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BENZENE AND TOLUENE REMOVAL BY CARBON NANOTUBES FROM AQUEOUS SOLUTION

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Abstract: The removal of benzene (B) and toluene (T) from aqueous solution by multi walled, single walled, and hybrid carbon nanotubes (MWCNTs, SWCNTs, and HCNTs) was evaluated for a nanomaterial dose of 1 g/l, concentration of 10−100 mg/l, and pH 7. The equilibrium amount removed by SWCNTs (B: 9.98 mg/g and T: 9.96 mg/g) was higher than for MWCNTs and HCNTs. Toluene has a higher adsorption tendency on CNTs than benzene, which is related to the increasing water solubility and the decreasing molecular weight of the compounds. The SWCNTs performed better for B and T sorption than the MWCNTs and HCNTs. Isotherms study based on isofit program indicate that the Generalized Langmuir-Freundlich (GLF) isotherm expression provides the best fit for benzene sorption, and that Brunauer-Emmett-Teller (BET) isotherm is the best fit for toluene adsorption by SWCNT. SWCNTs are efficient B and T adsorbents and possess good potential applications to water and wastewater treatment and maintain water of high quality that could be used for cleaning up environmental pollution.

INTRODUCTION

Benzene and toluene (aromatic organic compounds) are important materials in the chemical process industries. These compounds are usually used as raw materials in numerous chemical productions and also often as solvent in a wide variety of manufacturing processes [12]. Benzene and toluene are widely used in industry as solvents for organic synthesis, equipment cleaning, and other downstream processing purposes. They are frequently found in groundwater because of leaks in underground storage tanks and pipelines, improper waste disposal practices, inadvertent spills and leaching from landfills [10]. These pollutants cause many serious health side effects to humans (e.g., skin and sensory irritation, central nervous system depression, respiratory problems, leukemia, cancer and disturbance of the kidney, liver and blood systems) [1]. Since benzene and toluene compounds are classified as flammable, toxic, carcinogenic, and/or mutagenic agents, their presence in aqueous solution even at low concentrations is of major environmental concern. Hence, the removal of these organic pollutants from the water and wastewater is critical to ensure the safety of water supplies [12]. Due to these health concerns, a maximum contaminant level of 5 µg/l for benzene is set as the standard for drinking water by

the U.S.EPA. The U.S. Public Health Service (1989) has also recommended that drinking water contains no more than 2 mg/l of toluene for lifetime exposure [8, 10].

Carbon nanotubes (CNTs) have attracted great interest because of their unique chemical structure and intriguing physical properties [13]. The large adsorption capacity of CNTs for organic pollutant is primarily due to their pore structure and the existence of a wide spectrum of surface functional groups. The adsorption mechanism of benzene and toluene on CNTs is mainly attributed to the π–π electron donor–acceptor interaction between the aromatic ring of benzene and toluene and the surface carboxylic groups of CNTs [4]. It has been found that CNTs are more effective for the removal of natural organic matter (NOM) than activated carbon [7]. Lu *et al.* used surface modification of carbon nanotubes to enhance B and T adsorption from aqueous solutions. The NaOCl-oxidized CNTs have superior adsorption performance toward B and T compared with many types of carbon and silica adsorbents reported in the literature [6]. Su *et al.* employed multi-walled carbon nanotubes (MWCNTs) that were oxidized by sodium hypochlorite (NaOCl) solution to enhance the adsorption of benzene and toluene in an aqueous solution [11].

These studies indicate that CNTs have high affinity with organic chemicals and they show the potential for developing carbon nanotube technologies for treating benzene and toluene in water. However, such studies are still very limited in the literature. There are numerous types of CNTs that can be used for contaminant removal, but it is not known which of them is better for removing specific contaminants (such studies have not been conducted in the literature). Therefore, a test of the benzene and toluene removal efficiency of different types of CNTs is needed to employ the most efficient CNTs in water and wastewater treatment.

The present study aimed to determine the removal efficiency for benzene and toluene using single-walled and multi-walled carbon nanotubes and hybrid carbon nanotubes and to rank their benzene and toluene removal abilities. The contribution of this study is the evaluation of hybrid CNTs (HCNT) which was not found in the literature.

EXPERIMENTAL

Materials

A mixed suite of 2 organic compounds was employed to evaluate the different nanomaterials. These compounds were chosen to relative importance as an environmental pollutant. The chemicals tested in this study were benzene (Merck, purity: 99.7%) and toluene (Merck, purity: 99.7%). A stock solution of approximately 100 mg/l of B and T was prepared by dissolving appropriate amounts of each substance in a standard solution that contained 100 mg/l of benzene + 100 mg/l of toluene in deionized H_2O. The mixture was mixed thoroughly by using an ultrasonic bath (BANDELIN Sonorex Digtec) for 60 min. Then, it was stirred continuously for 24 hrs at 25°C. After shaking, the solution was put in the ultrasonic bath again for 30 min and was used to prepare the initial B and T solution with a 10 mg/l concentration. Finally, standard series and samples were prepared using deionized H_2O to achieve the desired concentrations.

Experimental condition

Batch experiments for adsorption were conducted using 110 ml glass bottles with the addition of 1000 mg of adsorbents and 100 ml of B and T solution at an initial concen-

tration (C_0) of 10 mg/l, which was chosen to be representative of low B and T levels in water polluted with gasoline. The glass bottles were sealed with 20 mm stoppers. The headspace within each beaker was minimized to exclude any contaminant volatilization phenomena. The glass bottles from the batch experiments were placed on a shaker (Orbital Shaker Model OS625) and were stirred at 240 rpm at room temperature for 10 minutes. The solution samples were then allowed to settle for 2 min. The supernatant was filtered through 0.45 µm filters to remove suspended CNTs. Finally, the B and T concentration in the liquid phase was determined using GC/MS chromatography. All of the experiments were repeated three times, and only the mean values were reported. Blank experiments, without the addition of adsorbents, were also conducted to ensure that the decrease in B and T concentration was not due to adsorption on the wall of the glass bottle or volatilization. The solution pH was measured at the beginning (pH_{in}) and at the end (pH_{fin}) of each experiment. The pH_{in} was adjusted to neutral using 0.05 M HCl or 0.05 M NaOH. The amounts of adsorbed B and T on the adsorbents (q_e, mg/g) were calculated as follows:

$$q_e = (C_0 - C_t) \times \frac{v}{m} \tag{1}$$

Where C_0 and C_t (mg/l) are the B and T concentrations at the beginning and after a certain period of time, V is the initial solution volume (li), and m is the adsorbent weight (g).

Chemical analysis

An Agilent technologies system consisting of a 5975C Inert MSD with a Triple Axis Detector, equipped with a 7890A gas chromatograph with a split/splitless injector, was used for the quantification and confirmation of the polycyclic aromatic hydrocarbons (B and T). A fused silica column, HP-5 ms (5% phenyl-95% dimethylpolysiloxane; 30 m × 0.25 mm I.D, 0.25 µm), was employed with helium (purity 99.995%) as the carrier gas at a flow rate of 1 ml/min. The column temperature was programmed as follows: 40°C for 10 min, increasing to 120°C at 10°C/min and holding for 2 min. The injector port was maintained at 250°C, and a 1 ml volume of headspace was injected in splitless mode (2.0 min). The effluent from the GC column was transferred via a transfer line held at 280°C and fed into a 70 eV electron impact ionization source held at 280°C. The analysis was performed in the selected ion monitoring (SIM) mode. The data were acquired and processed by the data analysis software.

Static headspace analysis was performed using a CTC PAL-Combi PAL headspace sampler. The experimental parameters of the headspace sampler were as follows: incubation time − 25 min; incubation temperature − 70°C; sample loop volume − 1 ml; syringe/transfer line temperature − 110°C; flash time − 2 min with N_2; loop fill time, 0.03 min; injection time − 1 min; injection volume 1 ml, and sample volume − 2 ml in 10 ml vials. No NaCl was added to the samples.

