



Linear solvation energy relationships (LSER) for adsorption of organic compounds by carbon nanotubes



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ABSTRACT

The objective of this paper was to create a comprehensive database for the adsorption of organic compounds by carbon nanotubes (CNTs) and to use the Linear Solvation Energy Relationship (LSER) technique for developing predictive adsorption models of organic compounds (OCs) by multi-walled carbon nanotubes (MWCNTs) and single-walled carbon nanotubes (SWCNTs). Adsorption data for 123 OCs by MWCNTs and 48 OCs by SWCNTs were compiled from the literature, including some experimental results obtained in our laboratory. The roles of selected OCs properties and CNT types were examined with LSER models. The results showed that the r^2 values of the LSER models displayed small variability for aromatic compounds smaller than 220 g/mol, after which a decreasing trend was observed. The data available for aliphatics was mainly for molecular weights smaller than 250 g/mol, which showed a similar trend to that of aromatics. The r^2 values for the LSER model on the adsorption of aromatic and aliphatic OCs by SWCNTs and MWCNTs were relatively similar indicating the linearity of LSER models did not depend on the CNT types. Among all LSER model descriptors, V term (molecular volume) for aromatic OCs and B term (basicity) for aliphatic OCs were the most predominant descriptors on both type of CNTs. The presence of R term (excess molar refractivity) in LSER model equations resulted in decreases for both V and P (polarizability) parameters without affecting the r^2 values. Overall, the results demonstrate that successful predictive models can be developed for the adsorption of OCs by MWCNTs and SWCNTs with LSER techniques.

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1. Introduction

Carbon nanotubes (CNTs) show a great affinity for adsorption of organic compounds (OCs) in water (Pan et al., 2008; Apul et al., 2013a,b; 2015). Adsorption of more than one hundred OCs by CNTs have been extensively investigated in the literature in more than 50 studies (e.g., Yang et al., 2006; Peng et al., 2003; Su et al., 2010; Yu et al., 2011; 2012a,b; Wang et al., 2012; Abdel Salam and Burk, 2010; Chen et al., 2009; Lin et al., 2008; Pyrzynska et al., 2007; Lu et al., 2006; Liu et al., 2014; Carabineiro et al., 2012; Long and Yang, 2001). Collecting OC adsorption data experimentally is a cost, labor and time intensive task. Therefore, linear solvation energy relationships (LSER) can be developed utilizing the available adsorption isotherms of the literature, and these models can be used for predicting the adsorption of untested OCs by CNTs.

In addition, LSER models can be instrumental in examining the adsorption mechanism(s) of OCs onto CNTs.

LSER is a poly-parameter equation that is developed using ordinary linear regression and a predetermined set of solvatochromic descriptors as independent variables. In the past, LSER models have been developed for predicting OCs adsorption by activated carbons (ACs) (Kamlet et al., 1985; Blum et al., 1994; Shih and Gschwend, 2009; Dickenson and Drewes, 2010). In the last five years, they were also implemented for predicting adsorption of OCs by CNTs (Xia et al., 2010; Apul et al., 2013a,b; 2015; Zhao et al., 2014; Hüffer et al., 2014; Yu et al., 2015). These studies are summarized in Table 1. Of these studies, Xia et al (2010), Apul et al. (2013a,b), and Zhao et al. (2014) investigated the predictive model development for adsorption of aromatic OCs by MWCNTs, Hüffer et al. (2014) focused on adsorption of aromatic and aliphatic OCs by MWCNTs. Recently, Apul et al. (2015) evaluated the predictive model development for adsorption of aliphatic OCs by MWCNTs and SWCNTs and Yu et al. (2015) examined the adsorption of aromatic OCs by MWCNTs and SWCNTs (Table 1). To date, no study has been

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Table 1
Literature review on LSER models for adsorption of OCs by CNTs.

No	Authors	Type of OCs	Number of OCs	Type of CNT	Oxygen content (%)	Parameters used	Adsorption descriptors
1	Xia et al., 2010	Aromatic	28	MWCNTs	<5	A, B, V, P, C	logK
2	Apul et al., 2013a,b	Aromatic	29	MWCNTs	<5	A, B, V, P, C	logK _{inf} – K _{0.01} – K _{0.1}
		Aromatic	30	MWCNTs	<5	A, B, V, P, C	logK _{inf}
3	Zhao et al., 2014	Aromatic	16	MWCNT	–	A, B, V, P, R, C	C _e /C _s –(0–5)
		Aromatic	10	Oxidized-MWCNTs	–	A, B, V, P, R, C	C _e /C _s –(0–5)
4	Hüffer et al., 2014	Aromatic	14	MWCNT	<2	A, B, V, P, R, L, C	logK _{d/a} at 10 ⁶ Cs
		Aliphatic	20	MWCNT	<2	A, B, V, P, R, L, C	logK _{d,0.01,0.001}
5	Apul et al., 2015	Aliphatic	10	MWCNT	5	A, B, V, P, R, C	logK _{d,500,750,1000} ^a
		Aliphatic	10	SWCNT	9	A, B, V, P, R, C	logK _{d,5,10,25,50,100,250,500,750,1000} ^a
6	Yu et al., 2015	Aromatic	67	MWCNTs	<10	A, B, V, P, R, C	logK _{d,0.00001,0.0001,0.001,0.01,0.1}
		Aromatic	40	SWCNTs	<10	A, B, V, P, R, C	logK _{d,0.00001,0.0001,0.001,0.01,0.1}
7	This study	Aromatic	94	MWCNT	<5	A, B, V, P, R, C	logK _{d,0.0001,0.001,0.01}
			36	SWCNT	<10	A, B, V, P, R, C	logK _{d,0.0001,0.001,0.01}
		Aliphatic	29	MWCNTs	<5	A, B, V, P, R, C	logK _{d,0.0001,0.001,0.01}
			12	SWCNTs	<10	A, B, V, P, R, C	logK _{d,0.0001,0.001,0.01}

^a Single point adsorption descriptors were used at different aqueous concentrations (ppb).

conducted to develop LSER models and compare the molecular interactions for adsorption of aromatic and aliphatic OCs by SWCNTs and MWCNTs simultaneously. In this study, adsorption data of 123 OCs by MWCNTs and 48 OCs by SWCNTs were compiled from the literature, including some experimental results obtained in our laboratory (Apul et al., 2013a,b; 2015) and predictive LSER models were trained and validated. To the best of our knowledge, this study is currently the most comprehensive LSER modeling effort in the literature to elucidate the adsorption of OCs by CNTs (Table 1).

The main objectives of the study were to: (i) develop poly-parameter LSERs for adsorption of OCs by CNTs, (ii) evaluate the role of selected OC properties on LSER models, (iii) compare adsorption of OCs by MWCNTs and SWCNTs side-by-side, and (vi) compare the findings with the LSER models presented in the peer-reviewed literature.

