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Supporting Information

Superior Single- and Multi-component Siloxane Removal from Water using a Faulted Silica DON Zeolite Adsorbent

Dariana R. Vega-Santander, Rodinson Arrieta-Perez, Daniela Rivera-Mirabal, Gabriela Del Valle-Pérez , Miguel Sepúlveda-Pagán, Juan C. Muñoz-Senmache, Yomaira J. Pagán-Torres, and Arturo J. Hernández-Maldonado*

Department of Chemical Engineering, University of Puerto Rico, Mayagüez Campus, Mayagüez, PR 00681, USA

* To whom correspondence should be addressed. Email: arturoj.hernandez@upr.edu

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Experimental Section

Reagents and Materials. The following reagents were used for the synthesis of both UTD-1 with faults (UTD-$1_{faulted}$) and faultless (UTD-$1_{faultless}$): hydrochloric acid (HCl, 37 %), sodium hydroxide (NaOH, ≥98 %) and Ludox HS-40 colloidal silica (40 wt. % suspension in H_2O) and hydrofluoric acid (HF, 48%). The structure directing agent (SDA) required for the assembly of the UTD-1 DON framework (i.e., bis (pentamethyl- cyclopentadienyl) cobalt (III) hydroxide ($[(Cp^*)_2Co]OH$) was prepared using the following reagents: bis-(cyclopentadienyl) cobalt (III) hexafluorophosphate ($[(Cp^*)_2Co]PF_6$, 98%), acetone, and Dowex® Marathon™ hydroxide. All reagents, except the ($[(Cp^*)_2Co]PF_6$, 98%), were obtained from Sigma-Aldrich, USA, and used without further purification. The ($[(Cp^*)_2Co]PF_6$, 98%) was purchased from Strem Chemicals, USA. Ultra-pure dry air and nitrogen obtained from Praxair Inc. USA were used for sample calcination and analyses.

Siloxanes employed during the adsorption tests were monomethylsilanetriol (MMST), dimethylsilanediol (DMSD), and trimethylsilanol (TMS) (see Table 1 for relevant properties). MMST was purchased from Alfa Chemistry, and TMS was obtained from Sigma-Aldrich, USA; both were used as received. DMSD was prepared in-house using dimethoxydimethylsilane (TCI – Chemicals, USA) as the source and following procedures reported elsewhere.[1] The distilled/deionized water (18.2MΩcm) required for the adsorption tests was produced in-house.

Synthesis of UTD-1. A previously reported method[2] for synthesizing the SDA was modified to effectively produce $[(Cp^*)_2Co]OH$ and eventually assemble a DON framework. Briefly, the SDA was synthesized by dissolving 1.5g of $[(Cp^*)_2Co]PF_6$ in 250 mL of acetone and adding 500 mL of distilled/deionized water. The solution was slowly passed through 15 mL of a fixed-packed bed column containing wetted Dowex® Marathon™ hydroxide form. The resulting solution was evaporated until approximately 15 mL, and the concentration of the SDA was determined to be 10.86 wt. %, by mass balance. All further synthesis steps were performed following the methods reported by Freyhardt et al.[3] For a typical synthesis of UTD-$1_{faulted}$, 10 mL of the SDA, 99.4 mg of NaOH, 2.8 mL of 40 wt. % SiO_2 and 15.4 mL of pure water were carefully mixed while slowly stirring at room temperature for 1 hour. The mixture was transferred to a Teflon-lined pressure reactor and placed in a convection oven at 175 ˚C for 48 hours. The resulting yellow solid product was cooled to room temperature, washed with 1 L of distilled/deionized water using vacuum filtration, and dried at 90 ˚C for 2 hours.

For the synthesis of UTD-$1_{faultless}$, the SDA was prepared as described above. All subsequence UTD-$1_{faultless}$ synthesis steps were performed as reported by Wessels et al.[4] That is, 12 mL of 10.86 wt.% SDA and 1.2 mL of 40 wt. % SiO_2 were carefully mixed while slowly stirring at room temperature for 1.5 hours. Subsequently, 1.5 µL of HF was added, and the mixture was vigorously stirred for 20 minutes. The resulting mixture was transferred to a Teflon-lined pressure reactor and placed in a convection oven at 175 ˚C for 25 days. The resulting solid product was cooled to room temperature, washed with at least 1 L of deionized water using vacuum filtration, and dried at 90 ˚C for 2 hours.