The pH measurements were made with a pH meter (EUTECH, 1500).

Adsorbents

During the experimental procedure, three different nanomaterials were tested: (1) single--walled carbon nanotubes (SWCNTs), (2) multi-wall carbon nanotubes (MWCNTs), and

(3) hybrid carbon nanotubes (HCNTs). The SWCNTs with 1−2 nm diameter (Fig. 1), MWCNTs with 10 nm diameter (Fig. 2), and HCNTs was a hybrid of MWCNTs and Silica (Fig. 3) to open the tubes of MWCNT as a sheet instead of tube. These adsorbents were purchased from the Iranian Research Institute of the Petroleum Industry. The surface area, pore volume and pore size distribution were measured by nitrogen adsorption at 77 K using an ASAP-2010 porosimeter from the Micromeritics Corporation GA. The samples were degassed at 350°C and 1.33–0.67 kPa overnight prior to the adsorption experiments. The pore size distribution (PSD) was evaluated from the adsorption isotherms using the Barrett, Joyner and Halenda (BJH) algorithm (ASAP-2010) available as a built-in software from Micromeritics. The surface area, average pore size diameter and pore volume of the adsorbates are presented in Table 1.

Table 1. N_2 adsorption data of SWCNTs, HCNTs and MWNTs

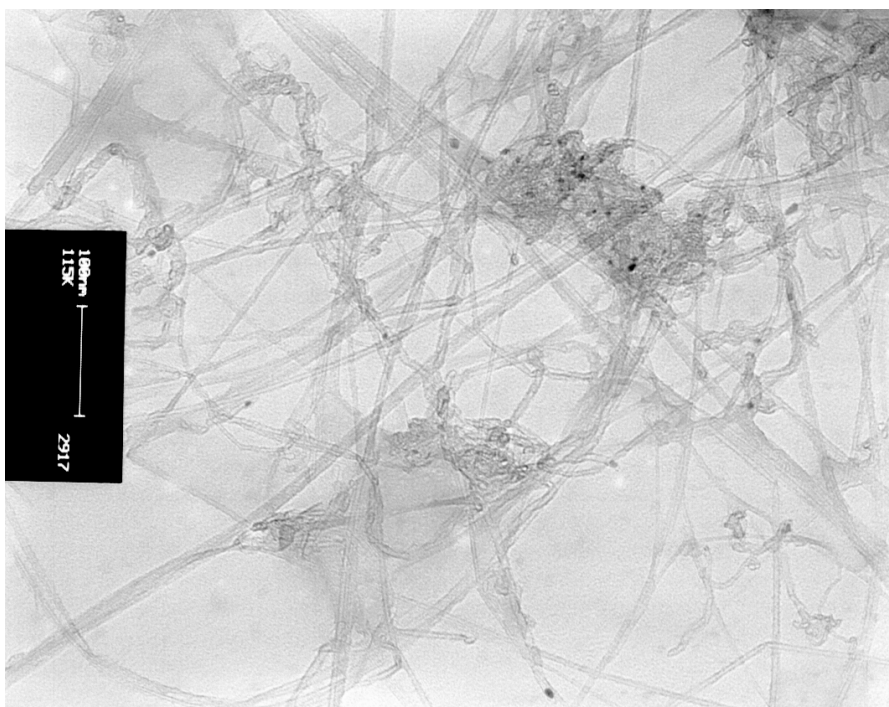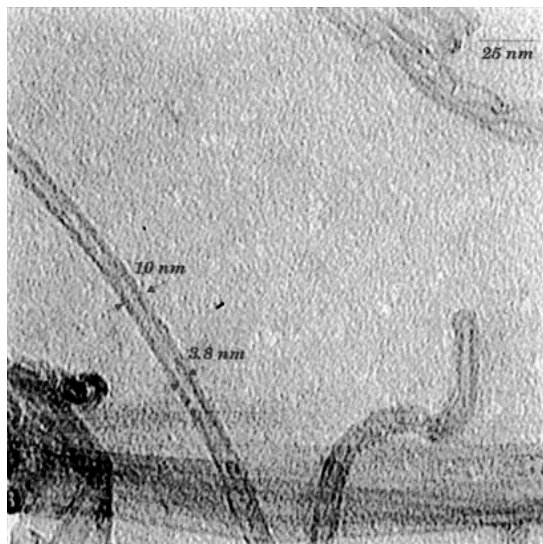| adsorbents	BET surface area (m^2/g)	Average pore diameter – by BET (nm)	BJH adsorption cumulative surface area of pores (m^2/g)	BJH adsorption average pore diameter (nm)	BJH adsorption cumulative pore volume of pores (cm^3/g)
SWCNTs	273.64	11.87	248.35	13.06	0.73
HCNTs	198.93	11.87	253.12	12.02	0.62
MWCNTs	132.42	13.21	175.74	13.57	0.58

Fig 1. TEM image of SWCNT
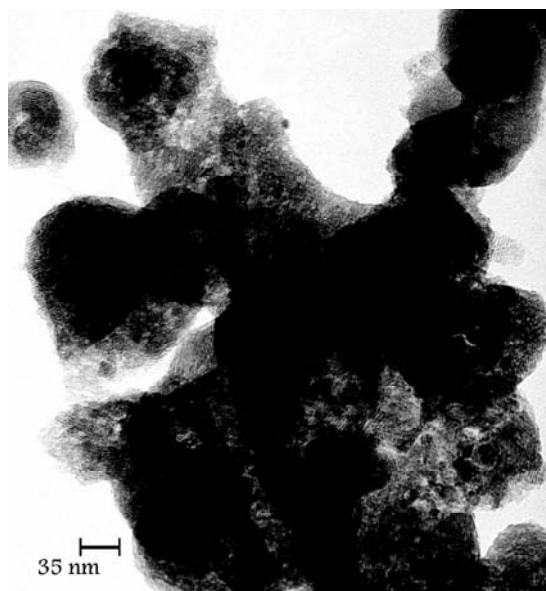
Fig. 2. TEM image of MWCNT

Fig. 3. TEM image of HCNT

Analysis of Data

For the data analysis, design of experiments (DOE) software (Design Expert 6) was used. In this software, the analysis was done with a general factorial plan.

Isotherm Fitting Tool (ISOFIT) is a software program that fits isotherm parameters to experimental data via the minimization of a weighted sum of squared error (WSSE) objective function. ISOFIT supports a number of isotherms, including (1) Brunauer-Em-

mett-Teller (BET), (2) Freundlich, (3) Freundlich with Linear Partitioning (F-P), (4) Generalized Langmuir-Freundlich (GLF), (5) Langmuir, (6) Langmuir with Linear Partitioning (L-P), (7) Linear, (8) Polanyi, (9) Polanyi with Linear Partitioning (P-P), and (10) Toth. Observation weights are ideally assigned according to individual estimates of measurement error, such that $w_i = 1/sd_i$, where sdi is the standard deviation of the i-th measurement.

RESULTS AND DISCUSSION

Adsorption Performance

Table 2 shows the B and T removal percent for MWCNTs, SWCNTs, and HCNTs under an initial B and T concentration of 10 mg/l, an adsorbent concentration of nanomaterial of 1000 mg/l, a contact time of 10 min and shaking at 240 rpm.

Table 2. B and T removal by MWCNT, SWCNT, and HCNT at C_0 = 10 mg/l – contact time of 10 min

adsorbent	Benzene		Toluene	
	C_t (mg/l)	Removal Percent (%)	C_t (mg/l)	Removal Percent (%)
MWCNT	0.23	97.66	0.15	98.5
SWCNT	0.03	99.74	0.02	99.8
HCNT	0.04	99.58	0.05	99.5

Based on the DOE analysis, there were differences between MWCNTs, SWCNTs and HCNTs for toluene removal (values of "Prob > |t|" less than 0.05). A comparison of benzene removal in carbon nanotubes indicated that only the performances of HCNTs and SWCNTs for benzene removal were not statistically different (values of "Prob > |t|" greater than 0.1). However, there was a difference between MWCNTs and SWCNTs for benzene removal (values of "Prob > |t|" less than 0.05).

