Modeling the transport of sodium dodecyl benzene sulfonate in riverine sediment in the presence of multi-walled carbon nanotubes

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Abstract

The environmental risks of carbon nanotubes have received considerable attention. In this work, the effects of multi-walled carbon nanotubes (MWCNTs) on the adsorption of sodium dodecyl benzene sulfonate (SDBS) by riverine sediment and the transport of SDBS in sediment were studied. MWCNTs could significantly increase the adsorption capacity of the sediment for SDBS, thus affecting the transport of SDBS in sediment. Maximum adsorption capacity of the sediment for SDBS increases from 2.29 to 2.99 mg/g with the increasing content of MWCNTs from 0% to 1.5%. Breakthrough curves (BTCs) of SDBS obtained from the column experiments were described by the convection-dispersion equation, Thomas model, and Yan model. The estimated retardation factor R increases with the incorporation of MWCNTs, either in water or sediment. Additionally, the value of R is well correlated to the content of MWCNTs in sediment. Compared with Thomas model, Yan model is more suitable for fitting the BTCs with all the values of $R^2 \geq 0.951$, but it tends to overestimate the maximum adsorption capacity when the content of MWCNTs in sediment is relatively higher. The results of SDBS retention in sediment indicate that MWCNTs can increase the accumulation of SDBS in the top sediment layer, while they can impede the transport of SDBS into deeper sediment layer when incorporated into the sediment. These effects should be taken into consideration for risk assessment of CNTs in the aquatic environment.

Keywords: Adsorption; Transport; Sodium dodecyl benzene sulfonate; Multi-walled carbon nanotubes; Sediment; Environmental risk

1. Introduction

Carbon nanotubes (CNTs), composed of carbon atoms in a periodic hexagonal arrangement, are hollow cylinders with a diameter in the nanometer range. Single-walled nanotubes (SWCNTs) and multi-walled nanotubes (MWCNTs) are two main types of CNTs. Since their observation was first reported by Iijima in 1991(Iijima 1991), CNTs have been attracting much attention of researchers because of their unique mechanical, thermal, optical, and electronic properties, as well as many potential applications (Popov 2004, Zhang et al. 2007, Huang et al. 2008, Tang et al. 2008, De Volder et al. 2013). Current production capacity of CNTs worldwide has exceeded 5,000 tonnes per year, and is increasing with an annual growth rate of 32.5% (Patel 2011, De Volder et al. 2013). Increasing production and application of CNTs will inevitably result in the release of these nanomaterials into the environment. In a multimedia environment (atmosphere, soil, water, and sediment), mass accumulation of CNTs was mostly in soil and sediment (Yang et al. 2010, Liu and Cohen 2014). Based on the research of Koelmans et al. (2009), the estimated concentrations of manufactured carbon-based nanoparticles in aquatic sediment are ranging from 1.2 to 2000 micrograms per kilogram of the dry sediment. And it is likely that the concentrations of CNTs in sediment will increase in the future.

CNTs have strong adsorption affinity for various organic and inorganic contaminants (Gong et al. 2009, Song et al. 2017a, Song et al. 2017b). As sediment is also the ultimate reservoir of various contaminants in aquatic ecosystem, the interaction between CNTs and contaminants may alter the fate and transport of these

contaminants, significantly influencing their mobility, toxicity, and bioavailability (Xu et al. 2012a, Zeng et al. 2013a, b, Cheng et al. 2016). For example, Sun et al. (2015) found that CNTs released into sediment would increase the adsorption capacity of Cd(II) by sediment. Fang et al. (2013) demonstrated that TX100 suspended MWCNTs could facilitate the transport of phenanthrene in soil columns, while Li et al. (2013) reported that 5 mg/g CNTs could significantly retain polycyclic aromatic hydrocarbons in soil. Recent research by Liang et al. (2016) showed that CNTs could enhance the mobility of tetrabromobisphenol A in saturated porous media. Zhang et al. (2017) also observed facilitated transport of chlordecone and sulfadiazine in the presence of CNTs in soil. However, studies investigating the effect of CNTs on the transport of contaminants in real riverine sediment were insufficient.

Since sodium dodecyl benzene sulfonate (SDBS) is commonly used to increase the dispersity and stability of CNTs in aqueous solutions, most of the current studies focused on the effect of SDBS on the properties, transport, and fate of CNTs (Tian et al. 2011, Ju et al. 2012, Wusiman et al. 2013). However, few studies investigated the effect of CNTs on the transport and fate of SDBS. As an anionic surfactant, SDBS is usually present in detergent, soap, as well as cosmetic, and widely used as emulsifier, dispersant, lubricant, and preservative in industrial processes (Myers 2005, Taffarel and Rubio 2010). Because of its extensive applications, a large amount of SDBS is released into the aquatic environment, causing serious environmental problems. The adverse effects of the surfactant on the aquatic environment and human health have been studied and reported elsewhere. According to the available literature, SDBS

exhibits toxic effects towards algae, benthic invertebrates, fishes, and human cells (Qv and Jiang 2013, Mu et al. 2014, Zhang et al. 2015, Zhang et al. 2016). Considering the ecological and human health risks of SDBS, the environmental behavior of SDBS in the presence of CNTs in the aquatic environment should be studied.

In this study, research on the transport of SDBS in riverine sediment in the presence of MWCNTs was conducted. The objectives of the present study were (1) to investigate the effect of MWCNTs on the adsorption of SDBS by sediment, and (2) to study the transport of SDBS in the presence and absence of MWCNTs in riverine sediment by column experiments and numerical modeling.

