

Sorption of triclosan by carbon nanotubes in dispersion: The importance of dispersing properties using different surfactants

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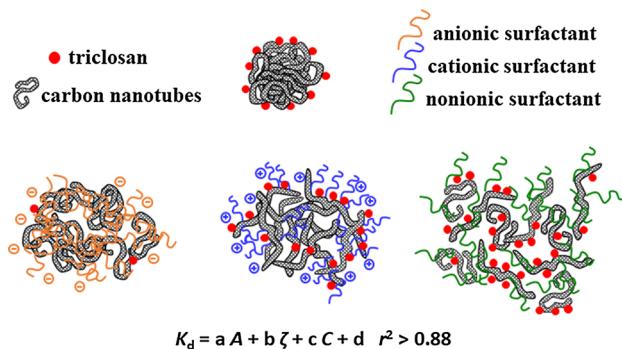
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GRAPHICAL ABSTRACT



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ABSTRACT

The production of carbon nanotubes (CNTs) increased rapidly due to the superior properties and was suggested to be the potential sorbents for environmental remediation. CNTs tend to form aggregates, thus CNTs dispersion was commonly produced by sonication with surfactant in industry for better application. In the present study, a novel passive sampling method was used to systematically study sorption of triclosan to CNTs dispersion to give a better understanding on their interactions especially with the presence of surface-active substances. With the increase of anionic surfactant concentration (SDBS or SDS), sorption of triclosan was gradually suppressed. CNTs dispersed by nonionic surfactant TX-100 increased or decreased sorption at different TX-100 and triclosan concentration. Little amount of cationic surfactant CTAB(1 mg/L) could sharply decrease triclosan sorption to CNTs but with larger CTAB concentration, sorption was continually increased. Sorption isotherms of triclosan to CNTs dispersion with 40 mg/L and 100 mg/L surfactant fitted well with Toth model show the existence of double competition in the sorption process. Different from the adsorption mechanism of previously aggregated CNTs and compounds. Sorption data combined with comprehensive characterization of CNTs dispersion and

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theoretical analysis, three effects referring to charge, dispersion and competition were proposed. Sorption coefficient was linearly correlated with the characterization parameters. Surface charge, dispersion status and surfactant concentration play the important role on triclosan sorption in CNTs dispersion in the presence of anionic, cationic and nonionic surfactant, respectively. The results provide basic supports on application of CNTs in remediation area and exploring the fate of both CNTs dispersion and pollutants.

1. Introduction

Triclosan (5-chloro-2-(2,4-dichlorophenoxy)-phenol) is a common synthetic antibacterial agent widely used in household and consumer care products [1–4], cosmetics and detergents [5]. Triclosan was reported to be associated with health and environmental effects such as skin irritation, allergies and other environmental toxicity in aquatic and terrestrial environments [6,7]. In recent years, triclosan has become more widely used. Several recent studies have demonstrated the widespread presence of triclosan in the environment, especially in wastewater, wastewater treatment plant effluents, rivers and sediments [8]. As typical antibacterial agent, triclosan has been shown to differentiated aquatic organisms by blocking enzyme carrying proteins, leading to concerns of the possible build-up of bacterial resistance in these people. Since triclosan has a long half-life and lipophilic properties, it may pose a long-term health risk to humans. Although a large number of studies have been conducted on triclosan, the removal effect of triclosan remains unsatisfactory [9–12]. The conventional sewage treatment methods cannot completely remove triclosan owing to its relatively high hydrophobicity. It was reported that the concentration of triclosan in the effluent of the wastewater treatment plants ranges from 9 ng/L to 6.7 µg/L [13,14]. Therefore, it is of great importance to find efficient adsorbent to deeply removal of triclosan.

Over the past decade, carbon nanotubes (CNTs) have gained increasing attention due to their unique properties [15–17]. CNTs were also suggested to be potential sorbents to remove different organic compounds such as phenolic compounds, aliphatic compounds, aromatic compounds and pharmaceutical and personal care products (PPCPs) [18,19]. Even though the sorption behavior between CNTs and those compounds were reported by numbers of studies, the sorption capacities of CNTs towards some compounds were still small (for example, compared to activated carbon) and remaining extension. As we all known, unlike normal sorbents, CNTs tend to form aggregates in water due to the strong Van der Waals along the tubes which might limit their sorption sites providing for the compounds. Sorption mechanisms between aggregated CNTs and compounds were well studied by previous studies. Gil. A et al. believe that the adsorption between CNTs and compounds is mainly dependent on van der Waals forces and electrostatic interactions [20]. Yu et al. believe that the cavity formation, hydrogen bond acidity interactions and π - π electron interactions are the most influential adsorption mechanisms [21]. However, the sorption mechanisms of CNTs dispersion and compounds remaining systematic investigated. In our previous study, we examined sorption of triclosan by sonication pretreated CNTs and found sonication could largely increase CNTs sorption capacities 1.3 times [22]. Though sonication could disperse CNTs but it could not produce stable CNTs dispersions since re-aggregation often occurs. To effectively break CNTs aggregates and achieve stable CNTs dispersion, CNTs were usually pretreated by various methods. The most usable method for dispersing CNTs is to sonicate them in the presence of certain amount of surfactant, and this is often applied in industry to prepare CNTs dispersions for different purpose. If CNTs were dispersed by dispersant, sorption of pollutants by CNTs could be influenced in two ways. First, the sorption sites of CNTs could be enlarged by dispersion, thus increase the sorption towards pollutants. Second, the sorption sites could be masked by dispersant. As a consequence, the available sorption sites for pollutants may be limited. How these two aspects interact together in the dispersion system still remaining investigation. The dispersant normally

used in industry is surfactant that could be classified in several types, anionic surfactant, nonionic surfactant and cationic surfactant. The different structure, properties and concentration of surfactant may act differently on CNTs dispersions thus influence CNTs sorption towards pollutants. The proper surfactant at certain concentration may promote CNTs sorption towards pollutants that might be a good way for deeply removal the persistent pollutants like triclosan. In addition, the CNTs dispersion may be occasionally released form industry and their interactions with pollutants could influence both CNTs and pollutants environmental behavior. Therefore, to study the interaction between triclosan to CNTs dispersion could also provide basic knowledge on the fate of materials.