Fig. 4 shows the B and T removal by MWCNTs, SWCNTs, and HCNTs and a comparison between them. SWCNTs were better than MWCNTs and HCNTs and also HCNT better than MWCNT at removing B and T.
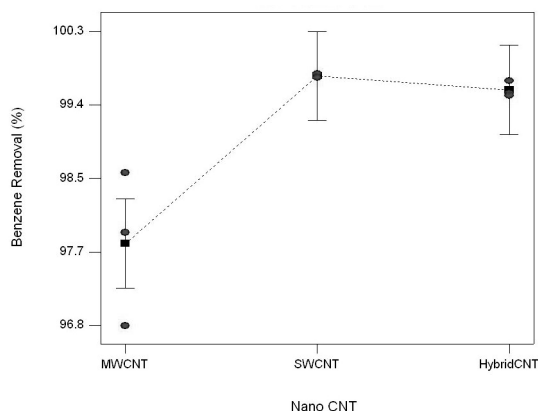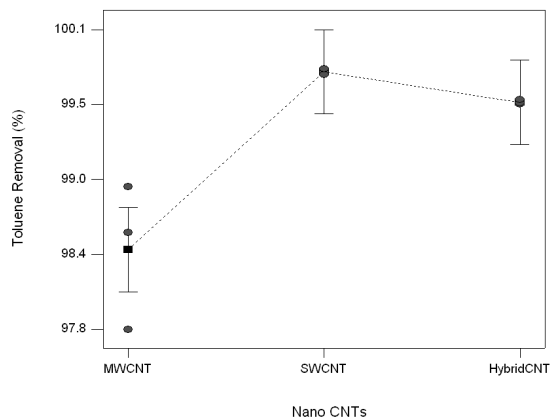
Fig. 4. Plots for MWCNT, SWCNT, and HCNT comparison in: (a) benzene and (b) toluene removal with C_0 of 10 mg/l

Fig. 5 indicates the equilibrium amounts of benzene and toluene adsorbed on MWCNTs, SWCNTs and HCNTs (q_e) with C_0 of 10 mg/l and a contact time of 10 min.
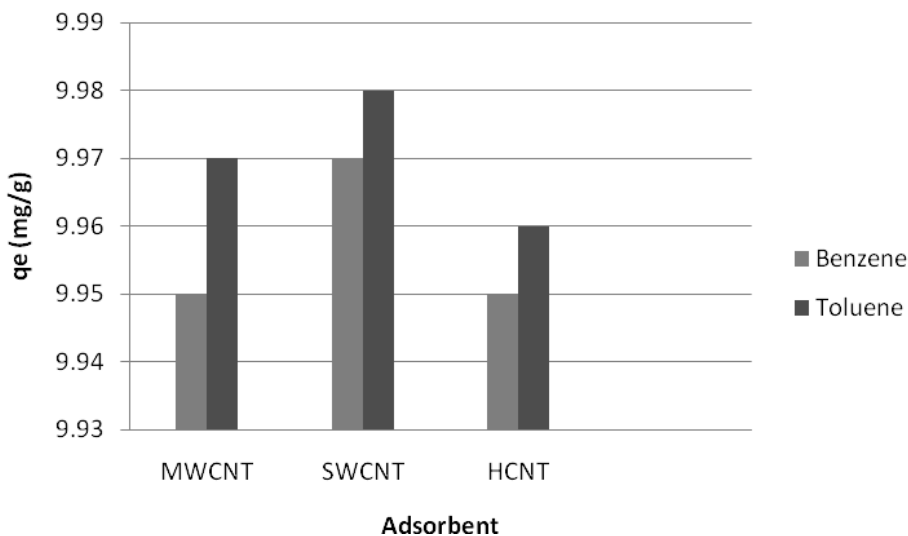

Fig. 5. Equilibrium amount of benzene and toluene adsorbed on CNTs with a C_0 of 10 mg/l

Based on Figure 5, it is evident that the q_e for MWCNTs, SWCNTs and for HCNT the order is T > B for C_0 of 10 mg/l B and T. This order of adsorption may be attributed to the decreased solubility (B, 1790 mg/l > T, 530 mg/l), the increased molecular weight (B, 78 g < T, 92 g) [1, 8] and the increased boiling point (B, 80.1°C < T, 110.7°C) of different compounds [4]. Equilibrium amount from Lu *et al.* study for surface modification of carbon nanotubes also showed that the q_e for toluene is higher than benzene for C_0 of

60 mg/l [6]. And study of Aivalioti *et al.* indicated that toluene has better adsorbent preference in raw (DR) and thermally modified diatomite than benzene [4]. Daifullah and Girgis indicated that the adsorption of B and T on activated carbon proceeds in the toluene > benzene order [3]. The equilibrium results from Su *et al.* study showed that the q_e of B and T adsorption (at a C_0 of 200 mg/l, contact time of 240 min and 600 mg/l of adsorbent concentration) by CNT (NaOCl) were 212 and 225 mg/g for B and T, respectively, and that favorable adsorption occurred in the T > B order [11].

The results from this study showed that the q_e for SWCNTs is higher than for HCNTs and MWCNTs. With C_0 of 10 mg/l, the SWCNTs showed the greatest q_e (B: 9.98 mg/g and T: 9.96 mg/g). The q_e of total B and T for SWCNTs was 19.94 mg/g. The equilibrium amount (q_e) sequence is SWCNTs > HCNTs > MWCNTs. This result implies the presence of chemically inherited groups that lead to direction of the affinity for B and T removal, irrespective of the texture characteristics. This indicates that the adsorption of B and T on CNTs is dependent on the surface chemical nature and the porosity characteristics. Similar findings have been reported in the literature for the adsorption of B and T on activated carbon [3]. Similar conclusions have been drawn in the literature for the adsorption of B and T on multi-walled carbon nanotubes (MWCNTs) [6, 11].

Silica opens the tubes of MWCNT to produce HCNTs. As shown in Fig. 3, HCNT has sheet shape that has more area than MWCNT for B and T adsorption. It is response for more removal of B and T by HCNT than MWCNT. Adding silica to MWCNTs (hybridization process) changes the physical properties of the MWCNTs such as specific surface area and pore size distribution. As shown in Table 1 the BET surface area and BJH cumulative surface area of pores of MWCNTs increased from 132 to 199 m^2/g and from 176 to 253 m^2/g, respectively. The BJH cumulative pore volume increased from 0.58 to 0.62 cm^3/g as a result of hybridization process. Therefore, the average pore diameter of MWCNTs was decreased.

The large adsorption capacity of CNTs for organic pollutant is primarily due to their pore structure and the existence of a wide spectrum of surface functional groups. The adsorption mechanism of B and T on CNTs is mainly attributed to the π–π electron donor–acceptor interaction between the aromatic ring of B and T and the surface carboxylic groups of CNTs [6]. Also because, there was no significant pH variation during experiments, it seems that the π-π electron donor–acceptor mechanism is responsible for the uptake of B and T by SWCNTs, HCNTs and MWCNTs. It involves the carboxylic oxygen atom on the CNT surface as the electron donor and the aromatic ring of B and T as the electron acceptor. Similar conclusions have been drawn in the literature for the adsorption of BTEX on multi-walled carbon nanotubes [6].

