HOCs) than natural organic matter (NOM), especially at low aqueous concentrations (Bucheli and Gustafsson, 2000; Cornelissen et al., 2004; Lohmann et al., 2005; Nguyen et al., 2004), indicating the environmental importance of BC. Accordingly, adsorption to BC contributes significantly to the total adsorption of HOCs in soils and sediments (Bucheli and Gustafsson, 2003; Gustafsson et al., 1997). Furthermore, oxygen-rich charcoal-BC with abundant carboxylic and phenolic groups resembling NOM adsorbs heavy metal cations (Chen et al., 2007), demonstrating that adsorption of cationic pollutant species should be accounted for when quantifying adsorption to charcoals.

Studies on TBT adsorption to soils (Huang and Matzner, 2004), sediments (Burton et al., 2004; Dowson et al., 1993), sand (Behra et al.,

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2003; Bueno et al., 1998, 2001), metal oxides (Weidenhaupt et al., 1997), clay minerals (Behra et al., 2003; Hoch and Schwesig, 2004; Weidenhaupt et al., 1997), humic acid (Arnold et al., 1998) and algae (StLouis et al., 1997) demonstrate that TBT adsorption is pH dependent. Although a study of TBT adsorption by a non-characterized BC has been performed (Brandli et al., 2009), it does not reveal the mechanism behind the adsorption process. Besides, information about the influence of pH on TBT adsorption to BC is still not available.

The aim of this investigation was to quantify and model the influence of TBT concentration and pH on the adsorption of TBT to three different BC samples including beech charcoal, wheat charcoal and soot. To avoid confusing, the terminology "TBT" is used for describing the total tributyltin, including ionic (TBT^+) and neutral (TBTOH) species in this paper.

2. The pH-dependent dual Langmuir model

Based on the results of preliminary investigations, a new simple model addressing different aspects of TBT–BC interactions was developed. The model is shortly described below; more details may be found in the Supplementary data (S1). TBT is a weak acid with $pK_a = 6.3$ (Arnold et al., 1997) composed of a cationic form (TBT^+, $(C_4H_9)_3Sn^+$) in equilibrium with a neutral form (TBTOH, $(C_4H_9)_3SnOH$) according to Eq. (1):

$$TBT^+ + H_2O \leftrightarrows TBTOH + H^+ \tag{1}$$

Hydrophobic (van der Waals) forces are considered to determine TBTOH adsorption by uncharged BC sites, whereas electrostatic forces govern adsorption of TBT^+ by negatively charged surface sites. Both adsorption reactions can be described by a Langmuir equation. The charcoals, but not the soot, possess pH-dependent negative surface sites due to dissociation of carboxylic and phenolic groups (Buffle, 1988). Consequently, modeling of TBT adsorption by BC includes Langmuir adsorption of the two TBT species and accounts for the influence of pH on the distribution between TBT^+ and TBTOH as well as the pH dependency of the surface charge of the BC. This is the case for the new pH-dependent dual Langmuir (pH-DL) model (Eq. (2)):

$$[TBT]_{BC} = \alpha_{TBTOH} \cdot \frac{\Gamma^{h}_{max} K^{h}_{L} [TBT]_{aq}}{1 + \left(K^{h}_{L} \alpha_{TBTOH} [TBT]_{aq}\right)} + \alpha_{TBT^+} \cdot \alpha_{charged} \frac{\Gamma^{e}_{max} K^{e}_{L} [TBT]_{aq}}{1 + \left(K^{e}_{L} \alpha_{TBT} [TBT]_{aq}\right)} \tag{2}$$

where $[TBT]_{BC}$ represents the adsorbed amount of TBT (in units of $\mu mol\ m^{-2}$), $[TBT]_{aq}$ ($\mu mol\ L^{-1}$) is the total aqueous concentration of TBT. Γ^{h}_{max} and Γ^{e}_{max} ($\mu mol\ m^{-2}$) are maxima of TBTOH and TBT^+ adsorption density, respectively, while K^{h}_{L} and K^{e}_{L} ($L\ \mu mol^{-1}$) are Langmuir binding coefficients for TBTOH and TBT^+, respectively. $\alpha_{charged}$ is the percentage of the negatively charged surfaces on BC obtained by means of titration, α_{TBTOH} and α_{TBT^+} are the fractions of TBTOH and TBT^+, respectively.

In the development of Eq. (2), TBT^+ was considered to interact only with the negatively charged BC sites, i.e. interactions between TBT^+ and relevant dissolved anions (nitrate and acetate, cf. Section 3.4.2) are considered negligible in accordance with the results of Arnold et al. (1997) and Shoukry (1993).

All adsorption data of each BC sample at three pHs were used to fit with the pH-DL model. In addition, the model was validated via predicting the adsorption edges of the BC samples and comparing with measured data obtained from adsorption edges experiments. The modeling was performed by using R version 2.10.0 (R Development Core Team, 2009).

