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Simulation-based evaluation of zeolite adsorbents for the removal of emerging contaminants

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SUPPORTING INFORMATION

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S1 Overview of atom types and force field parameters

S1.1 Atom types

The force field parameter assignment (atom typing) was done using the automated procedure implemented in *Materials Studio*. Table S1 gives an overview of the DREIDING atom types present in different pollutant molecules. The labelling used, which corresponds to that employed by Materials Studio, is largely consistent with the original DREIDING publication (S. L. Mayo, B. D. Olafson, W. A. Goddard III, *J. Phys. Chem.* **1990**, *94*, 8897–8909), with the exception of hydrogen atoms able to form hydrogen bonds: These are labelled H___A in Materials Studio, whereas the original publication used H___HB.

Table S1: Overview of DREIDING atom types present in pollutant molecules.

	H_	H___A	C_2	C_3	C_R	N_3	N_R	O_2	O_3	O_R	F_	P_3	S_3	Cl
Acetaminophen	X	X		X	X		X	X		X				
Atrazine	X	X		X	X		X							X
Caffeine	X			X	X		X	X						
Carbamazepine	X	X			X		X	X						
DEET	X			X	X		X	X						
Diazepam	X			X	X		X	X						X
Diclofenac	X	X		X	X		X	X		X				X
Dilantin	X	X		X	X		X	X						
Estrone	X	X	X	X	X			X		X				
Fluoxetine	X	X		X	X	X				X	X			
Gemfibrozil	X	X		X	X			X		X				
Hydrocodone	X		X	X	X	X		X		X				
Ibuprofen	X	X		X	X			X		X				
Meprobamate	X	X		X	X		X	X		X				
Naproxen	X	X		X	X			X		X				
Oxybenzone	X	X		X	X			X		X				
Pentoxifylline	X		X	X	X		X	X						
Sulfamethoxazole	X	X		X	X		X	X		X			X	
TCEP	X			X				X	X			X		X
Triclosan	X	X			X					X				X
Trimethoprim	X	X		X	X		X			X				

For the all-silica zeolite frameworks, the atom type Si3 was used for Si atoms, and O_3 was used for O atoms. As the zeolite frameworks were treated as rigid throughout the DREIDING-based simulations, only the vdW parameters of these atom types are relevant. They are included in Table S5.

S1.2 Bond stretching parameters

The DREIDING force field uses the following functional form for bond stretching:

$$E_{bond} = \frac{1}{2} k_{bond,AB} (R_{AB} - R_{0,AB})^2$$

Here, $k_{bond,AB}$ is the force constant of a given bond type, R_{AB} is the distance between the two bonded atoms A and B, and $R_{0,AB}$ is the equilibrium bond distance. Table S2 gives the parameters $k_{bond,AB}$ and $R_{0,AB}$ for all relevant bonds.

Table S2: DREIDING bond stretching parameters. Note that the force constants $k_{bond,AB}$ are given in (kcal/mol)/Å^2 to be consistent with the original publication and the Materials Studio force field file.

Atom A	**Atom B**	$k_{bond,AB}$ [(kcal/mol)/Å^2]	$R_{0,AB}$ [Å]
C_2	C_3	700	1.430
C_3	H_	700	1.090
C_3	H__A	700	1.090
C_3	C_3	700	1.530
C_R	H_	700	1.020
C_R	H__A	700	1.020
C_R	C_3	700	1.460
C_R	C_R	1050	1.390
N_3	H__A	700	1.022
N_3	C_3	700	1.462
N_R	H_	700	0.970
N_R	H__A	700	0.970
N_R	C_3	700	1.410
N_R	C_R	1050	1.340
O_2	H_	700	0.880
O_2	H__A	700	0.880
O_2	C_2	1400	1.220
O_2	C_3	700	1.320
O_2	C_R	1400	1.250
O_3	C_3	700	1.420
O_R	H_	700	0.980
O_R	H__A	700	0.980
O_R	C_3	700	1.420
O_R	C_R	1050	1.350
O_R	N_R	1050	1.300
F_	C_3	700	1.371
P_3	O_3	700	1.540
P_3	O_2	700	1.440
S_3	C_R	700	1.730
S_3	N_R	700	1.680
S_3	O_2	700	1.590
Cl	C_3	700	1.757
Cl	C_R	700	1.687

S1.3 Angle bending parameters

The DREIDING force field uses the following functional form for angle bending:

$$E_{angle} = \frac{1}{2} k_{angle,ABC} (\theta_{ABC} - \theta_{0,ABC})^2$$

Here, $k_{angle,ABC}$ is the force constant, θ_{ABC} is the bond angle defined by the three atoms A, B, and C (B = central atom), and $\theta_{0,ABC}$ is the equilibrium angle. In the DREIDING force field, one equilibrium angle is defined for each type of central atom B, regardless of the bonding partners A and C. Table S3 gives the parameters $k_{angle,ABC}$ and $\theta_{0,ABC}$ for all relevant atom types.

