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Regular Article

Carbon nanotube-impeded transport of non-steroidal anti-inflammatory drugs in Xiangjiang sediments

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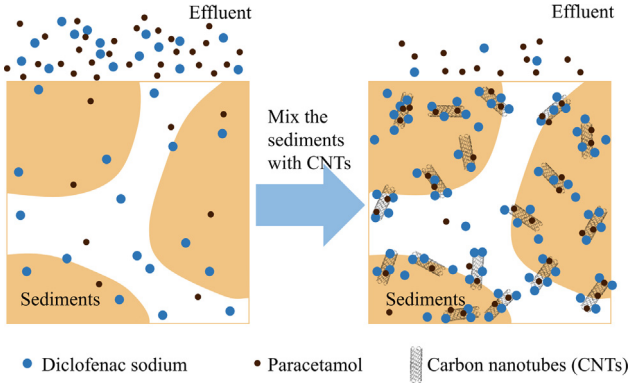
GRAPHICAL ABSTRACT



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ABSTRACT

Carbon nanotubes (CNTs), usually with a superior affinity with organic chemicals, are expected to ultimately released to the environment through their manufacturing, usage, and eventual disposal, which will influence the mobility and environmental risk of nonsteroidal anti-inflammatory drugs (NSAIDs). In this study, batch and column experiments were performed to examine the effects of two kinds of multi-walled carbon nanotubes (MWCNTs: MWCNT2040, MWCNT0815) and one kind of single-walled carbon nanotubes (SWCNTs) on the environmental fate of two NSAIDs, paracetamol (PA) and diclofenac sodium (DS), in sediments. Impact ways of CNTs including addition in inflow and mixing with sediments were investigated. The adsorption capacity of NSAIDs on sediments increased with increasing CNTs/sediments ratios and in an order of MWCNT2040 < MTWCNT0815 < SWCNT. In column tests, PA showed a higher mobility than DS. With CNTs in inflow, the amounts of NSAIDs leached from sediment columns reduced because of the association with CNTs. For the sediment columns mixed with CNTs, breakthrough of the two NSAIDs was dramatically retarded, and the NSAIDs were hard to separate from CNT-polluted sediments. Our work provides useful insights into fate, transport and risk assessment of NSAIDs in the presence of CNTs.

1. Introduction

Carbon nanotubes (CNTs) that contain one layer of rolled graphite sheet are called single-walled carbon nanotubes (SWCNTs).

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When several SWCNTs with different diameters nested together concentrically, the bundles are called multi-walled carbon nanotubes (MWCNTs) [1]. CNTs, with their high surface area to volume ratio, controlled pore size distribution, and manipulatable surface chemistry, have exceptional electrical, chemical, and physical properties, which are in turn utilized in various applications [2]. For example, polymeric materials containing CNTs are increasingly used for medical [3], aerospace, and other applications [4]. Increasing application of CNTs will inevitably lead to the release of these unique nanomaterials into the environment. However, this may result in adverse ecological risks to the organisms inhabiting in terrestrial, aquatic or sediment habitats from the aspect of either the CNTs themselves or the interaction with many other contaminants. Previous studies have demonstrated the potential health problems posed by CNTs, such as cytotoxicity, lung toxicity, and skin irritation [5]. Kennedy et al. indicated that surface modified CNTs are related to higher toxicity in *Ceriodaphnia dubia* [6]. For fish, CNT ingestion will results in the CNT precipitation in the intestinal tract and cause subtle neurotoxic or cardiovascular effects in brain as well as respiratory toxicity [7].

CNTs, mostly hydrophobic, are prone to aggregate with organic matters, suspended solids, or sediments in natural aquatic systems. Eventually, sediments are believed to be the ultimate sink of CNTs in aquatic environment [4,8]. Plenty of studies point out that CNTs have excellent adsorptive capability for organic contaminants because of their hydrophobic surfaces [9–14]. This strong adsorption affinity also largely affects the mobility, bioavailability, and environmental risk of organic chemicals [15,16]. Therefore, the released CNTs will influence the fate and impact of contaminants in the aquatic or soil environments [17].

Pharmaceuticals and personal care products (PPCPs) are labeled as emerging environmental contaminants as many of them are persistent in the body, and extensively used in human and veterinary medicine [18]. Non-steroidal anti-inflammatory drugs (NSAIDs) are one of the most prescribed pharmaceuticals detected in the environment, regarded as emerging pollutants, often prescribed for the treatment of headaches, arthritis, ankylosing spondylitis, sports injuries, and menstrual cramps. Paracetamol (PA) and diclofenac sodium (DS), belonging to NSAIDs drugs, are two of the most sold substances over the world and ubiquitously detected in effluents of sewage treatment plants (STPs), soils, surface and ground waters [19–24].

Unfortunately, as PA and DS applied in human medical care are not completely eliminated in the human body, they often make their way to representative end-points of receiving waters via incomplete treatment of human waste in STPs [25–27]. The occurrence and fate of PPCPs in the aquatic environment has been recognized as one of the emerging issues in environmental chemistry. If surface water is contaminated by PPCPs, these substances may reach the ground water by bank infiltration or artificial recharge of ground water on naturally occurring influent conditions [21]. The occurrence of the pharmaceutical compounds in surface waters has been proved to reach considerable levels (from ng/L to μg/L) in the environment [20,28–32]. They are known to cause significant renal, degenerative, and necrotic changes on vertebrates, considered potentially hazardous for the aquatic organisms and the ecosystem health [33,34]. Recently, diclofenac metabolites have been identified in fish bile [35]. Researchers found that residues of veterinary diclofenac are responsible for The Oriental white-backed vulture decline in the Indian subcontinent [33].

All in all, PA and DS as well as CNTs entering the aquatic environment may pose a threat for the ecosystem and it is critical to study and understand their fates in order to develop effective treatment and mitigation strategies [36].

