Fate kinetic coefficients and correlation models for tetrabromobisphenol A (TBBPA) in membrane bioreactors and conventional activated sludge process

Mohammad Showkatul Islam, Hongde Zhou and Richard G. Zytner

ABSTRACT

Tetrabromobisphenol A (TBBPA) is a fire retardant with endocrine disruption properties, which unfortunately has been detected in trace amounts in various environmental samples. Studies have shown that TBBPA enters the aquatic environment, sediments, soils and biota predominantly through the wastewater treatment process. The dominant contributor to the fate and transport of TBBPA in wastewater is biosorption by the sludge matrix. Accordingly, the goal of this research was to determine the fate kinetics, biosorption correlation models and mechanisms of TBBPA from both conventional activated sludge (CAS) and membrane bioreactor (MBR) systems. Experiments were conducted to determine different types of partitioning and fate kinetic coefficients such as solid–liquid phase coefficient, log K_p (4.53), sludge matrix organic carbon coefficient, log K_{oc} (6.05) and glass wall partition coefficient, K_w (0.053). The experimental values of these coefficients for TBBPA are not available in the literature for application to the models. The biosorption data were also verified and fitted to Freundlich, Langmuir, Temkin, Toth, Redlich–Peterson, Sips, Brunauer–Emmett–Teller (BET), Jovanovic and Dubinin–Radushkevich biosorption isotherm models to estimate the isotherm constants. These coefficients will allow engineering application for validation of various fate models for TBBPA.

Key words | biosorption, modeling, partitioning, tetrabromobisphenol A, wall loss coefficient

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MODEL NOTATION AND NOMENCLATURE

q_e Equilibrium sorbate conc. in the solid (ng of sorbate TBBPA/mg of sludge)

C_e Equilibrium sorbate conc. in the liquid (ng of sorbate/L of liquid phase)

K_F Freundlich isotherm constant (L liquid phase/mg sludge

n Freundlich biosorption intensity (-)

q_m Maximum biosorption capacity (ng sorbate/mg of sludge)

K_L Langmuir isotherm constant (L liquid/mg sludge)

R_L Separation factor (-)

C_O Initial sorbate concentration (ng sorbate/L liquid phase)

K_T Temkin isotherm binding constant (L liquid phase/mg sludge)

b Sorbate–biosorbent interaction energy (kJ energy/mol sorbate)

R Universal gas constant (kJ energy/mol sorbate/K temperature)

T Temperature (K)

K_t Toth equilibrium constant (ng sorbate/mg sludge)

t Toth isotherm heterogeneity factor (fractional value)

K_R Redlich–Peterson isotherm constant (L liquid/mg sludge)

α_R Redlich–Peterson model coefficient (L liquid/mg sludge)

β Redlich–Peterson model exponent (-)

K_S Sips isotherm constant (L liquid phase/mg sludge)

m Sips isotherm exponent (-)

B BET isotherm constant (L liquid phase/mg sludge)

q_s Biosorption saturation capacity (ng sorbate/mg of sludge)

C_s Saturation conc. for monolayer formation (ng sorbate/ L liquid)

K_J Jovanovic isotherm constant (-)

B_D Dubinin–Radushkevich constant (kJ energy/mol of sorbate)

E Polyani potential energy (kJ energy/mol of sorbate)

K_{HJ} Harkin-Jura isotherm constant (L liquid/mg sorbate)

A_{HJ} Harkin–Jura model coefficient (-)

K_H Halsey isotherm constant (-)

K Biosorption equilibrium constant (L liquid/mg sludge)

ΔG Gibbs free energy change (kJ energy/mol sorbate)

ΔH Enthalpy change of biosorption (kJ energy/mol sorbate)

ΔS Entropy change of biosorption (kJ energy/Kelvin temperature)

INTRODUCTION

The environmental fate and transport of tetrabromobis-phenol A (TBBPA) has a strong inter-relation to the partitioning of TBBPA in aqueous phase and wastewater sludge matrix. TBBPA is introduced to the aquatic environment and ultimately to the other environmental compartments through wastewater (Lee & Peart 2002; Covaci *et al.* 2009; Labadie *et al.* 2010; McPhedran *et al.* 2013). Essential plastic commodities of daily life containing TBBPA as a fire retardant component are the major cause of its increasing abundance either in wastewater or in land-fills. TBBPA has been found in biota, blood serum, human milk and adipose tissues (Thomsen *et al.* 2002; Cariou *et al.* 2005; Frederiksen *et al.* 2007). The adverse health and environmental consequences of TBBPA due to its ubiquitous nature is therefore an emerging concern. Accordingly, the investigation of the fate models and mechanisms of TBBPA was accomplished in this present study.

Organic carbon content may be the dominant constituent for the adsorption of TBBPA in activated sludge (Gao *et al.* 1997; Field 2006). As such, sludge-water partitioning and the fate of the analyte TBBPA was investigated in this research from experimentally determined pertinent physical

parameters. Schwarzenbach & Westall (1981) reported the relationship between partitioning of chemical pollutants and the fraction of organic carbon of the sorbent, where sorption is greatly affected by the presence of organic matter. The partition coefficients were significantly high for the sorbents containing greater than 0.1% organic carbon. However, relatively small partition coefficients were found when the organic fraction was less than 0.1%.

A great deal of sorption work has been reported in the literature with soils, but the structure, texture, physical and biological composition of the activated sludge matrix is quite different from the soil matrix. In the activated sludge process, the sorbent is completely suspended in wastewater. There are many other factors that may influence the normal distribution of pollutants differently in the sludge matrix. Activated sludge containing microbial consortia provides enhanced sorption, referred to as biosorption (Aksu 2005; Vijayaraghavan & Yun 2008; Srinivasan & Viraraghavan 2010; Islam *et al.* 2014). Activated sludge is a composite of live and dead microorganisms with a large surface area between 0.82 and 1.66 m^2/g (Wang & Govind 1993). Biosorption accompanied by diffusive penetration inside the cell membrane allows increased accumulation of organic contaminants into the sludge.

Biosorption depends on the chemical nature of the contaminant, the surface properties of biosorbent, diverse interactions and environmental conditions (Aksu & Isoglu 2007). As such, biosorption is a complex phenomenon involving physical, biological, chemical, kinetic, thermodynamic and mass transfer processes. Depending on the interpretation of the system interactions, there are numerous equations and models available in the literature (Foo & Hameed 2010; Paska *et al.* 2014). The applicability of various models was tested to determine different partitioning coefficients for the fate and transport of TBBPA. Isotherm model fittings demonstrate the potential of biosorption capacity for the candidate compound with respect to the sorbate–sorbent interactions of the fitted model. If the experimental data show goodness of fit with multiple models, then the potential of biosorption for the candidate compound becomes more obvious, i.e., highly favourable in terms of the theoretical model assumptions. Multiple model fittings indicate high possibilities of diverse combinations of binding sites availability and layer

formation for biosorption process (Samarghandi *et al.* 2009; Foo & Hameed 2010; Paska *et al.* 2014). Therefore, it can be concluded from the excellent curve fittings for TBBPA with a number of models that the dominant mechanism for the removal of TBBPA from wastewater process is biosorption.