The SDA was removed from both materials (i.e., detemplation) with a combination of thermal and acid treatments. The former was performed using flowing air (100 mL min^{-1}) in a tubular furnace, following a ramp and soak program: from 25 to 540 ˚C for a period of 1 hour and held at 540 ˚C for 1 hour, then heat from 540 ˚C to 600 ˚C for a period of 1 hour and held at 600 ˚C for 5 hours; finally, the product was cooled to 25 ˚C for 2 hours. The resulting solid product was then suspended and stirred in a 12 N hydrochloric acid solution (300 mL of solution for 1 g of material) for 2 hours (i.e., acid treatment). Afterward, the gray-colored solid was recovered via vacuum-assisted filtration and suspended overnight in a 7 N solution of hydrochloric acid (300 mL of solution for 1 g. of material) under vigorous stirring to remove traces of cobalt oxide remaining after the calcination of the organic fraction of the SDA. The final product was vacuum filtered, washed with 2 L of water, and dried in a forced convection oven at 90 ˚C overnight.

UTD-1 Characterization. The corresponding crystalline phases of the UTD-1 materials were identified via powder XRD. The data were collected using a Rigaku UTIMA III X-ray diffractometer fitted with a Cu kα anode (λ = 1.5418 Å). The anode was operated at 40 kV and 44 mA, and the patterns were gathered at a scanning speed of 0.5˚ min^{-1} in the 2θ range from 5 up to 45˚.

TGA tests were performed using a high-resolution TA Instruments D550 unit while operating with a constant gas flow of either nitrogen or air at 60 mL min^{-1}. Each UTD-1 sample material was heated from room temperature to 900 ˚C at a rate of 5 ˚C min^{-1}. TGA results allowed the determination of the stability of the UTD-1 samples, the amount of water adsorbed or coordinated to each material, and surface moiety decomposition pathways. TGA data were also used to elucidate regeneration options for spent adsorbents based on thermal purging and reactivation.

Textural properties were elucidated using nitrogen equilibrium adsorption-desorption isotherms gathered at -196 ˚C (77 K). The data were collected using a Micromeritics ASAP 2020 volumetric adsorption instrument fitted with turbomolecular drag pumps. Before each nitrogen adsorption measurement, the detemplated UTD-1 samples (i.e., no SDA) were degassed in a vacuum at 120 ˚C for 12 hours. This temperature was determined based on TGA tests, as indicated above. The BET (Brunauer, Emmett, and Teller) isotherm model was used to estimate surface area.[5] The corrected Horvath – Kawazoe approach[6] was used to determine the micropore volume and pore size distribution.

The hydrophobicity of the adsorbent materials was correlated through droplet water contact angle measurements using a Kruss DSA-25B contact angle meter equipped with a high-resolution/high-speed camera. Meanwhile, Zeta potential measurements were used to determine the behavior of the UTD-1 adsorbent's surface charge as a function of pH. A Brookhaven ZetaPals equipment was used. In a typical test, the materials were suspended in water (0.50 wt. %), and the data were collected in a 3-10 pH range; the ionic strength was maintained during tests using a 1 mM KCl solution.

FTIR spectroscopy was conducted to assess the interaction mechanism between the adsorbents and a target adsorbate (i.e., TMS@UTD-1$_{faulted}$ and TMS@UTD-1$_{faultless}$). The spectra were obtained using a Thermo Scientific Nicolet iS50 FTIR spectrometer equipped with an MCT detector. The sample preparation was conducted following the KBr pellet technique, mixing each material with KBr powder in a ratio of 1:10 (wt/wt). Samples were placed in a chamber equipped with ZnSe windows (Harrick Scientific), followed by pretreatment in a nitrogen flow at 20 cm^3 min^{-1} for 1 hour to remove moisture. Spectra were collected using 120 scans and a resolution of 4 cm^{-1}. Background spectra were recorded before each analysis at room temperature. The data collected were in Kubelka−Munk units.