2. Materials and methods

2.1. Chemicals, sediment, and carbon nanotubes

SDBS ($C_{18}H_{29}NaO_3S$, AR) was purchased from Sinopharm Chemical Reagent Co., Ltd., Shanghai, China. All other reagents in this study were of analytical grade or better and commercially available. Surface sediment samples (0−15 cm) were collected from Changsha section of the Xiangjiang River in Hunan Province, China. Sediment samples were air-dried at room temperature and then crushed in a porcelain mortar. Subsequently, the samples were sieved over a one mm mesh sieve and homogenized prior to use. Sediment properties including pH, zeta potential, electrical conductivity, organic carbon content, cation exchange capacity, and texture (sand, silt, and clay) were measured with the methods mentioned in previous literature (Song et

al. 2017b). Industrial grade MWCNTs with an outer diameter of 10−20 nm and a length of 5−10 μm were used in this study. They were purchased from Chengdu Organic Chemistry Co., Chinese Academy of Sciences, Chengdu, China.

2.2. Batch adsorption experiments

Kinetics experiments of SDBS adsorption onto MWCNTs, sediment, and sediment-MWCNTs mixtures (content of MWCNTs in sediment, w/w: 0.5%, 1.0%, and 1.5%) were performed in 250 mL conical flasks containing 20 mg/L SDBS on a shaker at 180 rpm, 25 ± 1 °C. Absorbent dosage of MWCNTs was 0.3 g/L, while the dosages of sediment, and sediment-MWCNTs were both 20 g/L. The samples were taken out from the flask after predetermined time intervals (from 30 s to 300 min), and the concentrations of SDBS were determined by high performance liquid chromatography (HPLC, Agilent 1100, USA) equipped with UV-vis variable wavelength detector (VWD) and reversed-phase C18 column. Methanol (90%, v/v) was used as the mobile phase at a flow rate of 1 mL/min with constant detection wavelength at 224 nm.

Adsorption isotherm experiments were conducted in conical flasks containing SDBS solutions of different concentrations (from 10 to 80 mg/L) on a shaker at 180 rpm, 25 ± 1 °C. The dosages of absorbents were the same as those in kinetics experiments. After a 2 h equilibrium, samples were taken out and the concentrations of SDBS were determined by the above-mentioned analytical method of HPLC.

2.3. Column experiments

Column transport experiments of SDBS in various sediment columns were carried out under saturated flow conditions. A Teflon column with a length of 300 mm and an inner diameter of 24 mm was used in the experiments. The column packing was based on previously reported methods with appropriate modifications (Zhuang et al. 2003, Tričković et al. 2016). Concretely, a stainless steel wire mesh with pore size of 0.14 mm was placed at the bottom of the column, and then a quartz sand (25−50 mesh) layer of 10 mm was added for supporting the sediment particles. Subsequently, ultrapure water was introduced into the column from the bottom to a certain height with a peristaltic pump (DDB-300, Zhisun Equipment Co., Ltd., Shanghai, China). After that, sediment was slowly poured into the column by 5−6 mm increments until the column was packed to a height of 48 mm. During the packing process, the sediment in the column was stirred with a glass rod to ensure homogeneous packing and to avoid air entrapment. After the sediment column was prepared, a potassium bromide (KBr) solution was used as a conservative tracer for characterizing the sediment column and the hydraulic conditions.

Two sets of column transport experiment, denoted as Set I and Set II, were conducted. In Set I, 50 mg/L SDBS, 50 mg/L SDBS containing 0.3 g/L MWCNTs (reached adsorption equilibrium in advance), and 32 mg/L SDBS (an equilibrium concentration of 50 mg/L SDBS containing 0.3 g/L MWCNTs) were pumped respectively to the top of the sediment columns. For Set II, sediment in the column was mixed with MWCNTs, and the contents of MWCNTs were 0.5%, 1.0%, and 1.5%

152 (w/w), respectively. In this set, 50 mg/L SDBS solutions were pumped to the columns
153 by peristaltic pump and transported from the top down. The duration of each column
154 transport experiment was 24 h for both Set I and Set II. During the column
155 experiments, a constant water head of 150 mm was maintained and the effluent was
156 collected at regular intervals for the measurement of SDBS concentrations.

157 At the end of the column experiment, sediment in the column was air-dried and
158 equally divided into 6 segments. Then SDBS concentrations in these segments were
159 analyzed based on previously reported method (Santos et al. 2007). In short, SDBS in
160 the sediment was extracted with methanol. For each extraction, 20 mL methanol was
161 added into the beaker containing the sediment, followed by shaking the beaker on a
162 shaker for 5 min. Afterwards, the sample was sonicated for 30 min and then
163 centrifuged to collect the supernatants. After filtered through 0.45 μm filter membrane,
164 the SDBS concentration in the filtrate was determined by HPLC.

165

166 *2.4. Numerical modeling*

167 The obtained data of adsorption kinetics were fitted with pseudo-first-order
168 kinetic model and pseudo-second-order kinetic model. The models are given by the
169 following equations (Hu et al. 2011, Xu et al. 2012b):

170 $$\ln(q_e - q_t) = \ln q_e - k_1 t \quad \text{(Pseudo-first-order kinetic model)} \tag{1}$$

171 $$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad \text{(Pseudo-second-order kinetic model)} \tag{2}$$

172 where q_e and q_t (mg/g) are the amount of adsorbed SDBS at equilibrium and time t
173 (min), k_1 and k_2 are the first-order rate constant (1/min) and second-order rate constant

(g/(mg min)), respectively.

Experimental results of the adsorption isotherms were described by Langmuir and Freundlich models, which are represented by the following equations (Hu et al. 2011, Xu et al. 2012b):

$$q_e = \frac{q_m K_L c_e}{1 + K_L c_e} \quad \text{(Langmuir model)} \tag{3}$$

$$q_e = K_F c_e^{\frac{1}{n}} \quad \text{(Freundlich model)} \tag{4}$$

where q_e (mg/g) is the amount of adsorbed SDBS at equilibrium, q_m (mg/g) is the maximum adsorption capacity, K_L (L/mg) is the Langmuir constant, c_e (mg/L) is the equilibrium concentration of SDBS, K_F (mg/g(mg/L)$^{-1/n}$) and n (dimensionless) are Freundlich constants.