Studies demonstrated that the partitioning parameters are directly related to the partition coefficients and constants (Birkett & Lester 2003). The distribution of the target compound depends on the extent of the increase or the decrease in the model constants at equilibrium. An excellent linear relationship from the regression analysis indicates high potential for the prediction of the parametric values by the correlation models (Schwarzenbach *et al.* 2003). The models developed from the experimental data produce more reliable results than empirical models and will be better predictors of what takes place in the field. Therefore, this research is valuable and promising for potential engineering application in the wastewater treatment process.

The biosorption isotherm models (Foo & Hameed 2010; Hadi *et al.* 2010; Paska *et al.* 2014) are generally justified from the curve fittings by plotting equilibrium sorbate concentrations in two phases (q_e, C_e). The equilibrium concentrations are measured after establishing the equilibrium in the system with sufficient mechanical mixing and reaction time.

The Freundlich isotherm equation is the best suited model for partitioning of the most organic compounds in activated sludge (Dobbs *et al.* 1989; Clara *et al.* 2004). According to Freundlich adsorption, the heat of sorption decreases exponentially with the coverage of the sorbent surface. In this case, the sorbate TBBPA undergoes interactions with the heterogeneous surface of the biosorbent activated sludge. The Freundlich isotherm model for activated sludge biosorption can be expressed as follows:

$$q_e = K_F C_e^{1/n} \tag{1}$$

where K_F (L/mg) is the Freundlich constant, indicating the biosorption capacity of sludge and $1/n$ is the exponent, indicating biosorption intensity of TBBPA.

The Langmuir isotherm model (Langmuir 1916) was formulated for the monolayer formation with the fixed maximum capacity of the surface coverage. The Langmuir isotherm equation can be represented as:

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \tag{2}$$

where q_m (ng/mg) is the maximum biosorption capacity of the sludge to form a monolayer with TBBPA and K_L (L/ng) is the Langmuir constant, indicating the affinity of the binding sites of sludge for TBBPA.

There are multiple models available from the modifications of widely used Freundlich and Langmuir isotherm equations. As such, suitability of Temkin, Toth, Redlich–Peterson, Sips, Brunauer–Emmett–Teller (BET), Jovanovic, Dubinin–Radushkevich, Harkin–Jura and Halsey isotherm models were verified in addition to Freundlich and Langmuir models.

Biosorption is a consequence of surface free energy change due to the interaction of sorbate–biosorbent molecules. The free energy change (ΔG^O), the enthalpy change (ΔH^O), and the entropy change (ΔS^O) were studied and calculated from the biosorption equation and thermodynamic relationships.

The fate and transport properties of organic pollutants in wastewater depend on the magnitude of partitioning coefficients. A number of transport and fate models are available for hydrophobic organic compounds in soil (Site 2001), whereas the fate model for the brominated flame retardants in activated sludge is very limited. The objective of this research was achieved by estimating the partition coefficients and developing the correlation models from the relevant experimental data. The ultimate engineering application of these outcomes will allow control and mitigation of environmental proliferation for TBBPA.

METHODOLOGY

Materials

All chemicals and reagents were purchased from Fischer Scientific Canada unless otherwise specified. Most chemicals were ACS grades and all solvents used were HPLC grades. Whatman GF/B filters, Whatman GF/F, Whatman 0.2 nylon membrane and nucleopore polycarbonate filters (Cat. No. 0930069) were purchased from Fisher Scientific.

Helium (99.9999%) and methane (99.9999%) were supplied by BOC Canada (Guelph, Ontario). Milli-Q water was produced from a Milli-pore Ultrapure Water System.

Extraction and analysis

The extraction and analysis of aqueous samples for injecting into the gas chromatography–mass spectrometry (GC-MS) system require multiple steps of processing. The first step of wastewater processing was filtration for applying to solid phase extraction. The captured fractions were eluted and liquid–liquid extraction (LLE) clean-up was performed before adding internal standards (ISTD). The sample was then evaporated to dryness for obtaining quantitative transfer of the reconstituted volume to the GC-MS system. The entire analysis process flow diagram is shown in Figure 1.

The quantitative estimation was performed by an Agilent 6890N GC equipped with an autosampler injector. The signal detector for quantification was an Agilent 5975 MSD. Helium was used as the carrier gas, under a constant pressure of 80 kPa. Methane was used as the reagent gas for the negative ion source and was maintained at 40% of flow. The system was run in negative chemical ionization (NCI) mode. The select ion monitoring (SIM) acquisition was chosen for higher sensitivity of the method. The interface, inlet and quadrupole temperatures were maintained at 250 °C, 250 °C and 150 °C, respectively. The ions monitored were 79 and 81 m/z for TBBPA, 71 and 74 m/z for DDT.
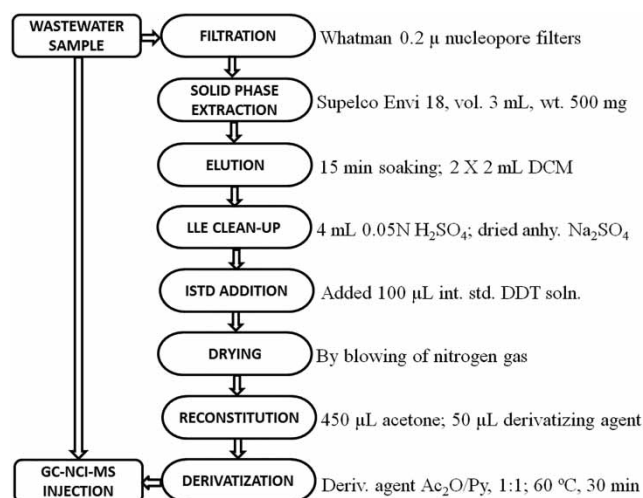

Figure 1 | Process flow diagram for wastewater sample.

Total organic carbon (TOC) was measured by a Shimadzu TOC-V unit equipped with a solid sample module 5000A. Calibration curves were developed and updated frequently as specified in *Standard Methods* (APHA 2012). Basic water quality parameters such as dissolved oxygen (DO), pH and temperature were recorded immediately after sample collection using a pH/conductivity/DO meter (probe model sensION6, Hach, USA).