The difficulty to study sorption in CNTs dispersion is to measure the sorption of pollutants towards colloidal CNTs in dispersion due to the difficulties on separation the colloidal CNTs and aqueous phase. The traditional separation methods in sorption batch experiments are centrifugation and filtration [23]. However, those methods cannot guarantee the separation of nano-sized colloidal CNTs from the liquid phase, and the mass of contaminants adsorbed on colloidal CNTs is difficult to detect. In our previous study, POM-SPE method as a passive sampling method was used to study sorption of polycyclic aromatic hydrocarbons on CNTs [15]. Solid-phase microextraction based on polyacrylate-coated fiber (SPME-fibers) as another passive sampling method was applied to determine sorption of polar and ionic organic contaminants to dissolved organic carbon (DOC) [24]. Application of passive sampling method on sorption batch experiment of CNTs dispersion towards pollutants may be a robust way to better investigation of sorption behavior of colloidal CNTs.

Surfactants are a group of organic compounds consisting of hydrophilic heads and hydrophobic tails. They have been widely used as detergents, wetting agents, emulsifiers, foaming agents as well as dispersants [17,25–27]. In this study, we aimed on examine the sorption behavior and mechanisms of triclosan to CNTs dispersions dispersed by different surfactant. We used four types of surfactants that normally used in dispersing CNTs as dispersants: anionic sodium dodecyl benzene sulfonate (SDBS), anionic sodium sodocetyl sulfate (SDS), cationic cetyl trimethyl ammonium bromide (CTAB) and nonionic octylphenol ethoxylate (TX-100). Passive sampling method solid-phase micro-extraction based on polyacrylate-coated fibers (SPME-fibers) was evaluated and applied in the sorption batch experiment to give an accurate examination on sorption coefficient between triclosan and colloidal CNTs. The objectives of this study are (i) to study the effect of different concentration and type of surfactants on the sorption process of triclosan to the CNTs; (ii) to investigate the sorption mechanisms of triclosan to CNTs in different dispersions; (iii) to generate the regulations on dispersion and sorption behavior in dispersion system.

2. Materials and methods

2.1. Materials

The analytical standard triclosan was purchased from Dr. Ehrenstorfer in Germany. The physicochemical properties of the CNTs and triclosan are shown in Tab.S1 and Tab.S2. Pristine multiwalled-CNTs with 95% purity were obtained from Chengdu Organic Chemistry Co. China. Four surfactants SDBS, SDS, CTAB, TX-100 were acquired from Sigma (Zwijndrecht, the Netherlands) and their properties were listed in Tab.S3. Glass optical fibers coated with polyacrylate (thickness

35 µm; volume 15.4 µL/m) were purchased from Polymicro Technologies (Phoenix, AZ, USA). Methanol (HPLC-grade) was obtained from Fisher Scientific, USA.

2.2. Batch experiments

2.2.1. Sorption to fibers

The SPME-fiber method outlined in Haftka and Jonker [24] was used to determine sorption of different kind of synthetic organic contaminants to dissolved organic carbon in different solution chemistry over a very wide concentration range. The SPME-fiber method was applied in the sorption batch experiment. The fibers were cut to 1 cm and cleaned three times with 50/50 methanol/water (v/v), then washed with ultrapure water to remove all the solvent, and stored in water until further use.

The 8 g/L triclosan stock solution was prepared by dissolving 800 mg of triclosan powder into 100 mL of methanol. The stock solution of triclosan was diluted successively to the required concentration levels and stored at 4 °C in the dark. To initiate a fiber sorption experiment, first 50 mL of electrolyte solution was transferred to a 50 mL glass scintillation vial. A stock solution of triclosan (in methanol) was added to the vial, and the volume percentage of methanol was kept below 0.1% (v/v) to minimize cosolvent effects. Then, a piece of fiber was added to the vial. The vial was capped and stirred on a horizontal shaker at 150 rpm until sorption equilibrium was reached. The time required to reach sorption equilibrium was predetermined. After 7 days, fibers were then taken out of the vials, wiped with a wet tissue and add to vials with 1 mL methanol. They were then extracted with sonication for 2 h. The extract was pursued for further analyze. The concentration in aqueous solution was also analyzed as dissolved phase. All experiments were run in duplicates. The sorption data was fitted with the linear sorption isotherm: $C_{\text{fiber}} = K_{\text{fiber}}/C_w$, where C_{fiber} (mg/L) and C_w (mg/L) are the equilibrium concentration of triclosan on the fiber and in the solution, respectively; K_{fiber} (L/L) is the fiber-water distribution coefficient

2.2.2. Sorption coefficient K_d of triclosan to CNTs in different dispersion

All sorption experiments were carried out at 25 °C using 50 mL Teflon-lined screw cap glass vials. 2.5 mg of pristine CNTs (weighed by a Mettler Toledo M X 5 micro balance) and 50 mL of surfactants solution were added to the vials. To prepare CNTs dispersions with different status, CNTs were sonicated for 2 h under a series of surfactants solutions with different concentration (SDBS/SDS/CTAB solution was 0 – 200 mg/L, TX-100 solution was 0 – 100 mg/L). When sonicating sample vials were immersed into the sonication bath, the water level in the bath was the same as in the samples. After sonication for 2 min, the samples were shaken by hand to ensure evenly distributed particles in suspension.

Sorption coefficient (K_d) under different dispersion status was measured at the initial triclosan concentration 8 mg/L. After sonication for 2 h, triclosan was added to all vials, and the volume percentage of methanol was kept below 0.1% to minimize cosolvent effects. At the same time, blank samples without sorbents were prepared to confirm that no sorption occurred in the glass vial. All samples with triclosan were added to the shaker and shaken at 150 rpm for 2 h. Samples including blanks were running in duplicates. The same concentration series of triclosan solutions without sorbent were run under the same condition as the controls, showing that the loss of the initially added amounts of triclosan was less than 3%. After shaken for 2 h, the cleaned 1 cm fiber was added to each sample. Then all the samples were placed in a shaker and shaken at 150 rpm for 7 days (The equilibrium time of fiber and triclosan sorption is 7 days that was confirmed in the pre-experiment). After 7 days, fibers were taken out to be analyzed in UPLC as described in 2.2.1.

The amount of triclosan adsorbed per unit sorbent mass after equilibration was calculated as follows:

$$q_e = (C_0 - C_e)V/m \quad (1)$$

$$K_d = q_e/C_e \quad (2)$$

$$C_e = m_{\text{fiber}} \times K_{\text{fiber}}/V_{\text{fiber}} \quad (3)$$

where q_e (mg/g) is the amount of sorbate adsorbed to the sorbent when the sorption equilibrium is reached; C_0 (mg/L) and C_e (mg/L) are the triclosan concentrations in the initial solution and at equilibrium, respectively; $V(L)$ is the volume of the solution; m (g) is the mass of the sorbent used for the experiment; and K_d (L/g) is the sorption coefficient. m_{fiber} (mg) is the mass of triclosan adsorbed on the fiber, V_{fiber} (µL/m) is the volume of the fiber, $V_{\text{fiber}} = 15.4 \mu\text{L}/\text{m}$. K_{fiber} is the partition coefficient of triclosan on the aqueous phase and the fiber. Test method refer to (2.2.1)

2.2.3. Sorption isotherms of triclosan to CNTs in different dispersion

Besides measuring the K_d at different surfactant solutions, sorption isotherms were also measured for CNTs with four surfactants under typical concentrations (0 mg/L, 40 mg/L and 100 mg/L). The typical concentrations of surfactant were selected according to the results of single sorption coefficients K_d at a series of surfactant concentrations. The concentration of triclosan is in the range of 0–13 mg/L. The batch experiment followed the procedure as described in 2.2.2.

