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Sorption of benzene, toluene, ethylbenzene from aqueous phase onto carbon nanotubes and the mutual effects of humic acid

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ABSTRACT

The adsorption behaviors of benzene (B), toluene (T), and ethylbenzene (E) onto carbon nanotubes (CNTs) were investigated in this study. To better disclose its sorption mechanism, the influences of aquatic conditions, including concentration, pH and temperature were studied. It was found that the adsorption capacity for BTE follows the order of B<T<E, which is mainly due to their water solubility. Langmuir model fitted adsorption isotherms well and was better used to quantify their adsorption capacities. In comparison, pH was found to influence the adsorption rather than temperature, which was mainly attributable by the π-π electron-donor-acceptor mechanism between the aromatic ring of benzene, toluene, and ethylbenzene and the functional groups on carbon nanotube surface. A higher adsorption for BTE achieved at higher pH values. When there exists B, T, and E, CNTs was more preferred to adsorb E, due to their water solubility. The addition sequences of BTE and humic acid (HA) sorption could affect their sorption mechanisms, with their competition effects occurred stronger at lower HA concentration. It was found that CNTs would be easier to bond HA molecules than BTE. The current study is of important to fully understand the adsorption behavior of BTE on CNTs and their mutual effects with HA, thus to better understand their co-existing effects in ecosystems.

Keywords: Carbon nanotubes; BTE; Adsorption; Humic acid

1. Introduction

Petroleum hydrocarbons in particular benzene, toluene and ethylbenzene (BTE) has been the most commonly contaminants in the past decades, due primarily to the wide use of petrol, gasoline, diesel, petrochemical products in industrial syntheses and operations [1,2]. Almost any of petrol or gasoline spill on the soil or the subsurface would cause the BTE pollution. Seriously, larger amount of BTE have been discharged from industrial manufacture and transportation wastewater during the many decade years [2], and may pose adverse effects on water quality, public health and live beings [3]. It was reported that the presence of BTE in environmental ecosystems would cause harmful effect on human health, leading to cancer, mucosal membranes irritation, impairment of the central nervous system, and liver and kidney disruption [4]. Removal of benzene, toluene and ethylbenzene (BTE) from aqueous and gas phase has, therefore, drawn increasingly attention by researchers. Since, various methods, include physical, chemical and biological approaches have been studied to eliminate BTE over the years [1].

Adsorption is a process that is considered to be the most feasible and conventional technique for the removal of organic matters, and has been extensively used in various fields, especially in water treatment processes with quite satisfactory removal efficiencies. The use of porous materials for the removal of benzene, toluene, and ethylbenzene (BTE) from aqueous solution has since aroused researchers' attention [4–7]. Among adsorbents, carbon nanotubes (CNTs) with porous property, nano-sized diameter, tubular microstructure, hence high surface area have been the worldwide hotspot of investigation on the removal

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of various organic contaminations, such as dioxin [8], trihalomethanes [9], chlorophenols [10], herbicide [11], dimethyl phthalate [12], phenolic compounds [13] and dyes [14], and metal ions, such as Pb^{2+} [15], Cd^{2+} [16], Cr^{6+} [17], and Zn^{2+} [18] from aqueous solution. Besides, as one-dimensional macromolecules CNTs provide strong thermal and chemical stability [19].

However, studies around the adsorption of BTE onto CNTs were mainly focused on the surface modification of CNTs [2,7]. There still lacked the comprehensive understanding of mutual effects of BTE adsorption in natural aquatic environments. It should be noted that the dissolved organic matters (DOM) exhibit a diversified water-solubility and reactivity in aquatic systems [15], and sorption of organic contaminants by CNTs was greatly influenced by the coexisting dissolved organic matter (DOM). Humic acid (HA) which contains many organic functional groups such as carboxylic, amine, quinone, and hydroxylare ubiquitous in natural environments (i.e., soils, rivers and wastewaters). It was reported due to its own structure effects, HA is ready to interact with CNTs in aquatic systems enhancing their stability and transport in aquatic system [20]. This posed the change of physicochemical behavior of CNTs due to the presence of HA. It was found that the presence of HA may also affect the adsorption of some chemical species, mainly metal ions, on CNTs by forming strong complexes with these ions on CNT surfaces [15]. The adsorbed HA on CNTs surface was showed to cause modification of adsorbent surface properties and have partial complexation with adsorbate [15]. Lin et al. [21] demonstrated that the surface-bound HA on CNTs (HA-CNTs) introduced oxygen containing functional groups and negative charges on the surface, thus greatly increasing the sorption of Pb^{2+}. Thereby, the study of the mutual effects of HA and BTE was significantly important to clear their sorption mechanism on CNTs, and the transport performance of BTE affected by HA in natural aqueous environments should be considered.