Pertinent equations for experimental measurements

Adsorption losses on to the container wall for organic compounds have been reported (Kerr *et al.* 2000; Kokkola *et al.* 2014). Similar to other organic compounds, TBBPA has a tendency to be adsorbed onto the surface of the glass vessel, indicating adsorptive losses (Covaci *et al.* 2009). Thus, care must be taken to compensate for these adsorption losses. As such, the vessel-wall partition coefficient K_W (mL/cm^2) was determined, which represents the partition coefficient between glass wall and the aqueous phase as represented by Equation (3) (Backhus & Gschwend 1990):

$$K_W = \frac{[TBBPA]_{Wall}}{[TBBPA]_{Aq.}[SA/V]} \tag{3}$$

The organic carbon partition coefficient (K_{OC}) of activated sludge was estimated from Equation (4):

$$\frac{[TBBPA]_{Tot}}{[TBBPA]_{Aq}} = 1 + K_{OC}[OC] + K_W[SA/V] \tag{4}$$

where K_{OC} = organic carbon partition coefficient; K_W = vessel-wall partition coefficient; $[OC]$ = organic carbon concentration; $[SA/V]$ = surface area to volume ratio of the container.

Sorptive partitioning to activated sludge was estimated from the sludge-water partition coefficient, K_P (L/mg). The solid-liquid partition coefficient is given by the following Equation (5):

$$K_P = \frac{[TBBPA]_{Sorp}}{[TBBPA]_{Aq}} = \frac{[TBBPA]_{Tot} - [TBBPA]_{Aq}}{[TBBPA]_{Aq}} \tag{5}$$

It should be noted that the solid phase concentration, C_s (ng/mg) was not measured in this study for the determination

of sludge-water partition coefficient. However, it was calculated from the difference of the total concentration and the dissolved phase aqueous concentration.

Batch experiments

Batch experiment for K_W

The wall loss coefficient was determined by spiking 100 μL of TBBPA solution in acetone to 500 mL Milli-Q water in borosilicate glass Erlenmeyer flasks. The equilibration period was over 24 h to achieve complete equilibrium before extraction and analysis. The time recommended for establishing equilibrium was the minimum mixing of half an hour (US EPA 1996). The flasks were wrapped with aluminum foil and placed in the dark chamber for 36 h in order to avoid photo-degradation losses. The concentration of the content by calculation was 100 ng/L after spiking. The initial aqueous concentration was estimated experimentally from the instantaneous extraction and quantification of the spiked solutions. Wall loss coefficient (K_W) was determined from the geometry and equilibrium concentrations between aqueous phase and borosilicate glass surface by using Equation (3).

Batch experiment for K_{OC} and K_P

The fraction of organic carbon in the sludge was obtained from the measurement of the organic carbon concentration. Organic carbon content in activated sludge was measured by a TOC analyser while the spiked concentration of TBBPA was extracted and analysed in parallel by GC-MS following the method protocol (Figure 1) for the determination of K_{OC}. For each sample analysis, diluted sludge (not filtered sludge) was used for organic carbon measurement by TOC analyser. One mL of fresh activated sludge was diluted to 1,000 mL in a volumetric flask. The diluted sludge was transferred to the bioreactor (300 mL biochemical oxygen demand (BOD) bottles) in varying amounts. TBBPA standard solution (90 μL) was spiked to each bioreactor while stirring. The TOC analyser suction tube was inserted into the continuously stirred bioreactors approximately at the midpoint for actual representation of the organic carbon. The organic carbon concentration was recorded from the analyser reading and

the remaining solution was used for extraction, analysis and quantification by GC-MS. Equation (4) was used for the computation of the organic carbon coefficient, K_{OC}.

Fate partitioning and distribution of TBBPA to activated sludge was estimated from the sludge-water partition coefficient (K_P). The concentrations of TBBPA in the aqueous phase and sludge were determined as detailed in the process flow diagram of Figure 1. Fresh activated sludge and membrane bioreactor (MBR) sludge was added to BOD bottles in varying amounts. A standard solution of TBBPA (50 μL) was added to each bioreactor bottles in stirred condition. The mixtures were extracted and analysed for TBBPA quantification in sludge phase and aqueous phase. The sludge phase TBBPA was estimated from the concentration difference of the total TBBPA and the dissolved phase TBBPA. In this study, only aqueous phase determination was accomplished by the developed method. Equation (5) was used for the computation of the required parameters.

Batch experiment for biosorption coefficients

Biosorption of TBBPA was studied by using fresh sludge collected from the aeration basin of the conventional activated sludge (CAS) process and from the aeration tank of the MBR pilot plants at the Guelph municipal wastewater treatment plant (GWWTP). Biosorption isotherms were developed to explain the partitioning behaviour of TBBPA in both MBR and CAS sludge. Different mathematical models have been applied to evaluate the goodness of fit for the experimental data. A set of biosorption partition coefficients for TBBPA were generated from the analysis of experimental data using isotherm equations.

Sludge samples from both biological reactors were collected in amber glass containers, and placed in an ice chamber. Samples were then brought immediately to the environmental engineering laboratory, University of Guelph for analysis.

US EPA (1996) guidelines recommend a minimum half an hour of stirring of the mixture to establish equilibrium for an adsorption study. Accordingly, the extraction was carried out after 2 h of spiking to allow enough time for achieving equilibrium. The reacting vessels were continuously stirred during the equilibration period. Fresh sludge in varying amounts was added to each reaction vessel for

developing the biosorption isotherms. The volumes of sludge directly added to each reactor were 0 mL, 1 mL, 2 mL, 4 mL, 6 mL, 8 mL, 10 mL, 12 mL and 15 mL, respectively. The spiked concentration of TBBPA in the reacting vessels was 30 ng/L. The pH and temperature of the test solutions were recorded at 7.1 °C and 21.5 °C for CAS sludge and 6.82 °C and 21.3 °C for MBR sludge, respectively.

The extraction, analysis and estimation of experimental samples were accomplished as shown in the process flow diagram of Figure 1. Biosorption coefficients were estimated from the experimental data using various isotherm model equations.

RESULTS AND DISCUSSION

Partitioning coefficients K_W, K_{OC}, K_P

The vessel-wall partition coefficient was determined in the laboratory. The measurement was done in triplicate experiments and the average experimental value was 0.053 mL/cm^2. This value serves as the correction coefficient for a unit volume of TBBPA solution per unit surface area of borosilicate glass. The correction coefficient compensates for the adsorptive losses onto the vessel wall for the determination of TBBPA. Table 1 shows the experimental result for the determination of the glass wall correction coefficient.