Table S3: DREIDING angle bending parameters. Note that the same force constant is used for all angle bending terms.

Atom B	$\boldsymbol{k_{angle,AB}}$ [(kcal/mol)/rad^2]	$\boldsymbol{\theta_{0,AB}}$ [deg]
C_2	100	120
C_3	100	109.471
C_R	100	120
N_3	100	106.7
N_R	100	120
O_3	100	104.51
O_2	100	120
O_R	100	120
P_3	100	93.3
S_3	100	92.1
C_2	100	120
C_3	100	109.471
C_R	100	120

S1.4 Torsions

The DREIDING force field uses the following functional form for torsions:

$$E_{torsion} = \frac{1}{2} V_{torsion,ABC-BCD}[1 - \cos(n_{ABC-BCD}(\varphi_{ABC-BCD} - \varphi_{0,ABC-BCD}))]$$

Here, $\varphi_{ABC\text{-}BCD}$ is the dihedral angle between the planes defined by atoms groups (A, B, C) and (B, C, D), $\varphi_{0,ABC\text{-}BCD}$ is the equilibrium dihedral angle, $n_{ABC\text{-}BCD}$ is the periodicity, and $V_{torsion,ABC\text{-}BCD}$ is the energy barrier to rotation. Table S4 lists these parameters for relevant combinations of atom types.

Table S4: DREIDING torsion parameters. Atom types of atoms B and C are always specified. Atom A is sometimes specified, if not, the label X represents any other atom type. Atom D is never specified (in other words, for a combination of atoms A, B, C, the torsion parameters are independent of D).

Atom A	**Atom B**	**Atom C**	**Atom D**	$V_{torsion,ABC\text{-}BCD}$ [(kcal/mol)]	$n_{ABC\text{-}BCD}$	$\varphi_{0,ABC\ BCD}$ [deg]
X	C_2	C_3	X	2	3	180
O_2	C_2	C_3	X	1	6	0
X	C_3	C_3	X	2	3	180
X	C_R	C_3	X	2	3	180
C_R	C_R	C_3	X	1	6	0
N_R	C_R	C_3	X	1	6	0
O_R	C_R	C_3	X	1	6	0
X	C_R	C_R	X	25	2	0
X	N_3	C_3	X	2	3	180
X	N_R	C_3	X	2	3	180
C_R	N_R	C_3	X	1	6	0
N_R	N_R	C_3	X	1	6	0
O_R	N_R	C_3	X	1	6	0
X	N_R	C_R	X	25	2	0
X	O_3	C_3	X	2	3	180
X	O_2	C_3	X	2	3	180
C_R	O_2	C_3	X	1	6	0
X	O_2	C_2	X	45	2	0
X	O_2	C_R	X	25	2	0
X	O_R	C_3	X	2	3	180
C_R	O_R	C_3	X	1	6	0
X	O_R	C_R	X	25	2	0
X	O_R	N_R	X	25	2	0
X	P_3	O_3	X	2	3	180
X	S_3	C_R	X	2	2	180
X	S_3	N_R	X	2	2	180
X	S_3	O_2	X	2	2	180

S1.5 Inversions

DREIDING uses an additional inversion term for atoms that can form three bonds. Assuming B to be bonded to atoms A, C, and D, the angle ψ is defined as the angle between the bond A-B and the plane B-C-D. This angle corresponds to 0 deg for a planar configuration and assumes non-zero values when displacing B from the plane. DREIDING uses the following functional form for planar environments:

$$E_{inv} = \frac{1}{2} K_{inv}(1 - \cos\psi)$$

An inversion term is considered for the following atom types used in the present work: C_2, C_R, N_R, O_2, O_R. For all these atom types, K_{inv} = 40 kcal/mol.

S1.6 Hydrogen bonds

The DREIDING force field employs a Lennard-Jones 12-10 potential for hydrogen bonds:

$$E_{hb} = D_{0,hb}\left[5\left(\frac{R_{0,hb}}{R_{DA}}\right)^{12} - 6\left(\frac{R_{0,hb}}{R_{DA}}\right)^{10}\right]\cos^4\phi_{DA}$$

Here, R_{DA} is the distance between the H-bond donor and acceptor, and ϕ_{DA} is the angle between H-bond donor, the hydrogen atom, and H-bond acceptor. $R_{0,hb}$ and $D_{0,hb}$ are the equilibrium donor-acceptor distance and the energy parameter, respectively.

Hydrogen bonds are considered only for hydrogen atoms having the atom type H___A. The universal parameters used are: $R_{0,hb}$ =2.75 Å and $D_{0,hb}$ = 4.0 kcal/mol.