The objective of this work is to systematically investigate the transport fate of B T and E adsorbed by carbon nanotubes (CNTs) influenced by aqueous environment conditions, including adsorbate concentrations, pH and temperature. Their competitive adsorption behaviors in the combination of B, T, and E due to their structure differences were studied. Finally, the mutual effects of BTE and HA sorption on CNTs were investigated.

2. Materials and methods

2.1. Reagents and materials

Humic acid (sodium salt) and benzene, toluene and ethylbenzene (analytical grade, purity > 99.9%.) were purchased from Sigma–Aldrich (Shanghai, China).

To keep the consistent property of CNTs in the studies for the comparison, a batch of mutiwalled carbon nanotubes (CNTs) were fabricated by dissociating methane in a hydrogen flow at 900 K. Ni nanoparticles which supported on diatomites were used as catalysts. The produced CNTs were suspended on the hydrofluoric acid firstly for at least 24 h to remove the catalyst support and then concentrated nitric acid to dissolve the Ni particles. After that, CNTs were dispersed in concentrated nitric acid and refluxed at 413 k for 1 h. The fabricated CNTs were washed to remove the residual acid until solution pH achieved the value of 7. Transmission electron microscopy (TEM) images show that the produced CNTs has inner diameter 5–10 nm and outer diameter 15–30 nm.

2.3. Adsorption experiments

Humic acid solution was prepared by dissolving 100 mg HA in 100 mL 0.1 mol/L NaOH solution. After the HA particles dissolved, the solution was diluted into 1 L with the pH was adjusted to 7 by using 0.01 mol/L HCl and/or NaOH. For each of the experiments, the prepared HA solution was filtrated with 0.45 µm filter.

The adsorption experiments were conducted by adding 50 mg CNTs into 100 mL of BTE and HA solution in the glass bottles, respectively, with initial concentration ranged from 20 to 150 mg/L. The concentrations of BTE solution were selected based on the levels of concentration in real industrial wastewater. The prepared glass bottles were covered and kept shaking at room temperature 25°C with 200 rpm. After 24 h until the adsorption achieved equilibrium, the supernatant solutions were filtrated by 0.45 µm syringe filter, and BTE concentrations were analyzed by gas chromatograph and flame ionization detection (GC-FID, Shimadzu, Japan).The operation injection and detector temperature were set at 200°C. The following temperature was used at 50°C for 8 min and 100°C for 5 min with 4°C/min. All experiments were repeated at least two times, and the calculated mean values were used for the analysis. The HA concentration in the supernatant were measured using a UV-vis spectrometer (UV-1800, Shimadzu, Japan) at 259 nm in a quartz cell.

The zeta potential (ξ) of CNTs were measured by a DB-525 Zeta Plus zeta potential analyzer (Brookhaven, USA) across the pH range 2–10. The solution pH was adjusted by using 0.1 mol/L NaOH and HCl solutions.

2.4. Effect of pH and temperature on adsorption of BTE

For each experiment, the adsorption protocol followed the same method as previous experiments by adding 50 mg CNTs into 100 mL of BTE solution in the glass bottles with initial concentration ranged from 20 to 150 mg/L. Regarding the effect of pH, the pH of the mixtures was adjusted to 3, 7 and 10, respectively. For the experiments of temperature effect, the mixtures were kept at 25°C, 35°C and 40°C until their adsorption equilibrium (i.e., 24 h).

2.5. Effect of the presence of HA on adsorption of BTE

The mutual effects of BTE and HA sorption on CNTs were conducted using four mixing sequences: (1) BTE, HA, and CNTs were prepared together (denoted as (BTE-HA-CNTs)). (2) BTE and CNT were pre-equilibrated for 24 h before the addition of BTE (denoted as (BTE-CNTs)-HA). (3) HA and CNTs were pre-equilibrated for 24 h before the addition of BTE (denoted as (HA-CNTs)-BTE).(4) BTE and HA were pre-equilibrated for 24 h before the addition of CNTs (denoted as (BTE-HA)-CNTs). To study the concentration effects, BTE solution with constant initial concentration 20 mg/L were investigated in sequences of 0–20 mg/L HA, which is near to the real TOC concentration in the environment.

2.6. Data analysis

The amount of BTE adsorbed on CNTs (q_e, mg/g) was determined from the changes of the initial concentration (C_0) and equilibrium concentration (C_e) by:

$$q_e = \frac{C_0 - C_e}{m} V \tag{1}$$

where V is the volume of solution (L), and m is the mass of adsorbent (g).

The most widely known isotherm equation Langmuir adsorption model was used to fit the adsorption isotherms:

$$q_\mathrm{e} = q_\mathrm{max} K_\mathrm{L} C_\mathrm{e} / (1 + K_\mathrm{L} C_\mathrm{e}) \tag{2}$$

where C_e (mg /L) is the liquid-phase equilibrium concentration, q_max(mg/g) is the maximum solid-phase concentration or the weight amount of adsorbed (mg) per one gram of adsorbent (g), K_L are the Langmuir constants of adsorption coefficient.

