Adsorption modeling of organic compounds (OCs) by carbon nanotubes (CNTs): role of OC and CNT properties on the linear solvation energy relationship

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ABSTRACT
This study evaluated a comprehensive database for the adsorption of polar and nonpolar organic compounds (OCs) by carbon nanotubes (CNTs) and to use the linear solvation energy relationship (LSER) technique for developing predictive adsorption models of OCs by multi-walled carbon nanotubes (MWCNTs) and single-walled carbon nanotubes (SWCNTs). The results showed that coefficient of determinations ($R^2$) values for all compounds are higher variability in the 200 g/mol molecular weight cutoff (74–99%). When the molecular weight cutoff of all OCs is higher than 200 g/mol, the trend of their $R^2$ values is decreased (less than 70%). Among all adsorbate descriptor coefficients, $V$ and $B$ terms are the most significant descriptors ($p$-values ≤ 0.05) in LSER equations for adsorption of low molecular weight polar and nonpolar OCs by both CNTs. Besides, $K_{OW}$ normalization of all $K_d$ values did not have significant impact on the regression of the LSER model, indicating that hydrophobic interactions are not sole mechanism for the adsorption of OCs on CNTs. Lastly, SWCNTs exhibited higher polar OCs uptake than MWCNTs, which was attributed to more polar surface of SWCNTs as suggested by its high oxygen content (%10).

Key words: adsorption, carbon nanotubes, LSER, modeling, organic compounds

HIGHLIGHTS
• Adsorption data for 119 OCs by MWCNTs and 45 OCs by SWCNTs were modeled.
• Adsorption of low/high molecular weight polar and nonpolar OCs by both CNTs predicted.
• $V$ and $B$ terms are the most significant descriptors ($p$-values ≤ 0.05) in LSER equations.
• $K_{OW}$ normalization of all $K_d$ values did not significant impact on the LSER model.
• SWCNTs exhibited higher polar OCs uptake than MWCNTs.

1. INTRODUCTION
Carbon nanotubes (CNTs) can be imagined as graphitic carbon sheets rolled into hollow cylinders with nanometer scale diameters and micrometer scale lengths (Iijima 1991; Terrones 2003), and are classified as multi-walled carbon nanotubes (MWCNTs) and single-walled carbon nanotubes (SWCNTs) (Ajayan 1999). Due to their structure and high adsorption affinity towards different organic compounds (OCs) in water (Lu et al. 2006), CNTs have been considered as promising adsorbents (Zhang et al. 2010; Wu et al. 2016; Zhao et al. 2014; Gao et al. 2012; Apul et al. 2013, 2015; Ersan et al. 2016b, 2019; Zhao et al. 2021). Up to now, the adsorption of OCs (100+) by CNTs have been widely investigated in the literature (Long & Yang 2001; Peng et al. 2003; Pyrzynska et al. 2007; Chen et al. 2009; Su et al. 2010; Yu et al. 2012; Liu et al. 2014; Ersan et al. 2019; Zhao et al. 2021). However, collecting the experimental adsorption data for OCs can be costly, laborious and time consuming as well as dangerous owing to the toxicity of both OCs and CNTs. Besides, multiple adsorption mechanisms can individually control the OC sorption onto carbon-based nanomaterials. These individual contributions are challenging task and can be addressed by quantitative structure–activity relationship (QSAR) modeling (Roy et al. 2019; Apul et al. 2020). Utilizes solvation theory of QSAR modeling is an accepted approach, and this specific approach is referred as linear solvation energy relationships (LSER) in the literature (Goss & Schwarzenbach 2001; Endo & Goss 2014; Nguyen et al. 2015; Jia et al. 2020). The principle

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behind of the LSER approach is that physicochemical properties of each OC (such as hydrogen-bond acidity, basicity, molecular volume, polarizability/dipolarity and excess molar refractivity) have been used to predict environmental partition and transport of OCs. The LSER equation expresses the application of adsorbate molecular descriptors in multiple linear regression (MLR), and it shows the adsorbate molecular descriptor impacts on the equilibrium concentration of CNTs (Wang et al. 2013, 2019; Apul et al. 2020). Therefore, LSER approach can be developed utilizing the available adsorption data of the literature and can be used for the predicting sorption of untested OCs on similar types of CNT (Ersan et al. 2016a, 2018).