Breakthrough curves (BTCs) are used to indicate the transport of SDBS through sediment columns. Under the condition of steady flow, the BTCs can be described by the convection-dispersion equation (CDE). BTC of the tracer (Br^-) is fitted with deterministic equilibrium CDE (Toride et al. 1995), which is written as

$$R\frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial x^2} - v\frac{\partial c}{\partial x} \tag{5}$$

where c (mg/L) is the Br^- concentration in effluent, R (dimensionless) is the retardation factor, D (cm^2/h) is the dispersion coefficient, v (cm/h) is the average pore water velocity, x (cm) is distance, and t (h) is time. Based on the assumption that Br^- is nonreactive and can not be adsorbed onto sediment (R = 1), the estimated D and v by the equilibrium CDE are 3.35 cm^2/h and 4.73 cm/h (Fig. 2a, R^2 = 0.982), respectively. These parameters are then used for understanding the dominant process

that impact the solute transport and analyzing the BTCs of SDBS transport.

The transport of SDBS in sediment can be described by a two-site chemical nonequilibrium model (TSM, a deterministic nonequilibrium CDE model), in which adsorption sites of the sediment are divided into two types: equilibrium adsorption sites and kinetic adsorption sites (Toride et al. 1995). Dimensionless form of the TSM is given by

$$\beta R\frac{\partial C_1}{\partial T}=\frac{1}{P}\frac{\partial^2 C_1}{\partial Z^2}-\frac{\partial C_1}{\partial Z}-\omega\left(C_1-C_2\right) \tag{6}$$

$$\left(1-\beta\right)R\frac{\partial C_2}{\partial T}=\omega\left(C_1-C_2\right) \tag{7}$$

$$\beta=\frac{\theta+fK_{\mathrm{d}}}{\theta+K_{\mathrm{d}}} \tag{8}$$

$$\omega=\frac{\alpha\left(1-\beta\right)RL}{v} \tag{9}$$

$$R=1+\frac{\rho_{\mathrm{b}}K_{\mathrm{d}}}{\theta} \tag{10}$$

$$T=\frac{vt}{L} \tag{11}$$

$$P=\frac{vL}{D} \tag{12}$$

$$Z=\frac{x}{L} \tag{13}$$

where β is a partitioning coefficient of equilibrium and kinetic adsorption sites, C is dimensionless concentration, T is dimensionless time, P is Peclet number, Z is dimensionless distance, ω is a dimensionless mass transfer coefficient, L (cm) represents a characteristic length, θ is volumetric water content, f is the fraction of exchange sites assumed to be at equilibrium, K_{d} is the distribution coefficient for linear adsorption, α is a first-order kinetic rate coefficient, ρ_{b} is the bulk density of sediment, and the subscripts 1 and 2 refer to equilibrium and kinetic adsorption sites,

respectively. Other symbols have the same meaning as those in Eq. (5). When fitting the BTCs of SDBS, the parameter D and v are fixed as the value obtained by the equilibrium CDE, and then the transport parameter R, β, and ω are estimated with TSM.

Thomas and Yan models are widely used for describing the adsorption process in a continuous system (Valizadeh et al. 2016). In this study, they are applied for modeling the BTCs concerning SDBS adsorption. The models are given by the following equations:

$$\frac{c}{c_0} = \frac{1}{1+\exp\left(\frac{K_T q_T m}{Q} - K_T c_0 t\right)} \quad \text{(Thomas model)} \tag{14}$$

$$\frac{c}{c_0} = 1 - \frac{1}{1+\left(\frac{Q^2 t}{K_Y q_Y m}\right)^{\left(\frac{K_Y c_0}{Q}\right)}} \quad \text{(Yan model)} \tag{15}$$

where c (mg/L) is the SDBS concentration in effluent, c_0 (mg/L) is the SDBS concentration in influent, K_T (L/h/mg) is the Thomas rate constant, K_Y (L/h/mg) is the Yan rate constant, m (g) is the mass of adsorbent, Q (L/h) is the influent flow rate, t (h) is time, and q_T (mg/g) and q_Y (mg/g) are the maximum adsorption capacity estimated by Thomas model and Yan model, respectively. Yan model is an empirical formula that overcomes some deficiencies of Thomas model, especially that of the prediction of solute concentration in effluent near time zero.

OriginPro 9.1 software (OriginLab Corporation, Massachusetts, USA) was used to fit the adsorption models and BTC models concerning SDBS adsorption. Fitting of BTC models concerning transport parameters was performed with the program

236 CXTFIT 2.0 executed in the software STANMOD (version 2.08) (Toride et al. 1995,
237 Simunek et al. 1999).
238
239 **3. Results and discussion**
240
241 *3.1. Characterization of the sediment and MWCNTs*
242 The measured pH value, organic carbon content, cation exchange capacity, zeta
243 potential, and electrical conductivity of the sediment are 7.92, 1.63%, 10.8 cmol/kg,
244 −18.4 mV, and 0.144 mS/cm, respectively. Additionally, the sediment sample has a
245 composition of 23.4% sand, 27.6% silt, and 49.0% clay. MWCNTs used in this study
246 were characterized by scanning electron microscope (SEM) and specific surface
247 analyzer. Typical tubular structure of the MWCNTs was observed with SEM images
248 shown in Fig. S1. According to the specific surface analysis, Brunauer-Emmett-Teller
249 (BET) specific surface area of the MWCNTs is 134 m^2/g.
250
251 *3.2. Effect of MWCNTs on the adsorption of SDBS by sediment*
252 The MWCNTs significantly influenced the adsorption of SDBS by sediment. As
253 shown in Fig. 1, the adsorption amount of SDBS increases with the increase of time.
254 The whole process of adsorption can be broadly divided onto three stages. During the
255 first stage (the first 20 min), a rapid increase of the adsorption amount of SDBS is
256 observed as a result of the high concentration gradient. In the second stage (20−50
257 min), the adsorption amount increases slowly until the arrival of the last stage (>50

min). The maximum adsorption amount is reached at the last stage, and the adsorption gets to an equilibrium state. Compared with the adsorption by sediment, the adsorption amount of SDBS by MWCNTs increases more quickly in the first stage.