Sorption coefficient (K_d) in unit of L/g of BTE and HA by CNTs was obtained from the equation:

$$K_d = \frac{q_e}{C_e} \tag{3}$$

3. Results and discussion

3.1. Adsorption of BTE on CNTs

Fig. 1 shows the adsorption results of BTE on the CNTs, respectively. The final pH of mixtures were measured around 7 with room temperature of 25°C. It is obvious that the trend of adsorption curves was not linear, and the nonlinear isotherms indicate the heterogeneous sorption sites on CNTs surfaces. The regression data fitted by Langmuir adsorption model are summarized in Table 1. As seen from the fitting results, Langmuir model could be well used for the simulation of BTE adsorption isotherm, with coefficients values ≥ 0.97 for three of them. It is obvious that the sorption capacity for BTE follows the order of B < T < E, with the maximum adsorption amount (q_{max}) were 118.01 mg/g, 132.61 mg/g, 199.30 mg/g for B, T and E, respectively. It has been suggested that this tendency happened presumably due to the effects of their water solubility, where B is 1790 mg/L larger than T (530 mg/L) and E (152 mg/L) [2]. Furthermore, the nature hydrophobicity of them (based on Log K_{ow}) were calculated as B = 2.13, T = 2.69, and E = 3.15, respectively. It should be worth noting that there exists positive correlation between hydrophobicity and adsorption capacity. Highest hydrophobicity of E achieved highest adsorption capacity on CNTs, and the results were consistent with some previous investigations of BTE adsorption [2,5,6].

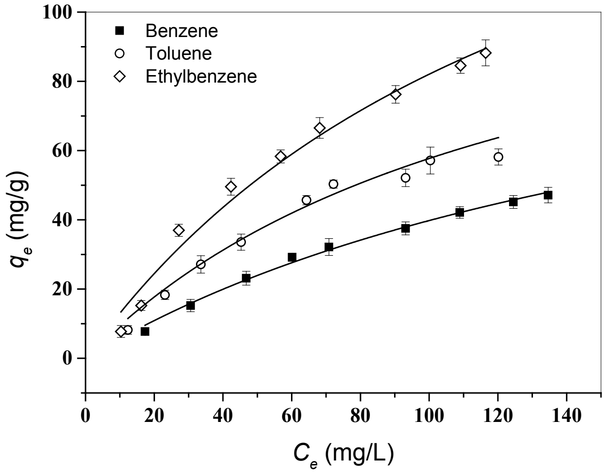

Fig. 1. Adsorption of BTE on CNTs with pH 7 at 25°C. Curves were based on fits obtained using Langmuir adsorption isotherm.

The adsorption capacities of BTE onto CNTs were much higher than other porous materials, such as the periodic mesoporous organosilica (PMO) [22], zeolite [23,24], thermally modified diatomite [25], montmorillonite (Mt) [26], and lignite [4], etc.,but lower than the use of macroreticular resins reported by Lin et al. [27]. This highlighted the potential use of carbon nanotubes than others. Benefit from its high adsorption capacity, carbon nanotubes such as multiwalled carbon nanotubes was successfully used for the extraction and preconcentration of metal ions from aqueous phase [28–30]. The use of CNTs is a promising method for the BTE removal from aqueous solution. To further improve its adsorption behavior, Su et al. [2] used sodium hypochlorite (NaClO) solution to oxidize carbon nanotubes (CNTs) surfaces and found that this oxidization method could enhance CNTs adsorption for BTE, and achieved a higher adsorption capacity of 212 mg/g, 225 mg/g and 255 mg/g, which are higher than the current results as well. Yu et al. [31] found that a little increase of oxygen content on CNTs surface (i.e., 3.2%) promoted the adsorption capacity for toluene, ethylbenzene and m-xylene (TEX) as dispersive interaction between CNTs and TEX was enhanced, while a further increase to 5.9% unexpectedly hindered their interaction thus reduced the adsorption capacity. However, due to the complexity of ecosystems, it is necessary to investigate the adsorption behavior at various aqueous environments.