The multiple adsorption mechanisms between OC and CNT (i.e., hydrophobic interaction, π-π interaction, π-π electron donor-acceptor interaction [π-π EDA], van der Waals interactions, electrostatic interactions [Coulomb force], Lewis acid-base interactions, and hydrogen bonding) can act simultaneously and/or separately with varying relative contribution for adsorption of OCs by CNTs (Ersan et al. 2017, 2018; Apul et al. 2020). However, only few studies were investigated the impact of OCs properties (aromatic vs aliphatic, polar vs nonpolar, or molecular weight cutoff) on the predictive LSER model for the OC adsorption by MWCNTs (Hüffer et al. 2014; Ersan et al. 2016b; Wu et al. 2016; Li et al. 2017) and/or SWCNTs (Ersan et al. 2016b; Wu et al. 2016; Wang et al. 2019). Besides, limited study has been investigated the impacts of CNT properties (i.e., MWCNTs, MWCNTs-COOH, MWCNTs-OH, and MWCNTs-NH2) on the prediction of OC adsorption (Zhao et al. 2014, 2021). Therefore, the impacts of OC properties on the prediction of OC adsorption by pristine (non-functionalized) CNTs could not be fully understood. This study is currently the most comprehensive LSER modeling effort in the literature to evaluate the role of OC properties (polarity, molecular weight cutoff and hydrophobicity) and CNT types (MWCNTs vs. SWCNTs) on the LSER models for the adsorption of OCs by pristine MWCNTs and SWCNTs, simultaneously.

The main objectives of the study were to examine the impact of (i) molecular weight for OCs, (ii) hydrophobicity of OCs, and (iii) polarity of OCs on the LSER models for the adsorption of OCs by both pristine MWCNTs (<5% of oxygen content) and SWCNTs (<10% of oxygen content).

2. MATERIALS AND METHODS

2.1. Data collection and analysis

A database for adsorption of 119 OCs (i.e., 69 polar and 50 nonpolar compounds) on MWCNTs and 45 OCs (i.e., 24 polar and 21 nonpolar compounds) on SWCNTs was obtained from the current literature. For MWCNTs, 90 out of 55 polar and 35 nonpolar compounds had aromatic OC, and the rest of them are aliphatic OC (14 polar and 15 nonpolar compounds). For SWCNTs, 33 out of 20 polar and 13 nonpolar compounds had aromatic OC, and the rest of them are aliphatic compounds (four polar and eight nonpolar compounds). The molecular weight, octanol/water partition coefficient (K_{ow}), solvatochromic parameters and logK_d values of all selected OCs were given in the Tables S1-S2 (Supporting Information (SI)).

For the LSER modeling efforts, the adsorption data of selected OCs from the literature was conducted under comparable experimental conditions (i.e., room temperature and in distilled deionized water). To prevent increasing polarity onto CNT surface, the adsorption data for both pristine MWCNTs and pristine SWCNTs with less than 5% and 10% of oxygen content were kept in the LSER modeling, respectively.

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 OC were calculated and shown with K_{d,0.0001}, K_{d,0.001} and K_{d,0.01}, respectively. The details of all K_d determination were given in the SI section and in previous publications (Ersan et al. 2016b; Ersan & Ersan 2021).

2.2. LSER model training

Adsorption of OCs by CNTs is controlled by physicochemical interactions, some of which are explicitly described with solvatochromic descriptors as independent variables in the LSER model (Apul et al. 2013, 2020). 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 is presented in Equation (1)

$$\log K_d = aA + bB + vV + pP + rR + c$$  (1)
where A, B, V, P and R terms are adsorbate molecular descriptors. A is the hydrogen (H)-bond acidity, B is the H-bond basicity, V is the molecular volume, P is the polarizability/dipolarity term, R is the excess molar refractivity. Lastly, c is the regression constant and carries the units of log\(K_d\). The corresponding regression coefficients \((a, b, v, p, r)\) describe the ‘differences’ between the CNTs and solvent to interact with the OCs. The R and V terms represent nonspecific interaction as the cavity formation energy and dispersive van der Waals interaction, whereas A, B and P terms indicate specific interaction energies. All solvatochromic descriptors were obtained from Absolv module of ADME Suite 5.0 software.