Backhus & Gschwend (1990) were the first to indicate the partitioning of polycyclic aromatic compounds to glass vessels with a wall loss coefficient, $K_W = 0.33$ mL/cm^2. TBBPA has a low K_W value as it is less hydrophobic than polycyclic aromatic compounds since it has two polar hydroxyl groups attached to each benzene ring. It was expected that the adsorption losses to glass vessels would be much less than polycyclic aromatic hydrocarbons. Accordingly, the estimated value $K_W = 0.053$ mL/cm^2 is acceptable for the compound TBBPA.

The organic carbon partition coefficients (K_{OC}) and sludge-water partition coefficients (K_P) for activated sludge determined in the laboratory are given in Table 2. The experimental data for the organic carbon partition coefficients (K_{OC}) and sludge-water partition coefficients (K_P) for MBR sludge are given in Table 3.

The resulting log K_{OC} value is 6.02, with log K_P equal to 4.54 for activated sludge. The corresponding values for MBR sludge are 5.76 and 4.31, respectively. The organic carbon partition coefficient, K_{OC} is more of an intrinsic parameter than K_P. K_{OC} is specific to the type of organic matter present in the biological process. The value of log $K_{OC} > 3$ provides a high potential for sorption to the sludge (Birkett & Lester 2003). Accordingly, the higher average value of K_{OC} for TBBPA indicates the higher biosorption potential in activated sludge (Islam *et al.* 2014).

The solid-water partition coefficient, K_P is a phase equilibrium constant which approaches to Freundlich constant (K_F) if the exponent of biosorption intensity ($1/n$) becomes unity. The linear partition coefficient K_P can be combined with Langmuir isotherm or Freundlich isotherm to model complex biosorption mechanisms covering a wide range of concentrations (Wang & Govind 1993; Schwarzenbach *et al.* 2003).

Partitioning parameters are empirically related to each other for developing the fate model. If the proportion of

Table 1 | Experimental data for wall loss coefficient

Aqueous phase TBBPA conc. [TBBPA]$_{Aq}$ ng/L	Vessel wall TBBPA conc. [TBBPA]$_{Wall}$ ng/L	Surface area to volume ratio [SA/V] cm^2/L	Wall loss coefficient $K_W = \dfrac{[TBBPA]_{Wall}}{[TBBPA]_{Aq}.[SA/V]}$ mL/cm^2
83.58	16.42	4.26	0.047
81.53	18.48	4.26	0.053
79.98	20.02	4.26	0.059
Average			0.053

Table 2 | Experimental data of activated sludge log K_{OC} and log K_P

No.	Vol. of sludge mL	[OC] mg/L	log K_{OC} L/mg	log K_P L/mg
1	1	0.523	5.80	4.32
2	2	0.615	5.87	4.50
3	4	1.427	5.98	4.51
4	6	1.743	6.00	4.54
5	8	2.161	6.01	4.57
6	10	2.299	6.10	4.61
7	12	3.220	6.20	4.62
8	15	3.717	6.21	4.63
Average			6.02	4.54

Table 3 | Experimental data of MBR sludge log K_{OC} and log K_P

No	Vol. of sludge mL	[OC] mg/L	log K_{OC} L/mg	log K_P L/mg
1	1	0.96	5.64	4.21
2	2	1.414	5.65	4.24
3	4	1.556	5.71	4.30
4	6	2.427	5.73	4.31
5	8	3.050	5.82	4.32
6	10	3.364	5.84	4.33
7	12	3.914	5.85	4.34
8	15	4.106	5.86	4.39
Average			5.76	4.31

Table 4 | Comparison of partitioning coefficients with literature values

Partitioning coefficients	Experimentally measured values	Literature values (estimated)
log K_{OC} (L/mg)	6.02	5.43[a] (KOCWIN, V.2.0, MCI) 6.80[a] (QSAR using log K_{OW}) 4.52[a] (derived from log K_{OW})
log K_P (L/mg)	4.54	6.49[b] (EPIWIN, V.3.04; BFRIP report)
K_W (mL/cm^2)	0.053	Not available

[a]Environment Canada: Physical and Chemical Properties of TBBPA.
[b]BFRIP (2001): Data Summary and Test Plan for TBBPA.

organic carbon content increases, the propensity of sorptive partitioning to sludge increases (Birkett & Lester 2003). The hydrophobicity of organic compounds is dependent on the organic carbon partition coefficient, K_{OC} (Field 2006). The sludge-water partition coefficient (K_P) is directly related to the organic fraction of the sludge. The relationship was expressed empirically by Karickhoff et al. (1979).

$$K_P = K_{OC} f_{OC} \qquad (6)$$

where f_{OC} is the organic fraction of the sludge.

K_P is a useful parameter for prediction partitioning of organic compounds in biological wastewater treatment systems. However, experimentally measuring the octanol-water partition coefficient (K_{OW}) is much easier than measuring K_{OC} and K_P from the sludge matrix. Accordingly, the empirical model given in Equation (7) was proposed for predicting K_P from K_{OW}, which is as follows (Karickhoff 1981):

$$K_P = f_{OC} \times 0.41 \times K_{OW} \qquad (7)$$

To overcome the limitation of the empirical modelling and to establish reliable experimental values for the partitioning fate model of TBBPA, the partition coefficients have been estimated in the laboratory.

Table 4 provides a comparison of the experimental results of this study with that of the model estimated literature values. The values obtained in this research were within the expected range of the estimated literature values.

Correlation models

It was observed that the organic carbon partition coefficient for TBBPA was linearly influenced by the increase of sludge organic carbon concentration. The fate and partitioning correlation models for TBBPA in the MBR and activated sludge processes are shown in Figures 2 and 3. The log K_{OC} for TBBPA increases linearly ($R^2 = 0.94$ for MBR, $R^2 = 0.91$ for CAS) with the organic carbon content exhibiting similar correlation with the solid-water partition coefficient K_P ($R^2 = 0.83$ for MBR, $R^2 = 0.82$ for CAS) in both biological processes. Figure 3 shows the linear relationship of log K_{OC} with organic carbon for MBR sludge and CAS sludge.