3.2. Effects of pH and temperature on the adsorption of BTE on CNTs

The impacts of the pH on the adsorption of BTE onto CNTs are shown in Fig. 2. The method of adsorption iso-

Table 1
Results of Langmuir adsorption

Solution	q_max(mg/g)	K_L (L/mg)	r^2
B	118.01 ± 15.3	0.005 ± 0.001	0.991
T	132.61 ± 26.7	0.008 ± 0.002	0.973
E	199.30 ± 40.5	0.007 ± 0.002	0.974

therm was used to compare the adsorption properties at three different pH ranges (acid, neutral and alkaline). The initial and final pH values of the mixtures were measured, and pH changes were negligible for each of the experiments. Results showed that the pH influenced the adsorption capacities obviously, that the adsorption of BTE was enhanced at higher pH values. The Langmuir model fitting results are summarized in Table 2. From the fitting results, the maximum adsorption amount (q_{max}) was promoted from 109.82 to 113.40 mg/g, 130.64 to 199.41 mg/g, and 196.95 to 214.96 mg/g for B, T and E, respectively. For the influence of pH on the CNTs adsorption, electrostatic force could play be a key between adsorbent and adsorbate. As shown from Fig. 3, the CNTs occurred positive charge at low pH ranges, while negatively charged at higher pH values. However, it has been suggested that the hat B, T and E are in the molecule form during adsorption processes and the ion exchange does not play a part in BTE adsorption [7]. Thereby, dispersive interactions are predominant. Concerning about the significant change of adsorption capacity with pH variation, it is of great important to clear the adsorption mechanism of BTE via CNTs. The π-π electron-donor-acceptor mechanism was regarded as the main mechanism dominant in the adsorption process. It should be noted that there are several functional groups on CNTs surfaces, such as, carboxylic groups, lactonic groups, and phenolic groups, etc. The π-π electron-donor-acceptor could be readily happened during the interaction of CNTs to BTE molecular, for example, the carboxylic oxygen-atom on CNTs surface could act as the electron-donor and the

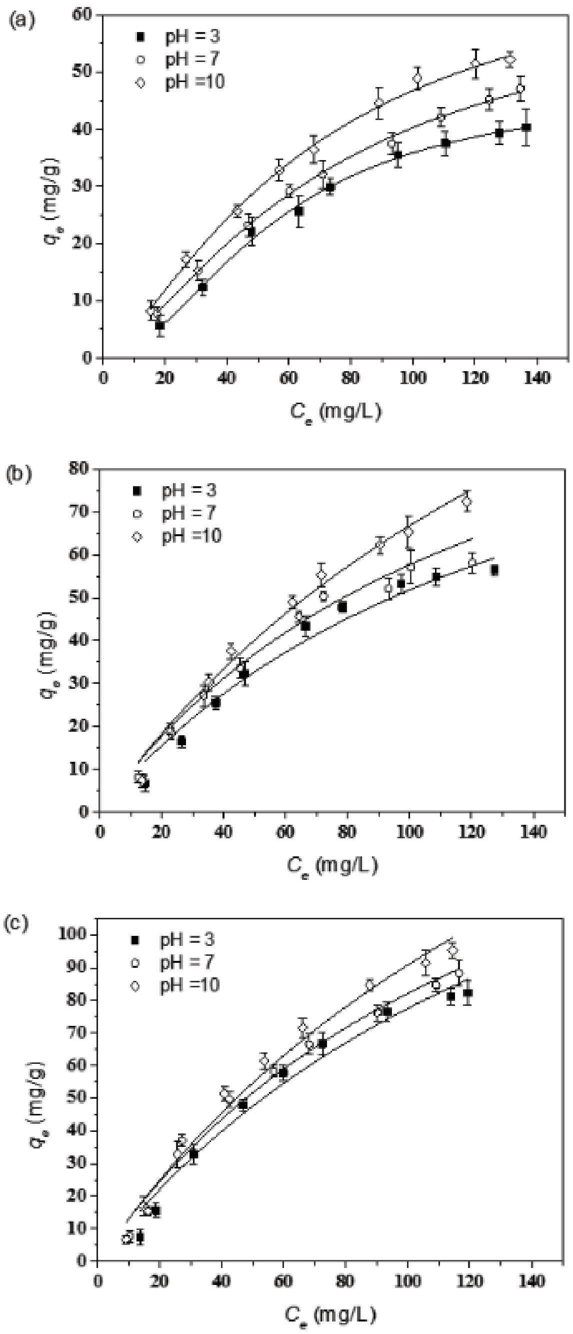

Fig. 2. Adsorption of (a) B, (b) T and (c) E on CNTs with various pH values at 25°C. Curves were based on fits obtained using Langmuir adsorption isotherm.

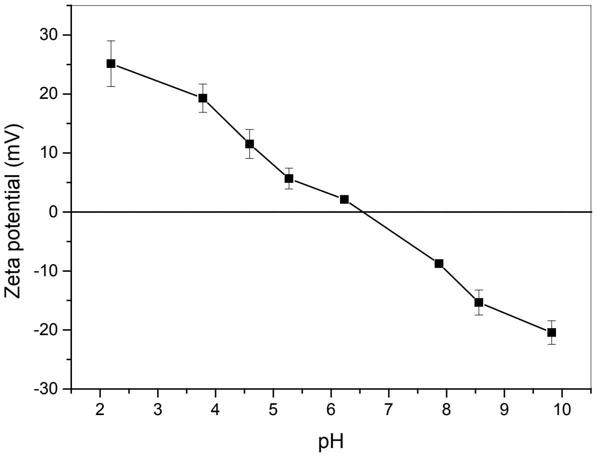

Fig. 3. Changes of zeta potential of CNTs with various pH values.