2. Materials and methods

2.1. Data collection and organization

A comprehensive literature review was conducted to collect adsorption isotherm data for aromatic and aliphatic compounds by SWCNTs and MWCNTs. A database was created for adsorption of 123 OCs (i.e., 94 aromatic and 29 aliphatic compounds) on MWCNTs from 59 studies and 48 OCs (i.e., 36 aromatic and 12 aliphatic compounds) on SWCNTs from 19 studies (Tables S1–S4 in the Supporting Information (SI)). For MWCNTs, 70 out of 94 aromatic compounds had molecular weight lower than 200 g/mol, and the rest higher than 200 g/mol. Aliphatic compounds, except 1,2-dibromo-3-chloropropane and hexachloroethane, had molecular weight lower than 200 g/mol. For SWCNTs, 23 out of 36 aromatic compounds had molecular weight lower than 200 g/mol. Aliphatic compounds, except 1,2-dibromo-3-chloropropane, had molecular weight lower than 200 g/mol. The adsorption isotherm data for single solute OCs were collected from literature under similar experimental conditions (i.e., temperature was about at 25–30 °C and in distilled deionized water) for the LSER modeling. Type and surface chemistry of the carbonaceous adsorbents have been shown to impact the adsorption of OCs (e.g., Karanfil and Kilduff, 1999; Zhang et al., 2009, 2010). The adsorption data for MWCNTs and SWCNTs with less than 5% and 10% of oxygen content were used in the modeling, respectively, to be able to compare the data obtained from literature (as shown in Table 1).

2.2. Determination of single point adsorption descriptor (K_d)

Single point adsorption descriptors ($K = q_e/C_e$, where q_e is solid phase equilibrium concentration and C_e is liquid phase equilibrium concentration) at three different C_e values, 0.01%, 0.1%, and 1% of the aqueous solubility of each adsorbate were calculated and represented with $K_{d,0.0001}$, $K_{d,0.001}$ and $K_{d,0.01}$, respectively. The details of $K_{d,0.0001}$, $K_{d,0.001}$ and $K_{d,0.01}$ determination were provided in the SI section and in one of our previous publications (Apul et al., 2013a,b).

2.3. LSER model training

Adsorption of OCs by CNTs is controlled by a number of physicochemical interactions, some of which are described with solvatochromic descriptors as independent variables in the LSER model (Apul et al., 2013a,b). Solvatochromic theory explains the adsorption interactions among adsorbate, adsorbent, and solvent with solute specific descriptors representing cavity formation, dipolar interactions and hydrogen bonding interactions. The LSER model has the following form:

$$\log K = aA + bB + vV + pP + rR + c$$

Briefly, A, B, V, P and R terms are adsorbate molecular descriptors. A is the hydrogen bond donating ability (acidity), B is the hydrogen bond accepting ability (basicity), V ((cm³ mol^{−1})/100) is the molecular volume, P is the polarizability and dipolarity term, R is the (cm³/10) excess molar refractivity. The R descriptor is inter-correlated with the V descriptor to some extent because the cavity term also captures the size-dependent non-specific interactions. Although these two descriptors (V and R) cannot be distinctly separated, they encompass both the cavity formation and non-specific attraction energies. Lastly, c is the regression constant and a, b, v, p and r are the regression coefficients. All solvatochromic descriptors were obtained from Absolv module of ADME Suite 5.0 software.

2.4. Statistical methods

Multiple linear regression was employed to develop correlations between adsorption descriptors and solvatochromic descriptors. Fitting equations were obtained using SAS v.9.3 software. The goodness of the fit was examined by the coefficient of determination (r²). The regression models were evaluated by the p-values presented in analysis of variance (ANOVA). The p-value less than

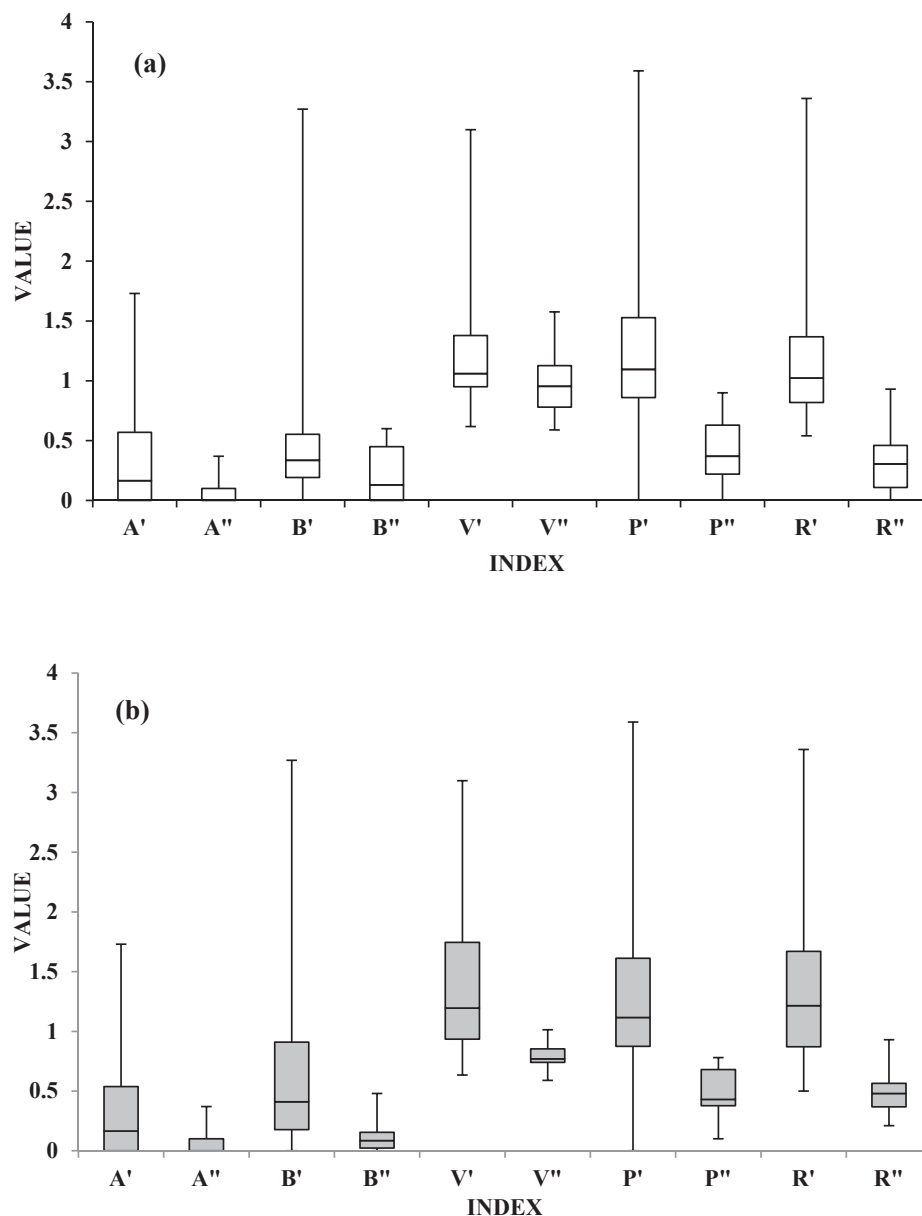


Fig. 1. Box and whisker plots for LSER descriptors for (a) MWCNT and (b) SWCNT datasets. A, B, V, P and R are the solvatochromic descriptors for all (<450 g/mol) of aromatic and aliphatic OCs. The descriptors representing the aromatic compounds are labeled with ('), and the descriptors representing the aliphatic compounds are shown with (''). Bottom and top of the boxes represent 25th and 75th percentiles, respectively. Bottom and top of the whiskers represent 10th and 90th percentiles, respectively. Lines inside the boxes represent mean values.

