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A. Oezguer Yazaydin

Robert W. Thompson

Worcester Polytechnic Institute, rwt@wpi.edu

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

A. Özgür Yazaydin and Robert W. Thompson*

Department of Chemical Engineering, Worcester Polytechnic Institute, Worcester, Massachusetts.

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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 contaminated water. However, some organic compounds are resilient to removal by some carbons for a variety of reasons. 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. Additionally, binding energies and Henry's Law constants were determined for 1,1-dichloroethylene (1,1-DCE) and perfluorooctanoic (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 rational selection of remediation systems.

Key words: adsorption; gas-phase reactions; chemical-organic; sorption; analytical methods; biological treatment 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 pharmaceuticals, insecticides, pesticides, solvents, industrial chemicals, 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 vertigo 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 squamous cell carcinomas (NCI, 1978). As a result the EPA has classified 1,4-dioxane as a Group B2, probable human carcinogen (US EPA, 1999).

1,1-DCE (C₂H₂Cl₂) is used in the production polyvinylidene 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, 1993a; US DHHS, 1993b). EPA considers 1,1-DCE to be a possible human carcinogen (US EPA, 1999).

PFOA (C₈HF₁₅O₂), shown in Figure 1, is an industrial surfactant. It is a fully fluorinated carboxylic acid and most commonly 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 removal capacity to persisting liquid phase concentration, as

*Corresponding author: Department of Chemical Engineering, Worcester Polytechnic Institute, 100 Institute Road, Worcester, MA 01609. Phone: 508-831-5525; Fax: 508-831-5853; E-mail: rwt@wpi.edu

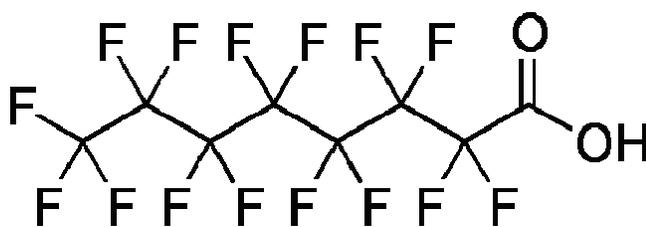


FIG. 1. Perfluorooctanoic acid.

in the case of Methyl Tertiary Butyl Ether and trichloroethylene removal by hydrophobic adsorbents (Erdem-Şenatarlar *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 slope 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.

$$H = \frac{\left\langle \exp\left(-\frac{U}{k_B T}\right) \right\rangle}{k_B T} \quad (1)$$

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 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-enatarlar *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 (>C=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; Kaminski *et al.*, 2001; Jorgensen, 1996). To model PFOA, parameters for fluorinated alkanes, and carboxylic acids, and to model 1,1-DCE parameters for chlori-

TABLE 1. GEOMETRIC PARAMETERS FOR POLAR SURFACE GROUPS ON GRAPHITE SURFACE[†]

| | Bond | Bond length (nm) | Angle | Amplitude, (deg) |
|----------|-------------------|------------------|---------------------|------------------|
| Carbonyl | C ^a =O | 0.1233 | | |
| Hydroxyl | C ^a —O | 0.1364 | C ^a —O—H | 110.5 |
| | O—H | 0.096 | | |
| Carboxyl | C ^a —C | 0.152 | C ^a —C=O | 111 |
| | C=O | 0.1214 | O—C=O | 123 |
| | C—O | 0.1364 | C—O—H | 107 |
| | O—H | 0.097 | | |

^aCarbon atom in the graphite basal plane.

[†]All geometric parameters were taken from Jorge *et al.*, 2002.

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:

$$V_{ij} = 4\epsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^6 \right] + \frac{q_i q_j}{4\epsilon_0 r_{ij}} \quad (2)$$

where i and j are atoms of adsorbate, adsorbent lattice and defects, and r_{ij} is the distance between atoms i and j . ϵ_{ij} and σ_{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):

$$V_{Ci}(z) = 2\pi\rho_C\epsilon_{Ci}\sigma_{Ci}^2\Delta \left[\frac{2}{5} \left(\frac{\sigma_{Ci}}{z} \right)^{10} - \left(\frac{\sigma_{Ci}}{z} \right)^4 - \left(\frac{\sigma_{Ci}^4}{3\Delta(z + 0.61\Delta)^3} \right) \right] \quad (3)$$

where V_{Ci} is the energy between the graphite plate and atom i , ρ_C is the density of the carbon atoms on the graphite plates which is 114 nm^{-3} , Δ 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 ϵ_{Ci} and σ_{Ci} 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 ϵ_{Ci} and σ_{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.

$$\epsilon_{ij} = \sqrt{\epsilon_{ii}\epsilon_{jj}} \quad \sigma_{ij} = \frac{\sigma_{ii} + \sigma_{jj}}{2} \quad (4)$$

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 used 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.

$$\epsilon_{ij} = \sqrt{\epsilon_{ii}\epsilon_{jj}} \quad \sigma_{ij} = \sqrt{\sigma_{ii}\sigma_{jj}} \quad (5)$$