Table 2
Results of Langmuir adsorption at different pHs

Solution	q_{max} (mg/g)			K_L (L/mg)		
	pH = 3	pH = 7	pH = 10	pH = 3	pH = 7	pH = 10
B	109.82 ±27.3	118.01 ± 15.3	113.40 ± 9.5	0.004 ± 0.001	0.005 ± 0.001	0.007 ± 0.001
T	130.64 ±24.9	132.61 ± 26.7	199.41± 39.9	0.003 ± 0.001	0.008 ± 0.002	0.005 ± 0.001
E	196.95 ±40.3	199.30 ± 40.5	214.96± 27.3	0.006 ± 0.002	0.007 ± 0.002	0.007 ± 0.001

aromatic ring of BTE acts as the electron-acceptor, and is responsible for the uptake of BTE by CNTs [32]. The changes of adsorption behavior in this study was mainly because of the attraction between the π orbital on the carbon basal planes and the electronic density in the benzene and toluene aromatic rings (π-π interactions). After donating the electron to benzene rings, H^+ would be readily attracted the negatively charged CNTs. This would result a higher adsorption behavior of CNTs for BTE molecular at higher pH values. It should be worth noting that adsorption induced by electrostatic, hydrophobic and hydrogen-bond interactions depends strongly on pH because of the changes of electrostatic repulsion and the hydrophobic and hydrogen-bond interactions as pH changes, resulting in the changes of BTE adsorption with pH.

Regarding the effects of temperature on CNTs adsorption, the results are presented in Fig. 4. The corresponding Langmuir fitting results are summarized in Table 3. It has been suggested that the adsorption of organics via CNTs tends to endothermic, in which higher temperature favor the adsorption processes [33]. However, our current results showed that the increase of temperature slightly enhanced the BTE adsorption for CNTs, and the adsorption behavior was found most significant with toluene, but still limited at higher temperature (from 35 to 40°C). This indicates that the influence of temperature was not quite significant between BTE and CNTs.

3.4. Competitive adsorption of BTE on CNTs

Fig. 5 shows the competitive adsorption of BTE onto CNTs. The first column showed the adsorption capacity, which was the adsorption capacity without others. However, with the presence of other compositions, such as, B+T, B+E, T+E, and B+T+E, the adsorption capacity decreased dramatically, which means some part of adsorption sites were occupied by other composition. From Fig. 1, the adsorption capacity for BTE follows the order of B < T < E, which suggests their adsorption preferences. The presence of their combination, the adsorption capacity decreased 10% and 11% when there were B and T, while, decreased 20% and 5% for B+E. This means that when there disperse several compositions, the adsorption of them via CNTs was readily happened from the higher adsorption capacity. For example, when there are B and E existed together in the aqueous solution, the adsorption sites were occupied by E first, and then B, due to their solubility tendency. As the CNTs has the highest adsorption capacity for E, it has the priority to adsorb E firstly. This was consistent with the case, that the adsorption capacity decreased 14% for T and only 7% for E, when T and E existed together, and the case that the adsorption capacity decreased dramatically when B T and E presented together (i.e., decreased 21%, 24% and 17%, respectively). This is of significant for the implication of CNTs for the removal of BTE from the aqueous solution. For the case of presence of B and T, the extent of adsorption capacity decreased was similar to each other, which implies that besides the adsorption preference, the other factor like the disperse interaction could also influence the competitive adsorption, as was suggested that a better dispersive interaction increases the available adsorption sites, which consequently can be favorable for the aqueous phase adsorption [31].