To date, few data are available covering the effect of CNTs on the transport and retention of NSAIDs in sediments. We have reported that CNTs can dramatically retain sulfonamide antibiotics in sediments [37]. However, further research is needed to study the effects of CNT content on the mobility of pollutants and the effects of CNTs on the binding force between sediments and pollutants. Because of effective retention by the sediment matrix, transport of CNTs can hardly occur in the vadose zone [38]. Consequently, the CNT transport is limited in a sediment column [39]. Mechanisms of colloidal retention in saturated porous media include attachment to solid-water interface, ripening, straining, etc. Due to the exceptional adsorptive capability of CNTs, the transport behavior of NSAIDs in sediments might be changed and needs extended study to clarify the mechanisms during the transport process.

The objective of this study is to research the effects of CNTs on the transport of the two aforementioned NSAIDs through sediment columns and understand the mechanisms involved. We conducted both laboratory scale batch and column tests using Xiangjiang sediments in order to assess the mobility of the NSAIDs for the given site conditions. The dosing ways of CNTs in column tests including addition in inflow and mix with sediment columns were investigated. Results of this study will help to assess the environmental transport and ecological risks of NSAIDs affected by CNTs.

2. Materials and methods

2.1. Materials

CNTs in this study included two kinds of MWCNTs (MWCNT2040: purity > 90%, length 10–30 μm, outer diameter 20–40 nm, specific surface area 80 m^2/g; MWCNT0815: purity > 90%, length 30–50 μm, outer diameter 8–15 nm, specific surface area 230 m^2/g) and one kind of SWCNT (purity > 90%, length 5–30 μm, outer diameter 1–2 nm, specific surface area 380 m^2/g), and were purchased from Chinese academy of sciences, Chengdu Organic Chemistry Co. Ltd.. Morphological properties of the CNTs were characterized using a scanning transmission electron microscopy (STEM, Tecnai G2 F20 S-TWIX).

Paracetamol (PA) was obtained from TCI Japan (Tokyo, Japan), and diclofenac sodium (DS) were purchased from Aladdin Industrial Corporation (Shanghai, China). Both of the chemicals were in analytical grade and used directly without further purification.

2.2. Sediment sample collection and characterization

Surface sediment samples were collected from Changsha section of Xiangjiang River, the largest river in Hunan province, China. The sampled sediments were air-dried, ground and sequentially passed through a 0.9 mm sieve prior to experimental use. Sediment pH value was measured at a sediment to ultrapure water ratio of 1:2.5 (w/v) using a digital pH meter. Zeta potential was measured using a ZetaSizer Nano Series Instrument (Malvern Instrument Ltd. UK) [40]. Sediment organic matter (SOM) was quantified using the potassium dichromate volumetric method [41]. Cation-exchange capacity (CEC) of the sediments was determined by the EDTA-ammonium method [42]. Sediment texture (sand, silt and clay contents) was measured using a hydrometer method [43].

2.3. Adsorption of pharmaceuticals on CNTs, sediments and sediment-CNTs mixture

Adsorption experiments were performed in duplicates at a constant temperature of 25 °C in 50-mL glass vessels using ultrapure water as a background solution. The adsorption suspension in the vessels consisted of 25 mL background solution, 0.4 g/L CNTs or 40 g/L sediment-CNTs mixture (the CNTs/sediments ratios: 0%, 0.9%, 1.8%, and 2.7%), and NSAIDs with various concentrations

ranging from 10 to 50 mg/L. The glass vessels were kept in a thermostated shaker at a shaking speed of 225 rpm for 24 h to obtain adsorption equilibrium. A contact time of 24 h was sufficient for equilibrium based upon preliminary kinetics studies conducted over a 72 h period. After the equilibrium was achieved, the solutions were then filtered through a 0.45 μm syringe filter and the concentrations of the pharmaceuticals were analyzed by a high performance liquid chromatography (HPLC) system.

2.4. Column experiments

Breakthrough experiments of NSAIDs in the presence and absence of CNTs were performed under saturated flow conditions at room temperature (25 ± 1 °C). A Teflon column with a transport length of 6.3 cm and an inner diameter of 2.4 cm was used in this study. A stainless wire net with pore size of 75 mm as well as quartz sands were used to support the sediment particles, preventing migration of fine particles. When the column was packed, deaerated ultrapure water was introduced into the column using a peristaltic pump (LEAD-2, Baoding Longer Precision Pump Co. China) from the bottom to a certain height, and then sediments were slowly poured into the solution. During packing, the content in the column was continuously stirred with a glass rod to ensure a homogenous compaction and to avoid air entrapment in the column [44]. Subsequently, in order to establish a steady-state flow and to standardize the conditions of the experimental system, the column was leached with ultrapure water for about 10 pore volumes (PVs) until the pH value of the effluent became the same as that of the influent [40]. After that, leaching suspensions (prepared previously) were pumped into the sediment column to reach a constant water head on the top of the column, and the effluent samples were collected at discrete leaching time intervals for the measurement of pharmaceutical concentrations. The pore volume of the packed column was determined by the weight difference of the water-saturated column versus the dry column, the porosity was determined to be 0.58, and the sediment bulk density ρ_b was 1.21 g/cm^3.

Two sets of column experiments were performed according to the different CNT-dosing ways: addition in inflow and mixing with sediments. For the first set of experiments, NSAIDs-CNTs mixture (50 mg/L and 333.3 mg/L, respectively) which had reached equilibrium was pumped onto the top of the sediments columns. In the second set of experiments, sediments in the columns were mixed with different CNT contents (the CNTs/sediments ratios were 0%, 0.9%, 1.8%, and 2.7%, respectively). 50 mg/L NSAID suspensions were then steadily introduced into the columns using the peristaltic pump and transported top-down through the columns. The samples of the effluent were collected at regular time intervals and then filtered with a 0.45 μm membrane for analysis. To test the mass balance of the retained pharmaceuticals, columns were air-dried and dissected into 6 equal segments at the end of the experiment, ready for extraction. Extraction of NSAIDs was performed according to the method reported by Al-Rajab et al. [45]. In short, the segments were extracted 3 times with 15 mL of ethyl acetate. For each extraction, samples were sonicated for 30 min. Samples were then centrifuged for 10 min at 8820 × *g*. The supernatants were transferred to a clean 250 mL glass round bottle. The extract was dried down to 1.5 mL using a rotary evaporator and stored at 4 °C until HPLC analysis.