Furthermore, the electrostatic interaction between the B and T molecules and the SWCNT surface may also explain the observation of high B and T adsorption via the single-wall CNTs. Because the B and T molecules are positively charged [6], the adsorption of B and T is thus favored for adsorbents with a negative surface charge. This results in more electrostatic attraction and thus leads to a higher B and T adsorption.

Comparisons for qe from this study with various adsorbents, such as SWCNTs, MWCNTs, powdered activated carbon (PAC) and granular activated carbon (GAC) reported in the literature are given in Table 3. Under analogous conditions, the present SWCNTs show better performance for B and T adsorption than do other adsorbents. This suggests that the SWCNTs are efficient B and T adsorbents. Because the costs of

commercially available CNTs are continuously decreasing, it may be possible to utilize these novel nanomaterials for B and T removal in water and wastewater treatment in the near future.

Table 3. Comparisons of qe via various adsorbents

adsorbents	q_e (mg/l)		condition	reference
	Benzene	Toluene		
MWCNT	9.95	9.97	pH:7, T:10, S/L:0.1/100, C_0 =10	This study
SWCNT	9.98	9.96	pH:7, T:10, S/L:0.1/100, C_0=10	This study
HCNT	9.97	9.95	pH:7, T:10, S/L:0.1/100, C_0=10	This study
MWCNT	18.1	80.1	pH:7, T:25, S/L:0.06/100, C_0=200	[6]
GAC	183.3	194.1	pH: 7, T: 30, S/L: 0.15/100, C_0=35–442	[12]
PAC	40	40	S/L: 0.1/40, C_0=100	[5]
activated carbons	4.76	5.5	T:25, S/L:0.1/100, C_0=10	[3]

Note: T = temperature (°C); S/L = solid/liquid (g/ml); C_0 = initial concentration (mg/l).

Isotherm study

The adsorption equilibrium data of benzene and toluene on SWCNT samples were fitted by several well-known isotherm models to assess their efficacies. In this study, ISOFIT was applied to involving the adsorption of benzene and toluene with initial concentration of 10−100 mg/l (10, 20, 30, 40, 50, 60, 70, 80, 90, and 100 mg/l) by SWCNT (because of best B and T adsorption). Water solubility (S_w) of benzene and toluene were estimated 1790 and 530 mg/L respectively at pH 7. Numerous studies have considered one or more of the supported isotherms in the context of a water/wastewater system. The dual-mode isotherms reflect recently developed models for the sorption of hydrophobic organic solutes [9].

To characterize parameter uncertainty, ISOFIT reports parameter correlation coefficients and 95% linear confidence intervals for each isotherm parameter. The correlation coefficient (CORij) between parameters Xi and Xj is a measure of the linear dependence between the two parameters, values range from –1 to 1, with a value of zero (0) indicating no correlation. Tables 4 and 5 summarize the resulting parameter estimated for each isotherm, along with linear confidence intervals.

Isotherm expressions are important for describing the partitioning of contaminants in environmental systems. Tables 6 and 7 summarize some of the diagnostic statistics computed by ISOFIT and reported in the output file for benzene and toluene respectively. The AICc values indicate that the GLF isotherm expression provides the best fit of the sorption data for benzene and BET isotherm is the best fit for toluene adsorption.

In particular, ISOFIT provided superior fits for the GLF isotherm for benzene removal by SWCNT and fits for BET isotherm for toluene removal by SWCNT.

Table 8 contains selected ISOFIT output for the GLF isotherm in benzene adsorption by SWCNT and Table 9 shows selected ISOFIT output for the GLF isotherm in

Table 4. Summary of parameters estimated for benzene adsorbed by SWCNT

Isotherms	Parameters	Estimate	CI_{low}	CI_{high}
BET	bQ_0	2.5×10^3	$+2.3\times10^3$	$+2.6\times10^3$
	b	1×10^{-3}	n/a	n/a
Freundlich	K_f	1.5	-4.7×10^{-1}	$+3.5$
	$(1/n_f)$	1×10^{-1}	$+7\times10^{-1}$	$+1.3$
F-P	K_f	7.1×10^{-7}	n/a	n/a
	$(1/n_f)$	3.2×10^{-1}	n/a	n/a
	K_p	1.5	$+1.3$	$+1.6$
GLF	Q_0	1.5×10^3	-6.8×10^3	$+9.8\times10^3$
	b	2.4×10^{-3}	-9×10^{-3}	$+1.4\times10^{-2}$
	$(1/n_g)$	1.5	$+9.1\times10^{-1}$	$+2.1$
Langmuir	bQ_0	1.5	$+1.4$	$+1.6$
	b	2.8×10^{-9}	n/a	n/a
Linear	K_p	1.5	$+1.4$	$+1.6$

Isotherms	Parameters	Estimate	CI_{low}	CI_{high}
L-P	bQ_0	1.5	-1.5×10^{-1}	$+2.5$
	b	5×10^{-10}	-1.4×10^{-2}	2.6×10^{-2}
	K_p	1×10^{-3}	n/a	n/a
Polanyi	Q_0	8×10^1	$+4\times10^1$	$+1.2\times10^2$
	A	-1×10^{-8}	n/a	n/a
	B	1.5×10^{-1}	n/a	n/a
P-P	Q_0	1	-2×10^1	$+2\times10^1$
	A	-7×10^{-8}	n/a	n/a
	B	2.8×10^{-1}	n/a	n/a
	K_p	1.5	$+1.2$	$+1.8$
Toth	bQ_0	1.5	$+1.2$	1.8
	b	4.2×10^{-5}	-2×10^{-2}	$+2\times10^{-2}$
	n_T	1.7	-5.6×10^2	$+5.7\times10^2$

CI_{low}, CI_{high}: lower and upper 95% confidence bounds; Q_0: (mg/g); b: (li/g); K_f: $[(mg/g)/(mg/l)]^{(1/n)}$; $(1/n_f)$, $(1/n_g)$, Kp, A, B, and n_T: no units

Table 5. Summary of parameters estimated for toluene adsorbed by SWCNT

Isotherms	Parameters	Estimate	CI_{low}	CI_{high}	Isotherms	Parameters	Estimate	CI_{low}	CI_{high}
BET	bQ_0	5.5×10^2	$+5.3 \times 10^2$	$+5.8 \times 10^2$	L-P	bQ_0	7.1×10^{-5}	n/a	n/a
	b	2×10^{-4}	n/a	n/a		b	1.9×10^1	n/a	n/a
Freundlich	K_f	1.4	-2.9×10^{-1}	$+3.2$		K_p	1.4	1.3	1.6
	$(1/n_f)$	1×10^{-1}	$+7 \times 10^{-1}$	$+1.3$	Polanyi	Q_0	7.6×10^1	$+4 \times 10^1$	$+1.1 \times 10^2$
F-P	K_f	1.5×10^{-6}	n/a	n/a		A	-5.1×10^{-6}	n/a	n/a
	$(1/n_f)$	4.7×10^{-2}	n/a	n/a		B	8.4×10^{-4}	n/a	n/a
	K_p	1.4	$+1.3$	$+1.6$	P-P	Q_0	1	-2×10^1	$+2 \times 10^1$
GLF	Q_0	9.5×10^2	-3.8×10^3	$+5.7 \times 10^3$		A	-7.4×10^{-7}	n/a	n/a
	b	3.3×10^{-3}	-1.2×10^{-2}	$+1.9 \times 10^{-2}$		B	3.6×10^{-4}	n/a	n/a
	$(1/n_g)$	1.5	$+6.4 \times 10^{-1}$	$+2.3$		K_p	1.4	$+1.1$	$+1.7$
Langmuir	bQ_0	1.4	$+1.3$	$+1.6$	Toth	bQ_0	1.4	$+1.3$	1.6
	b	2.9×10^{-9}	n/a	n/a		b	1.3×10^{-4}	n/a	n/a
Linear	K_p	1.4	$+1.3$	$+1.6$		n_T	3.8	n/a	n/a