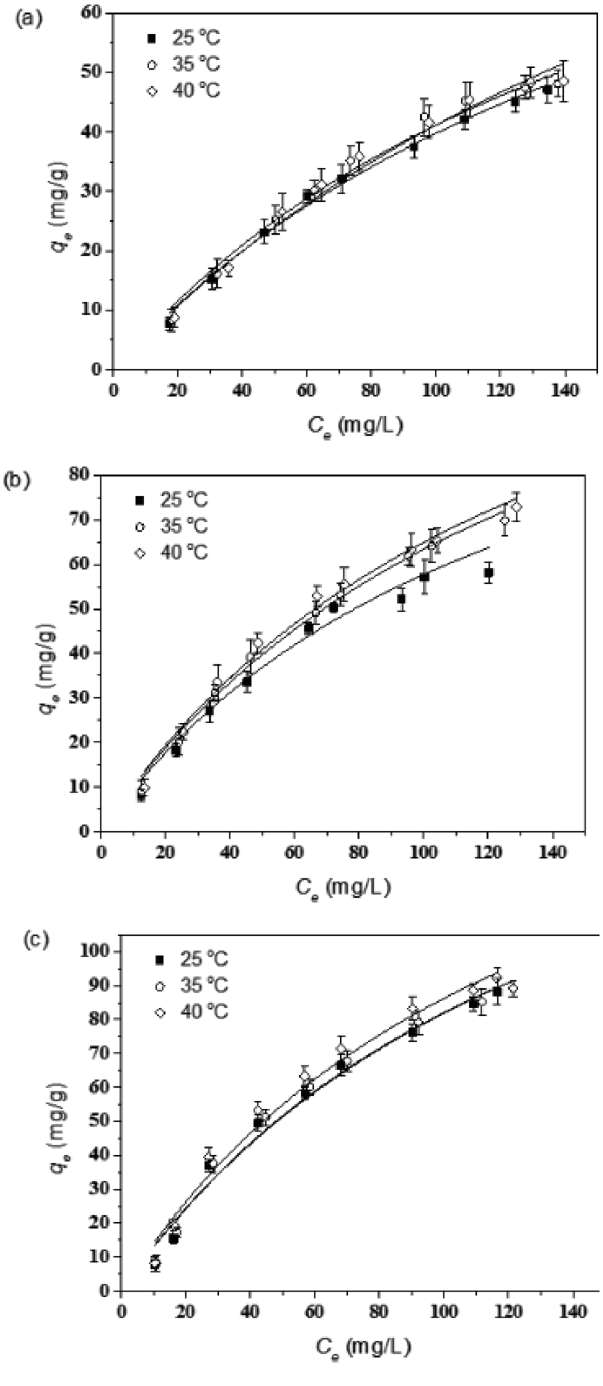

Fig. 4. Adsorption of (a) B, (b) T and (c) E on CNTs with various pH values at 25°C. Curves were based on fits obtained using Langmuir adsorption isotherm.

3.5. Mutual sorption effects of HA and BTE on CNTs

As shown in Fig. 6, the sorption coefficient (K_d) values for the sorption of BTE onto CNTs follow the order of B > T > E, which in agreement with previous results from adsorption isotherms. It is obvious from Fig. 6 that the effects of HA in the addition sequences are different with highest K_d occurred at (BTE-HA-CNTs). This implies that the presence

Table 3
Results of Langmuir adsorption at different temperature

Solution	$q_{\max}$ (mg/g)			K_L (L/mg)		
	25°C	35°C	40°C	25°C	35°C	40°C
B	118.01 ± 15.3	115.09 ± 14.3	116.68 ± 14.6	0.005 ± 0.001	0.006 ± 0.001	0.005 ± 0.001
T	132.61 ± 26.7	156.07± 14.6	157.50 ± 19.8	0.008 ± 0.002	0.007 ± 0.001	0.007 ± 0.001
E	199.30 ± 40.5	202.18± 34.5	200.41 ± 31.8	0.007 ± 0.002	0.006 ± 0.001	0.007 ± 0.001

