Computing Adsorbate/Adsorbent Binding Energies and Henry's Law Constants From Molecular Simulations

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Computing Adsorbate/Adsorbent Binding Energies 
and Henry’s Law Constants from Molecular Simulations

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Abstract

Numerous organic contaminants are increasingly found in U.S. waterways; some of these pose health hazards 
to plants, animals, or humans. Removal of some organics by adsorption onto activated carbons is a standard 
technique used to remediate some waters, depending on the organics involved, and the volume of contami-
nated water. However, some organic compounds are resilient to removal by some carbons for a variety of rea-
sons. In this study, the molecular interactions of 1,4-dioxane and water with various functional groups known 
to exist on some activated carbon surfaces (carbonyls, carboxyls, and hydroxyls) were investigated. Addition-
ally, binding energies and Henry’s Law constants were determined for 1,1-dichloroethylene (1,1-DCE) and per-
fluorooctanoic (PFOA) acid in all-silica molecular sieve zeolites to predict adsorption affinities in an attempt to 
design suitable adsorbents for their removal. It is shown that these relatively less demanding calculations are 
sufficient to reveal favorable and unfavorable sorbate/sorbent combinations, which can ultimately lead to ra-
tional selection of remediation systems.

Key words: adsorption; gas-phase reactions; chemical-organic; sorption; analytical methods; biological treat-
ment processes; drinking-water quality; environmental microbiology

Introduction

A recent survey by USGS scientists resulted in identifying the presence of over 100 organic compounds in U.S. 
waterways (Kolpin et al., 2002). Among these were pharmaceuthicals, insecticides, pesticides, solvents, industrial chemi-
cals, foodstuff (e.g., caffeine), and naturally occurring hormones and medical wastes. Some of the compounds 
identified were benign, but some could pose health concerns to plants, animals, and humans. In this study, three organic 
compounds of concern were investigated.

1,4-Dioxane is a cyclic ether, listed as one of the emerging contaminants by the U.S. Environmental Protection 
Agency (EPA), and reported to be difficult to remove from water with conventional water treatment methods and resistant to 
biodegradation (Zenker et al., 2003). By emerging, it is meant that it has only recently been seen as a chemical of concern 
for the EPA’s remedial action programs (US EPA, 2005). Even short exposure to high levels of 1,4-Dioxane has caused verti-
go and irritation of the eyes, nose, throat, lungs, and skin in humans (Calabrese and Kenyon, 1991; Budavari, 1989).

Rats and mice exposed to 1,4-Dioxane in their drinking water developed liver carcinomas and adenomas and nasal cavity 
quamous cell carcinomas (NCI, 1978). As a result the, EPA has classified 1,4-dioxane as a Group B2, probable hu-
man carcinogen (US EPA, 1999).

1,1-DCE (C₂H₂Cl₂) is used in the production polyvinylidiene chloride copolymers which are used in the production 
of flexible films for food packaging. It is also used as an intermediate for organic chemical synthesis (ATSDR, 1994). 
Animal studies have shown that 1,1-DCE has a toxic effect on kidneys, liver, CNS and lungs (ATSDR, 1994; US DHHS, 

PFOA (C₈HF₁₅O₂), shown in Figure 1, is an industrial surfactant. It is a fully fluorinated carboxylic acid and most com-
monly used for processing polytetrafluoroethylene, PTFE. The durability of PFOA prevents it from breaking down once 
in the environment, leading to widespread buildup and bioaccumulation in food chains. Traces of PFOA-family 
chemicals can now be found in the blood of nearly all Americans and in the environment worldwide. The U.S. EPA has 
identified potential human health concerns from exposure to PFOA and its salts (US EPA, 2006).

