1   **Supporting Information for:**

2   **The adsorption mechanisms of organic micropollutants on high-silica zeolites**

3   **causing S-shaped adsorption isotherms: An experimental and Monte Carlo**

4   **simulation study**

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16   S1 Simulation details

17   In force field based Monte Carlo simulations the total interaction energy, E_{tot}, between atoms

18   and molecules is computed from:

$$E_{tot} = E_{nonbonded} + E_{bonded} \tag{S1}$$

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21   S1.1 Nonbonded interactions

22   To calculate the nonbonded interactions between two atoms, the short-range van der Waals

23   interactions are taken into account by the (12-6) Lennard-Jones potential (E_{LJ}). The

24   electrostatic interactions are calculated using the Coulomb's law ($E_{electrostatic}$).

$$E_{nonbonded} = E_{LJ}(r_{ij}) + E_{electrostatic}(r_{ij}) = 4\varepsilon_{ij}\left(\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}}\right)^{6}\right) + \frac{q_i q_j}{4\pi\epsilon_0 r_{ij}} \tag{S2}$$

26   where ε_{ij} and σ_{ij} are the LJ parameters, and r_{ij} is the distance between atomos i and j, q_i.is

27   the atomic charge of atom i, ϵ_0 is the permittivity of vacuum. The LJ parameters for the

28   interaction between different types of particles is calculated according to the Lorentz-

29   Berthelot mixing rules:

$$\varepsilon_{ij} = \sqrt{\varepsilon_{ii}\varepsilon_{jj}} \tag{S3}$$

$$\sigma_{ij} = \frac{\sigma_{ii} + \sigma_{jj}}{2} \tag{S4}$$

32   The LJ parameters and atomic charges used in this study are listed in Table S1.

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34   S1.2 Bonded interactions

35   Two types of bonded interactions, the bond-angle bending and dihedral angle torsion, are

36   taken into account:

$$E_{bonded} = E_{angle} + E_{dihedral} \tag{S5}$$

38   where,

$$E_{angle} = \Sigma_{angles} \, k_\theta (\theta - \theta_0)^2 \tag{S6}$$

40   and

$$E_{dihedral} = \Sigma_{dihedrals} \, a_0 (1 + \cos(a_1 \phi - \delta)) \tag{S7}$$

42   where, K_θ is the force constant for bond-angle bending, θ is the bond angle, θ_0 is the

43   equilibrium bond angle, ϕ is the dihedral angle, and a_0, a_1, δ are coefficients of the dihedral

44   angle potential. The bond lengths are fixed in all simulations. The parameters used to

45   calculate the bonded interactions in this study are listed in Table S2 and Table S3.

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47   **S2 Chemical potential conversion to concentration**

48   S2.1 Obtaining chemical potential from the shifted chemical potential

49   In the Cassandra software package the chemical potential is defined as:

$$\mu' = \mu + k_B T \ln \left(Q_{rot+int} \frac{Z_{frag}\Omega_{dih}}{Z_{int}} \right) \tag{S8}$$

51   where μ' is the shifted chemical potential, μ is the chemical potential, $Q_{rot+int}$ is the

52   rotational and internal degrees of freedom partition function, Z_{int} is the internal degrees of

53   freedom configurational partition function, Ω_{dih} is equal to $(2\pi)^{N_{frag}-1}$, Z_{frag} is the

configurational partition function of the fragments of the molecule. To obtain the chemical potential based on Equation S8, the following steps were followed in this work:

1. Monte Carlo (MC) simulations are carried out in the grand canonical (GC) ensemble for a range of shifted chemical potentials at temperature T inserting TCP as an ideal gas.

2. Based on the results obtained in the GCMC simulations (the number of inserted molecules, and the pressure) the chemical potential of an ideal gas is calculated.

3. The shift in the chemical potential is calculated as the difference between the imposed shifted chemical potential and corresponding ideal gas chemical potential.

S2.2 Converting chemical potential

The conversion of the chemical potential to equilibrium concentration is based on the work of Xiong et al. (2011) To obtain the equilibrium concentration, the following steps were carried out:

1. The excess chemical potential of TCP in water is calculated by using the Continuous Fractional Component Monte Carlo (CFCMC) method (μ_A^{∞} in the work of Xiong et. al.).