3. Materials and methods

3.1. Reagents

TBT was purchased as liquid tributyltin chloride ($(C_4H_9)_3SnCl$; density: 1.2 g mL^{-1}) (96%) from Sigma Aldrich (Denmark). Palladium nitrate (2% $Pd(NO_3)_2$ in 5% HNO_3) and Triton X-100 ($C_{14}H_{22}O(C_2H_4O)_n$) were obtained from Perkin Elmer (Denmark). NaOH and HCl solutions used for titration, and concentrated HNO_3 (69%) were obtained from J.T. Baker (Netherlands), and HPLC-grade methanol was purchased from Sigma Aldrich (Denmark). All chemicals were pro analysis or better and triple deionized water (conductivity below 0.1 $\mu S\ cm^{-1}$) was used throughout the experiments.

An 8.8 mmol L^{-1} TBT stock solution was prepared by dissolving 250 μL TBT in 100 mL methanol, and stored in the dark at 5 °C.

The buffer solutions used contained 0.01 M $NaNO_3$ and 0.01 M CH_3COONa for pH 4 and pH 6, and 0.01 M CH_3COONH_4 for pH 8. The pH values were adjusted by adding small amounts of 1 M HNO_3 or 1 M NaOH solutions. The ionic strength (I) of the buffer solutions was equivalent to 0.02 M $NaNO_3$.

3.2. BC adsorbents

Wheat charcoal (WBC) was produced as described by Bruun et al. (2008). Briefly, portions of 10 g finely ground wheat straw in a steel dish (30 cm × 20 cm × 2 cm) covered with a steel lid was heated in a muffle furnace at 300 °C for 24 h. The resulting BC (~4.0 g) was stored in a dessicator over silica gel. Beech charcoal (BBC) produced by a method similar to Hammes et al. (2006) was donated by Institute of Forest and Landscape Center (University of Copenhagen, Denmark). Soot black carbon (SBC) produced via combustion of acetylene was donated by TIMCAL Ltd. (Switzerland).

The two charcoals were finely ground in an agate ball mill, and washed with 1 M HCl (2 × 100 mL), 1 M HF (2 × 100 mL) and triple deionized water (4 × 100 mL) in polyethylene bottles to remove silica and salts (Yang et al., 2004). Finally, the charcoal was dried at 100 °C until constant weight was achieved.

3.3. Characterization of the BC samples

The elemental composition of the three BC samples was determined on a Flash EA 1112 CHN elemental analyzer (Thermo Fisher Scientific, Italy) with a combustion temperature around 1800 °C.

The concentrations of carboxylic acid (–COOH) and phenolic groups (Ar-OH) in the BC samples were determined by potentiometric titration of BC suspensions. Briefly, 0.1 g BC was added to 40 mL 0.01 M $NaNO_3$ solution. The mixture was ultrasonically dispersed for 1 min using Branson sonifier 150 (Branson Ultrasonics Co. Ltd, USA) with 60 W output power and shaken over night before titration. To get an initial $pH > 11$, 0.5 mL of NaOH (1 M) was added to the suspension and then the BC suspension was titrated with 0.02 M HCl using a Metrohm 665 Dosimate (Metrohm Inc, USA) under argon flushing and a Metrohm 691 pH meter (Metrohm Inc, USA). The concentrations of carboxylic and phenolic groups were determined as titratable acidity between pH 3 and 7, and between pH 7 and 11, respectively (Buffle, 1988).

Fourier-Transform Infrared (FTIR) absorption spectra were obtained using the KBr pellet method with 0.1–0.3 mg of BC mixed with 300 mg of KBr compressed at 150 MPa under vacuum in an evacuated die to produce a pellet (13 mm diameter). Spectra were recorded as the averages of 10 scans measured against a blind over the range 4000–400 cm^{-1} using a Perkin Elmer FTIR 2000 spectrometer (Perkin Elmer, Denmark).

The specific surface area (SSA) of the BC samples was measured by water sorption (Pyman and Posner, 1978). Briefly, 1.0 g of the BC sample was dried over P_2O_5 in an evacuated dessicator (22 ± 1 °C) until constant weight was achieved, then the BC sample was placed in an evacuated dessicator over saturated $CaBr_2$ solution until it again reached constant weight. The increment of the weight of the BC sample between the two treatments is considered to correspond to the weight of a monolayer of water molecules (Quirk, 1955). Taking the area of a H_2O molecule as 0.108 nm^2, the SSA can then be calculated. The SSAs of the BC samples were also measured by conventional N_2 sorption procedure using a Gemini 2375 V4.01 surface area analyzer (Micromeritics Inc., USA). Prior to N_2-BET measurement, the BC samples were degassed over night under N_2 flow at 105 °C. The SSAs were calculated from a BET plot of N_2 sorption at relative N_2 gas pressures (P/P_o) ranging from 0.05 to 0.35.

X-ray diffraction (XRD) diffractograms of the three BC samples were recorded in the range of 5–90° 2θ with a speed of 0.3° (2θ) min^{-1} using a Siemens D5000 Diffractometer (Siemens, Germany) and Co Kα radiation at 40 kV and 40 mA.

Microscopic analysis was conducted using a Quanta 200 scanning electron microscope (FEI, USA) at ambient temperature and 15 kV. Samples were prepared on 12 mm carbon adhesive tabs and sputter-coated with 5 nm of gold using a Polaron SC 7640 (Quorum Tech., UK).

3.4. Adsorption experiments

3.4.1. Preparation of BC stock suspensions

Stock suspensions of the two charcoals were prepared by adding known amounts of WBC or BBC to 1 L pH 4, pH 6 or pH 8 buffer solutions, respectively. Then the