0.05 indicated that at 95% level of significance at least one of the independent variables of the developed equation is useful in predicting the dependent variable. The multicollinearity or correlations of independent variables with each other were tested by variation inflation factor (VIF). Higher VIF values indicate higher correlations with one or more of the remaining independent variables. The independent variables were accepted as correlated if the VIF values were larger than 10. The predictive precision of the models was quantified by the prediction error sum of squares (PRESS). A smaller PRESS value indicates a stronger prediction tendency of a model, and PRESS values were used to quantify the internal validation strength. The predictive precision of the models for external validation data were checked by root mean squared error (RMSE). RMSE is calculated by taking the square root of the

squared sum of residuals. The robustness and goodness-of-fits for models using statistical parameters and these regression model techniques were provided in our previous publication (Apul et al., 2013a,b).

3. Results and discussion

3.1. The effect of OC properties on LSER models

Single point adsorption descriptors (i.e., $\log K_d$ values) and solvatochromic descriptor values (A, B, V, P and R) of all OCs used for modeling (original dataset), are listed in Tables S1–S4. The parametric ranges of solvatochromic descriptors for all (<450 g/mol) of aromatic and aliphatic OCs are presented with box and whisker

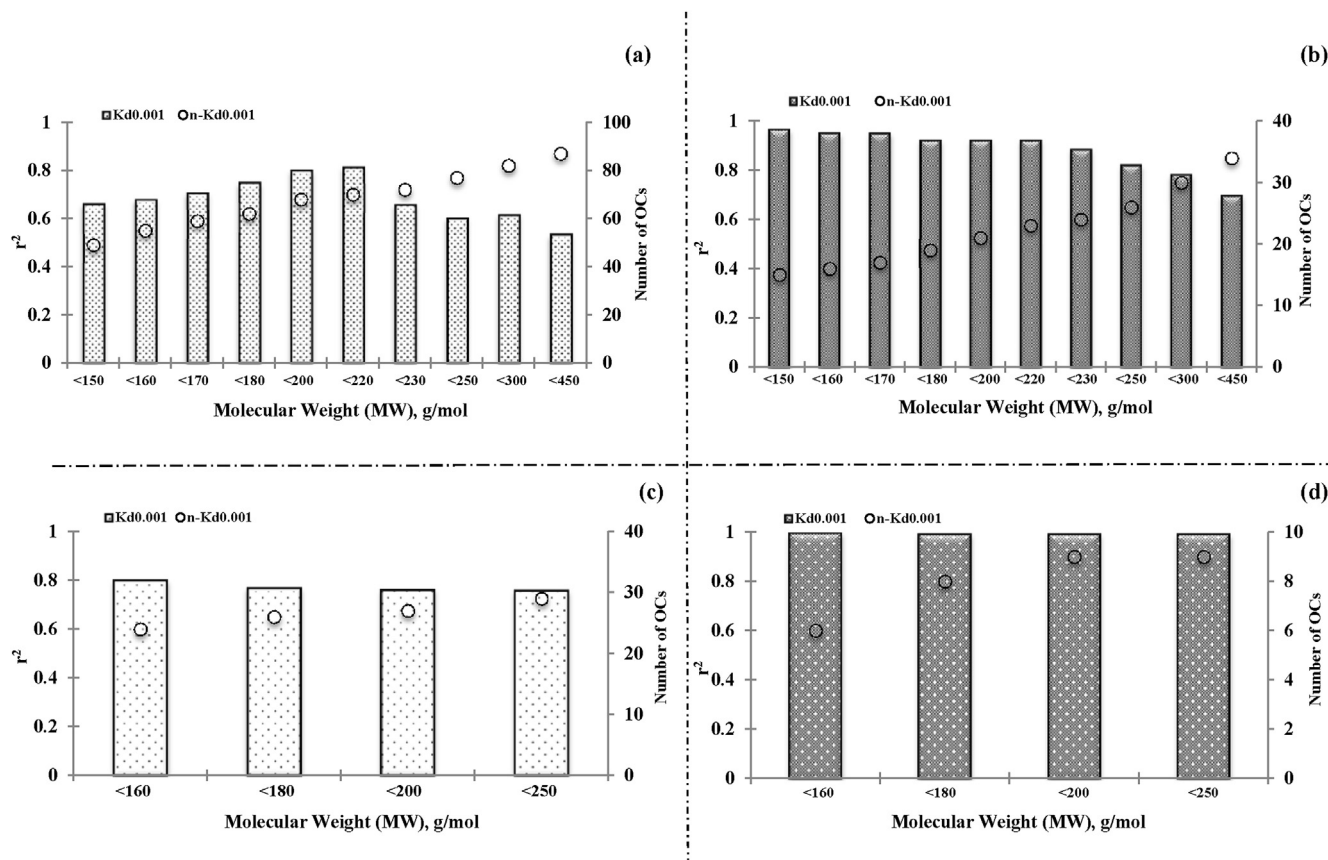


Fig. 2. Effect of molecular weight cutoff on the LSER models for adsorption of (a) aromatic OCs by MWCNTs, (b) aromatic OCs by SWCNTs, (c) aliphatic OCs by MWCNTs, and (d) aliphatic OCs by SWCNTs. 'n' represents the cumulative number of OCs.

Table 2

LSER model parameters for OCs adsorption by MWCNTs and SWCNTs at different equilibrium concentrations.

	Type of CNTs	Type of OCs	a	±	b	±	v	±	p	±	r	±	c	±	r ²	n
logK _{d0.0001}	MWCNTs	Aromatic	-1.2	0.66	-1.11	1.91	3.74	1.16	0.3	0.55	-0.08	0.6	-1.84	0.81	0.79	18
logK _{d0.001}			-0.17	0.21	-1.95	0.41	3.21	0.48	0.56	0.23	0.82	0.24	-3.27	0.37	0.8	68
logK _{d0.01}			-1.32	0.39	-2.36	0.73	4.03	0.76	-0.1	0.32	0.57	0.36	-3.36	0.53	0.88	32
logK _{d0.0001}			1.28	1.52	-4.03	1.13	3.69	0.99	-0.09	0.82	-3.07	1.17	-1.09	1.02	0.76	20
logK _{d0.001}		Aliphatic	0.45	1.48	-3.13	1.11	3.67	0.9	-0.89	0.79	-1.63	0.98	-1.66	0.92	0.76	27
logK _{d0.01}			0.81	1.25	-3.29	0.96	2.07	0.83	-0.92	0.73	-1.46	0.85	-0.3	0.85	0.76	20
logK _{d0.0001}		Aromatic + Aliphatic	-0.46	0.58	-3.14	0.9	4.08	0.63	0.32	0.47	0.09	0.43	-2.15	0.58	0.64	38
logK _{d0.001}			0.19	0.25	-2.57	0.45	4.46	0.39	0.12	0.27	0.24	0.24	-3.44	0.36	0.67	95
logK _{d0.01}		SWCNTs	-1.12	0.38	-3	0.55	3.91	0.45	-0.32	0.3	0.49	0.25	-2.75	0.42	0.78	52
logK _{d0.0001}		Aromatic	-3.6	1.14	3.78	3.32	9.12	4	-4.71	2.58	0.75	1.76	-3.51	1.19	0.85	17
logK _{d0.001}			-1.59	0.67	-1.81	1.41	5.16	1.55	-0.4	1.05	1.09	0.73	-3.62	0.68	0.92	21
logK _{d0.01}		Aliphatic	-3.17	0.67	-0.45	1.34	4.42	1.55	-0.72	1.16	1.16	0.87	-3.41	0.79	0.94	16
logK _{d0.0001}			-2.63	4.95	-19.94	4.73	-2.18	2.77	5.49	1.97	2.2	2.35	1.07	2.14	0.99	10
logK _{d0.001}		Aromatic + Aliphatic	-1.59	2.7	-14.14	2.61	1.23	1.52	2.01	1.08	2.6	1.29	-0.97	1.17	0.99	9
logK _{d0.01}			n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	3
logK _{d0.0001}			-2.41	1.76	-9.01	2.05	-6.12	1.97	3.48	1.72	6.28	1.26	1.55	1.23	0.8	27
logK _{d0.001}			-1.37	1.06	-6.96	1.33	-1.16	1.24	2.37	1.03	3.51	0.75	-0.96	0.8	0.85	30
logK _{d0.01}			-2.97	0.88	-1.74	1.1	1.93	1.19	-0.91	1.03	2.63	0.87	-1.94	0.88	0.89	19

n: number of OCs, n.d.: not determined. The OCs molecular weight lower than 200 g/mol. ±: standard errors of coefficients.