3. Results and discussion

3.1. Properties of CNTs, NSAIDs, and sediments

Each type of CNTs used in this study was different in the outer diameters, and the specific surface areas decreased with the increased outer diameters. STEM images of the used CNTs are shown in Fig. 1. The physico-chemical properties of NSAIDs are shown in Table 1, and the selected sediment properties are given in Table 2. Sediment used in this study belonged to loamy clay and contained no detectable level of NSAIDs.

3.2. Adsorption isotherms of NSAIDs

Adsorption data were fitted using the Freundlich and Langmuir isotherm models.

Freundlich isotherm model:

$$Q_e = K_F C_e^n \quad (1)$$

where Q_e is the amount of NSAIDs adsorbed (mg/g), C_e is the aqueous equilibrium concentration of NSAIDs (mg/L), K_F ((mg/g)(L/mg)^n) is the Freundlich distribution coefficient, and n is the Freundlich exponent which indicates whether the adsorption is linear.

Langmuir isotherm model:

$$Q_e = \frac{Q_{max} K_L C_e}{1 + K_L C_e} \quad (2)$$

where Q_{max} (mg/g) is the adsorption capacity and K_L (L/mg) is the Langmuir adsorption affinity parameter.

The adsorption affinity of NSAIDs between different adsorbents can be compared through a distribution coefficient K_d [46].

$$K_d = \frac{Q_e}{C_e} \quad (3)$$

The adsorption isotherms of the selected NSAIDs onto CNTs (Fig. 2), sediment (Fig. 3), and sediment-CNTs mixtures (Fig. 3) were obtained. For the tested NSAIDs, higher correlation coefficients and better fitting were observed with the Freundlich equation, which was chosen as the preferred model for further investigation (Tables 3 and 4). The Freundlich adsorption coefficients K_F reflected the affinity of each NSAID to CNTs and sediments. The Freundlich constant n is a joint measure of both the relative magnitude and diversity of energies associated with a particular adsorption process [47]. The index n = 1 indicates linear adsorption and, therefore, equal adsorption energies for all sites. Linear adsorption generally occurs at very low solute concentrations and low loading of the adsorbent. The observed nonlinear adsorption behavior, however, indicated the presence of multiple types of NSAID adsorption sites on the CNTs and sediments.

The affinity between organic compounds and sediments is determined by partition and adsorption. And adsorption of organic compounds onto sediments can be described by "dual-mode sorption": adsorption in amorphous organic matter and adsorption to carbonaceous materials such as black carbon, coal, and kerogen, which were collectively termed as "carbonaceous geosorbents" [48]. The adsorption affinity of PA (K_d = 1.47) on sediments was found to be lower than that of DS (K_d = 3.07). This could be attributed to the higher hydrophobic effects of DS than PA apart from the above-mentioned adsorption mechanisms, which is indicated by the higher K_{OW} value of DS (Table 1). However, the relatively low K_d values for NSAIDs suggested a low adsorption affinity to sediment particles and high mobility in sediments. In addition, the affinity between NSAIDs and sediments was much weak than that between NSAIDs and CNTs. This was attributed to the much stronger π-π bonding between NSAID molecules and the CNTs [49]. Besides, other mechanisms explaining the bonding of organic compounds by CNTs were proposed, such as hydrogen bonding and electrostatic interactions [50,51]. Chen et al. suggested that, besides the hydrophobic effect, there are other mechanisms controlling the adsorption of the chemicals to CNTs, and those additional mechanisms are possibly related to the π-electron polarizability typically associated with the aromatic compounds

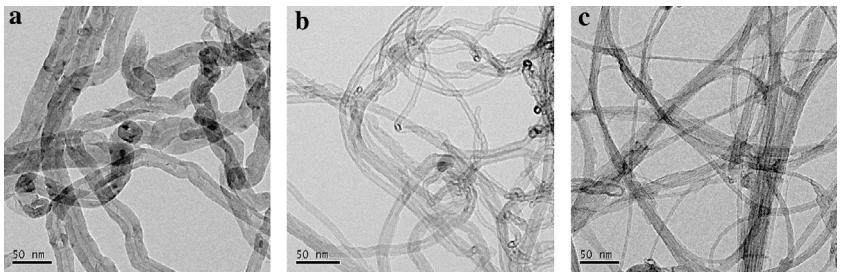
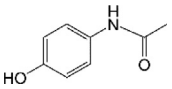
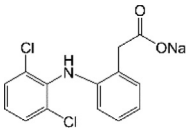


Fig. 1. STEM images of MWCNT2040 (a), MWCNT0815 (b) and SWCNT (c).

Table 1
Physico-chemical properties of DS and PA molecules.

Compound	Molecular formulae	Molecular weight[a] (g/mol)	Structural formula	Log K_{OW}[a]	p*Ka*[a]	Water solubility[a] (mg/L)
Paracetamol	$C_8H_9NO_2$	151.17		0.46	9.38	14000
Diclofenac sodium	$C_{14}H_{10}Cl_2NNaO_2$	318.14		0.70	4.15	2425

[a] Values obtained from SRC physical properties database: http://www.srcinc.com/what-we-do/environmental/scientific-databases.html.