One way to characterize the remediation capacity of a solid adsorbent is to generate adsorption isotherms relating re-
moval capacity to persisting liquid phase concentration, as
in the case of Methyl Tertiary Butyl Ether and trichloroethylene removal by hydrophobic adsorbents (Erdem-Şenatalar et al., 2004). Equilibrium adsorption isotherms give important information about the characteristics of an adsorbent-sorbate relation over a broad range of concentrations. In the very low concentration region of a “favorable” adsorption isotherm a rapid increase in the amount of the sorbate molecule is usually observed, which eventually reaches a limiting capacity at higher concentrations. The behavior of the isotherm in the very low concentration region, which is usually linear, is closely related to the affinity between the adsorbent and sorbate molecule, and the scope of this linear part of the isotherm is known as the Henry’s Law constant. Considering that this study is focused on contaminants which are present in water or air in low concentrations, investigating the affinity between an adsorbent and a sorbate molecule can be more convenient and easier than obtaining the full isotherm. And, these parameters are sufficient to identify unfavorable adsorbate/adsorbent pairs and predict those pairs that might be favorable.

Affinity between an adsorbent and a sorbate molecule can be expressed in terms of the binding energy between two of them. This binding energy can be computed by inserting a sorbate molecule in to the adsorbent many times in a Monte Carlo simulation and taking the average interaction energy between the sorbate molecule and adsorbent. Once binding energy is computed, using a Monte Carlo integration method Henry’s Law constant can be calculated (Smit and Siepmann, 1994; Jorge et al., 2002), which contains important information for designing industrial adsorption processes.

\[
H = \frac{\exp\left(-\frac{U}{k_BT}\right)}{k_BT}
\]

In the above equation \(H\) is Henry’s Law constant, \(U\) is the binding energy computed during the insertion of the sorbate molecule, and \(k_B\) is Boltzmann’s constant. This method was used to compute the Henry’s Law constant of several alkanes in silicalite (Vlugt et al., 1999; Smit and Siepmann, 1999) and Henry’s Law constant of water in activated carbon (Jorge et al., 2002).

In this study we utilized the computational methods described below to compute the binding energies and Henry’s Law constants for 1,4-Dioxane and water in activated carbon possessing different surface groups to investigate why activated carbon is ineffective in removing 1,4-Dioxane from water (Zenker et al., 2003). We also computed the binding energies and Henry’s Law constants for 1,1-Dichloroethylene (1,1-DCE) and Perfluorooctanoic Acid (PFOA) in all-silica silicalite, mordenite, zeolite beta, and zeolite Y to predict the efficiency of hydrophobic zeolites to remove these organic compounds from water or air streams. The choice of zeolites was motivated by our previous studies which illustrated their efficacy in removing organic contaminants from water (Giaya et al., 2000; Erdem-Şenatalar et al., 2004). In those studies, we concluded that condensed liquid organic phases were formed, and that, as a result, water was essentially excluded from the pores. By restricting these evaluations to the individual components, we seek to establish those adsorbents that would not effectively sequester particular adsorbates, and to predict which pairs might have strong affinity. The success of these pairs may be impacted by the environment in which the adsorbate exists.

Models and Methods

Activated carbon and zeolites

The activated carbon pore was modeled with two graphite plates, with each plate having three layers of graphitic carbon sheets above or below them. The length and width of the plates are constituted by hexagonal arrays set to give dimensions of \(a = 2.456\) nm, \(b = 2.456\) nm, and they were separated with a distance of \(c = 1.2\) nm, i.e., the pore dimension. Jorge et al. (2002) used dimensions of \(a = b = 3.0\) nm and Striolo et al. (2003) used dimensions of \(a = 2.95\) nm and \(b = 2.98\) nm which are similar to the values we used. It was reported that using larger values (\(a = 4.69\) nm, \(b = 4.43\) nm) did not result in significant differences (Striolo et al. 2003). The above references varied the distance between two plates; however, since we are interested in investigating the effects of the functional groups only, we fixed the separation of the plates at 1.2 nm.