CI_{low}, CI_{high}: lower and upper 95% confidence bounds; Q_0: (mg/g); b: (li/g); K_f: [(mg/g)/(mg/l)]$^{(1/n)}$; $(1/n_f)$, $(1/n_g)$, K_p, A, B, and n_T: no units

Table 6. Summary of selected diagnostics for benzene adsorbed by SWCNT

Isotherms	Multi model ranking (AICc)	Correlation between measured and simulated observation (R_y^2)	Correlation between residual and normality (R_N^2)	Linssen measure of non-linearity (M²)	Linearity assessment
GLF	38.3	0.994	0.875	6.4×10^1	Non-linear
BET	47.4	0.986	0.923	1.5×10^{-8}	linear
Linear	51.3	0.980	0.905	2.6×10^{-8}	linear
Langmuir	51.3	0.980	09.5	5.4×10^{-8}	linear
F-P	51.3	0.980	0.905	2.9×10^{-8}	linear
L-P	54.5	0.980	0905	6.8×10^{-1}	Non-linear
Freundlich	54.5	0.980	0.905	8.4	Non-linear
P-P	55.15	0.980	0.903	4.7×10^{-1}	Non-linear
Toth	58.8	0.980	0.906	8.5	Non-linear
Polanyi	81.3	-	0.963	2.8×10^{-10}	linear

Table 7. Summary of selected diagnostics for toluene adsorbed by SWCNT

Isotherms	Multi model ranking (AICc)	Correlation between measured and simulated observation (R_y^2)	Correlation between residual and normality (R_N^2)	Linssen measure of non-linearity (M²)	Linearity assessment
BET	35.9	0.988	0.944	6.2×10^{-9}	linear
Toth	48.8	0.977	0.891	2.8×10^{-8}	linear
GLF	44.7	0.987	0.973	3.1×10^1	Non-linear
Linear	48.8	0.977	0.891	2.6×10^{-8}	linear
Langmuir	48.8	0.977	0.891	5.2×10^{-8}	linear
F-P	48.7	0.977	0.891	2.7×10^{-8}	linear
L-P	48.8	0.977	0.891	2.7×10^{-8}	linear
Freundlich	52	0.977	0.891	9.6	Non-linear
P-P	52.6	0.977	0.890	4.7×10^{-1}	Non-linear
Polanyi	80	-	0.961	3.1×10^{-11}	linear

toluene adsorbtion by SWCNT. ISOFIT provides two 'standard' measures for evaluating isotherm goodness-of-fit, namely the root-mean-squared error (RMSE, Eq. (2)) and the correlation between measured and fitted observations (R_y, Eq. (3)).

$$RMSE = \sqrt{\frac{WSSE}{(m-p)}} \qquad (2)$$

$$R_y = \frac{\sum_{i=1}^{m}(w_i S_{i,obs} - S_{obs}^{avg})(w_i S_i - S^{avg})}{\sqrt{\sum_{i=1}^{m}(w_i S_{i,obs} - S_{obs}^{avg})^2 \sum_{i=1}^{m}(w_i S_{i,obs} - S^{avg})^2}} \qquad (3)$$

where WSSE is a weighted sum of squared error, m is the total number of experimental observations, p is the number of isotherm parameters, w_i is the weight given to observation i, $S_{i,obs}$ is the i-th experimentally measured sorbed concentration, S_i is the i-th simulated sorbed concentration computed via an isotherm expression, S_{obs}^{avg}, S^{avg} are the averages of the weighted measured and weighted isotherm-simulated sorbed concentrations, respectively.

Table 8. Selected ISOFIT post-regression output for benzene adsorption by SWCNT (GLF isotherm)

Parameter or statistics		ISOFIT result
Overall quality of fit	WSSE	1.7×10^2
	RMSE	21.25
	R_y	0.997
Parameter statistics	Q_0	1.5×10^3
	b	2.4×10^{-3}
	$(1/n_g)$	1.5
Parameter std. error	Q_0	3.5×10^3
	b	4.8×10^{-3}
	$(1/n_g)$	-2.5×10^{-1}
Test of assumptions Linssen (M^2)	M^2	64
	threshold	0.2
	assessment	Non-linear
Normality (R_N^2)	R_N^2	0.875
	critical value	0.861
	assessment	Normal residuals
Runs test	Number of runs	7
	p-value	0.8816
	assessment	No correlation
Durbine Watson test (D)	D	2.7
	p-value	0.82
	assessment	No correlation

In Table 8, the Linssen measure indicates significant WSSE nonlinearity near the optimal parameter values. Such nonlinearity invalidates the quantitative use of linear confidence intervals and observation influence measures. As such, these statistics were

regarded in a more qualitative manner. The remaining statistical measures in Table 8 (i.e. the R_N^2 measure and the Runs and Durbine Watson tests) imply normally distributed weighted residuals with no serial autocorrelation, necessary conditions for producing unbiased regression-based parameter estimates. The parameter statistics indicate high correlation among all three parameters with a relatively narrow confidence interval for the GLF exponent parameter ($1/n_g$), and relatively wide confidence intervals for the Q_0 and b terms.

Table 9. Selected ISOFIT post-regression output for toluene adsorption by SWCNT (BET isotherm)

Parameter or statistics		ISOFIT result
Overall quality of fit	WSSE	2.8×10^2
	RMSE	31.1
	R_y	0.994
Parameter statistics	bQ_0	5.5×10^2
	b	2.4×10^{-4}
Parameter std. error	bQ_0	10
	B	n/a
Test of assumptions Linssen (M^2)	M^2	6.2×10^{-9}
	threshold	0.2
	assessment	linear
Normality (R_N^2)	R_N^2	0.944
	critical value	0.861
	assessment	Normal residuals
Runs test	Number of runs	6
	p-value	0.833
	assessment	No correlation
Durbine Watson test (D)	D	2.9
	p-value	0.94
	assessment	No correlation

In Table 9, the Linssen measure indicates significant WSSE linearity near the optimum parameter values. Such linearity invalidates the quantitative use of linear confidence intervals and observation influence measures. As such, these statistics were regarded in a more qualitative manner. The remaining statistical measures in Table 9 (i.e. the R_N^2 measure and the Runs and Durbine Watson tests) imply normally distributed weighted residuals with no serial autocorrelation, necessary conditions for producing unbiased regression-based parameter estimates.