The nonlinear forms of the Toth Model (TM) Eq. (4) and Polanyi Manesmodel (PMM) Eq. (5) were used to fit the sorption isotherms. The models are expressed as follows:

$$q_e = Q_0 C_e / (1/K_t + C_e)^{1/t} \quad (4)$$

$$q_e = Q_0 \exp(a(RT \ln(C_s/C_e))^b) \quad (5)$$

Where Q_0 (mg/g) is the maximum sorption capacities; K_t (L/mg) is Toth equilibrium constant, t is Toth exponent, a and b are PMM sorption constants, R is the universal gas constant (8.314×10^{-3} kJ/(mol K)), T is room temperature (K), and C_s stands for solubility at 20 °C.

2.3. Analytical methods for triclosan

The concentration of triclosan in the fiber extraction solution was measured using ultra-high-performance liquid chromatography (UPLC, Waters, USA). The mobile phases used for elution were Milli-Q deionized water and methanol (10:90 v/v) with a flow rate of 0.4 mL/min. The injection volume of the sample was 10 µL, and the column temperature was maintained at 30 °C. The UV–Vis detector was set at a wavelength of 280 nm.

2.4. Characterization of CNTs dispersion

The dispersion state of CNTs under different conditions was characterized by different methods. The microstructure of the CNTs was measured by a field emission scanning electron microscope (SEM, SU8020). The zeta potential and size distribution of CNTs in the suspension were measured by a dynamic light scattering device (Zeta sizer 90, Malvern). The absorbance of CNTs in the suspension was determined by UV-vis spectrometer (UV759 UV-VIS) at 800 nm. The functional group of the CNTs was measured by Fourier transform infrared spectroscopy (FTIR, Nicolet IS10). The BET surface area of CNTs was measured by N₂ sorption at 77 K using a surface area analyzer (Quantachrome NOVA 2000, USA).

3. Results and discussion

3.1. Characterization of CNTs dispersion

The dispersion state of CNTs dispersion is an important factor in the sorption process of triclosan on CNTs. CNTs suspensions with different degrees of dispersion have different sorption capacities towards triclosan due to their different surface morphology and characteristics.

3.1.1. Visual assessment

It can be clearly observed from Fig.S1 that the dispersion states of CNTs after sonication treatment with different surfactants is significantly different. Among them, CNTs sonicated with TX-100 were the best dispersed and the dispersion almost reaches the state of ink (Fig.S1 h-i). SDBS dispersed CNTs were observed to be rank the second dispersed suspension. The dispersion states of SDS and CTAB cannot be distinguished by visual assessment. Sonication without surfactant significantly dispersed CNTs but reaggregation occurred immediately which could be observed in Fig.S1 a.

3.1.2. SEM images

SEM images of CNTs dispersed by other concentrations were shown in Fig.S2. Sonicated CNTs are slightly more dispersed than ordinary CNTs. After the addition of the anionic surfactant SDBS/SDS, CNTs surfaces turned to be thicker and it was supposed to be the macromolecular SDBS/SDS adsorbed onto the CNTs surface. From the image of CNTs with nonionic surfactant TX-100, the dispersibility of the CNTs is significantly improved as indicated by the well separation of each tubes, which is consistent with the results of the visual assessment. In the system in which cationic surfactants are present, the dispersion state of CNTs is also ideal, and there is not much macromolecular CTAB adsorbed on the surface of CNTs. Research by Xing et al. [28] showed that the anionic surfactant SDBS is more easily adsorbed on the surface of CNTs, while CTAB is hardly adsorbed by CNTs. Since SEM images acquired dry CNTs samples other than directly observation in CNTs dispersion, one should notice that the image could only reflect the morphologies of CNTs dispersion to some extent.

3.1.3. Zeta potential

From Fig.1, sonicated CNTs without surfactant were negatively charged with zeta potential -9.97 mV. Because SDBS/SDS is negatively charged, the zeta potential of CNTs dispersion with SDBS/SDS was negative and the absolute value was increased with the increase of surfactant concentration. The negative charge of CNTs with SDBS was larger than with SDS indicated that CNTs dispersion with SDBS was more dispersed than with SDS, that was consistent with the visually assessment. Zeta potential of CNTs with nonionic surfactant TX 100 was independent with the TX 100 concentration and the value is -15.63 mV, which is a bit lower than CNTs without surfactant. CNTs with cationic surfactant were positively charged and the value was increased with the increase of CTAB concentration that was due to the positively charged CTAB itself.

3.1.4. UV absorbance

A number of studies have indicated that the larger the absorbance value of suspensions, the more dispersed of CNTs dispersions. As shown in Fig.2, different types of surfactants exhibit different dispersion states, the absorbance is decremented in the following order: CNTs-TX-100 > CNTs-CTAB > CNTs-SDBS > CNTs-SDS > sonicated CNTs. Generally, CNTs dispersed by TX100 exhibit the largest absorbance value among four surfactants. As the TX-100 concentration increased from 0 to 200 mg/L, the absorbance of CNTs increased from 0.152 to 0.530. This indicates that the CNTs suspension becomes more dispersed as the TX-100 concentration increases. However, for SDBS, SDS and CTAB, the absorbance increased slightly with increasing surfactant concentration. This is mainly due to the electrostatic interaction and

steric forces between the surfactant molecules and the CNTs [17]. The dispersion mechanisms of the four surfactants on CNTs are different, so leading to the different dispersing states of each dispersion.