Equilibrium Single-Component Siloxane Adsorption. Single-component siloxane adsorption tests were conducted by mixing 35 mg of the adsorbent with 35 mL of solutions containing MMST, DMSD, or TMS (10 to 150 mg L^{-1}) using 50 mL borosilicates centrifuges tubes and shaken for 24 hours in room temperature and neutral pH conditions. The liquid and solid phases were separated via centrifugation (8500 rpm for 10 min), and aliquots of 25 mL were transferred to clear glass vials and sealed with an open-top polypropylene closure (PTFE/silicone lined). These tests were conducted in triplicates. The equilibrium concentration of the corresponding siloxane in the liquid phase was estimated using a Fusion Total Organic Carbon (TOC) analyzer (Teledyne Tekmar Inc.) following standard procedures. Finally, the siloxane adsorbed amounts were calculated based on a mass balance as follows:

$$q_e = \frac{V_i\left(C_i - C_e\right)}{m_{ads}} \tag{S1}$$

where q_e is the siloxane adsorbed amount (mg g^{-1}), C_i is the initial siloxane concentration in solution (mg L^{-1}), and C_e is the concentration of siloxane at equilibrium (mg L^{-1}), V_i is the liquid volume of the siloxane solution (L) and m_{ads} is the mass of the adsorbent (g). Given the pore dimensions and surface heterogeneity of UTD-1, the resulting siloxane adsorption isotherms were fitted using the modified Dubinin-Astakhov isotherm model (MDA). The MDA isotherm model is as follows:

$$\begin{aligned} q_{MDA} &= q_0\beta_1\left[exp\left[-\left(C\ln\left(\frac{S}{C_e}\right)\right)^n\right] + \beta_2 kC_e\right] \\ \beta_1 &= 1 - exp\left(-\alpha\frac{C_e}{S}\right) \\ \beta_2 &= exp\left(-\alpha\frac{C_e}{S}\right) \\ k &= \frac{q_1}{C_0} \\ C &= \frac{RT}{\beta E} \end{aligned} \tag{S2}$$

where q_{MDA} is the equilibrium adsorbed amount, q_0 is the siloxane maximum adsorbed amount (complete pore filling, mg g^{-1}), k is the Henry's Law constant, R is the universal gas constant,

β is the affinity coefficient of adsorbate, E is the energy of adsorption (kJ mol^{-1}), C_e is the equilibrium concentration (mg L^{-1}), S is the siloxane water solubility (mg L^{-1}), n is the heterogeneity coefficient, and α is a fitting parameter. The siloxane maximum adsorbed amount q_0 was estimated assuming full occupancy of the UTD-1 micropore volume and based on the kinetic diameters of MMST, DMSD, and TMS molecules, which are 4.30, 4.34, and 4.55 Å, respectively.

Equilibrium Multi-Component Siloxanes Adsorption. Multi-component siloxane adsorption was evaluated via single-point equilibrium adsorption of binary and ternary mixtures of the monomeric siloxanes with equivalent carbon concentrations of 1 or 10 mg per liter of solution (i.e., 1 and 10 mg C L^{-1}) of each contaminant. The tests were performed at room temperature and neutral pH conditions. The solution's final total concentration of siloxanes was estimated using the TOC analyzer and procedure described above. From these results, a qualitative analysis was conducted to evaluate the UTD-1 selectivity of the adsorbents toward the adsorbates. The overall percentage of removal of siloxanes was calculated based on a mass balance as follows:

$$\%\ Removal = \frac{C_0 - C_f}{C_0} x100 \tag{S3}$$

where C_0 is the initial siloxane concentration in the binary or ternary solution (mg C L^{-1}), and C_f is the final concentration of siloxane after the adsorption process (mg C L^{-1}).