Parameters of the fitted models for SDBS adsorption are listed in Table S1 and Table S2. It can be found that experimental data of adsorption kinetics are better fitted by pseudo-second-order kinetic model ($R^2 \geq 0.911$) than pseudo-first-order kinetic model ($R^2 \geq 0.828$). Such result indicates that rate-limiting step of the adsorption processes is a chemical adsorption in which valence forces generated by exchanging or sharing electrons are involved (Fan et al. 2008, Feng et al. 2010, Xu et al. 2012b). Langmuir and Freundlich models could be well used to fit the isotherm data with all the values of $R^2 \geq 0.926$. The estimated q_m of MWCNTs for SDBS adsorption is 115 mg/g, which is much more than that of sediment (2.29 mg/g). This could be due to the specific molecular structure of SDBS. On the one hand, the strong π-π electron-donor-acceptor interaction between the benzene ring of SDBS molecule and the highly polarizable graphene sheets of MWCNTs can facilitate the adsorption processes (Lin et al. 2015). On the other hand, the hydrophobic tail (12-carbon alkyl chain) of SDBS may be bound to the surface of MWCNTs through hydrophobic attraction (Lin et al. 2010). Additionally, the values of q_m (from 2.29 to 2.99 mg/g) and K_F (from 0.0713 to 0.844 mg/g $(mg/L)^{-1/n}$) increase with the increasing content of MWCNTs in sediment (from 0% to 1.5%), implying that the adsorption capacity of sediment for SDBS was enhanced as a result of the incorporation of MWCNTs.

3.3. Effect of MWCNTs on the transport of SDBS in sediment

3.3.1. Analysis and modeling of the BTCs concerning transport parameters

The experimental and CDE fitting results of SDBS transport through sediment columns in Set I and Set II are shown in Fig. 2, and associated parameters estimated by the model are listed in Table 1. It is observed from the table that the experimental data are well fitted by TSM with all the values of $R^2 \geq 0.927$. However, the equilibrium CDE is not suitable for describing the BTCs of SDBS (data not shown). Retardation factor R is a derived parameter to quantify the slowing down of solute transport. In the experimental results of Set I, a lower value of R (5.10) is obtained with an initial SDBS concentration of 50 mg/L, while the value of R increases to 5.62 with an initial SDBS concentration of 32 mg/L. Thus, it can be regarded that a slightly higher concentration of SDBS is able to overcome part of the mass transfer resistance, resulting in a lower value of R. Similar results can be found in previous literature (Fonseca et al. 2009, Florido et al. 2010). Considering the surfactant characteristic of SDBS, the effect of the critical micelle concentration (CMC) on the transport of SDBS were investigated (Fig. S2). We determined the CMC of SDBS through conductivity measurement, and the result is 1.72 mmol/L (599.16 mg/L). Thus, SDBS aqueous solutions with three different concentrations (200, 600, and 1000 mg/L) were used and transported through the sediment columns. Compared with 32 and 50 mg/L SDBS, higher SDBS concentration near CMC leads to an increase in R value (> 5.62), and the value decreases with the increasing SDBS concentration (11.3, 7.00, and 5.91). When SDBS concentration increases but is below the CMC, the surfactant may

increase the dispersion of colloidal-size sediment particles, leading to sediment pore clogging. And when the concentration up to the CMC, clay-size sediment particles can be trapped in the SDBS micelles and cannot settle out of the solution (Abdul et al. 1990). Using 50 mg/L SDBS containing 0.3 g/L MWCNTs as the influent significantly increases calculated R to 37.0 (c_0 = 50 mg/L). This is mainly because of the strong adsorption affinity of MWCNTs towards SDBS.

Partitioning coefficient β and mass transfer coefficient ω can be used for evaluating the validity of equilibrium assumption for the transport conditions (Pang and Close 1999). When $\beta = 1$, the transport is under an equilibrium condition and all the adsorption sites are instantaneous. When $0 < \beta < 1$, a nonequilibrium condition exists and there are some rate-limited adsorption sites. A higher value of ω corresponds to faster adsorption of the solute during transport process, and when $\omega \geq 100$, the transport is considered to be under an equilibrium condition (Pang and Close 1999). The calculated values of β for Set I (Table 1) indicated that more than 80% of the adsorption sites were rate-limited and less than 10% of the adsorption sites were instantaneous. The lower values of β ($\beta < 0.196$) and ω ($\omega < 9.53$) in the experiment results of Set I provide evidence for the nonequilibrium transport of SDBS in the sediment columns. Additionally, it is interesting that the calculated R, β, and ω for the influent with 50 mg/L SDBS containing 0.3 g/L MWCNTs (c_0 = 32 mg/L) are very similar to those obtained with 32 mg/L SDBS as influent when using the equilibrium concentration as initial concentration for modeling. We assume that the SDBS in the influent can be divided into an adsorbed part and a free part. Based on the above

result, only the free part participated in the transport, while the adsorbed part deposited with MWCNTs on the top of the sediment column. The result also shows that the adsorption affinity between SDBS and MWCNTs is relatively stronger and SDBS is not easy to be desorbed from MWCNTs under natural conditions.