Table 2
Selected properties of sediment used in this experiment.

pH	CEC (cmol/kg)	SOM (%)	Zeta potential (mV)	Texture (% mass)		
				Clay (< 2 μm)	Silt (2–20 μm)	Sand (20–900 μm)
7.1	21.3	1.6	−12.4	25.9	38.1	36.0

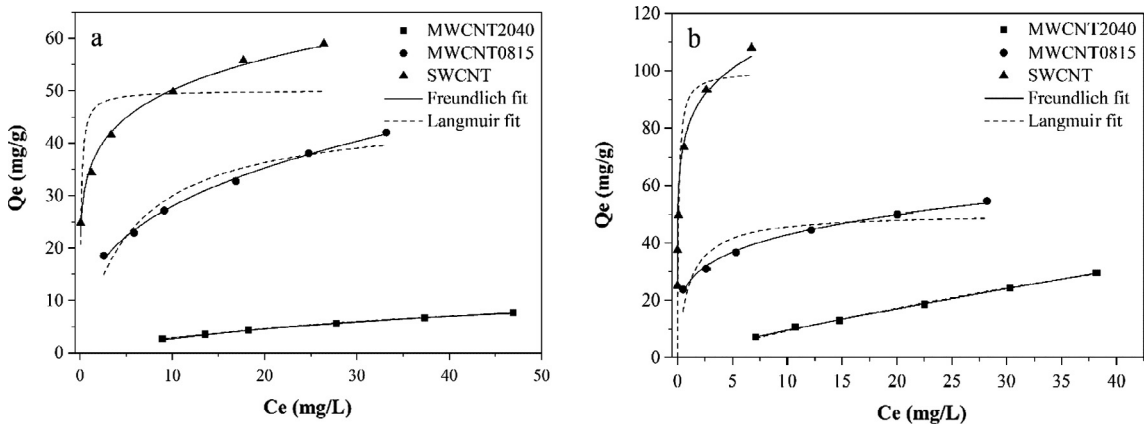


Fig. 2. Adsorption isotherms of PA (a) and DS (b) onto CNTs.

as well as the strong electron-accepting property associated with the aromatic compounds containing one or more nitro groups [51]. Both PA and DS have multiple polar functional groups, and DS has one more benzene ring than PA, generating a stronger connection with CNTs. The K_d values (Table 5) for the two NSAIDs adsorbed on CNTs are in a descending order: SWCNT > MWCNT0815 > MWCNT2040. The results also correlate well with specific surface areas of the adsorbents (Table 2), which also decrease with the order above. In order to explain the impact of surface area, surface area normalized K_F values (K_{FSA}) were examined: 0.009, 0.056, 0.091 for PA, and 0.018, 0.112, 0.213 for DS on MWCNT2040, MWCNT0815, and SWCNT, respectively. Surface area normalization suppressed the differences in adsorption capacities, indicating that specific surface area played an essential role on the adsorption of NSAIDs on CNTs.

When it comes to the sediments mixed with CNTs, the adsorption ability for NSAIDs were increased with increasing CNTs/sediments ratio. Comparing the K_d values for PA at the same initial CNT content, it can be found out that the values for sediment-SWCNT mixture are almost twice higher than those for sediment-MWCNT0815 mixture and over 10-fold higher than those for sediment-MWCNT2040 mixture. The results above showing the adsorption gap are also similar with that for DS, yet not so obvious. This indicates that more NSAIDs could be adsorbed with