2.3. Statistical data analysis

Multiple linear regression analysis was employed to develop correlations between adsorption and solvatochromic descriptors. Fitting equations were collected using Minitab 19.2020.1.0 software. The goodness of fit was examined by the coefficient of determination \((R^2)\). The regression models were examined by the \(p\)-values represented in analysis of variance (ANOVA). The \(p\)-value less than 0.05 referred that at 95% level of significance at least one of the independent variables of the developed equation is useful in predicting the dependent variable (Ersan et al. 2016b, 2019). The correlations of independent variables with each other were tested by variation in inflation factor (VIF). Higher VIF values represent higher correlations with one or more of the remaining independent variables. The independent variables were correlated if the VIF values were larger than 10. Besides, 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 was used to quantify the internal validation strength. Lastly, root mean squared error (RMSE) value was represented the predictive precision of the models for external validation data. The robustness and goodness of fit for models using statistical parameters and these regression model techniques were given and explained well in Ersan et al. 2021.

3. RESULTS AND DISCUSSION

3.1. The role of polar and nonpolar OCs on the 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-S2. The parametric ranges of solvatochromic descriptors are presented with box and whisker plots in Figure 1. The OCs graded as polar and nonpolar both datasets are shown to cover distinct and broad ranges of physicochemical properties as referred by the solvatochromic descriptors (Figure 1). The range of the solvatochromic descriptors for all OCs was also shown in Fig. S1. The distinction was more evident when P and R terms of polar and nonpolar OCs were compared. These terms represent polarizability and refractive properties of OCs, which typically capture the delocalization of electrons that is connatural higher in polar than nonpolar compounds.

Figure 2 showed the coefficient of determinations or \(R^2\) as the key output of regression analysis to examine the developed LSER models. The \(R^2\) values were presented individually for aromatic, aliphatic and all OCs, and were plotted for different subsets of the original dataset according to the molecular weight cutoff values. Only, \(\log K_{d,0.001}\) values were presented to demonstrate the effect of molecular weight cutoff on LSER modeling (Figure 2). Because, among all saturation concentrations, the number of available OCs adsorption data was highest at 0.001\% of aqueous solubility. Moreover, the \(\log K_{d,0.001}\) values have been used in previous LSER models providing the comparison of findings with other LSER models (Apul et al. 2013; Hüffer et al. 2014; Yu et al. 2015; Ersan et al. 2016b). The \(R^2\) values for aromatic and/or aliphatic compounds are higher variability in the 200 g/mol molecular weight cutoff. When the molecular weight cutoff of aromatic and/or aliphatic is higher than 200 g/mol, the trend of their \(R^2\) values is decreased (Figure 2). This decline can be attributed to the increase in the complexity of intermolecular interactions caused by large and/or branched OCs in the dataset. Modeling intermolecular interactions of a complex molecular structure is innately more difficult because different regions of the OC molecule may simultaneously expose to different molecular interactions. The complexity of adsorptive interactions between OCs and CNTs decreases the chances of success for a model strength (i.e., \(R^2\) of regression equations). Besides, there was no difference in \(R^2\) values at lower than 200 g/mol molecular weight cutoffs and all aliphatic OCs, for the limited number of available data in the literature (Figure 2). The \(R^2\) values of LSER models for adsorption of aromatic and aliphatic OCs by both CNTs at different equilibrium concentrations were also examined and found similar trends (see Table S3 and S4).

The values of \(R^2\) and adsorbate descriptor coefficients \((a, b, v, p, \text{ and } r)\) on the LSER models for all aromatic and aliphatic OCs, at different saturation levels, were tabulated in Tables S3 and S4 for the different range of molecular weight cutoff of aromatic and/or 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 (<200 g/mol) aromatic OCs adsorption by both CNT. When the
aromatic OC molecular weight was 450 g/mol, the correlation for CNTs was less than 70%. For the aliphatic OCs, the R² values of LSER model for aliphatic OCs ranged between 74 and 99%. And less than 68% correlation was observed for both CNTs at different saturation levels, when all aromatic and aliphatic OCs (<450 g/mol) were modeled together with LSER. Overall, aromatic OCs having low molecular weights (<200 g/mol) were showed better correlation for modeling OC adsorption by both CNTs at different equilibrium concentrations (Table S3-S4). This may be due to simpler adsorption interactions between OCs and the CNT surfaces that can be captured with solvatochromic parameters especially when compared to high molecular weight OCs. In addition, the adsorption dataset for aliphatic OCs was much smaller as compared to aromatic OCs, and the modeling of aliphatic OCs adsorption by CNTs assures further investigation especially when data for additional aliphatic OCs becomes available in the literature.