S1.7 van der Waals interactions

A Lennard-Jones 12-6 potential is used for van der Waals (vdW) interactions:

$$E_{vdW} = D_{0,AB}\left[\left(\frac{R_{0,AB}}{R_{AB}}\right)^{12} - 2\left(\frac{R_{0,AB}}{R_{AB}}\right)^{6}\right]$$

$R_{0,AB}$ and $D_{0,AB}$ are the equilibrium non-bonded A-B distance and the energy parameter, respectively, and R_{AB} is the distance between atoms A and B. vdW interactions are computed for all combinations of atoms except nearest (1-2) and next-nearest (1-3) neighbours.

For combinations of A and B having different atoms types, the parameters $R_{0,AB}$ and $D_{0,AB}$ are calculated from atomic parameters using the following (Lorentz-Berthelot) combination rules:

$$D_{0,AB} = \sqrt{D_{0,AA} \cdot D_{0,BB}}$$

$$R_{0,AB} = \frac{1}{2}(R_{0,AA} + R_{0,BB})$$

The vdW parameters of relevant atom types are tabulated in Table S5.

Table S5: DREIDING parameters for van der Waals interactions.

	R_0 [Å]	D_0 [kcal/mol]
Pollutants		
H_	3.195	0.0152
H___A	3.195	0.0001
C_2, C_3, C_R	3.8983	0.0951
N_3, N_R	3.6621	0.0774
O_2, O_3, O_R	3.4046	0.0957
F_	3.472	0.0725
P_3	4.15	0.3200
S_3	4.03	0.3440
Cl	3.9503	0.2833
Zeolites		
O_3	3.4046	0.0957
Si3	4.27	0.3100

S2 Dependence of E_{zg} on vdW interaction cutoff

Table S6: E_{zg} values (in kJ/mol) obtained for lowest-energy configurations using different cutoffs for vdW interactions. The columns Δ(10-15) and Δ(12.5-15) give the difference between results obtained with smaller cutoffs and the highest cutoff of 15 Å.

	Cutoff = 10 Å	**Δ(10-15)**	**Cutoff = 12.5 Å**	**Δ (12.5-15)**	**Cutoff = 15 Å**
MOR					
Acetaminophen	-150.5	1.4	-151.6	0.3	-151.9
Caffeine	-157.7	1.7	-159.1	0.3	-159.4
Fluoxetine	-249.2	2.7	-251.4	0.5	-251.9
Ibuprofen	-226.2	2.1	-227.9	0.4	-228.3
Triclosan	-228.7	2.3	-230.5	0.5	-230.9
FAU					
Acetaminophen	-112.3	1.5	-113.5	0.3	-113.8
Caffeine	-125.6	2.1	-127.4	0.3	-127.7
Fluoxetine	-212.5	3.3	-215.2	0.5	-215.7
Ibuprofen	-154.3	2.4	-156.2	0.5	-156.7
Triclosan	-165.8	2.7	-168.0	0.5	-168.5

S3 Results of DREIDING+QEq and PBE-D3 calculations

Table S7: E_{zg} values (in kJ/mol) obtained with the DREIDING force field E_{zg}(DR), the DREIDING force field in conjunction with QEq charges E_{zg}(DR+Q), and from DFT calculations using the PBE-D3 functional E_{zg}(DFT). The columns DR+Q/DR and DFT/DR report the ratios of the E_{zg} values, using the DREIDING values as reference. Individual results discussed in the main text are highlighted in bold. Experimental removal efficiencies from A. Rossner, S. A. Snyder, D. R. U. Knappe, *Water Res.* **2009**, *43*, 3787–3796 are given for comparison.

	η [%]	E_{zg}(DR)	E_{zg}(DR+Q)	DR+Q/DR	E_{zg}(DFT)	DFT/DR
ACA@MOR	-6	-151.6	-158.5	1.05	**-145.5**	**0.96**
ACA@FAU	-12	-113.5	**-135.3**	**1.19**	-98.9	0.87
CAF@MOR	12	-159.1	-150.8	0.95	-142.1	0.89
CAF@FAU	5	-127.4	**-144.3**	**1.13**	-112.6	0.88
FLX@MOR	100	-251.4	**-224.6**	**0.89**	-222.0	0.88
FLX@FAU	98	-215.2	-212.5	0.99	**-180.3**	**0.84**
IBU@MOR	98	-227.9	-227.8	1.00	-205.1	0.90
IBU@FAU	6	-156.2	-166.5	1.07	-136.0	0.87
SMX@MOR	13	-224.6	-230.9	1.03	**-181.7**	**0.81**
SMX@FAU	0	-172.4	-175.8	1.02	**-140.9**	**0.82**
TCEP@MOR	21	-207.9	**-157.7**	**0.76**	-179.9	0.87
TCEP@FAU	7	-167.7	-172.9	1.03	-151.6	0.90
TCL@MOR	99	-230.5	-240.4	1.04	-205.3	0.89
TCL@FAU	45	-168.0	**-192.9**	**1.15**	-146.3	0.87