3.2. Effect of surfactants on sorption coefficient of triclosan to CNTs

As shown in Fig.3, surfactants have significant effect on sorption behavior of CNTs, and the effects of the four surfactants on K_d of triclosan to CNTs were different. For the two types of anionic surfactants SDBS and SDS, sorption of the CNTs decreased with the increasing of surfactant concentration. In the presence of SDBS, the K_d of triclosan to CNTs sharply decreased from 74.68 L/g to 11.12 L/g with the SDBS concentration decreased from 0 to 40 mg/L. Then the K_d remained almost stable with the increasing of SDBS concentration from 40 to 200 mg/L. In the presence of SDS, the K_d of triclosan to CNTs sharply decreased from 74.68 L/g to 32.63 L/g with the SDS concentration decreased from 0 to 100 mg/L. Then the K_d remained unchanged with the increasing of SDS concentration from 100 to 200 mg/L. This phenomenon may be due to the fact that the SDBS/SDS occupies the active site on the surface of the CNTs due to the action of the $\pi-\pi$ bond when the concentration of the surfactant SDBS/SDS is increased from 0 to 40 mg/L. As a result, the sorption sites of triclosan on the CNTs reduced, so that the sorption decreased. Interestingly, for SDBS or SDS, the K_d did not further decreased with the increase of SDBS/SDS concentration from 40 mg/L. It might be explained by the already saturated surface of CNTs towards both anionic surfactants at the concentration studied. It has been reported that the sorption of CNTs by SDBS/SDS is related to the concentration ratio between surfactants and CNTs [28]. As the concentration of surfactant increases, the removal rate of surfactant from CNTs increases first and then decreases. For SDBS, the sorption of CNTs by SDBS at 40 mg/L might be saturated. This was also confirmed by the not further dramatically decreased zeta potential of CNTs dispersion with the increased of SDBS/SDS concentration from 40 mg/L (Fig.1).

In the dispersing procedure, CNTs were sonicated in surfactant solution that allowing surfactant molecules adsorb onto CNTs. From SEM images (Fig.S2), the thick cover-like substance could be seen along the tubes after CNTs dispersed with SDBS/SDS and that might be the surfactant molecules. Some researchers explained that the sorption of CNTs by SDS and SDBS is a process of reducing the pore size of CNTs by the action of $\pi-\pi$ bond of CNTs [28,29]. This can fully explain the sorption of SDBS/SDS occupying the sorption sites of CNTs. In addition, the dispersion by anionic surfactant could be also attributed to the steric forces between SDBS/SDS and CNTs. The dispersion form of CNTs was different at different surfactant concentration (Fig.S1). The dispersion form of CNTs cannot effectively expose the CNTs activated sites available for triclosan to form $\pi-\pi$ interaction. Sorption of SDBS/SDS

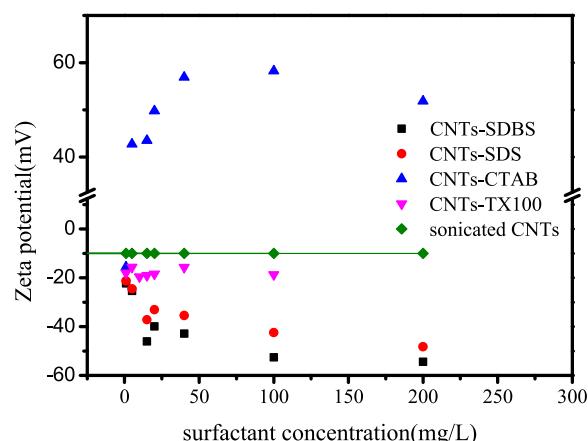


Fig. 1. Zeta potential of CNTs suspensions with the presence of four surfactants.

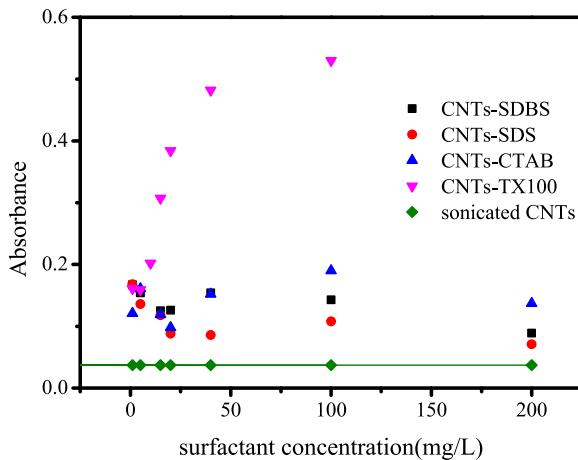


Fig. 2. Absorbance of the CNTs suspensions at 800 nm with the presence of four surfactants.

was first occupied the sorption sites of CNTs and triclosan could only adsorb to the sorption sites that SDBS/SDS not occupied. As consequence, the presence of SDBS/SDS decrease triclosan sorption to CNTs.

From the data, with the increase of anionic surfactant concentration, SDBS suppress sorption more than SDS that indicates that the competition effect of SDBS is much larger than SDS. This phenomenon may be explained by the much larger sorption of SDBS on CNTs than

SDS that leading to the more occupation on CNTs sorption sites. Visual assessment confirmed that the CNTs with SDBS were more dispersed than SDS. From the results of UV-absorbance of CNTs suspension (Fig.2), we observed that the UV absorbance of CNTs in SDBS is larger than SDS. At the same concentration, more SDBS adsorbed on CNTs than SDS. In addition, SDBS has one more benzene ring than the structure of SDS to interact with CNTs by $\pi-\pi$ bond thus it could improve CNTs dispersion [17]. Xing et al. [28] showed that the presence of benzene ring makes SDBS more easily adsorbed on CNTs than SDS. Therefore, CNTs adsorbs SDBS more than SDS thus suppressed more sorption of triclosan.

Dispersed by CTAB, sorption of triclosan to CNTs decreased sharply from 72.45 L/g to 38.00 L/g with the increase of CTAB concentration from 0 to 1 mg/L, while sorption continuously increased from 38.00 L/g to 358.34 L/g with the concentration of CTAB from 1 to 200 mg/L (Fig.3 c). In the presence of sufficient CTAB (200 mg/L), sorption of triclosan to CNTs was improved by two-fold. The sharp decreased on sorption at very low CTAB concentration may be attributed to the low dispersion of CTAB on CNTs, and the positively charged CTAB and negatively charged CNTs counteract to reduce the sorption by triclosan. Adding more CTAB to the system may result in an increase in the overall positive charge of the system, the formation of intramolecular and intermolecular bridges between CTAB and CNTs, and electrostatic association [30]. At the same time, high concentrations of CTAB could make the CNTs dispersed better, the stability of space is improved. As we discussed above, competition and dispersion effect by surfactant are important in the sorption of triclosan to CNTs. In this case, CNTs were