Three types of polar surface sites were considered; carboxyl (-COOH), hydroxyl (-OH), and carbonyl (\(\text{C} = \text{O}\)) groups. Kotdawala et al. (2007) recently evaluated the effects of these surface groups on carbon for mercuric chloride adsorption, and noted that these three surface groups were predicted to increase mercuric chloride adsorption due to charge-induced dipole interactions. Jorge et al. (2002) performed a similar study for water molecules in active carbon and investigated the effect of the density and distribution of the polar sites, and the pore size. These surface groups are characterized in Table 1, which lists their geometric parameters.

Unit cell structures of silicalite, mordenite, zeolite beta, and zeolite Y were taken from the works of Artioli et al. (2000), Gramlich (1971), Newsam et al. (1998), and Hriljac et al. (1993), respectively. For simulations in silicalite the simulation box dimensions were obtained by using two unit cells, in mordenite and zeolite beta by using four unit cells, and in zeolite Y by using a single unit cell. The final simulation box dimensions are reported in Table 2.

1,4-Dioxane, 1,1-DCE, and PFOA

PFOA and 1,1-DCE were modeled by using OPLS-AA force field. OPLS-AA force field was developed by the Jorgensen group at Yale University and lists parameters to model several types of molecules and functional groups (Jorgensen, 2001; Kaminskii et al., 2001; Jorgensen, 1996). To model PFOA, parameters for fluorinated alkanes, and carboxylic acids, and to model 1,1-DCE parameters for chloro-
nated alkanes were used. Water molecule was modeled by using the SPC-E model (Berendsen et al., 1987), and 1,4-Dioxane was modeled by the model developed in our previous work (Yazaydin and Thompson, 2006).

**Force field potentials**

We used a pairwise-additive potential which is in the form of 12-6 Lennard-Jones (LJ) plus columbic potential to compute the site-site non-bonded interactions:

\[
V_{ij} = 4\varepsilon_{ij}\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}}\right)^{6} + \frac{q_i q_j}{4\varepsilon_{ij} r_{ij}}
\]

where \(i\) and \(j\) are atoms of adsorbate, adsorbent lattice and defects, and \(r_{ij}\) is the distance between atoms \(i\) and \(j\). \(r_{ij}\) and \(\sigma_{ij}\) are LJ well depth and diameter, respectively. \(q_i\) and \(q_j\) are the partial charges of the interacting sites.

The activated carbon pore interacted with molecules present within the pore through the Steele-Potential (Steele, 1974):

\[
V_C(z) = 2\pi \rho_C e_C \sigma_C^2 \Delta 
\]

\[
\left(\frac{2}{5} \left(\frac{\sigma_C}{z}\right)^{10} - \left(\frac{\sigma_C}{z}\right)^{4} - \left(\frac{\sigma_C^4}{3\Delta(z + 0.61\Delta)}\right)^{4}\right)
\]

where \(V_C(z)\) is the energy between the graphite plate and atom \(i\), \(\rho_C\) is the density of the carbon atoms on the graphite plates which is 114 nm\(^{-2}\), \(\Delta\) is the separation distance between carbon sheets in a single graphite plate which is 0.335 nm, \(z\) is the distance between the graphite plate and an atom of the sorbate molecule present in the pore in nm, and \(e_C\) and \(\sigma_C\) are LJ well depth and diameter of the interaction potential between the carbon atom of graphite plate and atom \(i\) in the pore, respectively (see Table 3 for the units and values of \(e_{Ci}\) and \(\sigma_{Ci}\)). The Steele-Potential models the interaction between the carbon atoms on the activated carbon surface and atoms of other molecules in the pore. Instead of computing the interaction between an atom of a molecule in the pore and all carbon atoms on the graphite surface one by one, Equation 3 is used to represent all carbon atoms as a field. This accelerates computation time significantly. The accuracy of Steele potential was investigated by Striolo et al. (2003). The results from simulations where the Steele potential was used did not differ significantly from the results of simulations where carbon atoms were treated explicitly provided that the plate separation was kept less than 1.6 nm, which was 1.2 nm in our simulations.