Xia et al. (2005) reported a linear relationship of log K_P with log K_{OW} for selected compounds similar to the TBBPA experimental results observed in this study. The parameter log K_{OW} is indeed indicative of the partitioning of the compound between organic and aqueous phases (Karickhoff 1981; Dobbs et al. 1989; Schnoor 1996). The relationship between organic carbon and octanol-water partition coefficient was reported for the non-polar organic compounds (Schwarzenbach & Westall 1981; Birkett & Lester 2003). The experimental data for a large set of organic compounds ($n = 186$) were summarized by Schwarzenbach et al. (2003) that follows the linear model equation:

$$\log K_{OC} = a \log K_{OW} + b \qquad (8)$$

The correlation models developed in this study from the plotting of the experimental data for TBBPA in activated
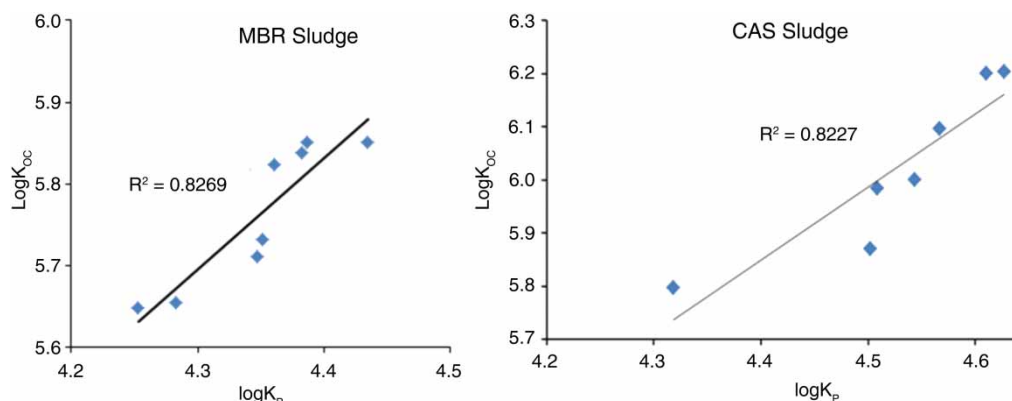
Figure 2 | Correlation of log K_{OC} with K_P for MBR sludge and activated sludge.
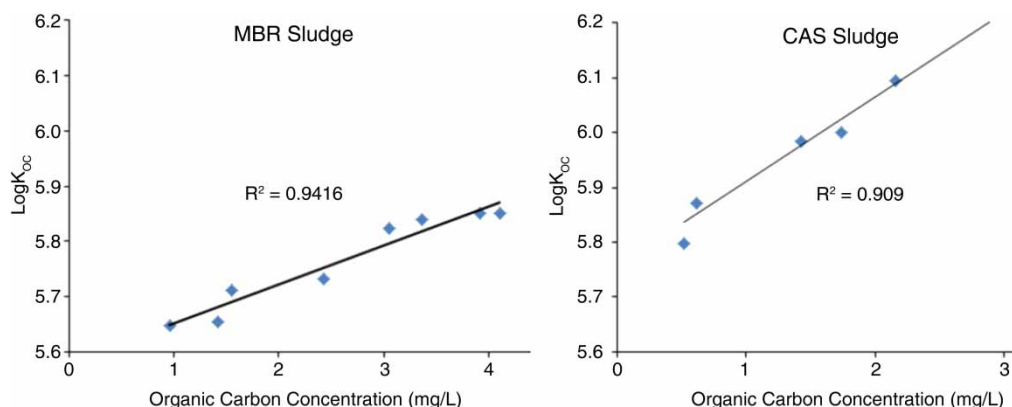

Figure 3 | Correlation of log K_{OC} with organic carbon for MBR sludge and CAS sludge.

sludge can be represented as:

$$\log K_{OC} = a \log K_P + b \qquad (9)$$

$$\log K_{OC} = c[OC] + d \qquad (10)$$

The correlation models developed for TBBPA in MBR sludge can be given as:

$$\log K_{OC} = e \log K_P + f \qquad (11)$$

$$\log K_{OC} = g[OC] + h \qquad (12)$$

Experimentally determined model coefficients will be helpful for environmental engineers to predict the fate of similar hydrophobic compounds in biological wastewater

treatment processes (Dobbs *et al.* 1989; Struijs *et al.* 1991). Schwarzenbach *et al.* (2003) have already shown the usefulness of the identical models developed from the experimental results. Table 5 shows the model constants for TBBPA of this study and other studies of linear regression fittings.

The developed linear correlation models with high values of R^2 indicate strong correlation among the measured partitioning parameters, supporting the evidence for the use of model constants for predicting the fate and partitioning of TBBPA in wastewater sludge. The environmental impacts of related compounds can be estimated from the experimental model coefficients. The equations presented in the present study will allow prediction of the fate, persistence and partitioning of nonvolatile, nonbiodegradable organic pollutants in wastewater process, sludge treatment process and landfill operation process (Dobbs *et al.* 1989; Wang & Govind 1993).

Table 5 | Comparison table of the model constants with other studies

Compounds	Slopes	Intercepts	Correlations	R^2
[a]Brominated compounds	0.50	0.81	log K_{OC} with log K_{OW}	0.49
[a]PCBs, chlorinated benzenes,	0.74	0.15	log K_{OC} with log K_{OW}	0.96
[a]Chlorinated phenols	0.89	−0.15	log K_{OC} with log K_{OW}	0.97
[a]PAHs	0.98	−0.32	log K_{OC} with log K_{OW}	0.98
[b]TBBPA	1.37	−0.20	log K_{OC} with log K_P (CAS)	0.82
[b]TBBPA	0.15	5.76	log K_{OC} with [OC] (CAS)	0.91
[b]TBBPA	1.36	−0.10	log K_{OC} with log K_P (MBR)	0.83
[b]TBBPA	0.07	5.58	log K_{OC} with [OC] (MBR)	0.94

PCBs: polychlorinated biphenyls; PAHs: polycyclic aromatic hydrocarbons.
[a]Schwarzenbach *et al.* (2003).
[b]Present study.

Isotherm coefficients

Isotherm models were verified for the curve fittings to extract the estimate of the isotherm coefficients. The experimental data for TBBPA biosorption have been fitted to linear regression analysis for determining isotherm model constants. These values are reported in Table 6 and compared with other studies for TBBPA and similar compounds. BPA is structurally similar to TBBPA with endocrine disrupting properties. Compounds having identical structural features generally display similar physicochemical and biological characteristics.

Biosorption is a complex process of physical, chemical and biological phenomena dependent on multiple factors of the system under study. Therefore, the results reported in the literature fall under a wide range in orders of magnitude. BPA is structurally similar to TBBPA, containing additional bromine atoms. The coefficients measured by Clara *et al.* (2004) were studied in sewage sludge which resembled the present study. The values of isotherm coefficients for TBBPA are 2.5 to 4.5 times higher in order of magnitude than BPA. This is reasonable with respect to the higher hydrophobicity of TBBPA compared to BPA. Other literature values were studied for the different sorbents but were very similar to the current study. Multiple model fittings were not available in the literature for TBBPA. It may be that the experimental data did not fit with models or the authors did not apply models other than the Freundlich and the Langmuir models.