Moreover, the R² values and adsorbate descriptor coefficients of the LSER models for low molecular weight aromatic and aliphatic OCs by both CNTs were given in Table 1 at different equilibrium concentrations. For MWCNTs, the R² values were 79–88% for aromatic OCs; 76% for aliphatic OCs, whereas for SWCNTs; R² values were 90–94% for aromatic OCs and 99% for aliphatic OCs. As a conclusion, the adsorption affinities of aromatic and aliphatic OC by SWCNTs at logK_{d,0.001} were designated to be higher than MWCNTs due to the higher surface area of SWCNTs.
Among all adsorbate descriptor coefficients, V and B terms are the most significant descriptors (p-values < 0.05) in LSER equations for adsorption of low molecular weight OCs by both 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 type of CNTs which captures hydrogen bonding accepting ability, as reported in other studies (Xia et al. 2010; Hüffer et al. 2014; Apul et al. 2015). V term had generally largest positive correlation that was relevant with the size of OCs, and it shows the hydrophobically driven adsorption, and nonspecific interactions between CNTs and OCs. These results also consisted with previous studies (Apul et al. 2015, Ersan et al. 2016b). According to the Table 1, the coefficients of A, P and R terms were generally smaller than V and P terms. Overall, all descriptors of LSER models for tor the adsorption of OCs by both pristine SWCNTs and MWCNTs were changed depending on CNT type (MWCNT vs SWCNT) and OC properties (molecular weight and polarity).

To examine the effect of equilibrium concentration on the LSER model, the results for modeling adsorption of low molecular weight aromatic and/or aliphatic compounds (<200 g/mol) on MWCNTs and SWCNTs were compared at different saturation levels (Table 1 and S3-4). As equilibrium concentration for modeling aromatic and/or aliphatic OCs adsorption on MWCNTs and SWCNTs increased, for aromatics, (i) no trends were observed on the A, V, P and R terms for MWCNTs, A, B, P and R terms for SWCNTs, (ii) the influence of V (from 5.25 to 4.89) for SWCNTs decreased, (iii) the influence of B (from -1.11 to -2.36) for MWCNTs increased. For aliphatics, their trends were not comparable at different saturation levels, due to the limited number of available data in the literature. The change in the coefficients with the equilibrium concentrations for aromatics may be partly owing to different number of adsorption isotherm data available at each equilibrium concentration for LSER modeling (Tables S3-S4).

![Figure 2](http://iwaponline.com/wst/article-pdf/84/7/1635/948301/wst084071635.pdf)
Table 1 | LSER model parameters for aromatic and/or aliphatic OCs adsorption by CNTs at different equilibrium concentration

<table>
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<th>CNT types</th>
<th>OC types</th>
<th>logK&lt;sub&gt;a&lt;/sub&gt;</th>
<th>±</th>
<th>b</th>
<th>±</th>
<th>v</th>
<th>±</th>
<th>P</th>
<th>±</th>
<th>r</th>
<th>±</th>
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<th>±</th>
<th>R&lt;sup&gt;2&lt;/sup&gt;</th>
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<td>MWCNTs</td>
<td>Aliphatic + Aromatic</td>
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<td>−0.46</td>
<td>0.58</td>
<td>−3.14</td>
<td>0.90</td>
<td>4.08</td>
<td>0.63</td>
<td>0.32</td>
<td>0.47</td>
<td>0.09</td>
<td>0.43</td>
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<td>0.58</td>
<td>0.64</td>
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<tr>
<td></td>
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<td>0.12</td>
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<td>−3.46</td>
<td>0.36</td>
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<td></td>
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<td>−3.00</td>
<td>0.55</td>
<td>3.91</td>
<td>0.45</td>
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<td>0.25</td>
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<td>1.91</td>
<td>3.74</td>
<td>1.16</td>
<td>0.30</td>
<td>0.55</td>
<td>−0.07</td>
<td>0.60</td>
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<td>0.49</td>
<td>0.56</td>
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<td>−0.92</td>
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*<sup>n</sup> number of OCs, n.d.: not determined. The OC’s molecular weight lower than 200 g/mol. ± standard errors of coefficients.
3.2. The role of hydrophobicity on the LSER models