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 2. SIMULATION BOX DIMENSIONS FOR EACH ZEOLITE STUDIED

| Zeolite | a (nm) | b (nm) | c (nm) |
|---------------------------|----------|----------|----------|
| Silicalite ¹ | 2.00511 | 1.987570 | 2.673640 |
| Mordenite ² | 1.8011 | 2.053 | 3.0112 |
| Zeolite beta ³ | 2.532278 | 2.532278 | 2.640612 |
| Zeolite Y ⁴ | 2.42576 | 2.42576 | 2.42576 |

Note: Unit cell dimensions of the listed zeolites were taken from (Artioli *et al.* 2000),¹ (Gramlich 1971),² (Newsam *et al.* 1998),³ and (Hriljac *et al.* 1993)⁴

TABLE 3. NON-BONDED FIELD PARAMETERS FOR GRAPHITE PLATES, POLAR SURFACE GROUPS, 1,4-DIOXANE AND WATER

| Interacting sites ^a | Lennard-Jones | | Columbic | |
|--------------------------------|---------------|----------------|------------------|---|
| | σ (nm) | ϵ (K) | Sites | $q(e)$ |
| C | 0.430 | 28.0 | C | 0.5/0.08/0.2 (carbonyl/carboxyl/hydroxyl) |
| Oonyl | 0.296 | 105.791 | Oonyl | -0.5 |
| H | 0.0 | 0.0 | H | 0.45/0.44 (carboxyl/hydroxyl) |
| Ca | 0.375 | 52.8 | Ca | 0.55 |
| Ohxyl | 0.3 | 85.6 | Ohxyl | -0.58 |
| Oxyl | 0.296 | 105.695 | Oxyl | -0.50 |
| Oh | 0.35 | 33.2123 | Oh | -0.64 |
| CH _{2c} | 0.385 | 51.3 | CH _{2c} | -0.25 |
| Oc | 0.28 | 98.0 | Oc | 0.5 |
| OW | 0.31656 | 78.197 | OW | -0.8476 |
| HW | 0.0 | 0.0 | HW | 0.4238 |

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; CH_{2c}: methylene united atom in 1,4-Dioxane; Oc: oxygen atom in 1,4-Dioxane.

^aLorentz-Berthelot mixing rules were used to calculate cross terms.

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, 5×10^6 insertions were performed, while in the case of PFOA the number of insertions was 2×10^5 . 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 computation-

ally 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 4. NON-BONDED FIELD PARAMETERS FOR ZEOLITE ATOMS, 1,1-DCE, AND PFOA

| Interacting sites ^a | Lennard-Jones | | Columbic | |
|--------------------------------|---------------|----------------|----------------|----------------------------------|
| | σ (nm) | ϵ (K) | Sites | $q(e)$ |
| Si | 0.0 | 0.0 | Si | 2.050 |
| OZ | 0.2806 | 89.6 | OZ | -1.025 |
| CM | 0.355 | 38.2445 | CM | 0.12/0.23 (bonded to Cl/H-C ~ 2) |
| Cl | 0.34 | 150.965 | Cl | -0.06 |
| H-C ~ 2 | 0.242 | 15.0965 | H-C ~ 2 | 0.115 |
| C_a | 0.375 | 52.8377 | C_a | 0.52 |
| CTf | 0.35 | 33.2123 | CTf | 0.36/0.24 (bonded to 3 Fpf/2Fpf) |
| Fpf | 0.295 | 26.6705 | Fpf | -0.12 |
| H-O | 0.0 | 0.0 | H-O | 0.45 |
| O ₂ | 0.296 | 105.6755 | O ₂ | -0.44 |
| O-Ha | 0.30 | 85.5468 | O-Ha | -0.53 |

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; O₂: oxygen double bonded to the carbon atom of carboxylic group in PFOA; O-Ha: oxygen atom bonded to carbon and hydrogen of carboxylic group in PFOA; H-O: hydrogen atom bonded to oxygen atom of carboxylic group in PFOA.

^aGeometric mixing rules were used to calculate cross terms.

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/m ³ 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/m ³ Pa) | 2.76×10^{-16} | 2.65×10^{-16} | 1.05×10^{-15} | 4.60×10^{-16} |

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 pres-

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 occupy pore volume and align with the surface sites, thus further 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 computed 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 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 perfect 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 alkanes 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 flexibility.

The binding energies for 1,1-DCE suggest that all of the zeolites considered have an affinity for 1,1-DCE. This affinity is in the order of zeolite-beta > silicalite > mordenite > zeolite-Y. Taken alone, these results would suggest that zeolite 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 zeolites 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 effectively than the other zeolites (Giaya and Thompson, 2002).

Conclusions

A strategy for predicting strong sorbate/sorbent interactions was demonstrated. The approach allows one to design suitable organics remediation systems, and to exclude from further consideration those pairs demonstrated to be unfavorable. 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 attached to the carbon surface for 1,4-Dioxane and water were investigated in an attempt to shed light on why activated carbons are not effective in removing 1,4-Dioxane from water. Results showed that the presence of carbonyl, carboxyl, and hydroxyl groups increased the affinity between water and activated carbon, while the affinity between 1,4-Dioxane 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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