The R_L value of 0.07 for activated sludge indicates favourable biosorption for TBBPA and 0.88 for MBR sludge indicates favourable biosorption but less favourable than

CAS sludge. The R_L values for TBBPA on a carbon nanotube sorbent surface were found to be 0.01 and 0.04 at temperature 25 °C and 45 °C, respectively (Fasfous *et al.* 2010).

The negative value of ΔG^O refers to the thermodynamic spontaneity of the biosorption process. Generally for physical biosorption, the values of ΔG^O are in the range of 0 to −20 kJ/mol (Yu *et al.* 2004). The negative values of $\Delta G^O = -7.79$ KJmol^{-1} (CAS) and $\Delta G^O = -10.84$ kJmol^{-1} (MBR) were calculated from the biosorption equilibrium. Therefore, the biosorption removal of TBBPA is a favourable thermodynamic process. Fasfous *et al.* (2010) reported ΔG^O values for TBBPA biosorption in the range of 10.2 to −17.9 kJ/mol.

The values of Freundlich intensity constant, n, equal 0.92 and 0.57 for the two types of sludge, indicate favourable biosorption (potentially chemisorption) and cooperative adsorption (Samarghandi *et al.* 2009; Foo & Hameed 2010). The positive values of adsorption energies: 2 kJ/mol and 5.1 kJ/mol, for the Temkin model constant b predict an exothermic biosorption process (Samarghandi *et al.* 2009). Therefore, the biosorption removal of TBBPA is a favourable process both kinetically and thermodynamically.

The higher order three parameter model equations did not allow linear plotting of the experimental data (Wang & Govind 1993). Thus, the complex model equations could not be solved for the linear regression curve fittings. Nonlinear regression analysis was applied to experimental data for extracting model constants using the MS Excel data solver (Wong *et al.* 2004). Most models were suitable for the curve fittings by nonlinear regression analysis

Table 6 | Comparison of biosorption coefficients with other studies

Compound (isotherm)	Constant	Unit/Unitless	Estimate	R^2	Sorbent	Reference
Bisphenol A (Freundlich)	$\log K_F$ n	L/mg –	−0.61 1.49	0.97	Activated sludge	Clara *et al.* (2004)
Bisphenol A (Freundlich)	$\log K_F$ n	L/mg –	1.83 4.55	0.94	Zeolite	Tsai *et al.* (2006)
(Langmuir)	q_{max} K_L	ng/mg L/mg	111.10 3.10	0.96		
(Redlich–Peterson)	K_R α β	L/mg – –	140.85 1.092 0.59	0.99		
TBBPA (Freundlich)	$\log K_F$ n	L/mg –	0.58 1.57	0.99	Carbon nanotube/$CoFe_2O_4$-NH_2	Zhou *et al.* (2014)
(Langmuir)	q_{max} K_L	ng/mg L/mg	30.65 0.12	0.98		
TBBPA (Freundlich)	$\log K_F$ n	L/mg –	1.74 3.60	0.94	Carbon nanotubes	Fasfous *et al.* (2010)
(Langmuir)	q_{max} K_L	ng/mg L/mg	64.40 8.00	0.97		
TBBPA (Freundlich)	$\log K_F$ n	L/mg –	1.89 0.75	0.99	Soil	Sun *et al.* (2008)
TBBPA (Freundlich)	$\log K_F$ n	L/mg –	−1.49 1.09	0.74	CAS sludge	This study
(Langmuir)	q_{max} K_L R_L	ng/mg L/mg –	4.90×10^{-1} 2.00×10^{-1} 7.00×10^{-2}	0.65		
(Temkin)	K_T b	L/mg kJ/mol	1.10×10^{-1} 2.00×10^{-3}	0.75		
TBBPA (Freundlich)	$\log K_F$ n	L/mg –	−2.92 1.75	0.86	MBR sludge	This study
(Langmuir)	q_{max} K_L R_L	ng/mg L/mg –	4.00×10^{-1} 2.70×10^{-3} 8.80×10^{-1}	0.90		
(Temkin)	K_T b	L/mg kJ/mol	8.60×10^{-1} 5.10×10^{-3}	0.85		

except the Harkin–Jura and the Halsey model isotherms. These two models account for the heteroporous nature of the adsorbent which is not the case for CAS sludge (Samarghandi *et al.* 2009). Thus, it is obvious that these two adsorption models, employing pore-filling mechanisms for heterogeneous porous media, will not be suitable for explaining biosorption processes of TBBPA by activated sludge and aerobic MBR sludge.

The estimated isotherm coefficients obtained from the experimental data by nonlinear analysis are reported in Table 7. The nonlinear regression analysis adopts a minimization approach for the sum of the squared errors (*SSE*) to attain the closest matching of the model equation to the experimental data. K_R (L/mg) is the isotherm equilibrium constant for the Redlich–Peterson equation similar to Freundlich constant, Langmuir constant or Henry's constant. The values of α (2.58, 2.57) are in the reasonable range as compared to the literature results (Wong *et al.* 2004). β is the exponent with a value between 1 and 0. When $\beta = 0$, then the isotherm equation becomes identical to the form of Freundlich equation. That was the case for the regression analysis of the experimental data for this study.

Table 7 │ Isotherm constants for TBBPA by nonlinear regression analysis

Isotherm model	Isotherm constant	Unit/Unitless	Value for activated sludge	Value for MBR sludge
Redlich–Peterson	K_R	L/mg	1.60×10^{-1}	6.00×10^{-2}
	α_R	–	2.58	3.57
	β	–	0	0
	SSE	–	6.50×10^{-1}	5.00×10^{-2}
Toth	q_{max}	ng/mg	4.00×10^{-2}	3.90×10^{-4}
	K_t	ng/mg	1.40	1.80
	t	–	2.40×10^{-1}	1.00×10^{-2}
	SSE	–	8.00×10^{-1}	5.00×10^{-2}
Sips	q_{max}	ng/mg	3.80×10^{3}	0.32×10^{-2}
	K_S	L/mg	6.50×10^{-3}	0.43
	m	–	5.40×10^{2}	1.00×10^{3}
	SSE	–	6.50×10^{-1}	5.00×10^{-2}
BET	q_{max}	ng/mg	4.00×10^{3}	5.80×10^{2}
	C_s	ng/L	6.60×10^{2}	0.78×10^{2}
	B	–	6.70×10^{-3}	7.90×10^{-4}
	SSE	–	6.20×10^{-1}	8.00×10^{-3}
Jovanovic	q_{max}	ng/mg	-2.40×10^{-2}	-5.80×10^{-2}
	K_J	–	1.00×10^{-1}	1.10×10^{-1}
	SSE	–	3.00×10^{-2}	7.70×10^{-1}
Dubinin–Radushkevich	q_s	ng/mg	9.40×10^{-1}	2.70
	B_D	kJ/mol	0.980×10^{2}	0.88×10^{2}
	SSE	–	1.50×10^{-1}	7.60×10^{-1}

Sum of the squared errors, $SSE = \sum_{i=1}^{n}(q_{\exp} - q_{\mod})^2$ where $q_{\exp}$ = experimental TBBPA biosorption and $q_{\mod}$ = TBBPA biosorption predicted by the model isotherm.