Adsorbent Regeneration. In the case of the single component adsorption results, regeneration experiments were performed to determine the recyclability of UTD-1$_{faulted}$ in the uptake of siloxanes. Regeneration experiments were carried out via multicycle batch equilibration adsorption of TMS solution at the initial concentration of 125 mg L^{-1}; for multicomponent adsorption, the ternary mixtures of the monomeric siloxanes had initial concentrations of 10 mg per liter of solution for each siloxane. For each cycle, 35 mg of UTD-1 and 35 mL of TMS solution were mixed in a centrifuge tube and shaken at room temperature for 24 hours. After the specified time, the spent adsorbent was recovered via centrifugation and thermally treated at 800°C under flowing air (100 mL min^{-1}) for 3 hours to remove TMS molecules from the surface. Thermal treatments can eliminate silanol groups on the UTD-1 surface by inducing their condensation at elevated temperatures,[7] subsequently, the regeneration of silanol groups or the rehydroxylation of the UTD-1 surface becomes necessary. It is achieved by placing the material in water and refluxing it at 100°C. Then, the adsorbent was recovered via centrifugation and dried at 160°C under flowing air for 3 hours to eliminate excess water. The re-hydroxylated UTD-1 was then used for the next adsorption cycle.

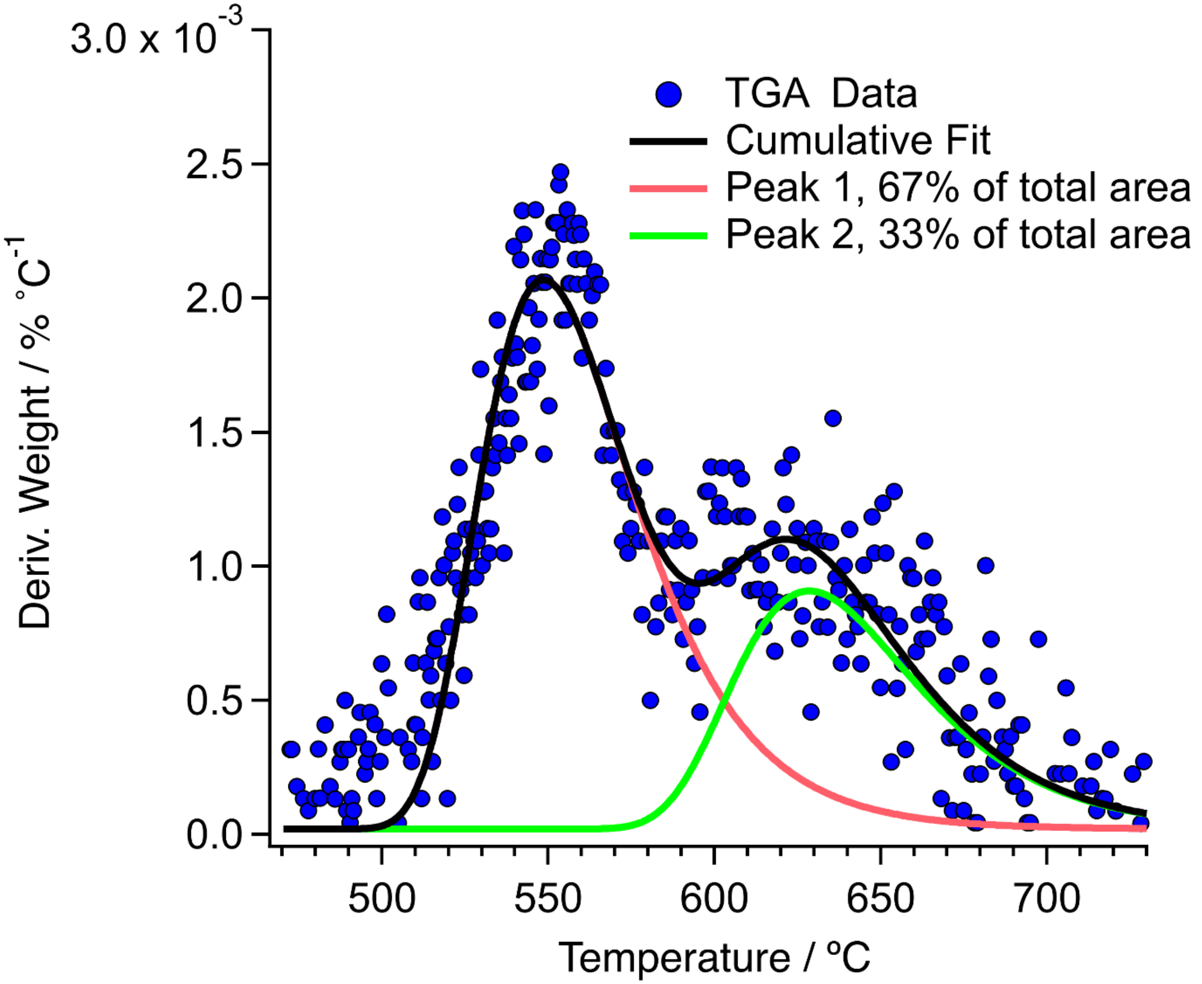

Figure S1. Deconvolution profiles for the derivative of weight with respect to temperature of thermal gravimetric analysis (TGA) data for detemplated UTD-1*faulted*. Full TGA profile is shown in Figure 2. Data gathered under air atmosphere. Deconvolution statistics: reduced $\chi^2 = 7.3906\ x\ 10^{-8}$ and coefficient of determination (or R^2) COD = 0.8675.

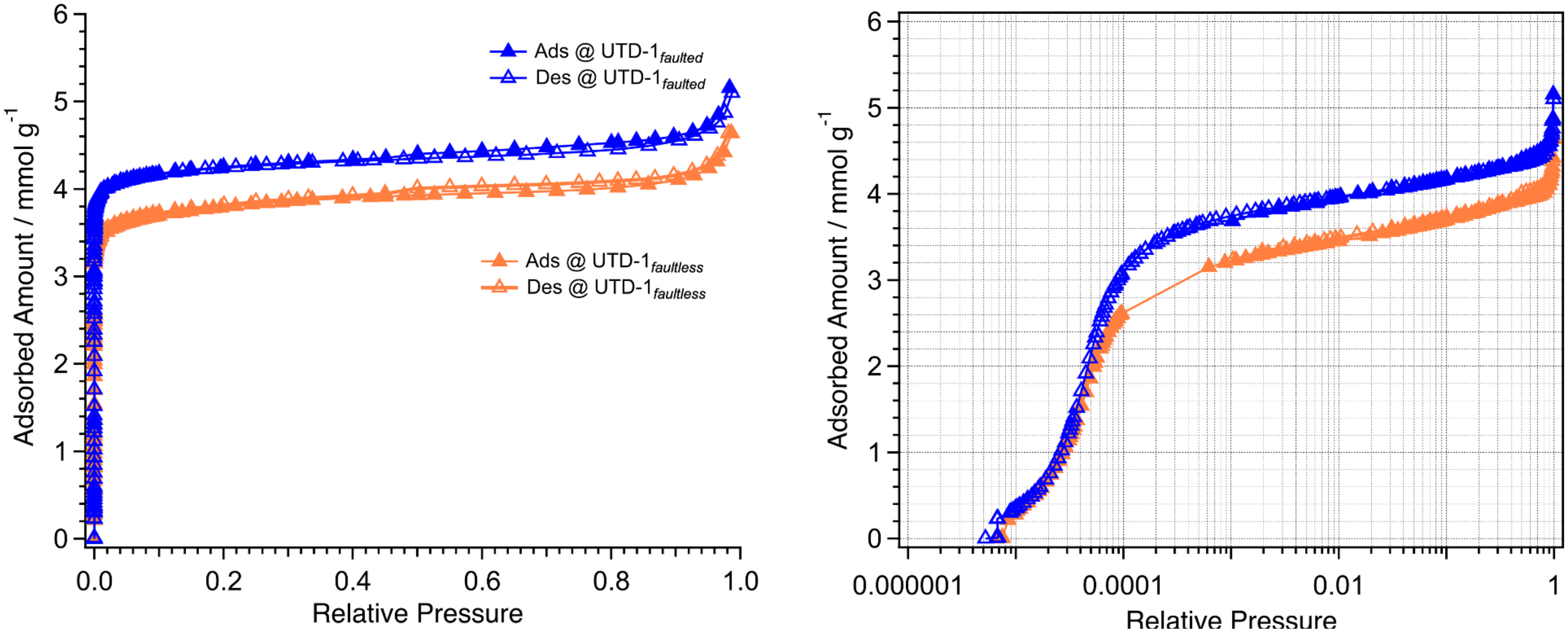

Figure S2. Nitrogen equilibrium adsorption–desorption isotherms for UTD-1 variants at -196˚C.