The adsorption coefficients of OCs with specific physicochemical properties could be normalized by aqueous solubility, $K_{\text{H/w}}$ (hexadecane-water partitioning coefficient), or $K_{\text{OW}}$ (octanol-water partitioning coefficient) to exclude hydrophobic effects (Chen et al. 2009; Pan et al. 2008). The peer-reviewed literature reported that $K_{\text{OW}}$ has been widely used to describe hydrophobicity. Conversely, some studies reported that the normalization of the adsorption coefficient by $K_{\text{H/w}}$ was unsuitable due to the possible interaction between -OH on octanol with OCs (Pan et al. 2008). Therefore, reliability of normalization of the adsorption coefficient by $K_{\text{OW}}$ can be depending on properties of OCs and type of CNTs (MWCNT vs SWCNT). In this study, the $K_{\text{H/w}}$ and $K_{\text{OW}}$ of all tested OCs were plotted for determining better and more reliable parameter (Fig. S2). According to the Table S1, the normalization of the adsorption coefficient by $K_{\text{OW}}$ are better correlated than $K_{\text{H/w}}$ for all tested OCs. Therefore, in this study was used $K_{\text{OW}}$ to normalize the adsorption to exclude hydrophobic effects.

The values of $R^2$ and adsorbate descriptor coefficients of the LSER models, at different saturation levels, were normalized by $K_{\text{OW}}$ and tabulated in Tables S5 and S6 for the different range of molecular weight cutoff of aromatic and/or aliphatic OCs. In addition, the results of low molecular weight (<200 g/mol) aromatic and aliphatic OCs by both MWCNTs and SWCNTs at different equilibrium concentrations were given in Table 2. According to all results, $K_{\text{OW}}$ normalization of $K_{\text{d,0.0001}}$, $K_{\text{d,0.001}}$ and $K_{\text{d,0.01}}$ did not have significant impact on the regression of the LSER model, indicating that hydrophobic interactions are not the only mechanism for the adsorption of OCs on SWCNTs. When compared to both pristine CNTs, the regression of the LSER models of low molecular weight (<200 g/mol) aromatic and aliphatic OCs by MWCNTs was slightly lower than SWCNTs (Table 2). Therefore, the hydrophobicity was a limiting factor for adsorption of aromatic and/or aliphatic OCs by MWCNTs due to the lower oxygen content (0.5%) of MWCNTs. Furthermore, the hydrophobicity of OCs can be a driving force for its accumulation on the CNTs surface, which is an important interaction in the adsorption of hydrophobic and OCs (especially nonpolar compounds) by CNTs from water (Zhang et al. 2010). The strong nonpolarity and hydrophobicity of CNTs can be described by using $K_{\text{OW}}$. However, there was no significant difference in $R^2$ values for nonpolar and polar OCs, due to the limited number of available nonpolar OCs data in the literature (data not shown).

Meanwhile, adsorbate descriptor coefficients of the LSER models of low molecular weight aromatic and aliphatic OCs by both MWCNTs and SWCNTs at log$K_{\text{d,0.001}}$ were normalized by $K_{\text{OW}}$ and demonstrated in Figure 3. Among all adsorbate descriptor coefficients, V and B terms are generally the most significant descriptors ($p$-values $\leq 0.05$) in LSER equations for adsorption of low molecular weight OCs by both CNTs. Specifically, comparing the B terms of different adsorbents and adsorbates (Figure 3), SWCNTs had the lowest B value for aliphatics, which exhibits that SWCNTs showed the lowest hydrogen-bond donating ability (least inclination to adsorb water). This is in accordance with the highest hydrophobicity (lowest cohesively) of SWCNTs indicated by the V terms. Besides, no clear trends were observed on the adsorbate descriptor coefficients of the LSER models by changing of aromatic and aliphatic OCs adsorption by both MWCNTs and SWCNTs at log$K_{\text{d,0.001}}$ and log$K_{\text{OW}}$ normalized. This difference may also be associated with the hydrophobic interactions between OC molecules and the along the nanotube axis depended on the properties of OC molecules (aromatic vs aliphatic, molecular weight cutoff) and CNTs (oxygen containing groups on SWCNTs and MWCNTs). Since oxygen containing groups on CNT surface are hydrophilic, they can form strong hydrogen bonds with water molecules, which result in the reduction of especially hydrophobic OC molecules (Apul et al. 2013; Ersan et al. 2016b).