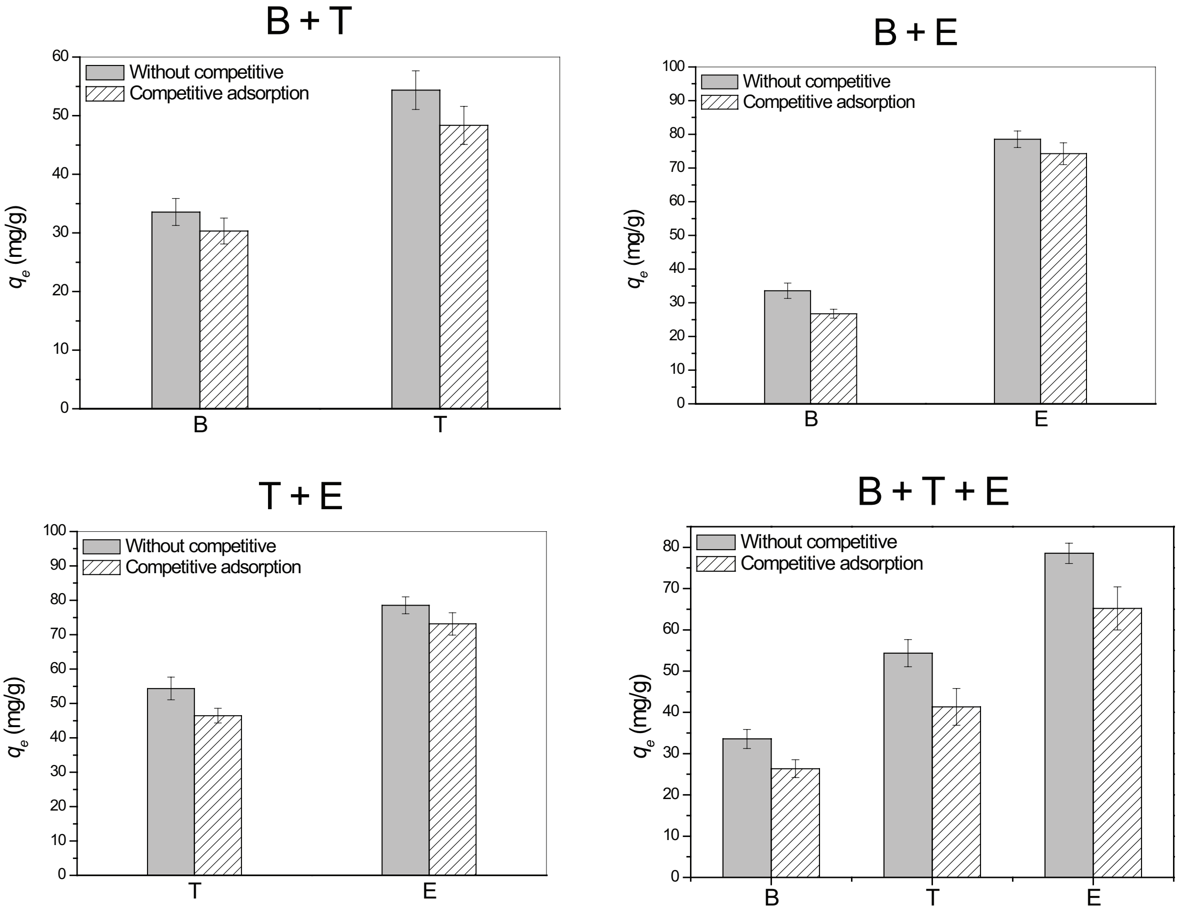

Fig. 5. Competitive adsorption of B, T, and E on CNTs. Experiments were conducted at pH 7 and temperature of 25°C.

of HA directly competes with BTE occupied the sorption sites on CNTs. It should be noted that due to its high hydrophobicity, CNTs can aggregate and form bundles in aquatic environments, which provides more adsorption sites (i.e., groove, interstitial, and inner areas). It was demonstrated that the surface sorption is the dominant mechanism for CNTs rather than others, such as pore filling [34]. The bundle interstitial and groove sorption sites offer much stronger force to trap sorbates. HA is a complex mixture of a heterogeneous natural continuum of high to low molecular weight species. The wide distribution of species would contribute to more sorption capacity. When there exists HA and BTE together with CNTs, competition for sorption sites of CNTs happened simultaneously.

The presence of various HA concentrations gave different trends of K_d values and the changes in the K_d values are smaller at relatively high HA concentration, which agrees well with the mutual effects of dialkylphthalate esters and humic acid sorption on CNTs by Wang et al. [35]. This is presumably due to the fact that at low HA concentration, the amount of HA molecules is not high enough to form complexes with all BTE molecules so that some free BTE molecules are left to sorb on the CNT surfaces. When the concentration of HA increases, more BTE are bound with HA, making the free BTE much harder to reach CNTs surface and thus weaken the competition. HA molecules, especially the soluble ones would be easily occupied on CNTs surface and govern the transportation behavior of