In the results of Set II in Table 1, retardation factor increases (from 5.10 to 92.6) with the increasing content of MWCNTs in sediment (from 0% to 1.5%). This is mainly because of the strong adsorption affinity of MWCNTs for SDBS. After the incorporation of MWCNTs into sediment, there is a consequential increase in the resistance of SDBS transport through the sediment columns. Retardation factor can also be estimated using Eq. (10) based on the batch adsorption experiments (Zhang et al. 2011). The calculated values of R are 39.66, 70.44, 106.5, and 182.2, which correspond to the MWCNTs content in sediment of 0%, 0.5%, 1.0%, and 1.5%, respectively (Table S3). It is found that the R values determined through the batch adsorption experiments are higher than those determined from the column experiments. Nonetheless, the changing trends are consistent. The difference could be due to a shorter retention time in column experiments (Pang and Close 1999).

3.3.2. Analysis and modeling of the BTCs concerning SDBS adsorption

Results of analysis and modeling of the BTCs concerning SDBS adsorption are shown in Fig. 3 and Table 2. Thomas model can well fit most BTCs except that using the influent of 50 mg/L SDBS containing 0.3 g/L MWCNTs and modeling with 50 mg/L as the initial concentration (R^2 = 0.752). Compared with Thomas model, Yan

model is more suitable for fitting the BTCs with all the values of $R^2 \geq 0.951$. In the experiment results of Set I, q_T and q_Y increase with the incorporation of MWCNTs in influent, while the rate constant K_T and K_Y vary inversely. For the influent with 50 mg/L SDBS containing 0.3 g/L MWCNTs (c_0 = 32 mg/L), the modeling results are also similar to those obtained with 32 mg/L SDBS as influent, which further confirms the foregoing conclusion. For Set II, 50 mg/L SDBS can completely (c/c_0 = 1) break through the sediment column without MWCNTs in about 12 hours, after which the concentration of SDBS in effluent reaches a stationary value of 50 mg/L. When MWCNTs were incorporated into the sediment, the transport of SDBS in sediment column was much slower. For sediment columns incorporated with 0.5%, 1.0%, and 1.5% MWCNTs, the values of c/c_0 are calculated to be 0.66, 0.25, and 0.09 after 24 hours, respectively (Fig. 3b). A higher content of MWCNTs in sediment leads to higher values of q_T and q_Y. Most values of maximum adsorption capacity estimated by Thomas model and Yan model (Table 2) are lower than those obtained from batch adsorption tests (Table S2) because of a shorter retention time. However, when the content of MWCNTs in sediment increase to 1.5%, the value of q_Y is estimated to be 9.96 mg/g, which is much higher than that (2.99 mg/g) obtained from the batch adsorption tests. The result suggests that Yan model tends to overestimate the maximum adsorption capacity when the content of MWCNTs in sediment is relatively higher. The rate constant K_T and K_Y, which characterize the rate of SDBS transfer from the liquid to sediment, decrease with the increase in content of MWCNTs in sediment. The lower values of rate constants indicate a greater decrease of the

adsorption rate with the increase of time due to fewer unoccupied adsorption sites (Shahbazi et al. 2011).

3.3.3. Retention of SDBS in sediment

MWCNTs have a remarkable influence on the retention of SDBS in sediment (Fig. 4). Under natural conditions, SDBS can be intercepted during the transport process due to mechanical resistance, adsorption, complexation, gravity sedimentation, etc. For influent with 50 mg/L SDBS, the final concentrations of SDBS in sediment segments from the top to the bottom are 0.39, 0.37, 0.37, 0.36, 0.27, 0.22 mg/g, respectively (Fig. 4a). For influent with 32 mg/L SDBS, the concentrations of SDBS in corresponding sediment segments decrease slightly. For example, SDBS concentrations of the top and the bottom segments are 0.35 and 0.19 mg/g, respectively. When MWCNTs were incorporated into the influent, transport of SDBS through the sediment column became more difficult. The adsorbed SDBS deposited with MWCNTs on the top of the sediment column, resulting in a high concentration of SDBS (1.96 mg/g) in the top sediment segment. For Set II, the concentrations of SDBS in the top segments are 0.39, 0.62, 0.82, and 1.10 mg/g, while those in the bottom segments are 0.22, 0.13, 0.09, and 0.07 mg/g when the contents of MWCNTs in sediment columns are 0%, 0.5%, 1.0%, and 1.5%, respectively (Fig. 4b). These results indicate that MWCNTs can increase the accumulation of SDBS in the top sediment layer, either in water or sediment. On the other hand, MWCNTs in sediment can impede the transport of SDBS into deeper sediment layer. This is mainly because

of strong adsorption affinity of MWCNTs for SDBS and low mobility of MWCNTs in riverine sediment.

Nevertheless, some previous studies reported the facilitated transport of contaminants in the presence of MWCNTs (Fang et al. 2013, Zhang et al. 2017). The different results can be attributed to that the MWCNTs were pretreated before the column experiments and the size of particles in porous media was relatively larger in these studies. As a result, MWCNTs showed high mobility in these porous media, leading to the co-transport of contaminants with MWCNTs. In our study, the MWCNTs used in the experiments showed no macroscopic transport in the riverine sediment, thus they impeded the transport of SDBS in sediment due to the increase of adsorption capacity of the sediment incorporated with MWCNTs.