3.3. The role of polarity on the LSER models

The $R^2$ values were presented individually for polar and/or nonpolar OCs by MWCNTs and SWCNTs at different equilibrium concentration and were summarized in Tables S7 and S8 for different subsets of the original dataset according to the molecular weight cutoff values. The $R^2$ values for polar and/or nonpolar OCs are higher variability in the 200 g/mol molecular weight cutoff. When the molecular weight cutoff of polar and/or nonpolar OCs is higher and/or lower than 200 g/mol, the trend of their $R^2$ values are decreased. And, among all saturation concentrations, the number of available adsorption data for low molecular weight cutoff OCs was highest at 0.001% of aqueous solubility. Therefore, log$K_{\text{d,0.001}}$ values were only presented to demonstrate the effect of polar and/or nonpolar OCs on LSER modeling in Figure 4. For both CNTs, the $R^2$ values of nonpolar OCs (0.91–0.99%) was always higher than polar OCs (0.65–0.66%) regardless of the aromatic and/or aliphatic OCs due to the hydrophobic interaction. The hydrophobicity of OCs can be a driving force for its accumulation on the CNTs surface, which is an important interaction in the adsorption of hydrophobic and nonpolar OCs from aqueous solution by CNTs (Chen et al. 2019; Apul et al. 2013; Ersan et al. 2016b). This is understandable...
Table 2 | Effect of hydrophobicity on the LSER models for adsorption of aromatic and/or aliphatic compounds by CNTs at different equilibrium concentration

| CNT types | OC types     | logK_a | a  | ±  | b  | ±  | v  | ±  | p  | ±  | r  | ±  | c  | ±  | R^2 | n |
|-----------|--------------|--------|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|
|           | Aliphatic+ Aromatic |        |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |
| MWCNTs    | logK_{0.0001,Kow} | −0.36  | 0.29 | −0.65 | 0.46 | 1.03 | 0.32 | 0.51 | 0.24 | −0.20 | 0.22 | −0.56 | 0.29 | 0.38 | 38 |
|           | logK_{0.001,Kow}  | 0.15   | 0.13 | −0.94 | 0.21 | 1.35 | 0.19 | 0.41 | 0.13 | −0.18 | 0.12 | −1.12 | 0.17 | 0.45 | 92 |
|           | logK_{0.01,Kow}   | −0.61  | 0.18 | −0.90 | 0.23 | 1.19 | 0.20 | 0.03 | 0.13 | 0.06  | 0.11 | −0.88 | 0.19 | 0.64 | 52 |
| Aromatic  | logK_{0.0001,Kow} | −0.70  | 0.47 | −0.10 | 1.35 | 0.95 | 0.82 | 0.59 | 0.39 | −0.45 | 0.43 | −0.30 | 0.57 | 0.49 | 18 |
|           | logK_{0.001,Kow}  | −0.01  | 0.14 | −0.68 | 0.25 | 0.83 | 0.27 | 0.60 | 0.15 | 0.02  | 0.15 | −1.02 | 0.21 | 0.49 | 65 |
|           | logK_{0.01,Kow}   | −0.78  | 0.24 | −0.78 | 0.36 | 1.11 | 0.35 | 0.17 | 0.18 | 0.04  | 0.18 | −0.91 | 0.27 | 0.69 | 32 |
| Aliphatic | logK_{0.0001,Kow} | 0.32   | 0.62 | −0.84 | 0.46 | 0.99 | 0.40 | 0.15 | 0.33 | −0.87 | 0.47 | −0.36 | 0.41 | 0.53 | 20 |
|           | logK_{0.001,Kow}  | 0.00   | 0.51 | −0.71 | 0.38 | 1.22 | 0.31 | −0.26 | 0.27 | −0.37 | 0.34 | −0.74 | 0.32 | 0.72 | 27 |
|           | logK_{0.01,Kow}   | 0.28   | 0.36 | −0.84 | 0.28 | 0.67 | 0.24 | −0.36 | 0.21 | −0.18 | 0.25 | −0.26 | 0.25 | 0.75 | 20 |
| SWCNTs    | Aliphatic+ Aromatic |        |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |
|           | logK_{0.0001,Kow} | −0.86  | 0.66 | −1.69 | 0.86 | −2.24 | 0.85 | 1.13 | 0.63 | 1.82  | 0.46 | 0.80  | 0.51 | 0.73 | 24 |
|           | logK_{0.001,Kow}  | −0.50  | 0.45 | −1.22 | 0.65 | −0.78 | 0.61 | 0.92 | 0.44 | 0.87  | 0.32 | 0.01  | 0.37 | 0.66 | 28 |
|           | logK_{0.01,Kow}   | −1.41  | 0.58 | −0.22 | 0.88 | 1.25 | 0.84 | −0.51 | 0.68 | 0.60  | 0.55 | −0.94 | 0.59 | 0.69 | 18 |
| Aromatic  | logK_{0.0001,Kow} | −1.20  | 0.46 | 1.45  | 1.43 | 1.31 | 1.63 | −0.49 | 1.09 | 0.61  | 0.69 | −0.84 | 0.47 | 0.81 | 14 |
|           | logK_{0.001,Kow}  | −0.60  | 0.36 | 0.70  | 0.81 | 1.37 | 0.87 | 0.05 | 0.56 | −0.02 | 0.39 | −0.92 | 0.39 | 0.70 | 19 |
|           | logK_{0.01,Kow}   | −1.61  | 0.57 | 0.90  | 1.21 | 2.48 | 1.27 | −0.57 | 0.98 | −0.19 | 0.70 | −1.53 | 0.63 | 0.76 | 15 |
| Aliphatic | logK_{0.0001,Kow} | 0.51   | 1.66 | −5.64 | 1.59 | −1.99 | 0.93 | 1.72 | 0.66 | 0.64  | 0.79 | 1.40  | 0.72 | 0.98 | 10 |
|           | logK_{0.001,Kow}  | 0.34   | 1.22 | −4.06 | 1.18 | −0.19 | 0.68 | 0.53 | 0.49 | 0.90  | 0.58 | 0.15  | 0.53 | 0.98 | 9  |