Figs 6 and 7 contain plots of the fitted isotherms for benzene and toluene respectively, (organized into visually indistinguishable groups) along with the observed data points.
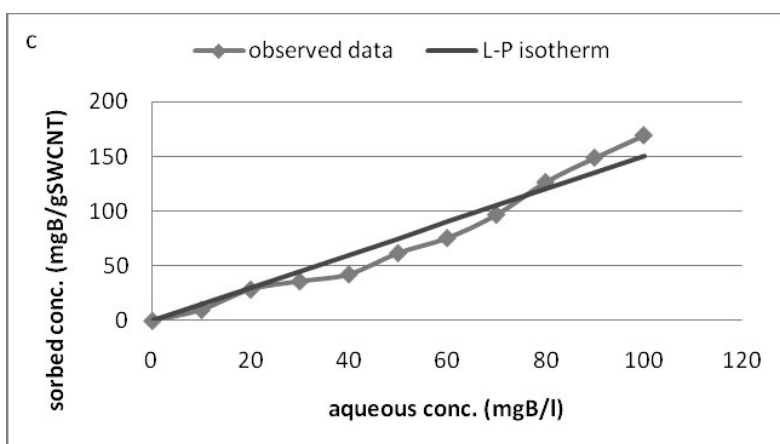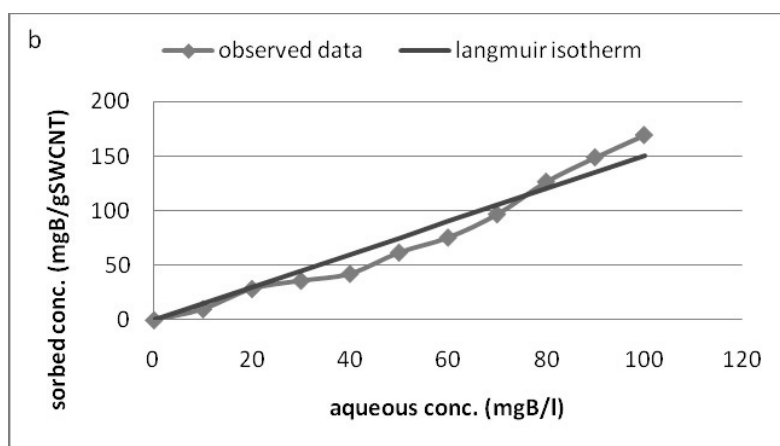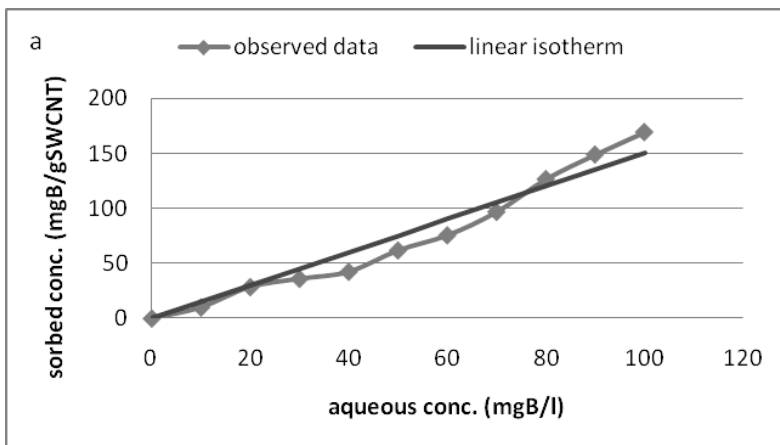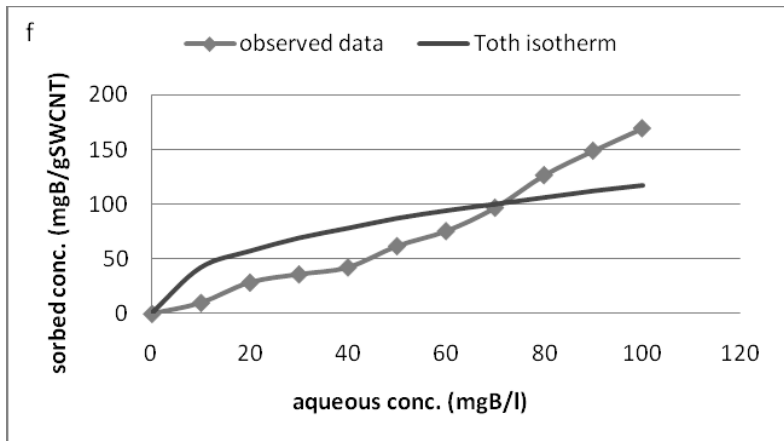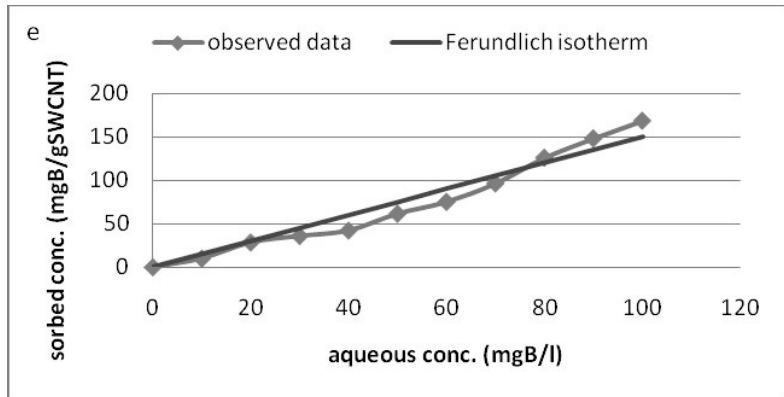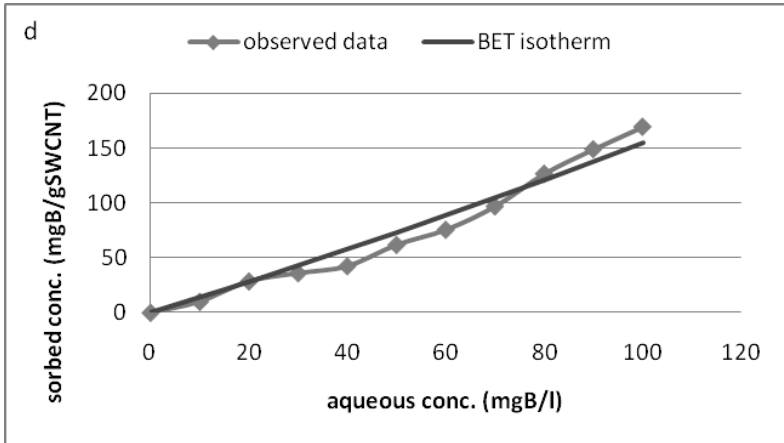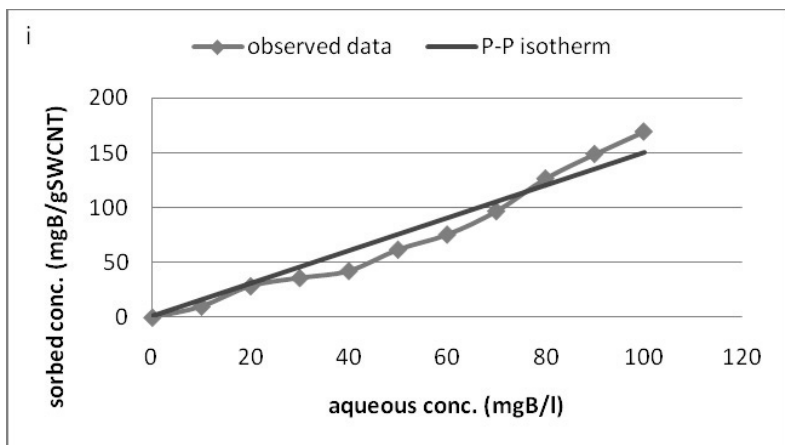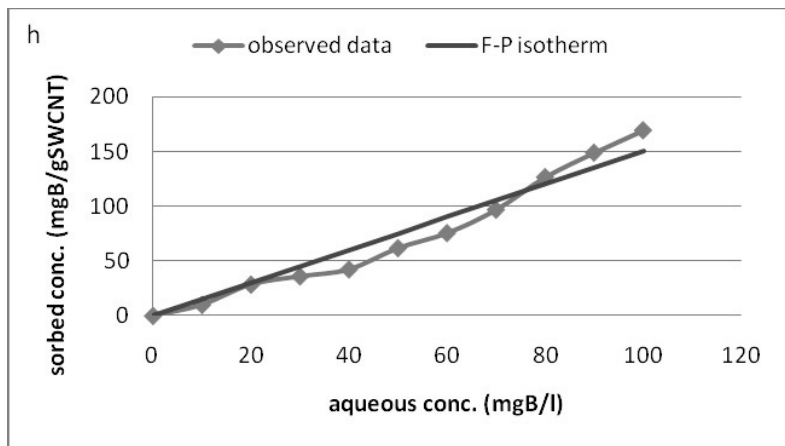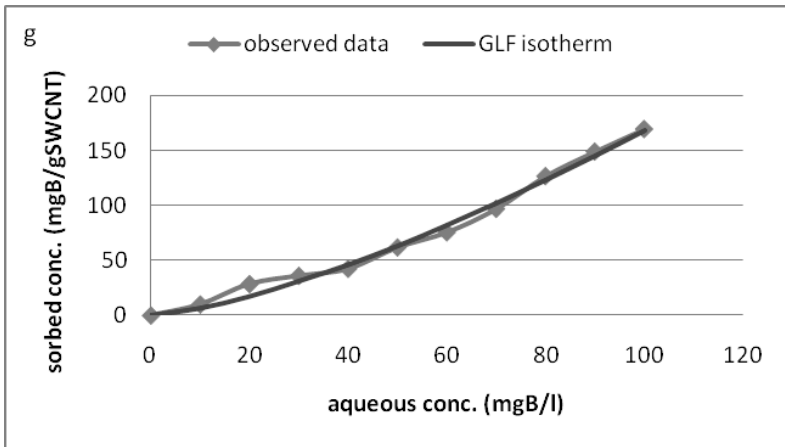