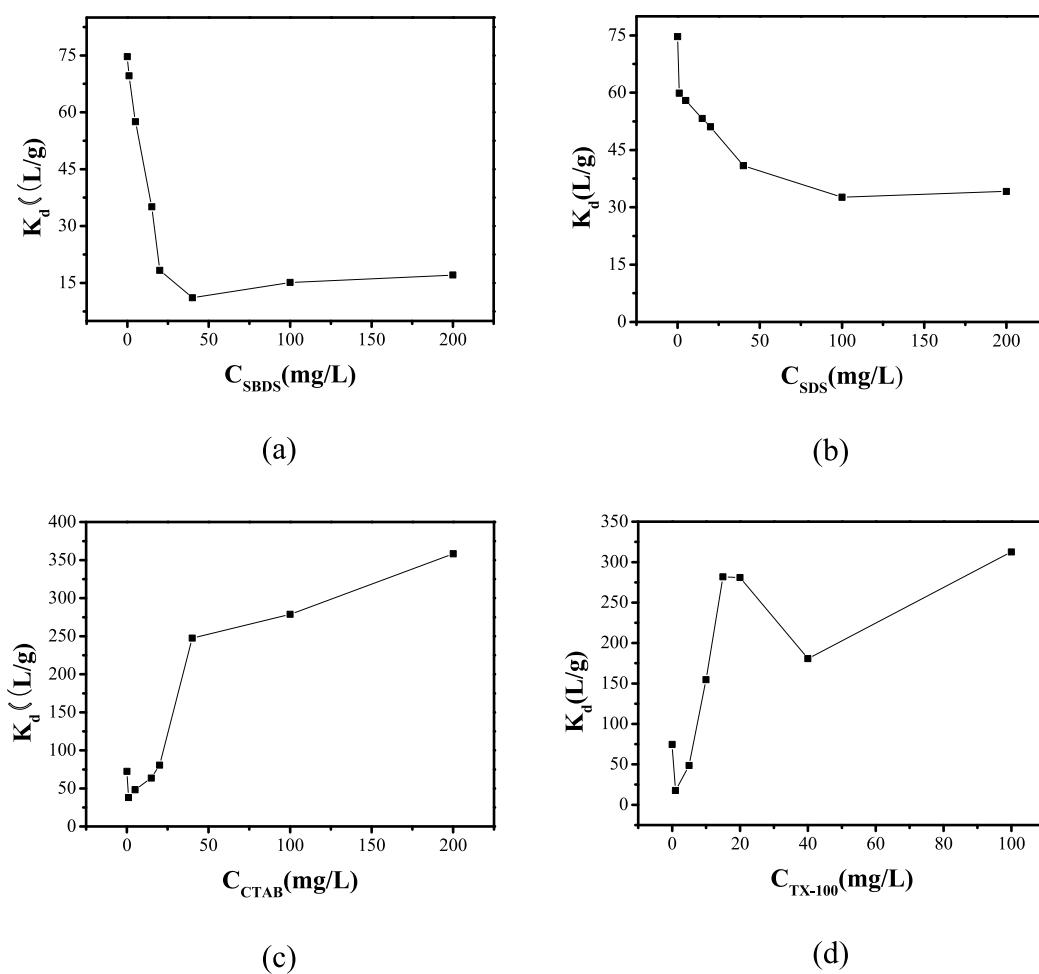


Fig. 3. Sorption coefficient of triclosan to CNTs with the presence of SDBS(a), SDS(b) and CTAB(c) solution from 0 to 200 mg/L, TX-100(d) solution from 0 to 100 mg/L in neutral pH.

also dispersed and dispersion effect was next to the TX-100 as demonstrated by the characterization results. B. Sohrabi et al. [31] reported that CTAB tends to lie flat on the surface of nanotubes or around CNTs at low concentrations of CTAB surface coverage. The tail section and most of the head set are located near the surface of the nanotube, with only a small amount of CTAB head positioned away from the surface of the nanotube and exposed to water. When increasing surface coverage, some of the CTAB molecules are preferably rotated away from the nanotube surface due to the reduced tube surface area available for each surfactant molecule, such that fewer tail particles are in direct contact with the CNTs surface. Therefore, at low CTAB concentration, the competition of sorption sites was the largest due to the flat coverage of CTAB molecules on the tubes and masked the available sites of CNTs (Fig. 4). With the increased of CTAB concentration, the CNTs become more dispersed which could be evidenced by visual assessment, the increased positive zeta potential and UV absorbance (Fig.S1, (Fig. 1 and 2). With the increase of CTAB concentration from 1 mg/L to 200 mg/L, the long tail of CTAB flouted in the dispersion and the available sorption sites for triclosan was exposed thus increase triclosan sorption. In summary, although positively and negatively charged surfactants can be adsorbed on CNTs, the adsorption mechanisms of surfactants with different charge on CNTs is different. The adsorption of CNTs by anionic surfactants is through the interaction of $\pi-\pi$ bonds with CNTs, which causes the anionic surfactants to compete with triclosan on the adsorption sites of CNTs. Adsorption of cationic surfactants with CNTs occurs only on the surface of CNTs. That is to say, the cationic surfactant covers only the surface of the CNTs, and as the concentration of the surfactant increases, the cationic surfactant tiled on the surface of the CNTs gradually rotates on the surface of the CNTs. In this process, cationic surfactants do not compete with triclosan for adsorption.

Besides dispersion mechanisms causing different sorption effect on CNTs, the surface charge of CNTs dispersion should also play a certain role on sorption. The presence of cationic CTAB makes the CNTs dispersion with positive charge as confirmed by the positive value of zeta potential. In the neutral system we studied, the triclosan (pK_a 7.9) should be positively charged. Therefore, if the electrostatic interactions between triclosan and positively charged CNTs dispersion played an important role, the sorption should be largely suppressed. Similarly, if the electrostatic interactions between triclosan and negatively charged CNTs dispersion played an important role, the sorption in SDBS/SDS should be improved. However, the results are contradictory. Therefore, it is different from the adsorption mechanism of the electrostatic interaction between the aggregated CNTs and the compound. In the surfactant-CNTs dispersion system, sorption of pollutants largely depends on the dispersion status and dispersion mechanisms other than electrostatic forces.