3.4. Environmental implications

The release of CNTs into sediment can significantly influence the adsorption behaviors of SDBS by sediment and the transport of SDBS in sediment. The q_m, q_T, q_Y, R estimated from the column experiments and the batch adsorption experiments, and retention amount of SDBS in sediment increased after the incorporation of CNTs. Relationships between the content of MWCNTs in sediment and these parameters were analyzed. The Pearson's correlation coefficients were calculated to be 0.957, 0.992, 0.975, 0.997, 0.860, and 0.990, respectively (Table S4). The results indicate a concentration-dependent effect of MWCNTs on SDBS transport in riverine sediment. Retardation factors estimated by the column experiments can be interpreted as the

transport distance of SDBS in sediment, since R is also expressed as the ratio of the velocity of pore water to that of solute (Baik and Lee 1994). In other words, for example, when the pore water flows for a distance of 92.6 cm in the sediment incorporated with 1.5% MWCNTs, SDBS can only be transported for one centimeter (R = 92.6). Although the ecological risks of CNTs are not fully understood, the retention of SDBS may increase the ecotoxicity of CNTs to the aquatic organisms due to the toxicity of SDBS and the prolonged contact time.

4. Conclusions

In this work, the effects of MWCNTs on the adsorption and transport of SDBS in riverine sediment were investigated. The main conclusions are as follows:

- MWCNTs significantly increase the adsorption capacity of the sediment for SDBS, thus affecting the transport of SDBS in sediment.
- The retardation factor R estimated by the CDE model increases with the incorporation of MWCNTs, either in water or sediment. Additionally, the value of R is well correlated to the content of MWCNTs in sediment.
- Compared with Thomas model, Yan model is more suitable for fitting the BTCs with all the values of $R^2 \geq 0.951$, but it tends to overestimate the maximum adsorption capacity when the content of MWCNTs in sediment is relatively higher.
- MWCNTs can increase the accumulation of SDBS in the top sediment layer, while they can impede the transport of SDBS into deeper sediment layer when incorporated into the sediment. Further studies on the potential ecological impacts

of CNTs and their mechanisms should be conducted.

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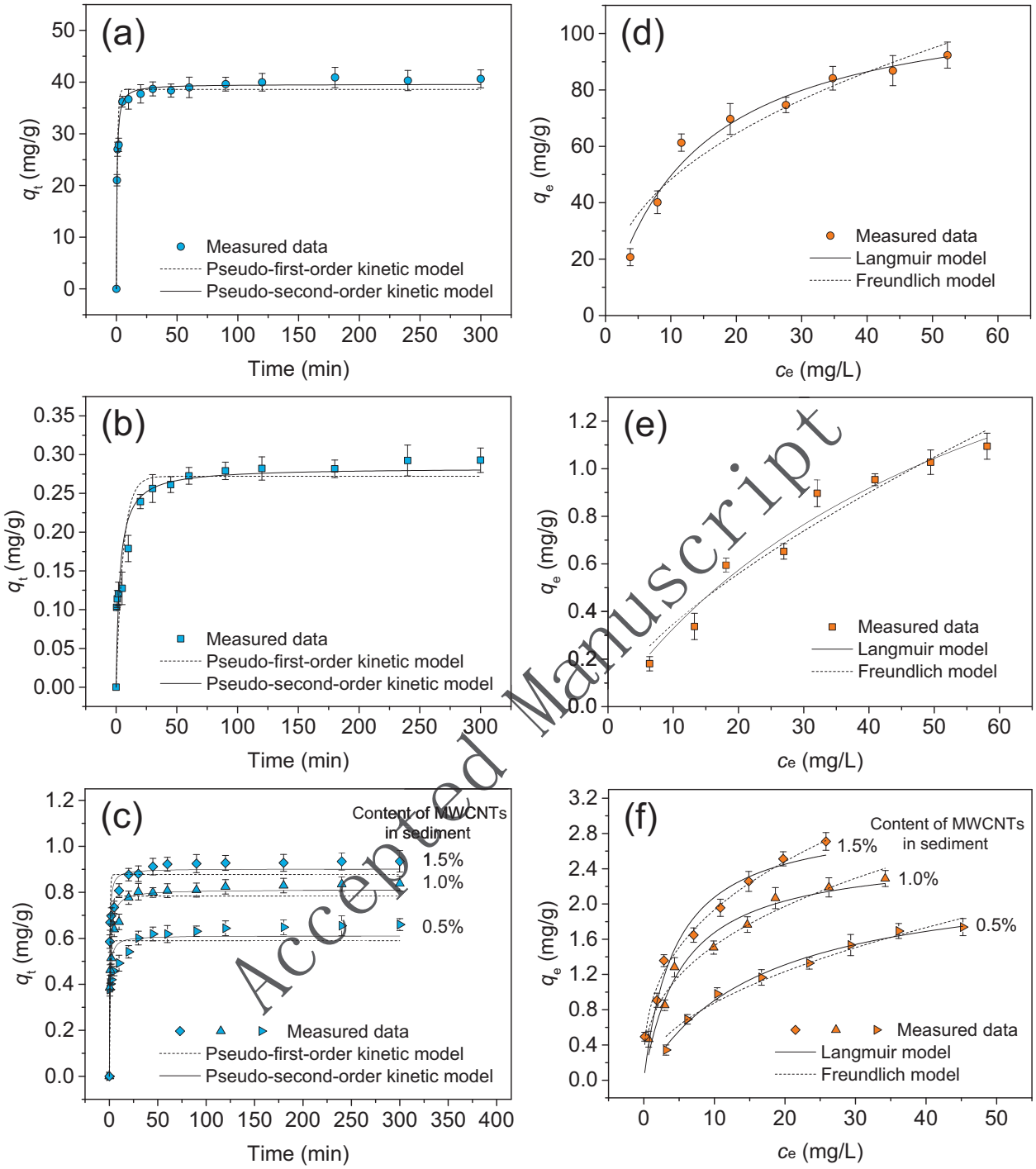
605 **Figure 1**