plots in Fig. 1. Besides, the box and whisker plots for the adsorbate molecular descriptors were also plotted and given for low molecular weight (i.e., <200 g/mol) aromatic and aliphatic OCs in Fig. S1. The OCs were classified as aromatic and aliphatic and both datasets are shown to cover distinct and broad ranges of physicochemical properties as indicated by the solvatochromic descriptors (Fig. 1). The distinction was more evident when P and R parameters of aromatic and aliphatic OCs were compared. These terms represent

polarizability and refractive properties of OCs, which typically capture the delocalization of electrons that is inherently higher in aromatics than aliphatics. Providing solvatochromic parameter ranges for LSER model development is important because models are valid for predicting adsorption of untested OCs as long as they fall within the reported solvatochromic descriptor ranges.

Fig. 2 shows the coefficient of determinations (r^2) as the key output of regression analysis to evaluate the developed LSER

Table 3

Adsorption descriptors of OCs data subset that was employed for comparison of CNT characteristics on the LSER models.

No	OCs	MW (g/mol)	logK _{0.001}		logK _{0.001}		logK _{0.01}	
			SWCNT	MWCNT	SWCNT	MWCNT	SWCNT	MWCNT
1	Benzene	78	0.951	0.729	0.313	−0.450	na	na
2	Toluene	92	na	na	0.919	0.270	0.317	0.070
3	Aniline	93	na	na	0.093	−0.770	na	na
4	Phenol	94	na	na	na	na	−2.296	−1.580
5	Chlorobenzene	113	na	na	1.089	−0.330	0.390	0.640
6	1,2,4,5-Tetrachlorobenzene	116	na	na	4.271	3.130	na	na
7	Nitrobenzene	123	1.444	1.092	0.832	0.330	na	na
8	1,3-Dichlorobenzene	125	na	na	2.167	0.650	na	na
9	Naphtaline	128	3.556	2.353	2.690	1.630	2.301	1.330
10	4-Nitrotoluene	137	na	na	2.170	1.440	na	na
11	1-Naphthylamine	143	na	na	na	na	2.404	0.440
12	2-Naphthol	144	3.062	1.600	2.159	1.380	na	na
13	1,2-Dichlorobenzene	147	na	na	2.050	0.560	na	na
14	Biphenyl	154	na	na	3.478	2.050	3.019	1.910
15	2,4-Dichlorophenol	163	1.745	1.261	1.222	0.960	0.368	0.010
16	2-Phenylphenol	170	2.699	1.854	2.030	1.630	1.196	0.820
17	Phenanthrene	178	na	na	4.459	3.290	3.843	3.040
18	1,2,4-Trichlorobenzene	182	na	na	2.520	1.170	1.894	1.230
19	2,4-Dinitrotoluene	182	2.939	3.376	2.559	2.380	na	na
20	Ibuprofen	206	na	na	3.076	1.979	2.678	1.456
21	Atrazine	216	na	na	3.184	2.627	2.417	2.234
22	Bisphenol A	228	na	na	1.374	0.295	1.295	−0.896
23	Diuron	233	3.979	3.803	0.257	2.929	2.331	2.104
24	Carbamazepine	236	na	na	3.090	2.048	2.191	1.112
25	Sulfamethoxazole	253	2.739	2.404	1.933	1.666	1.535	0.921
26	Pentachlorophenol	266	1.074	2.398	0.238	2.125	na	na
27	Triclosan	290	na	na	na	na	3.418	3.041
28	17 α -Ethinyl Estradiol	296	na	na	2.932	2.663	2.420	1.885
29	Norflurazon	304	4.074	3.840	3.126	2.982	2.402	2.126
30	Fluridone	329	5.222	4.805	4.501	4.116	3.699	3.383
31	Ciprofloxacin	331	0.523	0.222	−0.426	−0.737	−1.380	−1.675
32	Tetracycline	444	3.097	2.247	2.198	1.366	1.250	0.485
33	1,1-Dichloroethylene	97	na	na	0.374	−0.927	na	na
34	1,2-Dichloropropane	113	na	na	0.416	−0.362	na	na
35	Trichloroethylene	131	na	na	1.881	−0.119	na	na
36	1,1,1-Trichloroethane	133	na	na	0.504	−0.797	na	na
37	1,1,2-Trichloroethane	133	na	na	0.552	−0.863	na	na
38	Tetrachloroethylene	166	na	na	2.512	0.813	na	na
39	1,1,1,2-Tetrachloroethane	168	na	na	1.295	−0.580	na	na
40	1,2-Dibromoethane	188	na	na	0.839	−0.656	na	na

MW: Molecular weight (g/mol), na: data was not available within the experimental isotherm range, K is in mg/g.

models. The r^2 values were presented individually for aromatic and aliphatic OCs and they were plotted for different subsets of the original dataset according to the molecular weight cutoff values. Only, logK_{d,0.001} values were presented to demonstrate the effect of molecular weight cutoff on LSER modeling (Fig. 2), because among all saturation concentrations, the number of available OCs adsorption data was highest at 0.001% of aqueous solubility. Furthermore, the logK_{d,0.001} values have been used in previous LSER models enabling the comparison of our findings with other models (Apul et al., 2012; Hüffer et al., 2014; Yu et al., 2015). Fig. 2a – b indicate that there is a small variability in the r^2 values until 220 g/mol molecular weight cutoff for aromatic compounds. This is followed by a decreasing trend as the molecular weight cutoff reaches to 450 g/mol. This decrease can be attributed to the increase in the number of compounds (and associated uncertainty) included in the training dataset (n values) and/or the increase in the complexity of intermolecular interactions caused by large and branched OCs in the training dataset. Modeling intermolecular interactions of a complex molecular structure (e.g., amphiphilic molecules) is inherently more difficult because different regions of the molecule may undergo different molecular interactions concurrently. The complexity of adsorptive interactions between OCs and CNTs decreases the chances of success for a statistical model (i.e., r^2 of regression equations). Fig. 2c–d exhibit the r^2 values of LSER

models for adsorption of aliphatic OCs by CNTs at logK_{d,0.001}. There was no difference in r^2 values at different molecular weight cutoffs for aliphatic OCs, for the limited number of available data in the literature (n = 10–30). The r^2 values of LSER models for adsorption of aromatic and aliphatic OCs by CNTs at different equilibrium concentrations were also investigated and similar trends were observed (see Fig. S2). Overall, LSER approach was able to successfully train models for adsorption of aromatic and aliphatic OCs. The model linearity was notably better for smaller datasets; however, it should be noted that the prediction strength of the model will be diminished when compressing the variability in training datasets to obtain better linearity. The narrower descriptor ranges, in Fig. S1, resulted in a smaller prediction validity range.