*n: number of OCs, n.d.: not determined. The OCs molecular weight lower than 200 g/mol. ±: standard errors of coefficients.
Figure 3 | Effect of hydrophobicity of each regression coefficients (a, b, v, p and r) of the LSER models developed for adsorption of (a) aromatic and (b) aliphatic OCs by MWCNTs, (c) aromatic and (d) aliphatic OCs by SWCNTs at logK0.001 saturation level (MW cutoff <200 g/mol).

Figure 4 | The LSER models for adsorption of polar and/or nonpolar OCs by MWCNTs and SWCNTs at logK0.001 saturation level (MW cutoff <200 g/mol, n represents the ‘cumulative number of OCs’, n.d. represents ‘not determined’ due to limited number of available data).
considering the strong nonpolarity and hydrophobicity of CNTs, and polarizability seems to be a dominant parameter that can be used to predict the adsorption coefficients of even highly polar OCs to oxidized CNTs surface.

Figure 4 also demonstrated that SWCNTs exhibited higher polar OCs uptake than MWCNTs, which was attributed to more polar surface of SWCNTs as suggested by its high oxygen content (%10). More polar regions on SWCNTs increases adsorption of polar OCs due to the possible interaction between polar regions on SWCNTs with polar OCs. Besides, water molecules can also interact with polar surface functionalities of SWCNTs surface via hydrogen bonding (Yang et al. 2006; Ersan et al. 2016b). However, the results showed that polar OCs can strongly form than H-bonds with water molecules on the oxygen containing groups of SWCNT surface. The modeling results demonstrated that the linearity of LSER models for polar OCs depends on oxidized CNTs surface.