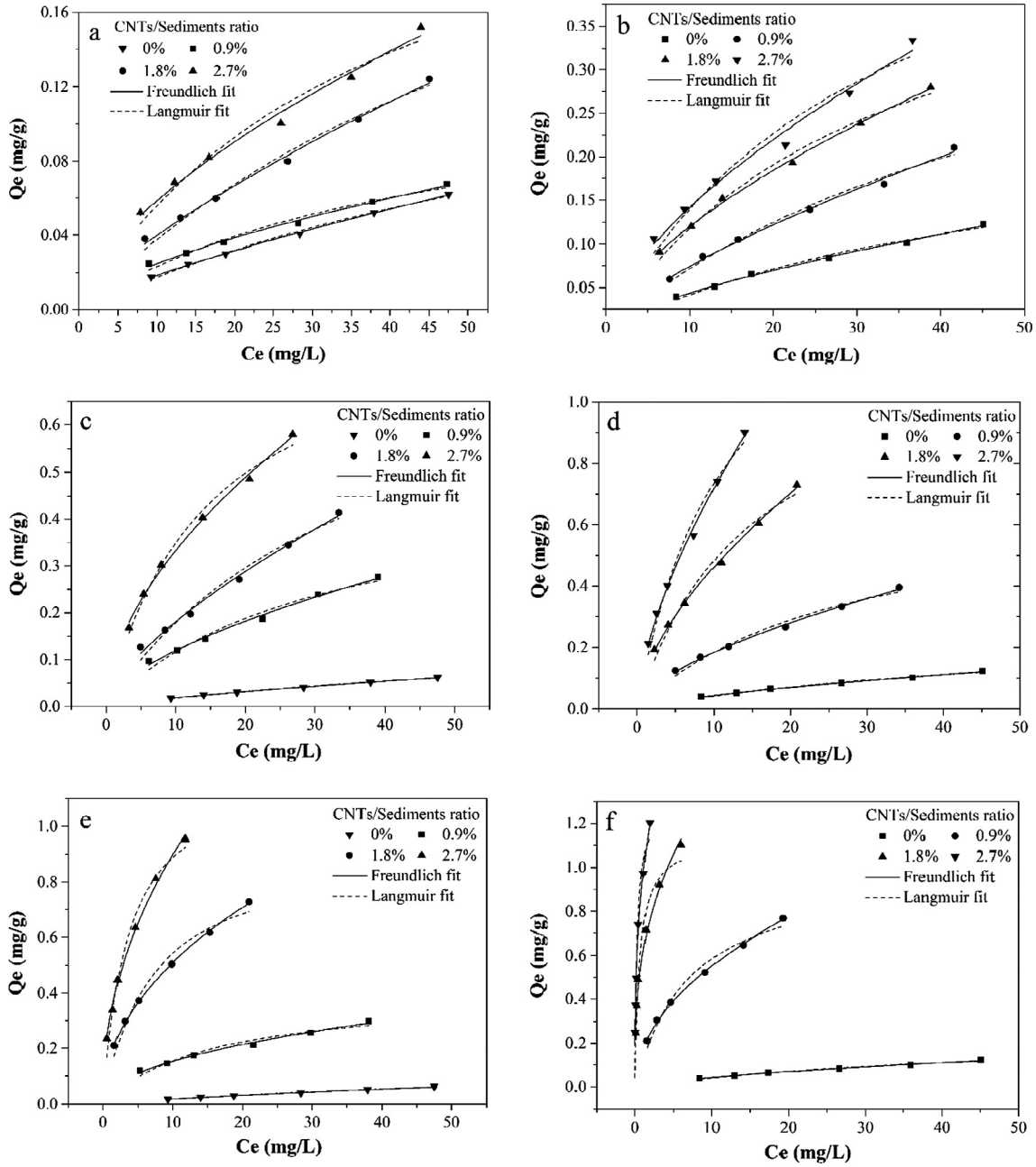


Fig. 3. Adsorption isotherms of PA (a, c, e) and DS (b, d, f) onto sediment-CNTs mixture with MWCNT2040 (a, b), MWCNT0815 (c, d), and SWCNT (e, f).

Table 3
Freundlich and Langmuir equation parameters for NSAID adsorption by CNTs.

Adsorbate	Adsorbent	Freundlich			Langmuir		
		K_F ((mg/g) (L/mg)^n)	n	R^2	K_L (L/mg)	Q_{max} (mg/g)	R^2
PA	MWCNT2040	0.708	0.62	0.999	0.025	14.03	0.996
	MWCNT0815	12.980	0.33	0.996	0.185	46.10	0.913
	SWCNT	34.671	0.16	0.990	8.836	50.02	0.540
DS	MWCNT2040	1.407	0.83	0.998	0.009	115.99	0.996
	MWCNT0815	25.859	0.22	0.993	0.931	50.56	0.727
	SWCNT	80.791	0.14	0.953	8.929	100.06	0.474

increasing CNTs content in sediments. The greater surface area of CNTs may account for the phenomenon. It is observed that the K_F values for sediment-CNTs mixture are higher than that for sediments, suggesting an increased NSAIDs-adsorbent interaction with addition of CNTs. Consequently, the addition of CNTs could increase the affinity between NSAIDs and sediments to a large extent, which indicated a potential environmental risk for NSAIDs and CNTs in sediments.

Table 4
Freundlich and Langmuir equation parameters for NSAID adsorption by sediments and sediment-CNTs mixtures.

Adsorbate	Adsorbent	CNTs/sediments ratio	Freundlich			Langmuir		
			K_F ((mg/g)(L/mg)^n)	n	R^2	K_L (L/mg)	Q_{max} (mg/g)	R^2
PA	Sediments	0%	0.003	0.77	0.999	0.011	0.18	0.994
	Sediment-MWCNT2040	0.9%	0.006	0.64	0.994	0.022	0.13	0.975
		1.8%	0.007	0.74	0.995	0.013	0.33	0.984
		2.7%	0.014	0.62	0.986	0.026	0.27	0.963
	Sediment-MWCNT0815	0.9%	0.029	0.61	0.991	0.032	0.49	0.966
		1.8%	0.039	0.67	0.992	0.027	0.85	0.972
		2.7%	0.093	0.55	0.996	0.068	0.87	0.987
	Sediment-SWCNT	0.9%	0.051	0.48	0.990	0.063	0.40	0.946
		1.8%	0.171	0.47	0.999	0.140	0.93	0.970
		2.7%	0.310	0.46	0.995	0.284	1.20	0.976
DS	Sediments	0%	0.009	0.67	0.996	0.020	0.25	0.987
	Sediment-MWCNT2040	0.9%	0.014	0.71	0.994	0.018	0.48	0.986
		1.8%	0.029	0.62	0.998	0.031	0.50	0.987
		2.7%	0.033	0.63	0.983	0.030	0.60	0.957
	Sediment-MWCNT0815	0.9%	0.045	0.61	0.997	0.037	0.68	0.977
		1.8%	0.114	0.61	0.998	0.066	1.22	0.979
		2.7%	0.164	0.64	0.996	0.083	1.62	0.979
	Sediment-SWCNT	0.9%	0.178	0.49	0.998	0.141	1.00	0.973
		1.8%	0.609	0.34	0.983	1.689	1.13	0.965
		2.7%	0.957	0.35	0.987	3.558	1.30	0.888

Table 5
The distribution coefficient (K_d) for sediments, sediment-CNTs mixtures, and CNTs.

Adsorbent		CNTs/sediments ratio	K_d	
			PA	DS
Sediments		0%	1.47	3.07
Sediment-CNTs mixtures	Sediment- MWCNT2040	0.9%	1.78	5.00
		1.8%	2.96	7.11
		2.7%	3.90	8.20
	Sediment-MWCNT0815	0.9%	7.11	9.82
		1.8%	9.89	16.73
		2.7%	14.19	19.57
	Sediment-SWCNT	0.9%	8.29	18.26
		1.8%	17.71	23.76
		2.7%	21.53	24.60
CNTs	MWCNT2040	–	204.94	649.57
	MWCNT0815	–	1270.06	1681.83
	SWCNT	–	1847.07	2405.73

3.3. Transport of NSAIDs through sediment columns

3.3.1. Transport of NSAIDs associated with CNTs through sediment columns

The breakthrough curves (BTCs) for the selected NSAIDs associated with CNTs are shown in Fig. 4. Concentrations of the influent and effluent NSAIDs were defined as C and C_0, respectively. The concentration of effluent NSAIDs increased with continuous flow of the suspension until reaching a stable plateau. The transport of DS through the columns was much slower than that of PA, with breakthrough time later than PA for about 3 PVs. The fate of PA and DS in natural systems, to a large degree, depends on their partitioning behavior between aqueous and immobile solid phases and the condition factors which affect the partitioning [52]. The delayed DS