The values of r^2 and adsorbate descriptor coefficients (a, b, v, p and r) of the LSER models, at different saturation levels, were given in Tables S5 and S6 for the different range of molecular weight cutoff of aromatic and aliphatic OCs. The r^2 values of LSER model within a range of 79–94% indicated the success of the LSER approach in the modeling low molecular weight (<220 g/mol) aromatic OCs adsorption by CNT. When the aromatic OC molecular weight reached 450 g/mol, the correlation for CNTs was less than 70%. For the aliphatic OCs, the r^2 values of LSER model for aliphatic OCs ranged between 76 and 99%. Overall, less than 65% correlation was observed for both CNTs at different saturation levels, when all

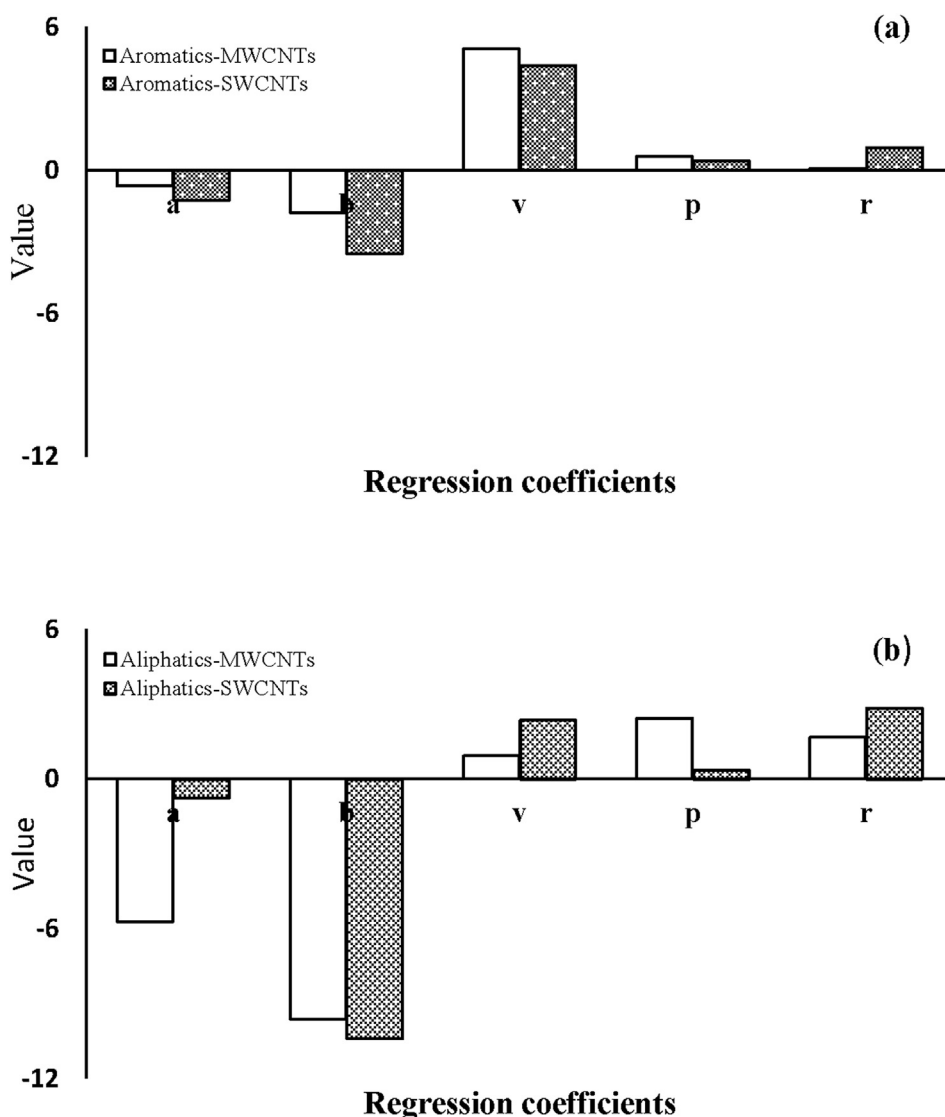


Fig. 3. The regression coefficients (a, b, v, p and r) of the LSER models developed for adsorption of (a) aromatic (b) aliphatic OCs by CNTs. (MW cutoff < 200 g/mol).

aromatic and aliphatic OCs (<450 g/mol) were modeled together with LSER. The wider molecular weight range of OCs resulted in decreasing correlations for both CNTs. Besides, the values of r^2 increased with increasing equilibrium concentration of low molecular weight aromatic OCs, while the r^2 values of aliphatic and high molecular weight aromatic OCs showed minor changes. Overall, aromatic OCs having low molecular weights (<220 g/mol) showed better correlation for modeling OC adsorption by CNTs at different equilibrium concentrations. This may be due to simpler sorption interactions between OCs and the CNT surfaces that can be captured with solvatochromic parameters especially when compared to high molecular weight OCs. It should be also noted that adsorption dataset for aliphatics was much smaller as compared to aromatics, and the modeling of aliphatic OCs adsorption by CNTs warrants further investigation especially when data for additional aliphatics becomes available in the literature.

Furthermore, the values of LSER model coefficients for adsorption of low molecular weight aromatic and aliphatic OCs by CNTs at different equilibrium concentrations were given in Table 2. Among all descriptors, V and B terms are the most significant descriptors (p values ≤ 0.05) in LSER equations for adsorption of low molecular

weight OCs by CNTs. Specifically, V term for aromatic OCs has the highest coefficients, whereas the absolute value of B term for aliphatic OCs was the most predominant descriptor, and was negatively correlated with adsorption on both CNTs. In addition, when the adsorption of low molecular weight cutoff OCs by CNTs were compared for their LSER descriptor coefficients with and without R term at $\log K_{0.001}$ saturation level (Tables S5 and S6), for MWCNTs; r^2 values were 80% and 76% for aromatic OCs; 76% and 73% for aliphatic OCs, respectively, whereas for SWCNTs; r^2 values were 92% and 91% for aromatic OCs and 99% and 98% for aliphatic OCs, respectively. R term did not have a significant effect on the LSER model at other studied saturation levels ($\log K_{0.0001}$ and $\log K_{0.01}$) for OCs adsorption by CNTs. The effect of R term on LSER models will be discussed in greater detail in Section 3.3.

3.2. The effect of CNT characteristics on LSER models

Among all OCs ($n = 123$), 40 of them had adsorption isotherm data both on MWCNTs and SWCNTs. Therefore, the effect of CNT types on the LSER model were examined by using this data subset of 40 OCs (Table 3). While the adsorption data of aromatic OCs were

Table 4
Comparison* of this study with literature in terms of LSER model parameters.