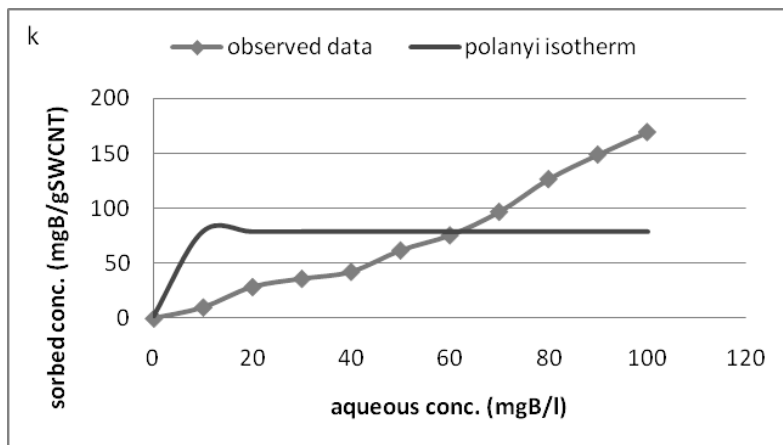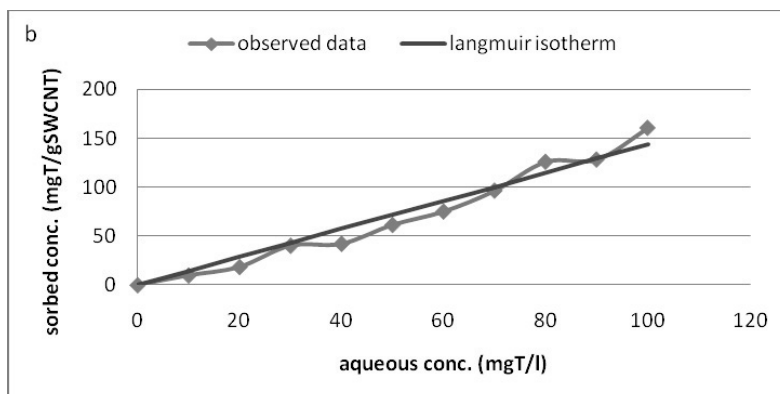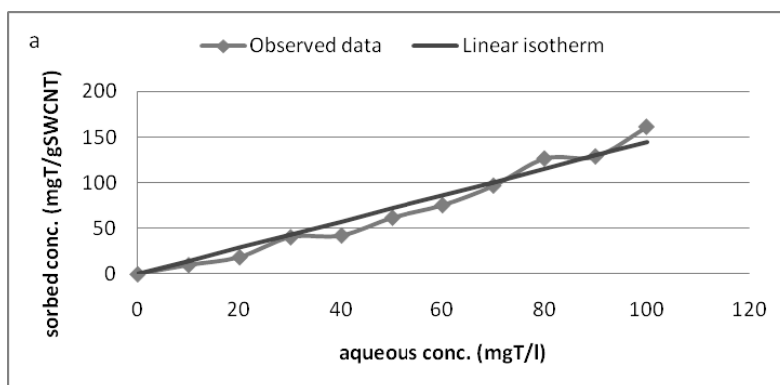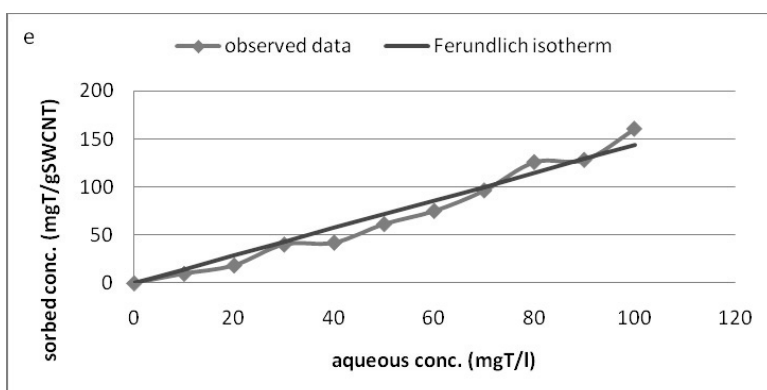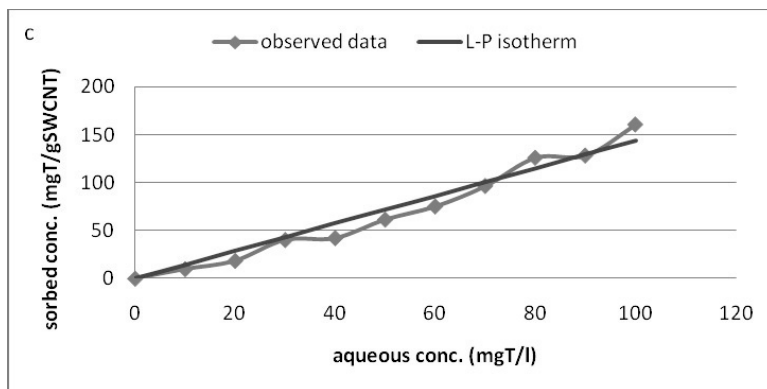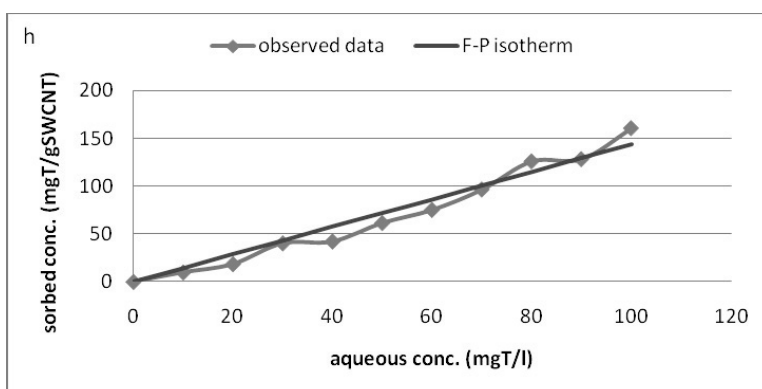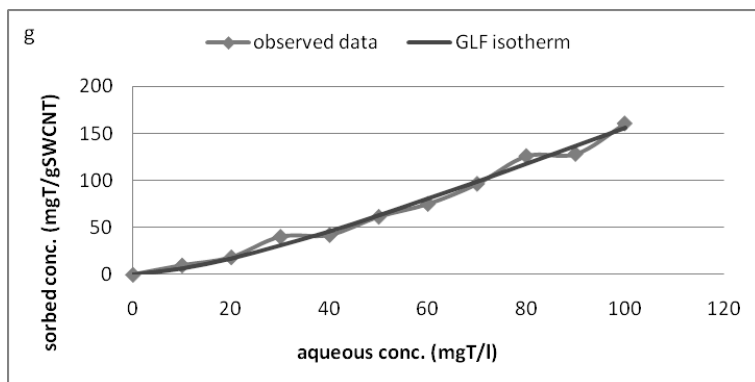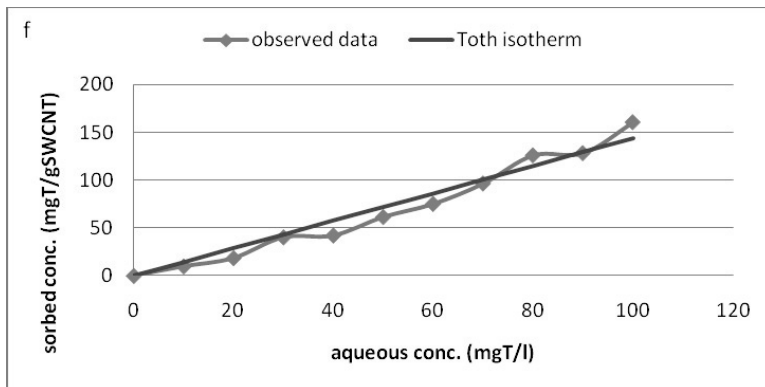
Fig. 6. Plots of fitted isotherms and observed data for benzene adsorption: (a) linear, (b) Langmuir, (c) L-P, (d) BET, (e) Freundlich, (f) Toth, (g) GLF, (h) F-P, (i) P-P, (k) Polanyi
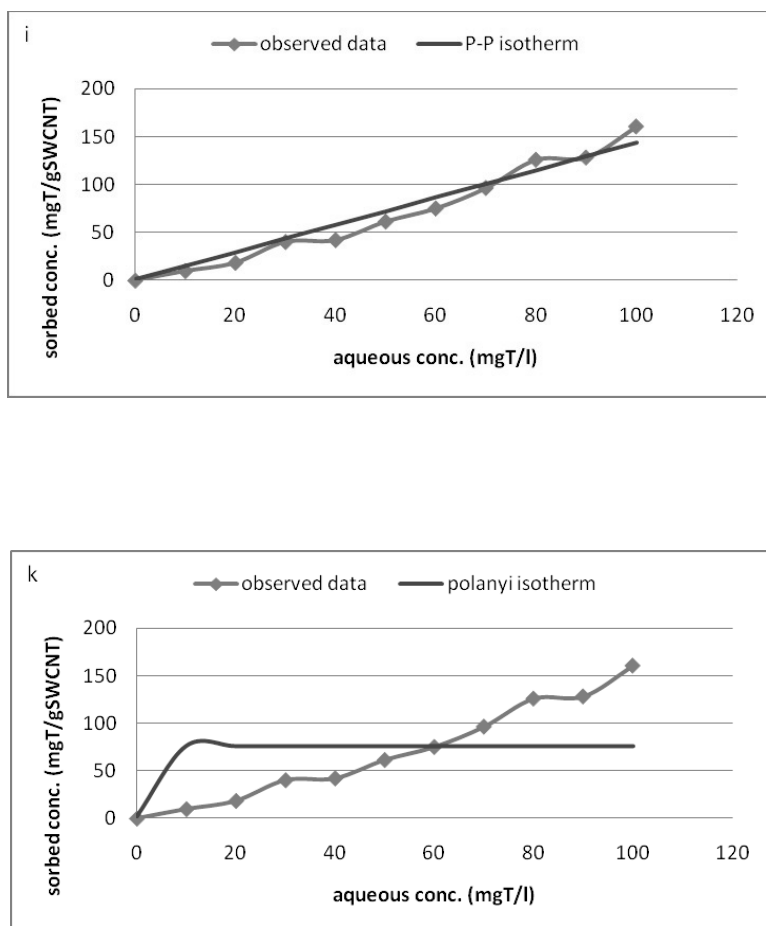
c