Partial charges and LJ parameters of the polar surface groups attached to graphite plates were taken from the work of Jorge et al. (2002). LJ terms between unlike atoms of water, 1,4-Dioxane, carbon atom of graphite plate and atoms of polar surface groups were computed using Lorentz-Berthelot mixing rules.

\[
e_{ij} = \sqrt{e_i e_j}, \quad \sigma_{ij} = \frac{\sigma_i + \sigma_j}{2}
\]

Table 3 lists all the non-bonded interaction parameters for graphite plates, polar surface groups, 1,4-Dioxane, and water.

Partial charges on the zeolite atoms were taken from the work of Jaramillo et al. (2001) and LJ parameters of the oxygen atom of the silicalite were taken from the work of Snurr et al. (1993). As noted previously, the silicon atom of silicalite interacted with the atoms of the sorbate molecules only through the electrostatic potential. OPLS-AA force field which was use to model 1,1-DCE, and PFOA uses geometric mixing rules so LJ terms between unlike atoms of 1,1-DCE, PFOA and oxygen of zeolites were computed using geometric mixing rules.

\[
e_{ij} = \sqrt{e_i e_j}, \quad \sigma_{ij} = \sqrt{\sigma_i \sigma_j}
\]

Table 4 lists all non-bonded interaction parameters for zeolite atoms and 1,1-DCE, and PFOA.

**Simulations**

Four different surface structures on activated carbon pores were considered in the simulations. One with no polar sites attached and one simulation for each type of polar site attached on the surface of the graphite plates. Four polar sites

---

**Table 1. Geometric Parameters for Polar Surface Groups on Graphite Surface**

<table>
<thead>
<tr>
<th>Bond</th>
<th>Bond length (nm)</th>
<th>Angle</th>
<th>Amplitude, (deg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbonyl</td>
<td>C=O</td>
<td>0.1233</td>
<td>C=O-H</td>
</tr>
<tr>
<td>Hydroxyl</td>
<td>C-O</td>
<td>0.1364</td>
<td>C=O-H</td>
</tr>
<tr>
<td></td>
<td>O-H</td>
<td>0.096</td>
<td></td>
</tr>
<tr>
<td>Carboxyl</td>
<td>C=C</td>
<td>0.152</td>
<td>C=C-O</td>
</tr>
<tr>
<td></td>
<td>C=O</td>
<td>0.1214</td>
<td>O=C-O</td>
</tr>
<tr>
<td></td>
<td>C=O</td>
<td>0.1364</td>
<td>C=O-H</td>
</tr>
<tr>
<td></td>
<td>O-H</td>
<td>0.097</td>
<td></td>
</tr>
</tbody>
</table>

*Note:* Unit cell dimensions of the listed zeolites were taken from (Artioli et al. 2000), (Gramlich 1971), (Newsam et al. 1998), and (Hrlijac et al. 1993).

**Table 2. Simulation Box Dimensions for Each Zeolite Studied**

<table>
<thead>
<tr>
<th>Zeolite</th>
<th>a (nm)</th>
<th>b (nm)</th>
<th>c (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silicalite</td>
<td>2.00511</td>
<td>1.98757</td>
<td>2.673640</td>
</tr>
<tr>
<td>Mordenite</td>
<td>1.8011</td>
<td>2.053</td>
<td>3.0112</td>
</tr>
<tr>
<td>Zeolite β</td>
<td>2.532278</td>
<td>2.532278</td>
<td>2.640612</td>
</tr>
<tr>
<td>Zeolite Y</td>
<td>2.42576</td>
<td>2.42576</td>
<td>2.42576</td>
</tr>
</tbody>
</table>
were placed on each graphite plate totaling in eight polar sites per pore. These polar sites were placed such that they are as far as possible from each other.