	Type of CNTs	Type of OCs	a	±	b	±	v	±	p	±	r	±	c	±	r ²	n
logK _{d,0.001} (This study)	MWCNTs	Aromatic	-1.20	0.66	-1.11	1.91	3.74	1.16	0.30	0.55	-0.08	0.60	-1.84	0.81	0.79	18
logK _{d,0.001} (Yu et al., 2015)			-0.83	0.18	-1.46	0.38	2.71	0.25	-0.40	0.15	0.97	0.15	-1.24	0.25	0.92	44
logK _{d,0.001} (This study)			-0.17	0.21	-1.95	0.41	3.21	0.48	0.56	0.23	0.82	0.24	-3.27	0.37	0.80	68
logK _{d,inf} (Apul et al., 2013a,b)			-0.06	0.21	-1.76	0.41	4.02	0.53	0.91	0.24	0.32	0.26	-4.07	0.43	0.83	58
logK _{d,0.001} (Yu et al., 2015)			-0.96	0.19	-1.77	0.40	2.96	0.26	-0.18	0.17	0.81	0.16	-1.99	0.26	0.92	44
logK _{d,0.01} (This study)			-1.32	0.39	-2.36	0.73	4.03	0.76	-0.1	0.32	0.57	0.36	-3.36	0.53	0.88	32
logK _{d,0.01} (Apul et al., 2013a,b)			-1.24	0.48	-2.86	1.06	2.29	1.08	0.43	0.42	1.20	0.49	-2.74	0.82	0.90	20
logK _{d,0.01} (Yu et al., 2015)			-1.07	0.18	-1.85	0.37	2.86	0.26	-0.20	0.15	0.74	0.15	-2.22	0.26	0.92	40
logK _{d,0.0001} (This study)		Aromatic + Aliphatic	-0.46	0.58	-3.14	0.90	4.08	0.63	0.32	0.47	0.09	0.43	-2.15	0.58	0.64	38
logK _{d,0.0001} (Hüffer et al., 2014)			-0.79	0.4	-3.66	0.48	4.83	0.39	0.46	0.38	0.43	0.33	0.1	0.39	0.86	34
logK _{d,0.01} (This study)			-1.12	0.38	-3.00	0.55	3.91	0.45	-0.32	0.30	0.49	0.25	-2.75	0.42	0.78	52
logK _{d,0.01} (Hüffer et al., 2014)			-0.93	0.41	-3.53	0.50	3.91	0.40	-0.26	0.39	0.37	0.35	0.35	0.40	0.85	34
logK _{d,0.001} (This study)	SWCNTs	Aliphatic	0.45	1.48	-3.13	1.11	3.67	0.90	-0.89	0.79	-1.63	0.98	-1.66	0.92	0.76	27
logK _{d,0.001} (Apul et al., 2015)			-3.51	7.56	18.35	17.07	21.79	6.05	-12.10	7.42	5.14	3.34	-17.41	3.48	0.92	9
logK _{d,0.0001} (This study)			-3.60	1.14	3.78	3.32	9.12	4.00	-4.71	2.58	0.75	1.76	-3.51	1.19	0.85	17
logK _{d,0.0001} (Yu et al., 2015)			-1.35	0.30	-1.82	0.61	3.30	0.72	0.21	0.44	1.33	0.43	-2.24	0.43	0.93	24
logK _{d,0.001} (This study)		Aromatic	-1.59	0.67	-1.81	1.41	5.16	1.55	-0.40	1.05	1.09	0.73	-3.62	0.68	0.92	21
logK _{d,0.001} (Yu et al., 2015)			-1.38	0.23	-2.01	0.47	3.69	0.56	-0.13	0.34	1.19	0.34	-2.67	0.33	0.96	24
logK _{d,0.01} (This study)			-3.17	0.67	-0.45	1.34	4.42	1.55	-0.72	1.16	1.16	0.87	-3.41	0.79	0.94	16
logK _{d,0.01} (Yu et al., 2015)			-1.42	0.22	-2.22	0.46	4.06	0.54	-0.46	0.33	1.04	0.32	-3.08	0.32	0.96	24

n: number of OCs,* data was obtained from their publication and remodeled with R. The OCs molecular weight lower than 200 g/mol. The LSER models were re-modeled given by Apul et al. (2013a,b and 2015) and Yu et al. (2015) taking the R term into account and selecting low molecular weight (<200 g/mol) of aromatic and aliphatic OCs adsorption by MWCNTs and SWCNTs from their studies. ±: standard errors of coefficients.

available at 1%, 0.1% and 0.01% of aqueous solubility, aliphatic OC data were available only at 0.1% of aqueous solubility. Therefore, only logK_{d,0.001} values were used to examine the effect of CNT types on the LSER models for aromatic and aliphatic OCs adsorption. The coefficients of LSER model descriptors at logK_{d,0.001} were presented in Fig. 3. The coefficients in all of the LSER models at three different saturation levels were also provided in Table S7. The adsorption affinities of aromatic and aliphatic OCs by SWCNTs at logK_{d,0.001} was shown to be greater than MWCNTs (Table 3). However, the r² values of LSER models for the adsorption of aromatic OCs by both SWCNTs and MWCNTs were similar indicating the linearity of LSER models does not strongly depend on the CNT type.

Among all descriptors, V and B terms are the most significant descriptors (p values ≤ 0.05) in LSER equations for adsorption of OCs by both MWCNTs and SWCNTs (Fig. 3). Specifically, V term for aromatic OCs had the highest coefficient, whereas the absolute value of B term for aliphatic OCs was the most predominant descriptor, and was negatively correlated with adsorption on both types of CNTs. Overall, the trends of model coefficients were generally similar for each CNT type; however, the values of A and P parameters were higher for aliphatics on MWCNTs than SWCNTs (Fig. 3).

In order to evaluate the effect of equilibrium concentration on the LSER model, the results for modeling adsorption of low molecular weight aromatic OCs (<200 g/mol) on MWCNTs and SWCNTs were compared at different saturation levels (Table S7). As equilibrium concentration for modeling aromatic OCs adsorption on MWCNTs and SWCNTs increased, i) no trends were observed on the B and V terms for MWCNTs, and R term for MWCNTs and SWCNTs, ii) the influence of A (from -0.97 to -1.35) and P (from 3.31 to -0.84) terms for MWCNTs and A (from -0.57 to -3.09) and P (from 3.29 to -1.07) terms for SWCNTs decreased, iii) the influence of V (from -4.23 to 4.65) and B (from -5.55 to -0.13) terms for SWCNTs increased. The change in the coefficients with the equilibrium concentrations may be partly due to different number of OC isotherm data available at each equilibrium concentration for modeling (Tables S1–S4). On the other hand, the effect of equilibrium concentration for the modeling aliphatic OCs adsorption by CNTs was not investigated due to limited aliphatic OCs adsorption data available at different equilibrium concentration.

3.3. Comparison of findings with the literature

Development of LSER model for adsorption of OCs by CNTs has recently attracted researchers' interest (Table 1). LSER models developed in this study are summarized in Table 4 along with other models developed in literature. A thorough discussion for the contribution of each descriptor will be difficult without taking into account the range of molecular weight of OCs (Apul et al., 2013a,b). Therefore, the corresponding LSER modeling data were collected and re-modeled within the studied range of OC molecular weight cutoffs. Additionally models were generated with and without R parameter to investigate its significance (Apul et al., 2013a,b; 2015 and Yu et al., 2015). Among all, V and B terms were the most influential descriptors in LSER equations for adsorption of OCs by CNTs (Table 4). V term had largest positive correlation that was associated with the size of the OCs molecule, and it exhibits the hydrophobically driven adsorption, and also nonspecific interactions between CNTs and OCs. The calculated V coefficients were also consistent with previous studies (Xia et al., 2010; Apul et al., 2013a,b; 2015; Hüffer et al., 2014). On the other hand, a negative correlation was observed for the B term, which captures hydrogen bonding accepting ability, as reported in other studies (Xia et al., 2010; Hüffer et al., 2014; Apul et al., 2015). As documented in Table 4, the coefficients of A, P, and R parameters were, in general, smaller than V and B coefficients.