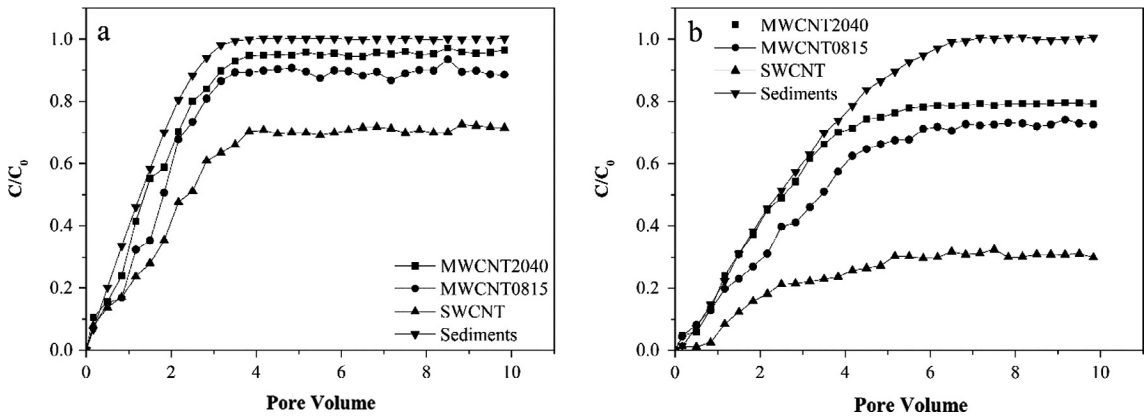


Fig. 4. Breakthrough curves of PA (a) and DS (b) in sediment columns with different inflows. 'MWCNT2040', 'MWCNT0815', and 'SWCNT' refer to inflow with MWCNT2040, MWCNT0815, and SWCNT, respectively. 'Sediments' refers to inflow without CNTs. C and C_0 represent the concentration of effluent and influent, respectively.

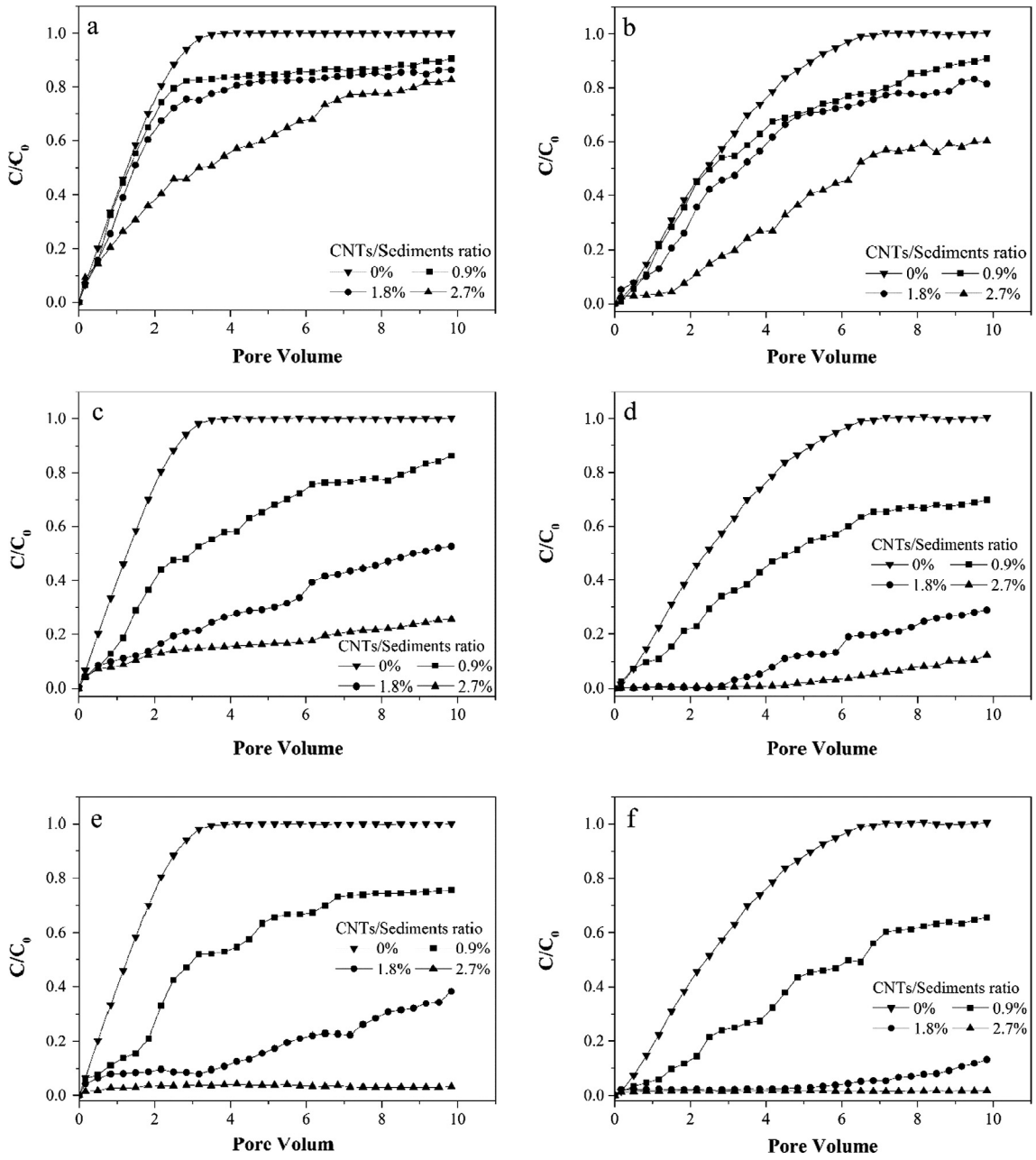


Fig. 5. Breakthrough curves of PA (a, c, e) and DS (b, d, f) in sediment columns mixed with MWCNT2040 (a, b), MWCNT0815 (c, d) and SWCNT (e, f) in different CNT ratios (0%, 0.9%, 1.8%, 2.7%). C and C_0 represent the concentration of effluent and influent, respectively.

transport in the water-saturated sediment columns suggested that the affinity between DS and sediments was stronger than that between PA and sediments, which conformed to the results in batch adsorption experiments.