In the present of nonionic surfactant TX-100, sorption of triclosan to

CNTs tends to be irregularly. Sorption of triclosan to CNTs decreased sharply from 74.68 L/g to 17.66 L/g with the increase of TX-100 concentration from 0 to 1 mg/L, while sorption continuously increased from 17.66 L/g to 281.93 L/g with the concentration of TX-100 from 1 to 15 mg/L. Then sorption decreased from 281.93 L/g to 180.75 L/g with the concentration of TX-100 increased from 15 to 40 mg/L. Finally, when the concentration of TX-100 reaches 100 mg/L, the sorption of triclosan on CNTs rose to 312.57 L/g. Dispersed by TX-100, the CNTs suspension is the most dispersed among all types of surfactant. The UV absorbance increased from 0.037 to 0.57, indicating that TX-100 plays a decisive role in the dispersion of CNTs. The ink-like dispersion was also observed by visual assessment. In addition, the characterization results of SEM confirmed that CNTs dispersed by TX-100 were the most dispersed. From the above results referring to SDBS and SDS, we highlighted the importance of competition between surfactant and triclosan on sorption sites along the tubes. In the case of TX-100, competition of TX-100 and triclosan should also occur. However, due to the well dispersion effect by TX-100, TX-100 was adsorbed to CNTs causing competition, in the mean well, CNTs aggregates were also detached to single tubes and allowing re-opening new sorption sites for triclosan. Little amount of TX-100 (1 mg/L) cannot effectively disperse CNTs and causing the stronger competition than re-opening new sites that results in a sharp decreased on triclosan sorption. Actually, the competition and re-opening by dispersion effect occurred simultaneously and that played more important role depending on the types and concentration of surfactant. Some studies have shown that the polyethoxyl moiety of TX-100 and the hydroxyl/carboxy group on the surface of the CNTs can form hydrogen bonds. The formation of hydrogen bonds increases the amount of TX-100 sorption of CNTs [32,33]. With the increase of TX-100 concentration from 1 to 100 mg/L, the K_d first increased at 20 mg/L and then decreased at 40 mg/L finally increased at 100 mg/L. The effect of TX-100 concentration on triclosan sorption to CNTs seems to be irregular. Besides the competition and dispersion effect, the activated sites triclosan adsorbed may be different in TX-100 dispersed CNTs system other than other surfactants. Besides sorption sites provided by CNTs, triclosan may also act with TX-100 adsorbed to CNTs that improves sorption to different extent. The presence of TX-100 almost all enhance sorption at a certain triclosan concentration to different extent, however, different concentration of triclosan could attribute to different extent of suppression on sorption. That could be due to the different weight on competition and dispersion effect at different TX-100 concentration.

Because CNTs have certain adsorption effect towards surfactants. The amount of surfactant adsorbed on CNTs may help us to assess the residual adsorption site provided for triclosan. We evaluated the sorption capacity of CNTs towards surfactants and found that the adsorption amount of absorbed surfactant decreases in the following order: TX-100 > CTAB > SDBS > SDS. We tried to associate this results with

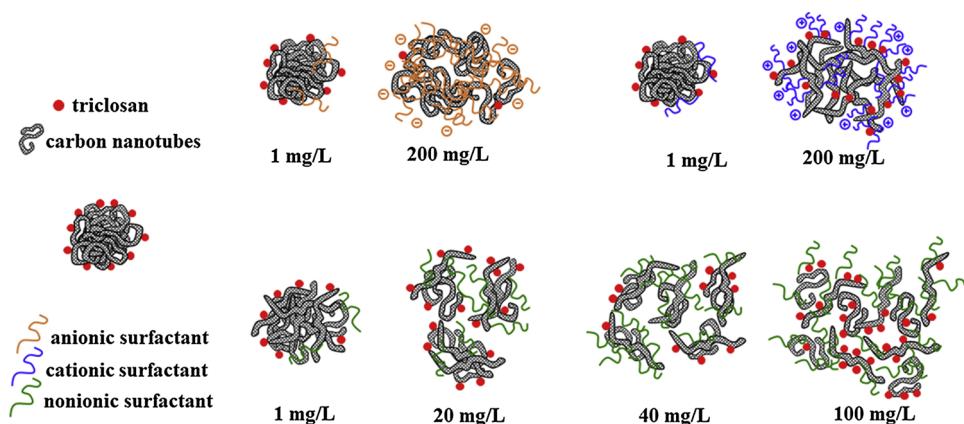


Fig. 4. Schematic diagram of sorption of triclosan to CNTs in the presence of different type and concentration of surfactants.

the adsorption of triclosan on CNTs. However, there is no apparent relationship between them. This indicates that although the amount of surfactant adsorbed on the CNTs is important for assess the adsorption of triclosan. However, due to the different adsorption modes of the surfactant on the CNTs, the adsorption sites of different surfactants on the CNTs may be different. Therefore, the amount of surfactant adsorbed on the CNTs is not a major factor affecting the adsorption of triclosan.

Besides the main interactions between aggregated CNTs and compounds, sorption mechanisms between CNT dispersion and compounds were also depends on the dispersion properties that the aggregated CNTs do not possess. Combined with dispersion characterization and sorption results we acquired, the charge, dispersion and competition could all affect sorption of triclosan in CNT dispersion. Comprehensive characterization of CNTs could give better understanding on their sorption behavior. SEM images (see Fig.S2), specific surface area (BET) (see Tab.S4) and FTIR (see Fig.S3) of CNTs and particle size distribution of dispersed CNTs (see Fig.S4) could give certain information on sorption. However, since most of the above characterization results were based on dry samples other than directly measure in dispersion, the information is limited. Among all the characterization properties, we found that the UV absorbance (A), zeta potential (ζ) and surfactant concentration (C) of the CNTs dispersion are the main factors affecting the sorption. As discussed above, we proposed that CNTs dispersion properties, the type and concentration of surfactant should have certain effect on sorption. The regulations were tried to generate between the dispersion properties and sorption. Linear regression analysis was performed using K_d as the dependent variable, UV absorbance (A), zeta potential (ζ) and surfactant concentration (C) as independent variables. The deduced linear equations were shown as follows:

$$\text{SDBS: } K_d = 126.73 - 118.819A + 2.004\zeta + 0.05C \quad r^2 = 0.885 \quad N = 14 \quad (6)$$

$$\text{SDS: } K_d = 69.316 + 31.103A + 0.67\zeta - 0.045C \quad r^2 = 0.904 \quad N = 14 \quad (7)$$

$$\text{CTAB: } K_d = -52.34 + 726.526A + 0.905\zeta + 1.504C \quad r^2 = 0.937 \quad N = 14 \quad (8)$$

$$\text{TX-100: } K_d = 731.292 + 785.63A - 37.683\zeta - 0.973C \quad r^2 = 0.920 \quad N = 14 \quad (9)$$

From the deduced Eqs. (6)–(9), the models have higher credibility with $r^2 > 0.88$. Different types of surfactants have different model equations, indicating that the type of surfactant is an important factor affecting sorption. K_d value is linear correlated with the UV absorbance, zeta potential and surfactant concentration. That is to say, the sorption of CNTs and triclosan is affected by the degree of dispersion of CNTs, charge and surfactant concentration.

In order to further analyze the weight of each factor on K_d for different type of surfactant, regression analysis was performed on single factors (A , ζ and C). The correlation coefficient (r^2) could be seen in Table 1.