Furthermore, adsorbate descriptor coefficients of the LSER models of low molecular weight polar and/or nonpolar OCs by both MWCNTs and SWCNTs at logKd,0.001 were given in Figure 5. Among all, V and B terms are the most significant descriptors (p-values ≤ 0.05) in LSER equations for adsorption of low molecular weight polar/or nonpolar OCs by both CNTs. Specifically, V term for adsorption of polar OCs by SWCNTs and nonpolar OCs by MWCNTs has the highest coefficients. V term had generally largest positive correlation that was relevant with the size of OCs, and it shows the hydrophobically driven adsorption, and nonspecific interactions between CNTs and OCs. These results also related with polarizability, as mentioned above. Besides, the absolute value of B term for polar and nonpolar OCs was the most predominant descriptor and was negatively correlated with adsorption on both type of CNTs which captures hydrogen bonding accepting ability, as reported in other studies (Xia et al. 2010; Hüffer et al. 2014; Apul et al. 2015; Ersan et al. 2016a). The coefficients of A and B terms for polar OCs were lower than nonpolar OCs for both CNTs. V and R terms for adsorption of nonpolar OCs by MWCNTs were higher than polar OCs, whereas V and R terms for adsorption of polar OCs by SWCNTs were higher than nonpolar OCs. Lastly, the P term of nonpolar and polar OCs adsorption by MWCNTs was not impact than
SWCNTs owing to the interaction between oxidized SWCNTs surface with polar OCs. Overall, all descriptors of LSER models for the adsorption of OCs by both SWCNTs and MWCNTs were changed depending on CNT types (MWCNTs vs SWCNTs) and OC properties (aromatic vs aliphatic, polar vs nonpolar, molecular weight cutoff).

CONCLUSIONS

This study is the first comprehensive LSER modeling effort in the literature to evaluate the role of OC properties (molecular weight cutoff, polarity, and hydrophobicity) and CNT types (SWCNTs vs. MWCNTs) on the LSER models for the adsorption of OCs on CNTs.

The LSER modeling results showed that adsorption affinities of aromatic and aliphatic OC by SWCNTs at logKd,0.001 were designated to be higher than MWCNTs, for low molecular weight (<200 g/mol) OCs. Besides, the R^2 values were 79–88% for aromatics and 76% for aliphatics adsorption by MWCNTs, whereas R^2 values were 90–94% for aromatics and 99% for aliphatics adsorption by SWCNTs. When the OC molecular weight was reached to 450 g/mol, the correlation for CNTs was less than 70%.

On the other side, K_{OW} normalization of all K_d values did not have significant impact on the regression of the LSER model, indicating that hydrophobic interactions are not the only mechanism for the adsorption of OCs on SWCNTs. When SWCNTs was compared with MWCNTs, the regression of the LSER models of low molecular weight (<200 g/mol) aromatic and aliphatic OCs by MWCNTs was slightly lower than SWCNTs. It might be due to the surface area of MWCNTs.

Furthermore, the R^2 values for polar and/or nonpolar OCs are higher variability in the 200 g/mol molecular weight cutoff. When the molecular weight cutoff of polar and/or nonpolar OCs is higher and/lower than 200 g/mol, the trend of their R^2 values are decreased. For both pristine CNTs, the R^2 values of nonpolar OCs (0.91–0.99%) was always higher than polar OCs (0.65–0.66%) regardless of the aromatic and/or aliphatic OCs due to the hydrophobic interaction. SWCNTs exhibited higher polar OCs uptake than MWCNTs, which was attributed to more polar surface of SWCNTs as suggested by its high oxygen content (%10). More polar regions on SWCNTs increases adsorption of polar OCs because of the possible interaction between polar regions on SWCNTs with polar OCs. Among all adsorbate descriptor coefficients, V and B terms are generally the most significant descriptors (p-values ≤0.05) in all LSER equations for adsorption of all low molecular weight OCs by both CNTs.

Overall, LSER approach was able to successfully train models for adsorption of low molecular weight OCs. The type of OCs (aromatic vs aliphatic, molecular weight cutoff, hydrophobicity, and polar vs nonpolar) and CNTs (SWCNTs vs. MWCNTs) influenced the coefficient values of the LSER equations. Additional data and further comparison of modeling adsorption of OCs (especially molecular weight >200 g/mol) by functionalized CNTs in different background water chemistry (i.e., natural organic matter, pH, and ionic strength) is warranted to investigate the impacts of functionalization of CNTs on the LSER models.

DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

REFERENCES

Endo, S. & Goss, K.-U. 2014 Applications of polyparameter linear free energy relationships in environmental chemistry. Environmental Science and Technology 48 (21), 12477–12491.
Ersan, G. & Ersan, M. S. 2021 Are carbon-based nanomaterials for the adsorption of organic contaminants perform better than nanoplastics (NPs) and microplastics (MPs)? Journal of International Environmental Engineering and Science 16 (2), 72–81.

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