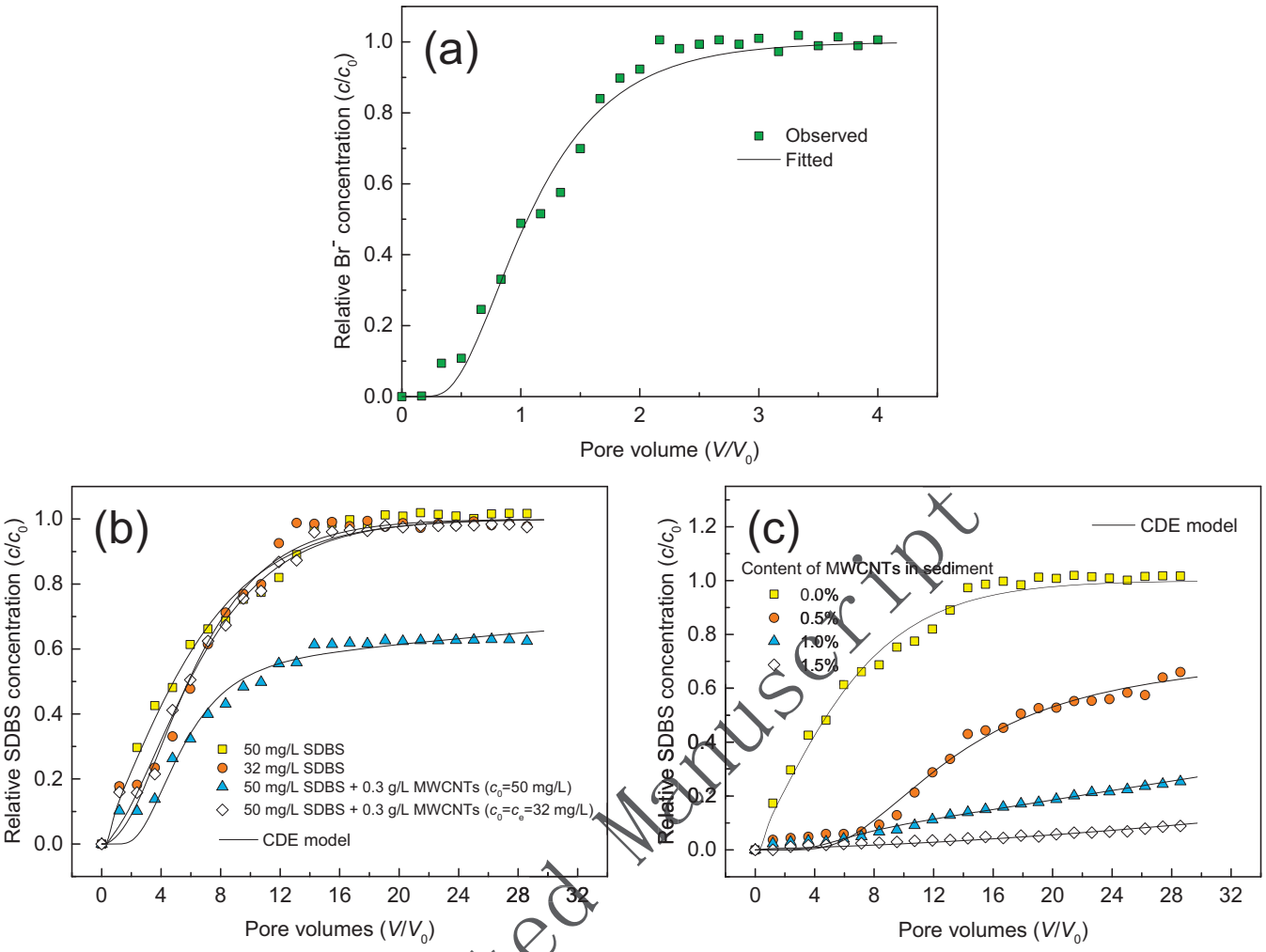


606 **Fig. 1.** Kinetic (a, b, and c) and isotherm (d, e, and f) studies of SDBS adsorption onto

607 MWCNTs (a and d), sediment (b and e), and sediment-MWCNTs mixtures (c and f).

608

609 **Figure 2**



610

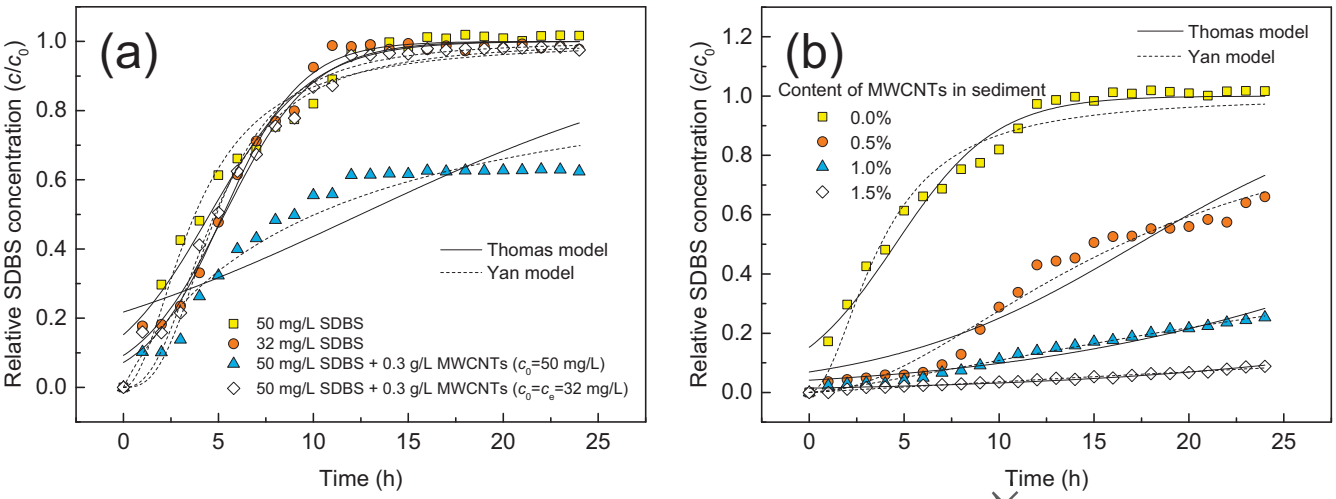
611 **Fig. 2.** Br^- breakthrough curve fitted with deterministic equilibrium CDE model (a)

612 and SDBS breakthrough curves fitted with deterministic nonequilibrium CDE model

613 (two-site chemical nonequilibrium model) for Set I (b) and Set II (c).