In the simulations of 1,4-Dioxane, water, and 1,1-DCE, $5 \times 10^6$ insertions were performed, while in the case of PFOA the number of insertions was $2 \times 10^5$. One should note that this insertion move is different than the one normally sampled in a Grand Canonical Monte Carlo (GCMC) simulation which is used to simulate the adsorption isotherms. In our simulations, a molecule was inserted into a randomly selected position in the simulation box, and after the energy between the inserted molecule and adsorbent was computed, the molecule was removed, whereas, in a GCMC simulation the inserted molecule can stay in the simulation box with a certain probability of acceptance. The method we followed to compute the Henry’s Law constant is less computationally demanding than that of computed for GCMC simulations. To compute the Henry’s Law constant with the GCMC method one must perform several simulations at the very low concentration region to generate the points on the adsorption isotherm and Henry’s Law constant is computed by taking the slope of the line fitted to these points. Whereas in the Monte Carlo integration method we used, only a single simulation is required. Jorge et al. (2002) compared the Henry’s Law constants obtained from both method and reported excellent agreement.

All simulations were performed in the NVT ensemble at 298.15 K. In this ensemble, the number of molecules, the volume of the system, and the temperature were kept fixed. Coulombic interactions were handled by the Ewald Sum method (Ewald, 1921). Periodic boundary conditions were applied in all directions in the simulations with zeolites. On

Table 3. Non-Bonded Field Parameters for Graphite Plates, Polar Surface Groups, 1,4-Dioxane and Water

<table>
<thead>
<tr>
<th>Interacting sites</th>
<th>Lennard-Jones</th>
<th>Columbic</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\sigma$ (nm)</td>
<td>$\varepsilon$ (K)</td>
</tr>
<tr>
<td>C</td>
<td>0.430</td>
<td>28.0</td>
</tr>
<tr>
<td>Oonyl</td>
<td>0.296</td>
<td>105.791</td>
</tr>
<tr>
<td>H</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>Ca</td>
<td>0.375</td>
<td>52.8</td>
</tr>
<tr>
<td>Ohxyl</td>
<td>0.3</td>
<td>85.6</td>
</tr>
<tr>
<td>Oxyl</td>
<td>0.296</td>
<td>105.695</td>
</tr>
<tr>
<td>Oh</td>
<td>0.35</td>
<td>33.2123</td>
</tr>
<tr>
<td>CH2c</td>
<td>0.385</td>
<td>51.3</td>
</tr>
<tr>
<td>Oc</td>
<td>0.28</td>
<td>98.0</td>
</tr>
<tr>
<td>OW</td>
<td>0.31656</td>
<td>78.197</td>
</tr>
<tr>
<td>HW</td>
<td>0.0</td>
<td>0.0</td>
</tr>
</tbody>
</table>

C: carbon atom on the basal plane of graphite connected to a polar group atom; Oonyl: oxygen atom of carbonyl group; Ca: carbon atom of the carboxyl group; Ohxyl: oxygen atom bonded to hydrogen in the carboxyl group; Oxyl: oxygen atom double bonded to carbon atom in the carboxyl group; Oh: oxygen atom in the hydroxyl group; H: hydrogen bonded to any oxygen atom; OW: oxygen atom of water; HW: hydrogen atom of water; CH2c: methylene united atom in 1,4-Dioxane; Oc: oxygen atom in 1,4-Dioxane.

$^a$Lorentz-Berthelot mixing rules were used to calculate cross terms.

Table 4. Non-Bonded Field Parameters for Zeolite Atoms, 1,1-DCE, and PFOA

<table>
<thead>
<tr>
<th>Interacting sites$^a$</th>
<th>Lennard-Jones</th>
<th>Columbic</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\sigma$ (nm)</td>
<td>$\varepsilon$ (K)</td>
</tr>
<tr>
<td>Si</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>OZ</td>
<td>0.2806</td>
<td>89.6</td>
</tr>
<tr>
<td>CM</td>
<td>0.355</td>
<td>38.2445</td>
</tr>
<tr>
<td>Cl</td>
<td>0.34</td>
<td>130.965</td>
</tr>
<tr>
<td>H-C ~ 2</td>
<td>0.242</td>
<td>15.0965</td>
</tr>
<tr>
<td>C_a</td>
<td>0.375</td>
<td>52.8377</td>
</tr>
<tr>
<td>CTf</td>
<td>0.35</td>
<td>33.2123</td>
</tr>
<tr>
<td>Fpf</td>
<td>0.295</td>
<td>26.6705</td>
</tr>
<tr>
<td>H-O</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>O2</td>
<td>0.296</td>
<td>105.6755</td>
</tr>
<tr>
<td>O-Ha</td>
<td>0.30</td>
<td>85.5468</td>
</tr>
</tbody>
</table>