d

e
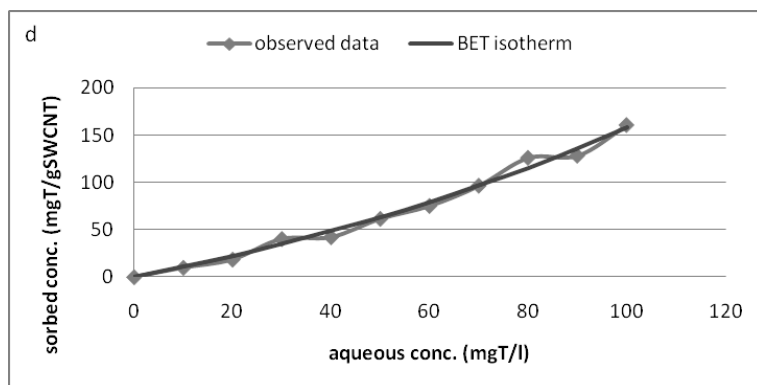
Fig. 7. Plots of fitted isotherms and observed data for toluene adsorption: (a) linear, (b) Langmuir, (c) L-P, (d) BET, (e) Freundlich, (f) Toth, (g) GLF, (h) F-P, (i) P-P, (k) Polanyi

In this study, the results showed that ISOFIT provided superior fits in benzene removal by SWCNT, for GLF, BET, Linear, Langmuir, F-P, L-P, Freundlich, P-P, and Toth isotherms and for toluene removal ISOFIT provided superior fits for BET, Toth, GLF, Linear, Langmuir, F-P, L-P, Freundlich, and P-P isotherms. ISOFIT was used by Shawn Matott to the adsorption of zinc by ferrihydrite. Results indicate that ISOFIT produced equivalent or better fits, in terms of minimum and median RMSE values. In particular, ISOFIT provided superior fits for the GLF, Toth, Polanyi and Polanyi-Partition isotherms [9].

The adsorption process of atrazine on CNTs studied by Yan *et al.* show that the adsorption equilibrium isotherms were nonlinear and were fitted by Freundlich, Langmuir, and Polanyi–Manes models. It was found that the Polanyi–Manes model described the adsorption process better than other two isotherm models [13].

Wibowo *et al.* studied the adsorption of benzene and toluene from aqueous solutions onto activated carbon; their study shows that the Langmuir equation can describe the experimental data fairly well than Freundlich [12]. It has been indicated that the Freundlich isotherm has a good linear relationship for Cr(VI) adsorption by magnetic nano particles [2].

Evidently, the global search capabilities of the hybrid method played an important role when fitting these more complicated three- and four-parameter expressions.

In the adsorption mechanism of aromatic compounds in a liquid phase on SWCNT there are two main types of interactions, including electrostatic and dispersive. The functional group linked to the adsorptive aromatic ring can activate or deactivate it that removes its electronic charge. Electrons with drawing groups on an aromatic ring create a partial positive charge in the ring, while deactivating groups produce the opposite effect, creating a partial negative charge [12].

Here, benzene and toluene are in the molecular form in the aqueous solution; in this case, dispersive interactions are predominant, mainly because of the attraction between the π orbital on the SWCNT basal planes and the electronic density in the benzene and toluene aromatic rings (π-π interactions) [12].

CONCLUSION

We concluded that SWCNTs showed a higher adsorption capacity for B and T removal than MWCNTs and HCNTs. Also between MWCNT and HCNT, HCNT shows better performance for B and T removal because of sheet shape produced by silica. The q_e for SWCNT, HCNT and MWCNTs follows the order T > B for a C_0 of 10 mg/l B and T. It appears that toluene is the component with higher adsorption tendency on CNTs and benzene is the component with lower adsorption tendency. The equilibrium amount (q_e) sequence is SWCNTs > HCNTs > MWCNTs.

ISOFIT provided superior fits for the GLF isotherm for benzene removal by SWCNT and fits for BET isotherm for toluene removal By SWCNT.

More research works on the toxicity of CNTs and CNT-related materials are needed before practical use of CNTs in water and wastewater treatment.

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