614

615 **Figure 3**

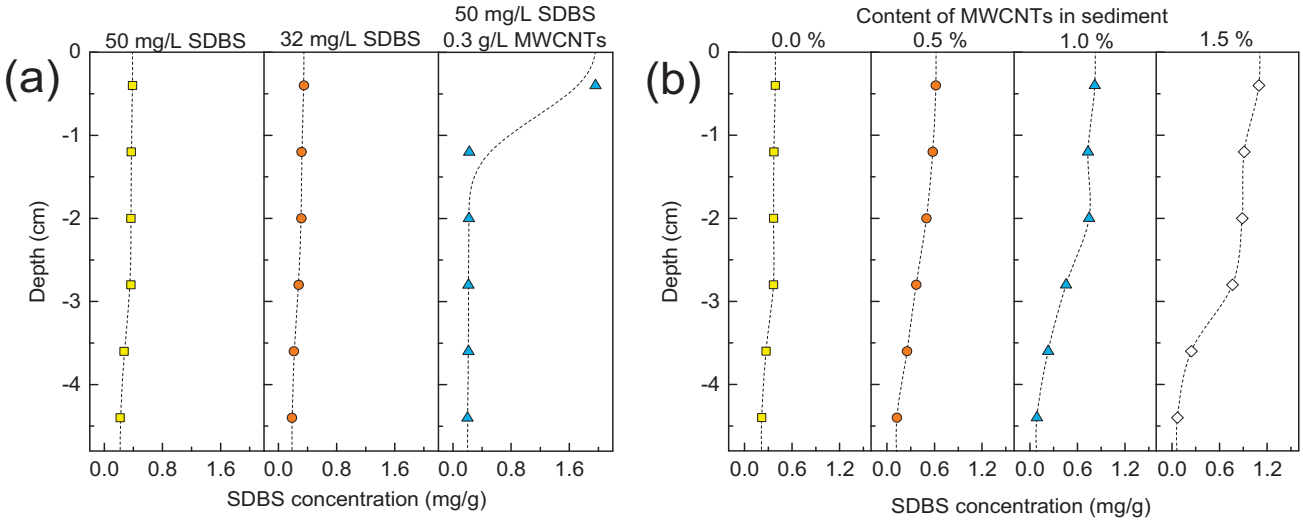


616 **Fig. 3.** SDBS breakthrough curves fitted with Thomas and Yan models for Set I (a)

617 and Set II (b).

618

619 **Figure 4**



620 **Fig. 4.** Retention profiles of SDBS in sediment columns for Set I (a) and Set II (b).

621

Table 1

Parameters of the two-site chemical nonequilibrium model for fitting breakthrough curves of SDBS.

		R	β	ω	R^2
Set I	Influent				
	50 mg/L SDBS	5.10	0.196	3.12	0.981
	32 mg/L SDBS	5.62	0.178	9.53	0.977
	50 mg/L SDBS + 0.3 g/L MWCNTs (c_0=50 mg/L) [a]	37.0	0.155	0.646	0.966
	50 mg/L SDBS + 0.3 g/L MWCNTs (c_0=c_e=32 mg/L) [b]	5.78	0.173	6.22	0.989
Set II	Content of MWCNTs in sediment (%, w/w)				
	0.0	5.10	0.196	3.12	0.981
	0.5	42.7	0.313	0.518	0.983
	1.0	60.6	0.158	3.53	0.980
	1.5	92.6	0.0108	10.3	0.927

[a] Using 50 mg/L as the initial concentration of SDBS for fitting the data.

[b] Using 32 mg/L (the equilibrium concentration) as the initial concentration of SDBS for fitting the data.

Table 2

Parameters of Thomas and Yan models for fitting breakthrough curves of SDBS.

		Thomas model			Yan model		
		$K_T \times 10^{-3}$ (L/h/mg)	q_T (mg/g)	R^2	$K_Y \times 10^{-3}$ (L/h/mg)	q_Y (mg/g)	R^2
Set I	Influent						
	50 mg/L SDBS	7.56	0.170	0.975	0.582	0.0730	0.962
	32 mg/L SDBS	15.2	0.126	0.992	1.32	0.0419	0.975
	50 mg/L SDBS + 0.3 g/L MWCNTs (c_0=50 mg/L) [a]	2.05	0.469	0.752	0.291	0.390	0.951
	50 mg/L SDBS + 0.3 g/L MWCNTs (c_0=c_e=32 mg/L) [b]	13.4	0.128	0.988	1.14	0.0474	0.985
Set II	Content of MWCNTs in sediment (%, w/w)						
	0.0	7.56	0.170	0.975	0.582	0.0730	0.962
	0.5	3.00	0.649	0.913	0.580	0.318	0.971
	1.0	1.84	1.28	0.933	0.360	1.81	0.992
	1.5	1.61	1.97	0.951	0.300	9.96	0.980

[a] Using 50 mg/L as the initial concentration of SDBS for fitting the data.

[b] Using 32 mg/L (the equilibrium concentration) as the initial concentration of SDBS for fitting the data.