Si, OZ: Silicon and Oxygen atoms of zeolites; CM, Cl, H-C ~ 2: carbon, chlorine, hydrogen atoms of 1,1-DCE; CTf: carbon atom bonded to fluorine in PFOA; Fpf: fluorine atom bonded to carbon in PFOA; C_a: carbon atom of carboxylic acid group in PFOA; O-H: hydrogen atom bonded to oxygen atom of carboxylic group in PFOA; O-H: hydrogen atom bonded to oxygen atom of carboxylic group in PFOA.

$^a$Geometric mixing rules were used to calculate cross terms.
the other hand, in the simulations with activated carbon pores, periodic boundary conditions were only applied in the two directions that were parallel to the graphite surface. The non-bonded potential cutoff distance was 0.95 nm for simulations with silicalite, 0.9 nm for simulations with mordenite, and 1.2 nm for simulations with zeolite beta, zeolite Y, and activated carbon.

In all simulations Towhee Monte Carlo simulation code was used (http://towhee.sourceforge.net).

Results and Discussion

1,4-Dioxane and Water

In Table 5 binding energies and Henry’s Law constants of water and 1,4-Dioxane are given in graphitic activated carbon and with carbonyl, carboxyl, and hydroxyl groups on the surface. Having an activated carbon surface with no impurities is highly unlikely, but it is included here for completeness and for comparison. While we can say that there is essentially no affinity between 1,4-Dioxane and graphitic activated carbon, the most important outcome of these figures can be seen when we examine the change in binding energies and Henry’s Law constants at the presence of the polar sites. The addition of polar sites increases the binding energy for water significantly, resulting in an increase of the Henry’s Law constants by one or two orders of magnitude. Jorge et al. (2002) reported similar increases in activated carbon’s affinity for water in the presence of these groups as well. By contrast, addition of polar sites had no effect on the binding energy of 1,4-Dioxane except for a minor change in the case of the carboxyl group. These polar groups are always present on the surface and, according to the simulation results, the polar groups favor the adsorption of water over 1,4-Dioxane. The groups’ affinities for water rather than 1,4-Dioxane might be one of the reasons why activated carbons are ineffective in removing 1,4-Dioxane from water (Zenker et al., 2003). That is, while activated carbon is predicted to have little affinity for 1,4-Dioxane in air, in the

| Table 5. Binding Energies and Henry’s Law Constants for 1,4-Dioxane and Water in Activated Carbon Pore with Polar Surfaces of Carbonyl, Carboxyl, and Hydroxyl |
|---|---|---|---|
| Water | No polar group | Carbonyl | Carboxyl | Hydroxyl |
| Binding energy (kcal/mol) | 0.14 | −1.20 | −2.77 | −1.52 |
| Henry’s constant (mol/m³ Pa) | 3.19 × 10⁻⁴ | 3.07 × 10⁻³ | 4.35 × 10⁻² | 5.28 × 10⁻³ |

| 1,4-Dioxane |
|---|---|---|---|
| No polar group | Carbonyl | Carboxyl | Hydroxyl |
| Binding energy (kcal/mol) | 16.61 | 16.62 | 15.80 | 16.29 |
| Henry’s constant (mol/m³ Pa) | 2.76 × 10⁻¹⁶ | 2.65 × 10⁻¹⁶ | 1.05 × 10⁻¹⁵ | 4.60 × 10⁻¹⁶ |