The BTCs for NSAIDs without CNTs in inflow could reach a steady relative concentration about one. However, when CNTs was present in inflow (and adsorption equilibrium of NSAIDs to CNTs was reached before the inflow was flushed into the column), all breakthrough curves reached a steady state concentration lower than one, indicating that CNTs might be retained in sediments and therefore markedly impeded the transport of the contaminants [37–39]. The critical PV (the number of pore volumes needed to reach the C_{max}, the maximum concentration of outflow) of a given NSAID not varies significantly with the CNT type, but different curves have different C_{max}, with a C_{max} order of SWCNT < MWCNT0815 < MWCNT2040. These observations were almost attributed to the straining effects of the CNTs; i.e., blocked pores act as dead ends for the CNTs [53]. It was proposed that the CNT shape and structure, particularly the large aspect ratio, the extreme variability in length, and their highly bundled state, play a significant role in straining [54]. Due to the strong binding force between CNTs and NSAIDs, part of NSAIDs adsorbed on CNTs was retained in sediment columns. Straining played an important role in the deposition of CNTs in sediment columns, contributed by not only the CNT shape and structure, but also heterogeneity in sediment particle size, porosity, and permeability [39]. Some studies observed more or less breakthrough of CNTs in porous media, but the used CNTs were functionalized by using strong acids and the acidification introduced oxygen containing functional groups on the CNTs which could facilitate the suspension and transport of the CNTs [55,56]. Furthermore, the porous medium used in those studies had a bigger grain size and less complex constitution

Table 6
The retardation factor (R) for PA and DS.

Adsorbent		CNTs/sediments ratio	R	
			PA	DS
Sediments		0%	4.07	7.40
Sediment-CNTs mixtures	Sediment-MWCNT2040	0.9%	4.71	11.44
		1.8%	7.18	15.84
		2.7%	9.14	18.10
	Sediment-MWCNT0815	0.9%	15.84	21.48
		1.8%	21.64	35.90
		2.7%	30.59	41.83
	Sediment-SWCNT	0.9%	18.30	39.10
		1.8%	37.94	50.60
		2.7%	45.91	52.33