In the peer-reviewed literature, LSER models for adsorption of OCs by CNTs with and without R term have been contemplated. Xia et al. (2010) and Apul et al. (2013a,b), investigated LSER modeling for adsorption of aromatic OCs by MWCNTs. They did not take R term into account for LSER development because the dataset was exclusively for aromatics, and lone pair electrons are assumed to be enclosed within the π-electron clouds of aromatic rings. Apul et al. (2015) reported that the effect of R term in the modeling of ten halogenated aliphatic OCs adsorption by SWCNTs was important, when the LSER equations with and without R term were compared. However, for MWCNTs, no notable effect of R term was observed. Hüffer et al. (2014) reported that R term cannot be fully separated by the LSER model due the inherent correlations between the descriptors. The authors argued that contribution of R term on LSER equation can be depending on types of CNTs and properties of OCs

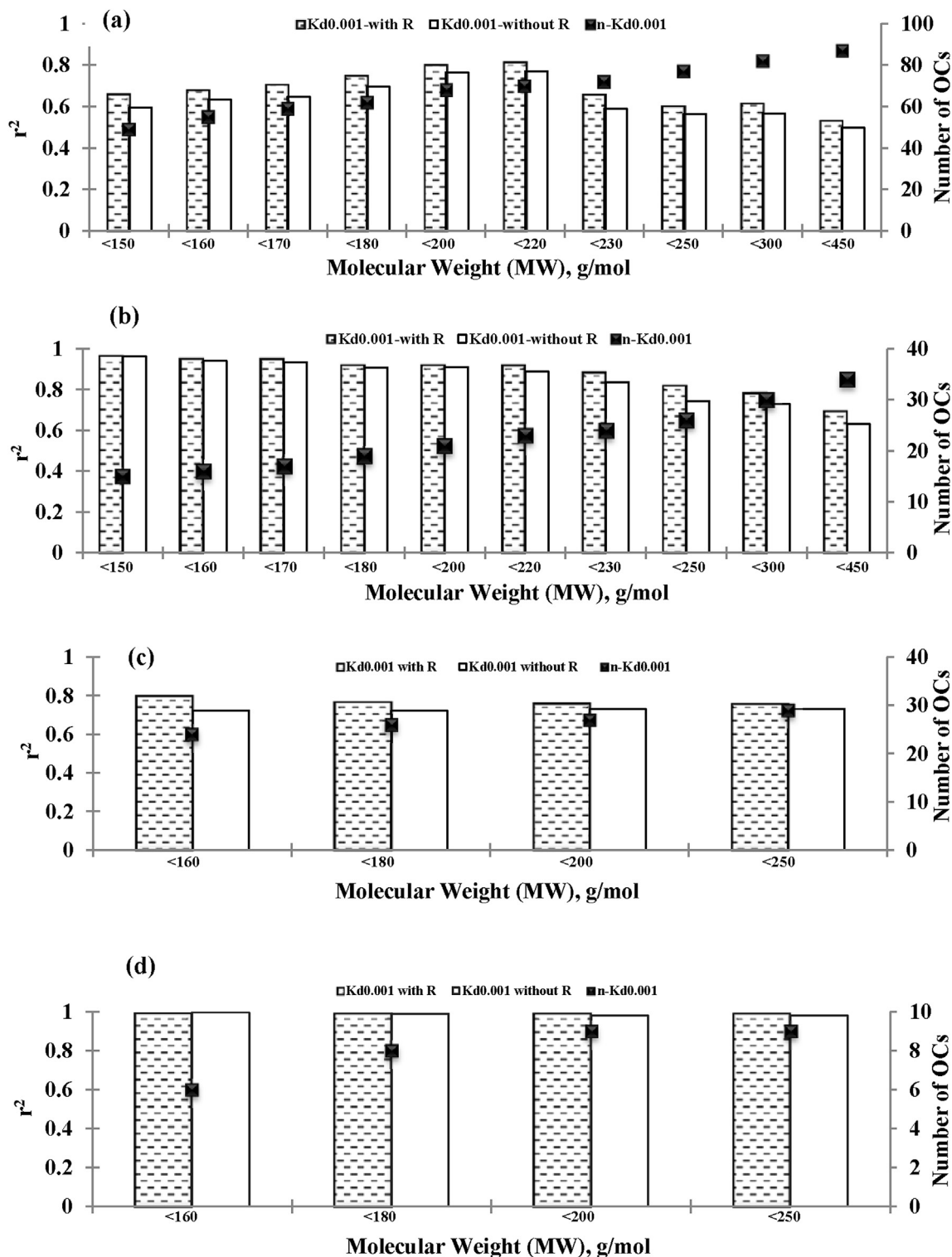


Fig. 4. Effect of R parameter on the LSER model for adsorption of OCs by CNTs. (a) and (b) represent aromatic OCs adsorption by MWCNTs and SWCNTs, respectively (c) and (d) represent aliphatic OCs adsorption by MWCNTs and SWCNTs, respectively. The number of OCs is labeled with n.

but the authors only examined MWCNTs (Table 1). In this study, we examined the effect of R parameter on the adsorption modeling of aromatic and aliphatic OCs by both SWCNTs and MWCNTs, and $\log K_{0.001}$ values were used as an example to develop the effect of R parameter on the LSER model. The r^2 values of LSER model descriptors at $\log K_{d,0.001}$ were provided in Fig. 4 for different OC

molecular weight cutoffs, and the LSER model coefficients with and without R for molecular weight smaller than <200 g/mol (a subset of the database) were shown in Fig. 5. The results indicate that the r^2 values of LSER models exhibited similar trends with and without R term. Therefore, the effect of R term on LSER model linearity was independent of the OC properties (i.e., aromatic vs. aliphatic and