Table 6. Binding Energies and Henry’s Constants of PFOA and 1,1-DCE in Silicalite, Mordenite, Zeolite-Beta, Zeolite-Y

| PFOA |
|---|---|---|---|
| Silicate | Mordenite | Zeolite-beta | Zeolite-y |
| Binding energy (kcal/mol) | 36.43 | −6.82 | −7.51 | −2.97 |
| Henry’s constant (mol/kg Pa) | 4.44 × 10⁻³⁴ | 2.36 × 10⁻² | 8.60 × 10⁻² | 4.50 × 10⁻⁵ |

| 1,1-DCE |
|---|---|---|---|
| Silicate | Mordenite | Zeolite-beta | Zeolite-y |
| Binding energy (kcal/mol) | −6.12 | −5.55 | −6.58 | −4.60 |
| Henry’s constant (mol/kg Pa) | 6.84 × 10⁻³ | 2.75 × 10⁻³ | 1.79 × 10⁻² | 7.06 × 10⁻⁴ |
ence of liquid water, the adsorption of water is likely to oc-
cupy pore volume and align with the surface sites, thus fur-
ther restricting access by the dioxane molecules. Kotdawal
et al. (2007) also noted that the affinities for these groups
and mercuric chloride increased in the same order as com-
puted here for water. Their results were attributed to high charge
densities and charge-induced dipole interactions.

1,1-DCE and PFOA

In Table 6 binding energies and Henry’s constants for 1,1-
DCE and PFOA are given in four different zeolites. The re-
results for PFOA reveal that zeolites beta and mordenite have
the highest affinities for PFOA followed by zeolite Y. On the
other hand silicalite has no affinity at all for PFOA. Zeolite
beta and zeolite Y have large pores to accommodate PFOA
and the straight channels of mordenite seem to have a per-
fec fit for PFOA. The pores at the intersection of the straight
and zigzag channels of silicalite are known to be favorable
sites for adsorbing molecules; however, they are not large
enough to accommodate a long chain. It is known that alka-
nes with long chains are flexible enough to bend themselves
(Maginn et al., 1995), but the value of the binding energy of
PFOA in silicalite suggest that PFOA does not have this flex-
ibility.

The binding energies for 1,1-DCE suggest that all of the
zeolites considered have an affinity for 1,1-DCE. This affin-
ity is in the order of zeolite-beta > silicalite > mordenite >
zeolite-Y. Taken alone, these results would suggest that ze-
olite beta is the best candidate for removing 1,1-DCE from
water. However, it is known that the competing effects of
water must be considered as well, even though these zeo-
lites are highly hydrophobic and some only permit liquid
water to exist at very high applied pressures (Desbiens et al.,
2005). In the case of trichloroethylene and methyl tertiary
butyl ether removal from water, for example, silicalite
proved to be better than these other three zeolites (Erdem-
Şenatalar et al., 2004), because it excluded water more effec-
tively than the other zeolites (Giaya and Thompson, 2002).

Conclusions

A strategy for predicting strong sorbate/sorbent interac-
tions was demonstrated. The approach allows one to design
suitable organics remediation systems, and to exclude from
further consideration those pairs demonstrated to be unfa-
vorable. Monte Carlo simulations were used to compute
binding energies and Henry’s Law constants for 1,4-dioxane
and water in activated carbons, and for PFOA and 1,1-DCE
in four zeolites: silicalite, mordenite, zeolite beta, and zeolite
Y. The affinity of activated carbon with polar groups at-
tached to the carbon surface for 1,4-Dioxyane and water were
investigated in an attempt to shed light on why activated
carbons are not effective in removing 1,4-Dioxane from wa-
ter. Results showed that the presence of carboxyl, carboxyl,
and hydroxyl groups increased the affinity between water
and activated carbon, while the affinity between 1,4-Dioxyane
and activated carbon was not effected by the presence of
these polar surface groups. Silicalite had no affinity for
PFOA, most likely due to size exclusion constraints. All four
zeolites had relatively high affinities for 1,1-DCE, however
zeolite-beta had the highest affinity for both PFOA and 1,1-
DCE.

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Author Disclosure Statement

No competing interests exist.

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