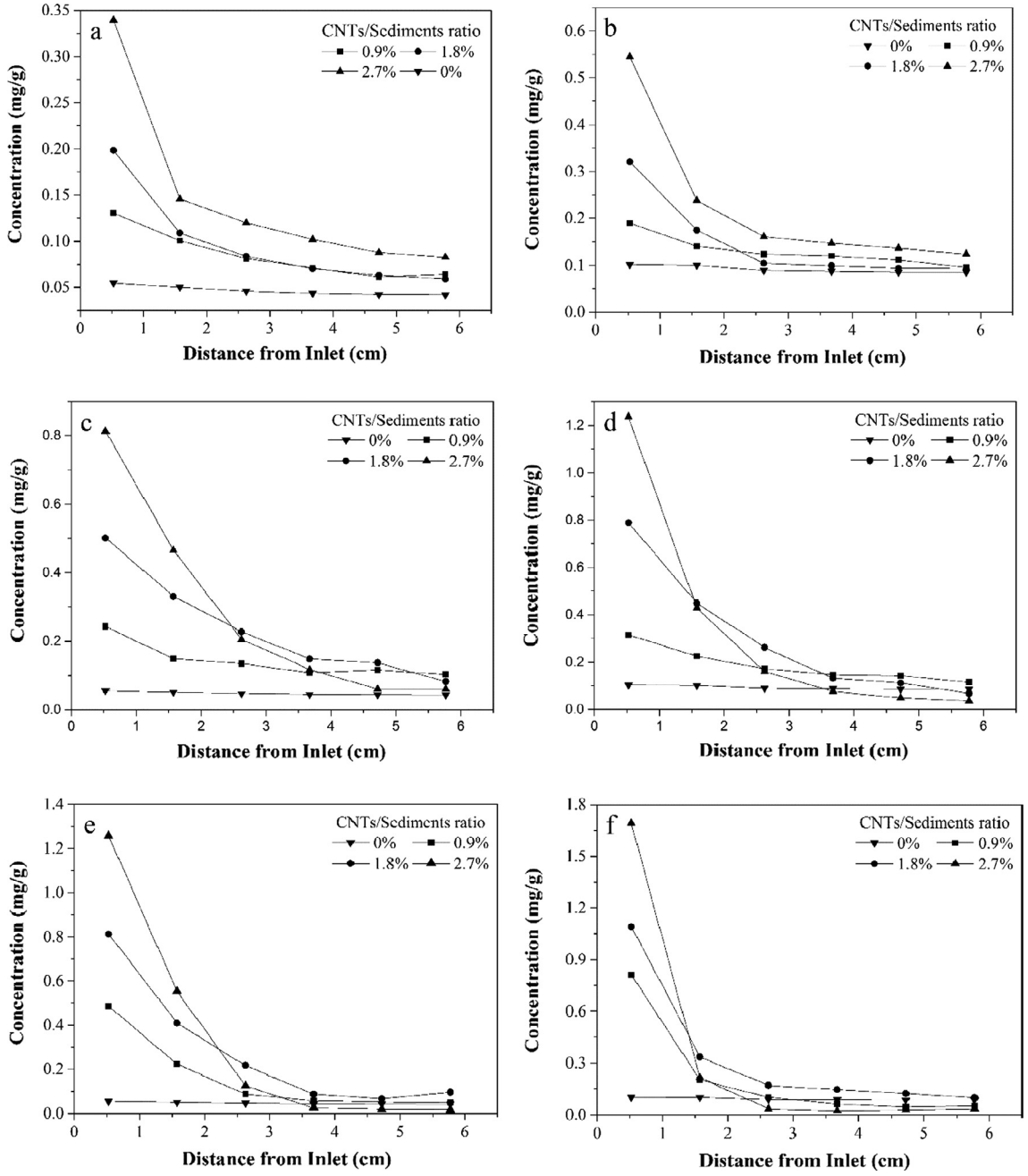


Fig. 6. Retention profiles of column transport tests for PA (a, c, e) and DS (b, d, f) through sediments mixed with MWCNT2040 (a, b), MWCNT0815 (c, d) and SWCNT (e, f) in different CNT ratios (0%, 0.9%, 1.8%, 2.7%).

than the sediments used in this study. Therefore, the straining effects played a more important role in the deposition of CNTs in Xiangjiang sediments.

3.3.2. NSAID transport in sediment columns mixed with CNTs

BTCs of the NSAID suspensions in the sediment columns with different CNT content are shown in Fig. 5. In the columns mixed with CNTs, C_{max} of PA were generally higher than that of DS, suggesting a higher mobility of PA than DS in all the columns. The retardation factor, R, was calculated using the measured K_d values to estimate the travel time of NSAIDs in sediments. The variable of ρ_b is sediment bulk density and θ is sediment porosity [46].

$$R = 1 + \frac{\rho_b K_d}{\theta} \quad (4)$$

The R values (Table 6) of DS were higher than those of PA in the water-saturated sediment columns under all of the circumstances, also suggesting stronger interactions between DS and the natural sediment media. It can be seen from Fig. 5 that the NSAID transport is CNT type dependent. C_{max} for different kinds of CNTs has an order of SWCNT < MWCNT0815 < MWCNT2040, following an opposite order of their surface area. No matter which kind of CNTs was mixed with the sediment columns, the NSAIDs were detected in the first PV of the effluents. Nonetheless, with continuous flow of the suspension, the concentrations of effluent NSAIDs were hard to reach a stable plateau within the studied PVs. The suspension without CNTs, however, could reach a stable plateau about one C/C_0. The effect of CNT content on the transport of NSAIDs is also shown in Fig. 5. With an increased CNTs/sediments ratio, the upward trend of outflow concentration for the three kinds of CNTs became more and more retarded. Especially, in the columns with SWCNT content of 2.7%, negligible breakthrough of NSAIDs was observed in 10 PVs. Furthermore, the R values increased greatly with an increasing CNTs/sediments ratio, informing that the CNT content played a key role for the resulted retarded transport of NSAIDs. CNTs, with superior affinity to NSAIDs, could impede the transport of NSAIDs through the sediment columns, and then entrap them within the columns. The above results indicated that CNTs can make NSAIDs retained in sediment columns to a large extent, thus affecting the mobility of NSAIDs.

3.3.3. Spatial distribution of NSAIDs

Fig. 6 shows the spatial distribution of NSAIDs in sediment columns. In columns without CNTs, the retention of NSAIDs was relatively uniform over the entire length of the column. The relatively constant deposition profile suggested that NSAID deposition approached a limiting capacity. In contrast, for the sediment columns mixed with CNTs, NSAID retention decreased with distance from the column inlet. In addition, the inlet NSAID mass retained is rather high compared with the outlet mass, and this phenomenon was especially obvious in the sediment columns mixed with SWCNTs. The NSAID mass retained in each segment increased in an order of MWCNT2040 < MTWCNT0815 < SWCNT, consistent with the tendency of their adsorption abilities. Moreover, the NSAID mass retained increased with an ascending CNTs/sediments ratio. The results indicated that, due to the great adsorption capacity, the adsorption condition of CNTs in the column inlet was much closer to saturation than the CNTs in the column outlet, and CNTs with more superior adsorption properties could lead to much greater difference. Therefore, the NSAID mass retained in the column inlet for a more excellent adsorbent was much higher than other adsorbents, and a higher content of CNTs in sediment columns could lead to a more obvious retention for NSAIDs.

To further evaluate the transport condition of the two selected NSAIDs, overall mass balance recoveries were computed from the ratio of the NSAID mass recovered from solid phase extraction and the NSAID mass difference of inflow versus effluent. For the sediment columns without CNTs, the ratio was 72% for PA, and 76% for DS. For the columns mixed with CNTs, however, the ratios only ranged from 40% to 55%. This circumstance clearly showed that CNTs could restrain NSAIDs from leaching out of the sediment columns, and the binding force between them was hard to break, manifesting a potential environmental risk of CNTs. In addition, although there are microbial activities in realistic fields, CNTs themselves have superior antibacterial effects [57], so the contaminants may persist in the aquifer over a longer time. Therefore, a long-term risk for sediment contamination by NSAIDs should be taken into account.

4. Conclusions

Investigation of the effects of CNTs on the fate of NSAIDs in sediments is essential to assessing their environmental risks. The presented results allowed us to conclude that CNTs could impede the transport of NSAIDs in sediment columns due to the superior adsorption ability of CNTs. Because of the complex texture of sediments, CNTs in this study could hardly breakthrough the columns by straining effects, therefore made NSAIDs retained in sediment columns. The results indicated that the affinity between CNTs and NSAIDs could be related to the CNT content and type. The C_{max} values of column tests decreased with increasing CNTs/sediments ratios. With larger specific surface area, SWCNTs possessed a more outstanding adsorption capacity among the three kinds of CNTs. Besides, PA showed a higher mobility than DS no matter whether CNTs were considered in sediment columns, indicating a lower affinity to CNTs and sediments than DS. Because of the strong binding force to adsorption sites, NSAIDs adsorbed could hardly depart from the CNTs, and this needs further investigation in our future work.

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