2. The chemical potential is calculated using the shift value (see Section S2.1) from the shifted chemical potential. The obtained chemical potential is converted into fugacity using the following equation:

$$\mu = \mu_{\text{ideal}} + \frac{\ln{(k_B T f_A)}}{k_B T}$$

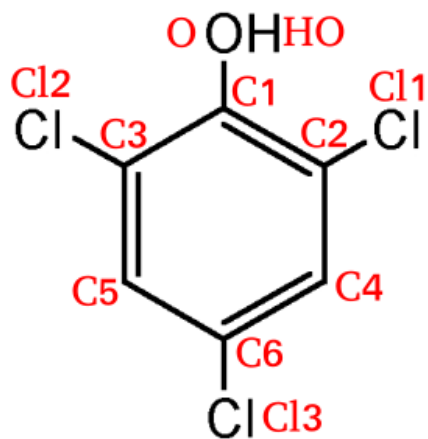where μ_{ideal} is the ideal gas chemical potential of TCP, f_A is the fugacity of TCP.

3. Based on the calculated fugacity, the mole fraction of TCP is calculated using the following equation:

75 $$f_A = \rho\, k_B T \exp\left(\frac{\mu_A^\infty}{k_B T}\right) x_A$$

76   where ρ is the number density of TCP in the bulk phase, k_B is the Boltzmann constant, T is

77   the temperature, x_A is the mol fraction of TCP in the bulk phase.

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80   **Figure S1.** Representation of the TCP molecule with atom names shown in red color.

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82   **Table S1** Lennard--Jones parameters and atomic charges used in the simulations. Atom names

83   are shown in Figure S1 for TCP.

Molecule	Atom name	Atom type	ε_{ii}/k_B / [K]	σ_{ii} / [Å]	q_i / [e]
2,4,6-trichlorophenol	C1	CA	43.277	3.400	0.543841
	C2	CA	43.277	3.400	-0.246516
	C3	CA	43.277	3.400	-0.246516
	C4	CA	43.277	3.400	0.073606
	C5	CA	43.277	3.400	0.073606
	C6	CA	43.277	3.400	-0.143285
	O	O	105.877	3.066	-0.524338
	Cl1	CL	85.547	3.475	-0.051323
	Cl2	CL	85.547	3.475	-0.051323
	Cl3	CL	85.547	3.475	-0.083382
	H1	HA	7.550	2.600	0.141479
	H2	HA	7.550	2.600	0.141479
	H3	HO	0.000	0.000	0.372672
Water	O	OW	78.208	3.166	-0.8476
	H	HOW	0.000	0.000	0.4238
Zeolite	Si	SI	0.0	3.302	2.1
	Al	AL	0.0	3.302	1.575
	O_{Si}	OSI	78.2	3.166	-1.05
	O_{Al}	OAL	78.2	3.166	-1.16875
	Na	NA	65.5	2.35	1

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85   **Table S2.** Bond angle bending parameters for all angle types used in this study. The atomtypes

86   are shown for each in Table S1.

Molecule	Bond	k_θ / [K rad^{-2}]	θ_0 / [degrees]
	CA-CA-CA	33806.3	120.00
	CA-O-CA	35149.9	120.00
2,4,6-trichlorophenol	CA-CA-CL	31662.6	120.00
	CA-CA-HA	24386.0	120.00
	CA-O-HO	24582.3	109.47
Water	HW-OW-HW	fixed	109.47

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88   **Table S3.** Dihedral angle torsion parameters for all dihedral type used in this study. The

89   atomtypes are shown for each in Table S1.

Molecule	Dihedral angle	a_0 / [kJ mol^{-1}]	a_1 / [-]	δ / [degrees]
	CA-CA-CA-CA	15.166	2	180
	CA-CA-O-HO	3.765	2	180
2,4,6-trichlorophenol	CA-CA-CA-CL	4.6	2	180
	CA-CA-O-CA	4.6	2	180
	CA-CA-CA-HA	4.6	2	180

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References

Xiong, R., Sandler, S.I. and Vlachos, D.G., 2011. Alcohol adsorption onto silicalite from aqueous solution. The Journal of Physical Chemistry C 115, 18659-18669.