The r^2 reduced followed by: $f(\zeta) > f(C) > f(A)$ for SDBS, $f(\zeta) > f(C) > f(A)$ for SDS, $f(C) > f(\zeta) > f(A)$ for CTAB and $f(A) > f(C) > f(\zeta)$ for TX-100. It can be seen that for anionic surfactant SDBS/SDS, zeta potential is the most important factor affecting the sorption of CNTs. For cationic surfactant CTAB, the concentration of surfactant in the system has the greatest effect on the sorption of triclosan to CNTs. For nonionic surfactant TX-100, UV absorbance dominates the sorption process of CNTs, which indicates that dispersion play the most important role on sorption of CNTs. The above discussion combined with theoretical analysis could give better understanding on the effect of surfactant on CNTs sorption.

3.3. Effect of surfactants on sorption isotherms of triclosan to CNTs

To study the effect of surfactants on the sorption behavior of CNTs at different triclosan concentrations, sorption isotherms of triclosan to

CNTs were measured in the presence of four surfactants at three typical concentrations. According to the above results, each surfactant concentration of 40 mg/L and 100 mg/L were selected. Isotherm without surfactant was also measured to compare. The sorption isotherms of triclosan to CNTs without and in the present of four surfactants were shown in Fig. 5. All isotherms were non-linear, the sorption data was fitted by Polanyi Manes model and Toth model. PMM was commonly used to describe sorption of viruses of pollutants on CNTs that reported by a great number of studies, while TM was used to describe heterogeneous sorption systems satisfying both low and high boundaries of the concentration. The Toth model as empirical modification of the Langmuir model aims of reducing the error between experimental data and predicted values of equilibrium data [34,35]. Only a few studies use TM to describe CNTs sorption towards pyrene and reported that the sorption of TM is mainly based on surface sorption [15,36].

The deduced parameters calculated from the sorption model were shown in Table 2 (TM) and Tab.S5 (PMM). The results of the sorption data and the Toth model are slightly better than the Polanyi Manes model, as indicated by the high r^2 (> 0.93 for TM and > 0.85 for PMM, respectively). We confirmed that sorption of CNTs could be well described by two models. Because the r^2 of TM was slightly larger than PMM, the parameters deduced from Toth model were adopted to discuss the sorption behavior. It can be observed by sorption isotherm that the sorption of triclosan on CNTs dispersed by SDBS, SDS, CTAB or TX-100 is different. In the present of 40 mg/L or 100 mg/L surfactant, the maximum sorption capacity (Q_0) of CNTs towards triclosan obtained from TM isotherms followed the order of CNTs-CTAB > CNTs-TX-100 > sonicated CNTs > CNTs-SDS > CNTs-SDBS. The effect of competition, dispersion and loadings caused by surfactant may affect the shape of sorption isotherms of triclosan to CNTs.

From Fig. 5 a–b, the presence of anionic surfactant SDBS/SDS significantly inhibited the sorption of chlorinated CNTs by triclosan. The occupancy of CNTs sorption sites by SDBS/SDS caused the sorption of CNTs by triclosan decreased by 0.86 fold and 0.97 fold than without dispersant, respectively. The presence of different concentrations of triclosan did not change the inhibition of SDBS/SDS. In addition, in the system of 40 mg/L and 100 mg/L SDBS/SDS, the sorption capacity of triclosan to CNTs at different equilibrium concentrations was not obvious change. Therefore, the concentration of triclosan is not a factor affecting sorption in the presence of anionic surfactants.

In the presence of cationic surfactant CTAB, sorption capacity of triclosan to CNTs largely enhanced by CTAB dispersed CNTs (Fig. 5 c). The presence of 40 mg/L CTAB increased the sorption capacity of CNTs by 1.34 fold than without dispersant. When the equilibrium concentration of triclosan < 1 mg/L, in the system in which 40 mg/L and 100 mg/L of CTAB exist, the sorption amount of triclosan to CNTs is almost equal. When the equilibrium concentration of triclosan was > 1 mg/L, the sorption capacity of triclosan on CNTs was significantly increased in the system in which 100 mg/L of CTAB was present. This indicates that when the concentration of triclosan is low, CNTs in different dispersed states can provide sufficient sorption sites for triclosan. When the concentration of triclosan increases, the sorption sites of CNTs are limited, and the sorption sites of 100 mg/L CTAB dispersed CNTs provide more sorption sites, so the sorption capacity of triclosan increases. In summary, in the system where CTAB exists, the concentration of triclosan affects the occurrence of sorption to some extent.

TX-100 was a type of surfactant without any charge. The presence of

Table 1
Correlation coefficient (r^2) between K_d and characterization parameters.

	SDBS	SDS	CTAB	TX-100
$K_d=f(A)$	0.535	0.745	0.453	0.775
$K_d=f(\zeta)$	0.869	0.891	0.555	0.466
$K_d=f(C)$	0.553	0.833	0.905	0.631