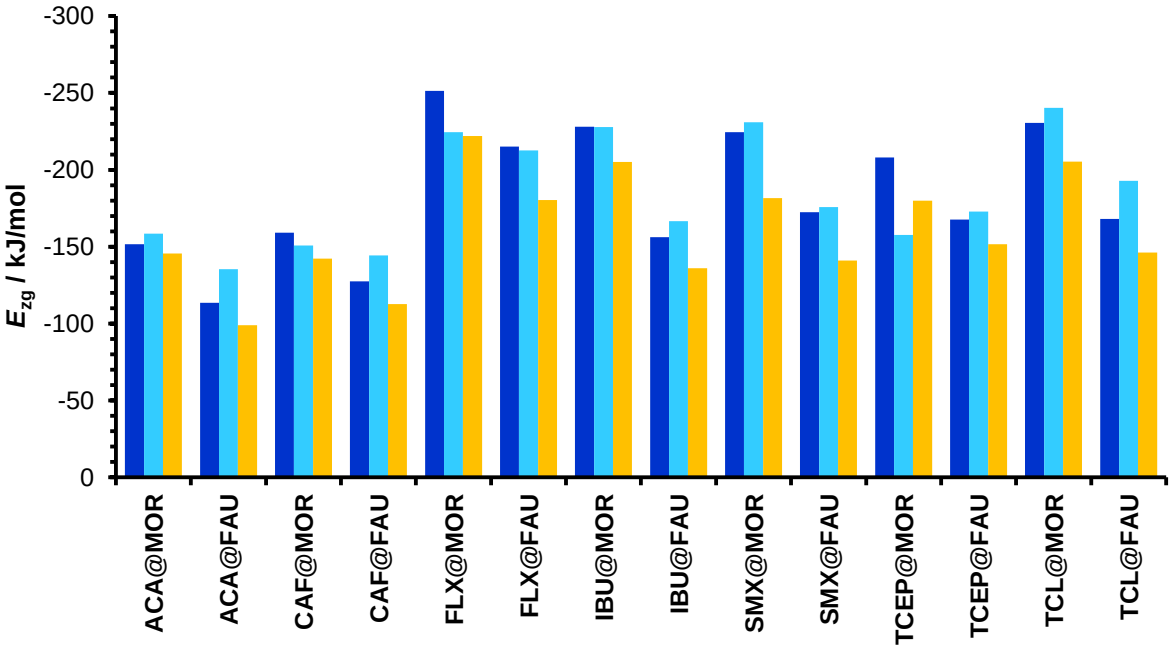

Fig. S1: Comparison of E_{zg} values obtained with different approaches: DREIDING = dark blue, DREIDING+QEq = light blue, DFT = yellow.

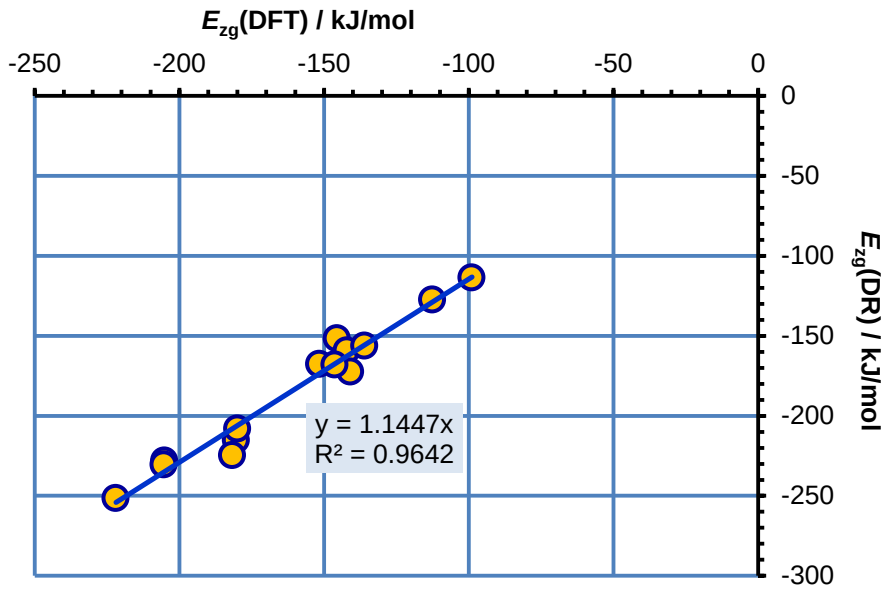

Fig. S2: Plot of E_{zg}(DR) as a function of E_{zg}(DFT). Parameters of a linear regression with intercept zero (blue line) are shown in the box.