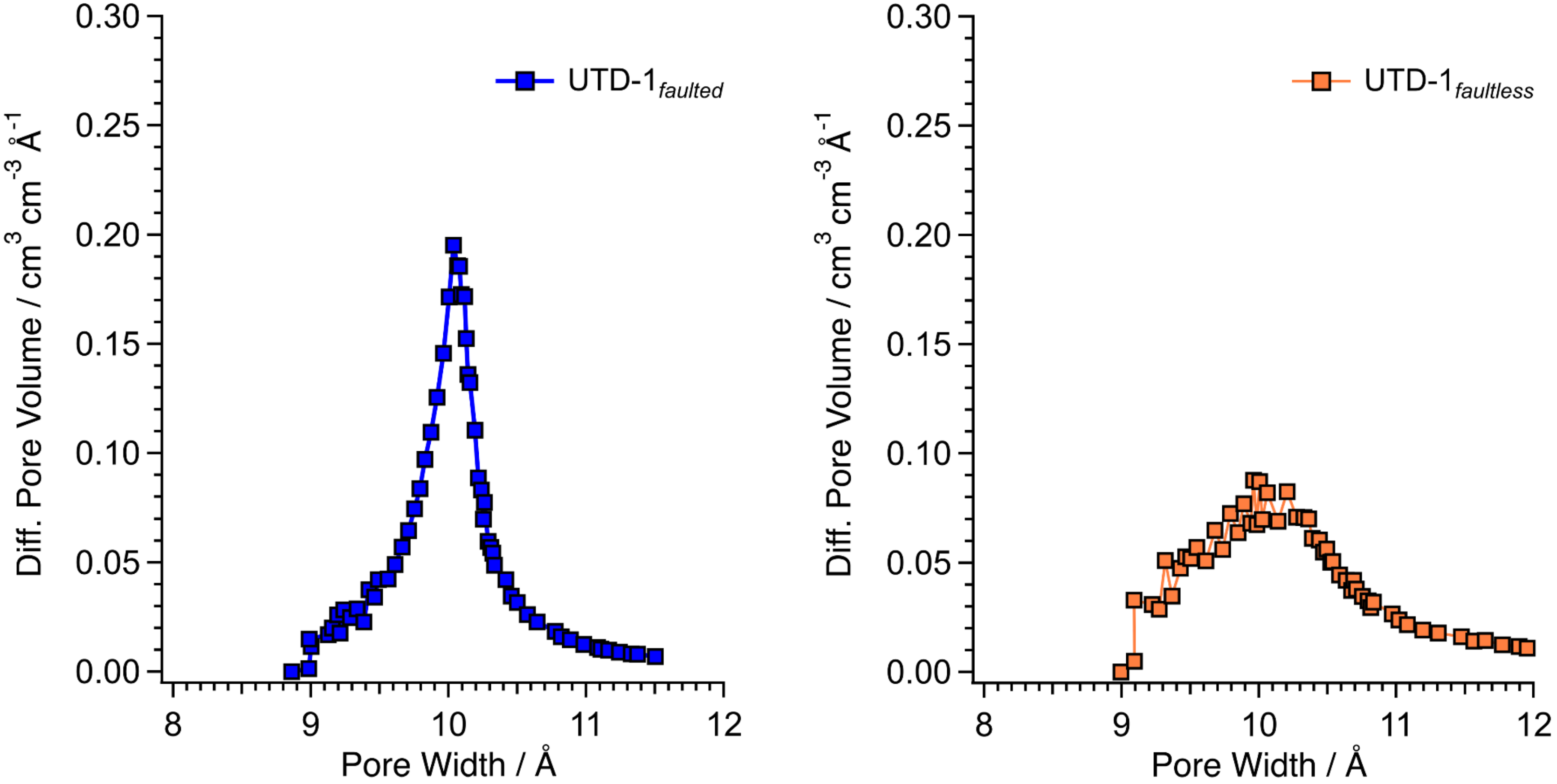

Figure S3. Pore size distribution (PSD) profiles for UTD-1 variants. PSD profiles were obtained from nitrogen adsorption data (Figure S1) and using the corrected Horvath−Kawasoe method.