The Toth isotherm is a modified form of the Langmuir equation with the heterogeneity factor, t. The magnitude of the factor can be between the values of a small fraction to unity. The other isotherm constants may acquire different values depending on the adsorption type. q_m (ng/mg) is the maximum adsorption capacity parameter applicable to all types of isotherm equations such as Sips, BET and Jovanovic models. The characteristic constant values obtained in this study for different isotherm models were in good agreement with the other adsorption studies (Wong *et al.* 2004; Samarghandi *et al.* 2009). However, those studies have been designed to interpret dye adsorption phenomena. These models are widely used in the treatment of wastewater from textiles, dye industries, agricultural wastes and pulp and paper industries (Foo & Hameed 2010; Dada *et al.* 2012; Paska *et al.* 2014). The present study will extend these applications to municipal wastewater for the removal of TBBPA and similar nonvolatile, nonbiodegradable hydrophobic compounds.

Overall the models have similarities and differences in comparison to each other. The correlations and the magnitude of the coefficients from different models clearly demonstrated the usefulness and applications of the research in the engineering field. Experimental values will help to validate and verify the empirical models. However, there are drawbacks and constraints to these constants for transferring laboratory data to the field. Aspects of variations and limitations to the application should be considered. Some modifications, adjustments or optimization may be required in the real engineering applications.

CONCLUSIONS

The partitioning coefficients presented in this paper were successfully measured experimentally. The experimental values showed excellent goodness of fit with the theoretical models for applying to biosorption process modelling, measuring and predicting of the persistent pollutants. In addition, the isotherm constant values were in the acceptable range according to the theories of those models. The

developed correlation models for partition coefficients will be useful to determine the fate, persistence and partitioning of TBBPA in wastewater treatment processes, sludge treatment processes and landfill applications.

The correlation models provide an easy means of assessing fate, partitioning and transport of the contaminant without time-consuming laboratory effort. The important purpose of the correlation models is to develop engineering tools for environmental management planning, monitoring, problem identification, impact assessment, risk assessment, pollution load evaluation and mitigation of transboundary migration. The kinetic coefficients determined in this research are valuable for potential engineering applications in tackling TBBPA proliferation in the environmental compartments. These models will also be applicable to the biosorption removal of contaminants in wastewater with properties similar to TBBPA.

REFERENCES

Aksu, Z. 2005 Application of biosorption for the removal of organic pollutants: a review. *Process Biochem.* **40**, 997–1026.

Aksu, Z. & Isoglu, I. A. 2007 Use of dried sugar beet pulp for binary biosorption of Gemazol Turquoise Blue-G reactive dye and copper (II) ions: equilibrium modeling. *Chem. Eng. J.* **127**, 177–188.

APHA 2012 *Standard Methods for the Examination of Water and Wastewater*, 22nd edn. American Public Health Association, Washington, DC, USA.

Backhus, D. A. & Gschwend, P. M. 1990 Fluorescent polycyclic aromatic hydrocarbons as probes for studying the impact of colloids on pollutant transport in groundwater. *Environ. Sci. Technol.* **24**, 1214–1223.

BFRIP 2001 *Summary and Test Plan for Tetrabromobisphenol A, TBBPA*. Brominated Flame Retardant Industry Panel, Arlington, VA, USA.

Birkett, J. W. & Lester, J. N. 2003 *Endocrine Disrupters in Wastewater and Sludge Treatment Processes*. CRC Press, Boca Raton, FL, USA.

Cariou, R., Antignac, J. P., Marchand, P., Berrebi, A., Zalko, D., Andre, F. & Bizec, B. L. 2005 New multiresidue analytical method dedicated to trace level measurement of brominated flame retardants in human biological matrices. *J. Chromatogr. A* **1100**, 144–152.

Clara, M., Strenn, B., Saracevic, E. & Kreuzinger, N. 2004 Adsorption of bisphenol-A, 17 β-estradiol and 17α-estradiol to sewage sludge. *Chemosphere* **56**, 843–851.

Covaci, M. A., Voorspoels, S., Abdallah, M. A.-E., Greens, T., Harrad, S. & Law, R. J. 2009 Analytical and environmental aspects of the flame retardant tetrabromobisphenol-A and its derivatives. *J. Chromatogr. A* **1216**, 346–363.

Dada, A. O., Olalekan, A. P., Olatunya, A. M. & Dada, O. 2012 Langmuir, Freundlich, Temkin and Dubinin–Radushkevich isotherms studies of equilibrium sorption of $Zn^{2}+$ unto phosphoric acid modified rice husk. *IOSR J. Appl. Chem.* **3** (1), 38–45.

Dobbs, R. A., Wang, L. & Govind, R. 1989 Sorption of toxic organic compounds on wastewater solids: correlation with fundamental properties. *Environ. Sci. Technol.* **23**, 1092–1097.

Environment Canada 2013 *Physical and chemical properties of TBBPA*. Screening Assessment Report, Environment Canada, Health Canada, Toronto.

Fasfous, I. I., Radwan, E. S. & Dawoud, J. N. 2010 Kinetics, equilibrium and thermodynamics of the sorption of tetrabromobisphenol A on multiwalled carbon nanotubes. *Appl. Surf. Sci.* **256**, 7246–7252.

Field, J. A. 2006 Groundbreaking papers in Water Research 1967–2006. *Water Res.* **40**, 3001.

Foo, K. Y. & Hameed, B. H. 2010 Insights into the modeling of adsorption isotherm systems. *Chem. Eng. J.* **156**, 2–10.

Frederiksen, M., Vorkamp, K., Bossi, R., Riget, F., Dam, M. & Svensmark, B. 2007 Method development for simultaneous analysis of HBCD, TBBPA, and dimethyl-TBBPA in marine biota from Greenland and the Faroe Islands. *Int. J. Environ. Anal. Chem.* **87**, 1095–1109.

Gao, J. P., Maguhn, J., Spitzauer, P. & Kettrup, A. 1997 Sorption of pesticides in the sediment of the Teufelsweiher pond (Southern Germany). I: equilibrium assessments, effect of organic carbon content and pH. *Water Res.* **32** (5), 1662–1672.