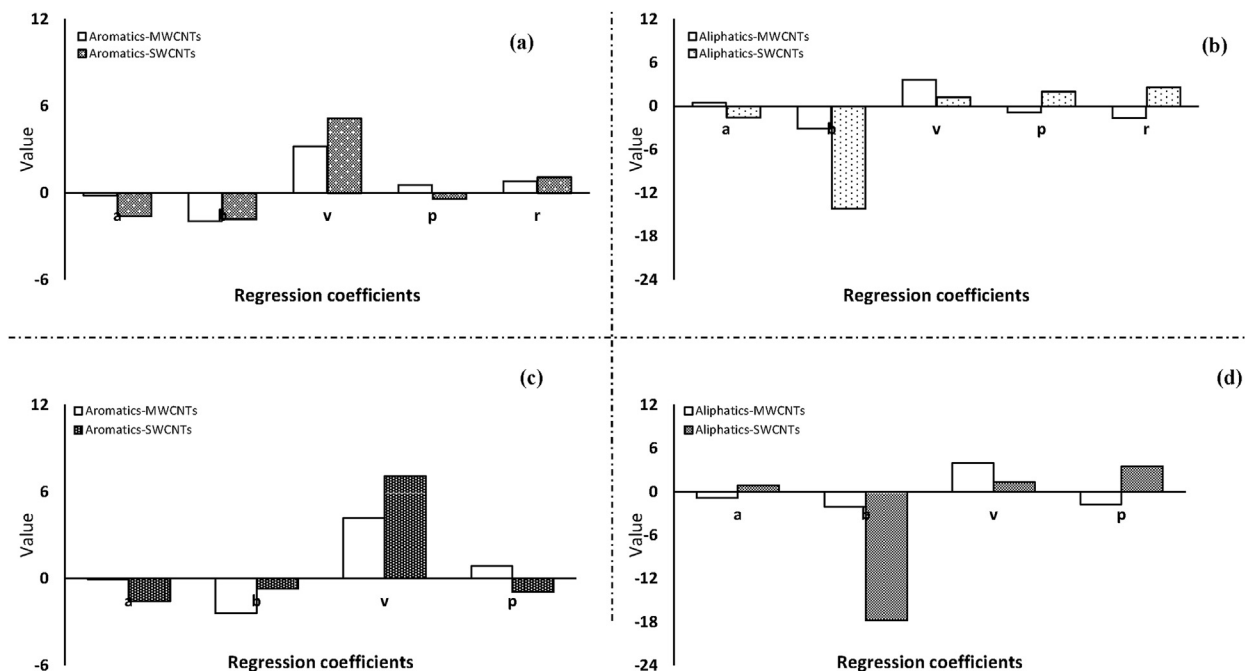


Fig. 5. (a) and (b) represent the regression coefficients (with r) of LSER model on the low molecular weight aromatic and aliphatic OCs adsorption by CNTs, respectively, (c) and (d) represent the regression coefficients (without r) of LSER model on the adsorption of aromatic and aliphatic OCs adsorption by CNTs, respectively (MW cutoff <200 g/mol for aromatic and aliphatic OCs).

molecular weight) or CNT properties (Fig. 4). The contribution of R term to adsorption onto both CNTs may be overshadowed by other interactions. According to Fig. 5, the trends of regression coefficients values (A , B , V , and P) for both CNTs were slightly changed with and without R term. Besides, the r^2 values were not significantly different in the absence and presence of R term at different saturation levels (Figs. S3–S6). An analysis of LSER model showed

that the coefficients of V and P decreased when R was included in the model (Fig. 5), while there was no consistent pattern for A and B . Although the presence of R may provide some additional mechanistic or predictive value to statistical models (i.e., a model with more terms that can have better predictive strength and/or the intermolecular interactions captured by these terms), researchers should be cautious about over parameterization of

VIF values-with R

VIF values-without R

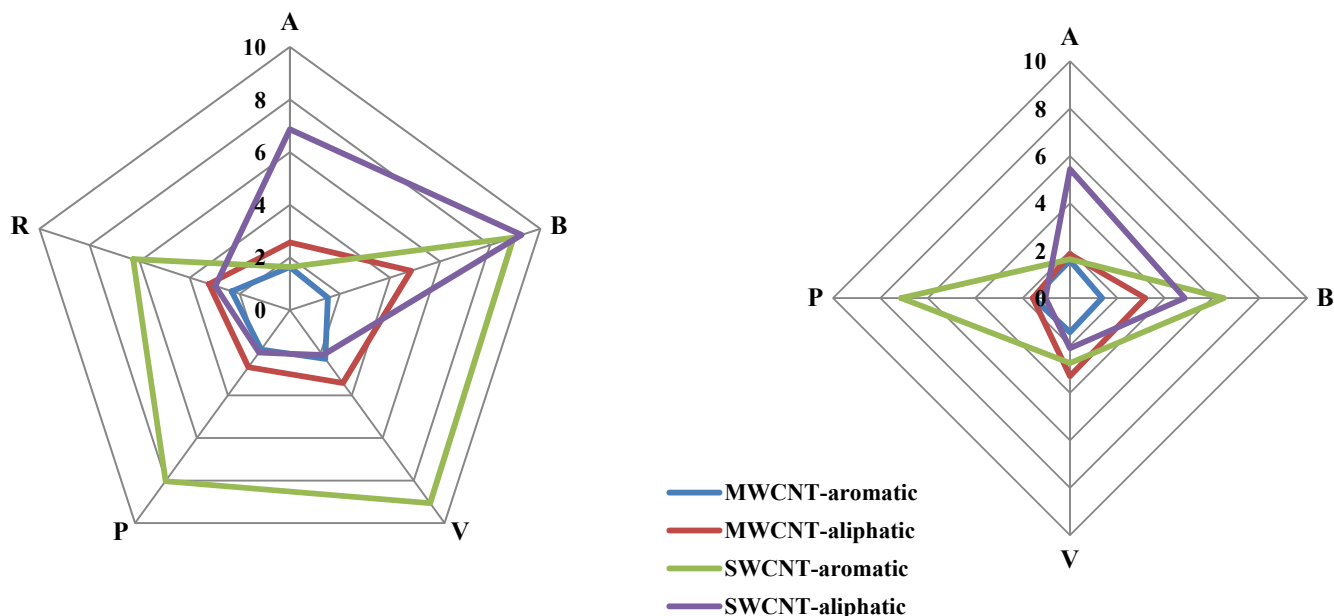


Fig. 6. The variation inflation factor (VIF) values for LSER model of aromatic and aliphatic OCs adsorption by MWCNTs and SWCNTs at $\log K_{0.001}$ saturation level.

models because of potential multicollinearity of least square regression correlations (i.e., correlation of independent variables).

To better visualize the multicollinearity, the change in VIF values during adsorption modeling (with and without R) was shown with radar chart in Fig. 6. The multicollinearity ($VIF > 10$) was not observed for both CNTs. Although the addition of the R term increased the VIF value of all model parameters, they still remained under the threshold value i.e., 10. This assessment indicates that R term may not present a very strong contribution to LSER models, and its addition does not cause a multicollinearity problem.

4. Conclusions

Poly-parameter LSER equations were developed for adsorption of different range of molecular weight cutoff of aromatic and aliphatic compounds by MWCNTs and SWCNTs at three different equilibrium concentrations. This comprehensive analysis showed that:

- LSER approach was able to successfully train models for adsorption of both aromatic and aliphatic OCs. The type of OCs (aromatic vs. aliphatic) did not influence the r^2 of the LSER equations.
- The model linearity was notably better for smaller datasets; however, the prediction strength of the models diminishes because of narrower model descriptor ranges.
- Adsorption affinity of OCs (K_d values) to SWCNTs were consistently higher than MWCNTs; however, the modeling results showed that the linearity of LSER models does not depend on the CNT type.
- V term for aromatic and B term for aliphatic compounds were found to be the predominant descriptors. The presence of R term in the LSER model resulted in decreases in both V and P parameters without affecting the r^2 values at different saturation levels. The effect of R term was independent of the OC properties (i.e., aromatic vs. aliphatic and molecular weight) or CNT properties.
- The addition of the R term increased the multicollinearity of the equations; however, they still remained under the threshold value i.e., 10. The presence of R term did not present a strong contribution to LSER models and did not cause a multicollinearity problem.
- This study presents the development of predictive LSER models for adsorption of OCs by CNTs in a simplified background matrix i.e., all adsorption data was collected in distilled and deionized water. The ability of LSER models predicting adsorption in natural waters in the presence of natural organic matter and other background components (calcium/ionic strength, alkalinity etc.) need to be further investigated. Some of these variables are currently under investigation in our laboratory and will be communicated in future publications.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.watres.2016.03.067>.

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