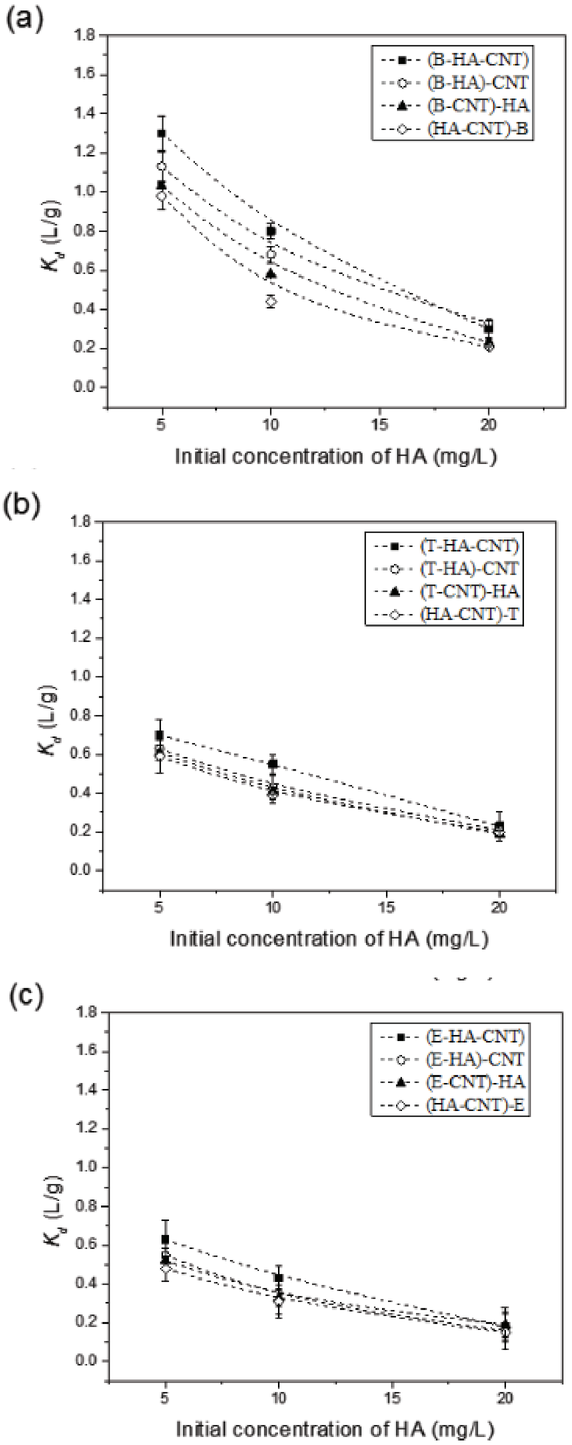

Fig. 6. Sorption coefficient of B (a), T (b) and E (c) in the sequences of HA on CNTs. Initial concentrations of HA are 5 mg/L, 10 mg/L and 20 mg/L.

organics, as was manifested by the K_d values at high HA concentrations.

It is obvious that K_d values decreased fast especially for B with the increase of HA concentration, implying the poor competition potential with HA. The results that the K_d values of (BTE-HA-CNT) were higher than that of (HA-CNT)-BTE in Fig. 6. When HA is initially adsorbed on CNTs surfaces, strong competition of BTE is needed. For the case of BTE was pre-equilibrated with HA which is (BTE-HA)-CNTs addition, the K_d values were the secondary high in the sequences. This indicates that complexation form of HA with BTE is possible. However, the decrease compared to (BTE-HA-CNT) may also harmed by the effects of complexation, that the BTE are first bound with HA causing BTE was harder to pass through to reach on CNTs sorption sites. It should be noted that HA may also affect the adsorption of some chemical species, mainly metal ions, on CNTs by forming strong complexes with these ions on CNT surfaces. The mutual effects of HA was reported to positively promote the sorption of Pb^{2+} on CNTs surface due to the interaction between HA and Pb^{2+}. The polar moieties in HAs can also interact with the O-containing hydrophilic functionalities at the graphene surfaces. More details of the mutual effects between HA and organic contaminants should be necessary to understand their transportation fate adsorbed on CNTs surface in aqueous environments.

4. Conclusions

The adsorption capacities of B, T and E on CNTs from aqueous solution were studied. The effects of aquatic environment including concentration, pH, and temperature on CNTs sorption were systematically investigated, which illuminates the transformation fate of BTE using carbon nanotubes. The mutual effects of BTE and HA on CNTs sorption were studied. The most widely used Langmuir adsorption isotherm model fitted the data well, which helped quantify the adsorption capacity for BTE. CNTs has the greatest adsorption capacity for E, which was quite important for the competitive adsorption, and the pH influenced the adsorption more than temperature. The adsorption of BTE was enhanced at higher pH values. The adsorption mechanism of BTE appears mainly attributable to π-π electron-donor-acceptor interaction, due to the presence of the aromatic ring of BTE molecules and the functional groups on CNTs surface. Therefore, the attraction between the π orbital on the carbon basal planes and the electronic density in the BTE aromatic rings (π-π interactions) changed with pH. After donating the electron to benzene rings, H^+ would be readily attracted the negatively charged CNTs. This would result a higher adsorption behavior of CNTs for BTE molecular at higher pH values.

The addition sequences of HA and BTE could affect their sorption mechanisms, with the competition occurred directly when HA presented. The change of adsorption coefficient are smaller at higher HA concentrations. This is presumably due to the fact that at low HA concentration, the amount of HA molecules is not high enough to form complexes with all BTE molecules so that some free BTE molecules are free adsorbed on the CNT surfaces. When the concentration of HA increases, more BTE are bound with HA, making the free BTE much harder to reach CNTs surface and thus weaken the competition. HA molecules, especially the soluble ones would be easily occupied on CNTs surface and govern the transportation behavior of organics. Results indicated that the complexation form of HA with

BTE is possible, and investigations about their co-existing effects on the ecosystems are necessarily needed.

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