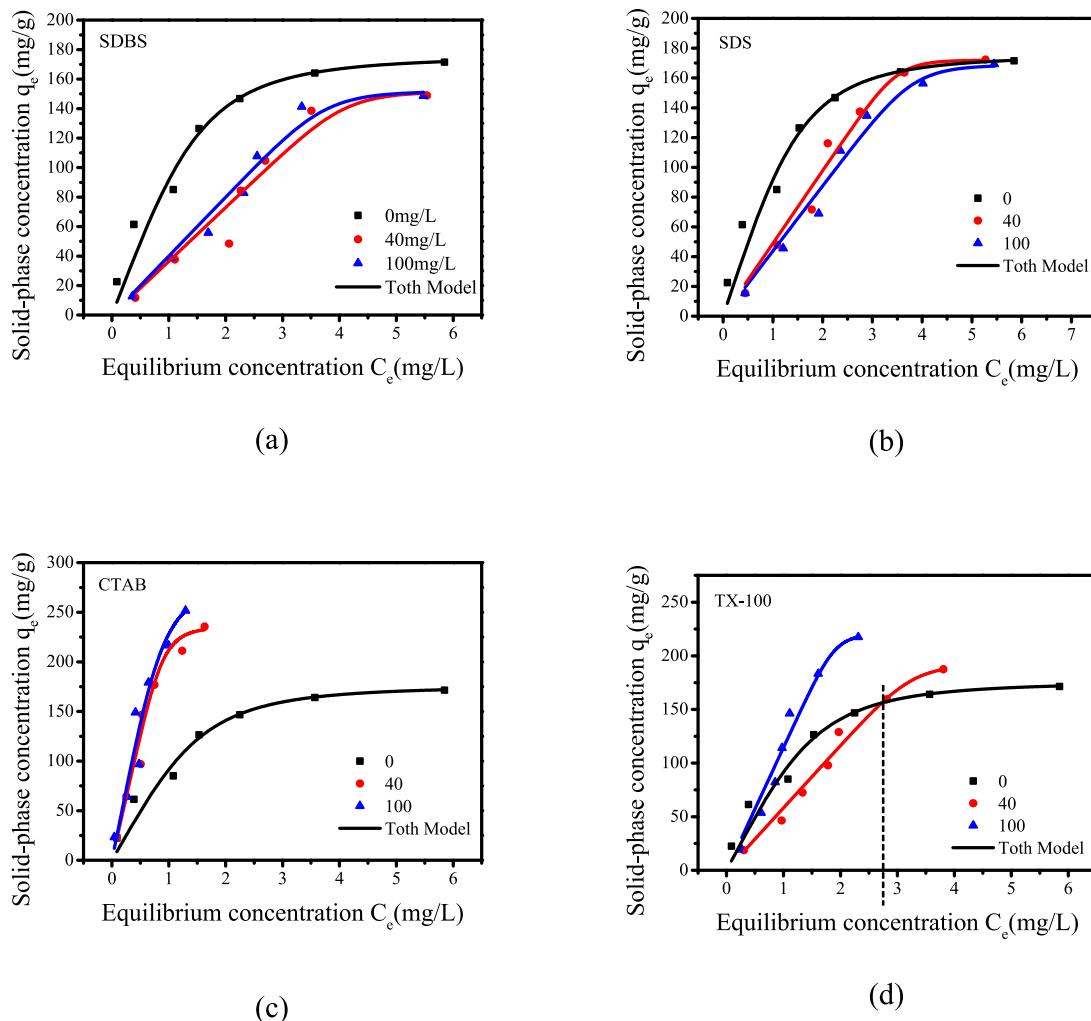


Fig. 5. Sorption isotherms of triclosan to CNTs without surfactant and the presence of 0, 40 mg/L, 100 mg/L SDBS(a), SDS(b), CTAB (c), TX-100 (d) and the data fitted with Toth Model.

Table 2

Fitting parameters for Toth model (TM) fitting the isotherms of triclosan to CNTs with the presence of four surfactants.

	Parameter concentration(mg/L)	Q_0 (mg/g)	t	K_t (L/mg)	r^2
SDBS	0	175.33 ± 14.33	2.48 ± 0.51	0.25 ± 0.24	0.94
	40	150.59 ± 14.26	11.36 ± 0.99	$1.00 \times 10^{-7} \pm 4.26 \times 10^{-6}$	0.93
	100	151.61 ± 15.83	8.64 ± 0.57	$1.00 \times 10^{-5} \pm 3.14 \times 10^{-4}$	0.97
SDS	40	172.02 ± 17.27	11.74 ± 1.24	$3.85 \times 10^{-7} \pm 8.50 \times 10^{-6}$	0.97
	100	168.64 ± 9.90	9.35 ± 0.59	$3.32 \times 10^{-6} \pm 4.53 \times 10^{-5}$	0.97
CTAB	40	235.12 ± 14.48	5.01 ± 0.35	1.45 ± 0.01	0.95
	100	277.34 ± 43.11	3.33 ± 3.34	1.09 ± 0.03	0.92
TX-100	40	191.95 ± 11.92	9.50 ± 0.65	$1.18 \times 10^{-5} \pm 3.73 \times 10^{-4}$	0.98
	100	220.34 ± 17.69	10.55 ± 1.69	$1.00 \times 10^{-3} \pm 0.06$	0.96

100 mg/L TX-100 increases the sorption capacity of CNTs towards triclosan. In the system with 40 mg/L TX-100, the sorption is inhibited when the concentration of triclosan is low, and the sorption is promoted when the concentration is high (Fig. 5 d, Table 2). The presence of 40 mg/L and 100 mg/L TX-100 increases maximum sorption capacity by 1.09 and 1.26 fold, respectively. For 100 mg/L TX-100, dispersion is the most important factor affecting sorption. Since the UV absorbance is maximized at 100 mg/L, this indicates that the degree of dispersion is large and the CNTs show the most sorption sites, which is sufficient to supply triclosan. In addition, the polyethoxy moiety of TX-100 and the hydroxyl/carboxy group on the surface of the CNTs can form a hydrogen bond. The formation of hydrogen bonds increases the amount of

sorption of CNTs. Therefore, in the system presence of 100 mg/L TX-100, the sorption amount of CNTs is remarkably improved. When the equilibrium concentration of triclosan is low ($C_e < 3$ mg/L), the dispersion effect of 100 mg/L TX-100 on CNTs is better than that of 40 mg/L TX-100, so in the system where 100 mg/L TX-100 exists, CNTs are exposed to more sorption sites and form more hydrogen bonds to promote the sorption of triclosan. However, in the system presence of 40 mg/L TX-100, CNTs are exposed to less sorption sites and fewer hydrogen bonds, and the lower concentration of triclosan is less competitive than TX-100, so the sorption capacity of triclosan declines. When the concentration of triclosan increased ($C_e > 3$ mg/L), the competitiveness of triclosan in the solution increased, thereby

promoting sorption. In summary, in the system in which TX-100 is present, the concentration of triclosan is also an important factor affecting adsorption.

4. Conclusion

The purpose of this study is to provide comprehensive information on the sorption of triclosan to CNTs dispersed with different types and concentration of surfactants. The main findings could be summarized as follows:

- (i) The presence of anionic surfactants SDBS and SDS significantly inhibits the sorption of CNTs by triclosan. The presence of cationic surfactants promotes the sorption of CNTs. For nonionic surfactants, sorption of CNTs is inhibited when the surfactant concentration is low, while sorption is promoted when the concentration is high.
- (ii) Sorption coefficient was linearly correlated to UV absorbance, zeta potential and surfactant concentration. That is to say, the sorption of CNTs and triclosan is affected by the degree of CNTs dispersion, charge and surfactant concentration.
- (iii) Surface charge is the most important for anionic surfactant (SDBS/SDS) affecting sorption. For the cationic surfactant CTAB, the concentration of the surfactant is the main factor affecting the sorption. For the nonionic surfactant TX-100, the dispersion state is the most important factor.
- (iv) Sorption isotherms of triclosan by CNTs dispersed by the three types of surfactants fitted well with the Toth model, and the cationic surfactant CTAB dispersed CNTs show the largest sorption capacity. The results provide basic supports on application of CNTs in remediation area and exploring the fate of both CNTs dispersion and pollutants.

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