Hadi, M., Samarghandi, M. R. & McKay, G. 2010 Equilibrium two-parameter isotherms of acid dyes sorption by activated carbons: study of residual errors. *Chem. Eng. J.* **160** (2), 408–416.

Islam, M. S., Zhou, H. & Zytner, R. G. 2014 Comparison of behaviour and fate of tetrabromobisphenol A (TBBPA) in membrane bioreactors and conventional activated sludge process. *J. Water Reuse Desal.* **4** (3), 164–173.

Karickhoff, S. W. 1981 Semi-empirical estimation of sorption of hydrophobic pollutants on natural sediments and soils. *Chemosphere* **10** (8), 833–846.

Karickhoff, S. W., Brown, D. S. & Scott, T. A. 1979 Sorption of hydrophobic pollutants on natural sediments. *Water Res.* **13**, 241–248.

Kerr, K. M., Larson, R. J. & McAvoy, D. C. 2000 Evaluation of an inactivation procedure for determining the sorption of organic compounds to activated sludge. *Ecotoxicol. Environ. Safety* **47**, 314–322.

Kokkola, H., Yli-Pirila, P., Vesterinen, M., Korhonen, H., Keskinen, H., Romakkaniemi, S., Hao, L., Kortelainen, A., Joutsensaari, J., Warsnop, D. R., Virtanen, A. & Lehtinen, K. E. J. 2014 The role of low volatile organics on secondary organic aerosol formation. *Atmos. Chem. Phys.* **14** (3), 1689–1700.

Labadie, P., Tlili, K., Alliot, F., Bourges, C., Desportes, A. & Chevreuili, M. 2010 Development of analytical procedures for

trace-level determination of polybrominated diphenyl ethers and tetrabromobisphenol A in river water and sediment. *Anal. Bioanal. Chem.* **396**, 865–875.

Langmuir, I. 1916 The constitution and fundamental properties of solids and liquids. Part I: solids. *J. Am. Chem. Soc.* **38** (11), 2221–2295.

Lee, H. B. & Peart, T. E. 2002 Organic contaminants in Canadian municipal sewage sludge. Part I. Toxic or endocrine-disrupting phenolic compounds. *Water Qual. Res. J. Can.* **37**, 681–696.

McPhedran, K., Seth, R., Song, M., Chu, S. & Letcherolo, R. J. 2013 Fate and mass balances of triclosan (TCS), tetrabromobisphenol A (TBBPA) and tribromobisphenol A (tri-BBPA) during the municipal wastewater treatment process. *Water Qual. Res. J. Can.* **48** (3), 255–265.

Paska, O. M., Pacurariu, C. & Muntean, S. G. 2014 Kinetic and thermodynamic studies on Methylene Blue biosorption using corn-husk. *RSC Adv.* **4**, 62621–62630.

Samarghandi, M. R., Hadi, M., Moayedi, S. & Askari, F. B. 2009 Two-parameter isotherms of methyl orange sorption by pinecone derived activated carbon. *Iran J. Environ. Health Sci. Eng.* **6** (5), 285–294.

Schnoor, J. L. 1996 *Environmental Modeling: Fate and Transport of Pollutants in Water, Air, and Soil.* John Wiley & Sons, New York, USA.

Schwarzenbach, P. R. & Westall, J. 1981 Transport of nonpolar organic compounds from surface water to groundwater. Laboratory sorption studies. *Environ. Sci. Technol.* **15** (11), 1360–1367.

Schwarzenbach, P. R., Gschwend, P. M. & Imboden, D. M. 2003 *Environmental Organic Chemistry*, 2nd edn. Wiley, New York, USA.

Site, A. D. 2001 Factors affecting sorption of organic compounds in natural sorbent/water systems and sorption coefficients for selected pollutants. *J. Phys. Chem. Ref. Data* **30** (1), 188–439.

Srinivasan, A. & Viraraghavan, T. 2010 Decolorization of dye wastewaters by biosorbents: A review. *J. Environ. Manage.* **91**, 1915–1929.

Struijs, J., Stroltenkamp, J. & Van de Meent, D. 1991 A spreadsheet-based box model to predict the fate of xenobiotics in a municipal wastewater treatment plant. *Water Res.* **25** (7), 891–900.

Sun, Z., Yu, Y., Mao, L., Feng, Z. & Yu, H. 2008 Sorption behavior of tetrabromobisphenol A in two soils with different characteristics. *J. Hazard. Mater.* **160**, 456–461.

Thomsen, M., Arias, P., Sjodin, A. & Bergman, A. 2002 An overview of commercially used brominated flame retardants, their application, their use patterns in different countries/regions and possible modes of release. *Environ. Int.* **29**, 683–689.

Tsai, W., Hsu, H., Su, T., Lin, K. & Lin, C. 2006 Adsorption characteristics of bisphenol-A in aqueous solutions onto hydrophobic zeolite. *J. Coll. Interf. Sci.* **299**, 513–519.

US EPA 1996 *Fate, Transport and Transformation Guidelines – Activated Sludge Sorption Isotherm. Prevention, Pesticide and Toxic Substances.* EPA-712-C-98-298. US Environmental Protection Agency, Washington, DC, USA.

Vijayaraghavan, K. & Yun, Y.-S. 2008 Bacterial biosorbents and biosorption. *Biotechnol. Adv.* **26**, 266–291.

Wang, L. & Govind, R. 1993 Sorption of toxic organic compounds on wastewater solids: mechanism and modeling. *Environ. Sci. Technol.* **27** (1), 152–158.

Wong, Y. C., Szeto, Y. S., Cheung, W. H. & McKay, G. 2004 Adsorption of acid dyes on chitosan-equilibrium isotherm analyses. *Process Biochem.* **39**, 693–702.

Xia, X. R., Baynes, R. E., Monterio-Reviere, N. A. & Reviere, J. E. 2005 Determination of the partition coefficients and absorption kinetic parameters of chemicals in a lipophilic membrane/water system by using a membrane-coated fiber technique. *Eur. J. Pharm. Sci.* **24**, 15–23.

Yu, Y., Zhuang, Y. Y., Wang, Z. H. & Qiu, M. Q. 2004 Adsorption of water-soluble dyes onto modified resin. *Chemosphere* **54**, 425–430.

Zhou, L., Ji, L., Ma, P., Shao, Y., Zhang, H., Gao, W. & Li, Y. 2014 Development of carbon nanotubes/$CoFe_2O_4$ magnetic hybrid material for removal of tetrabromobisphenol A and Pb(II). *J. Hazard. Mater.* **265**, 104–114.