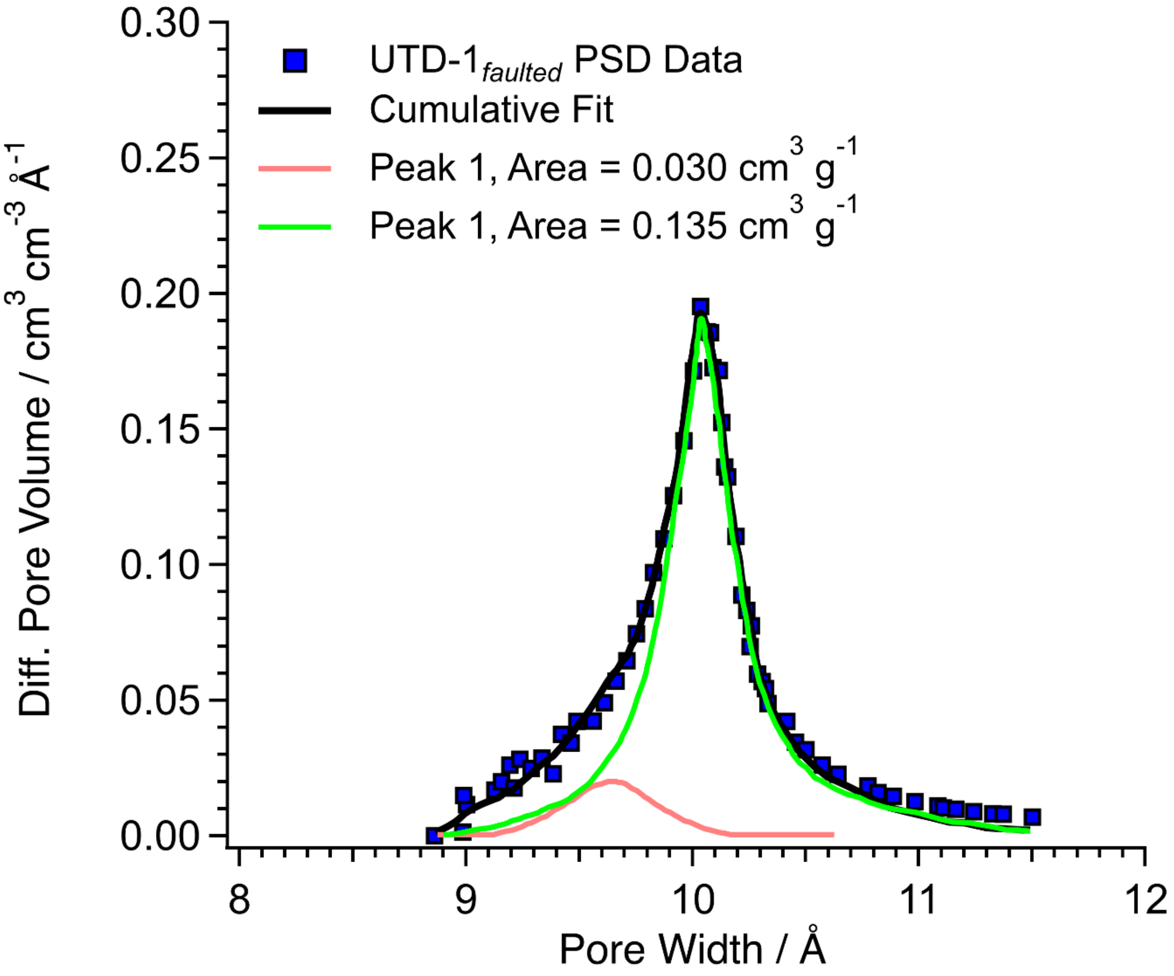

Figure S4. Deconvolution profiles for the pore size distribution of UTD-$1_{faulted}$.

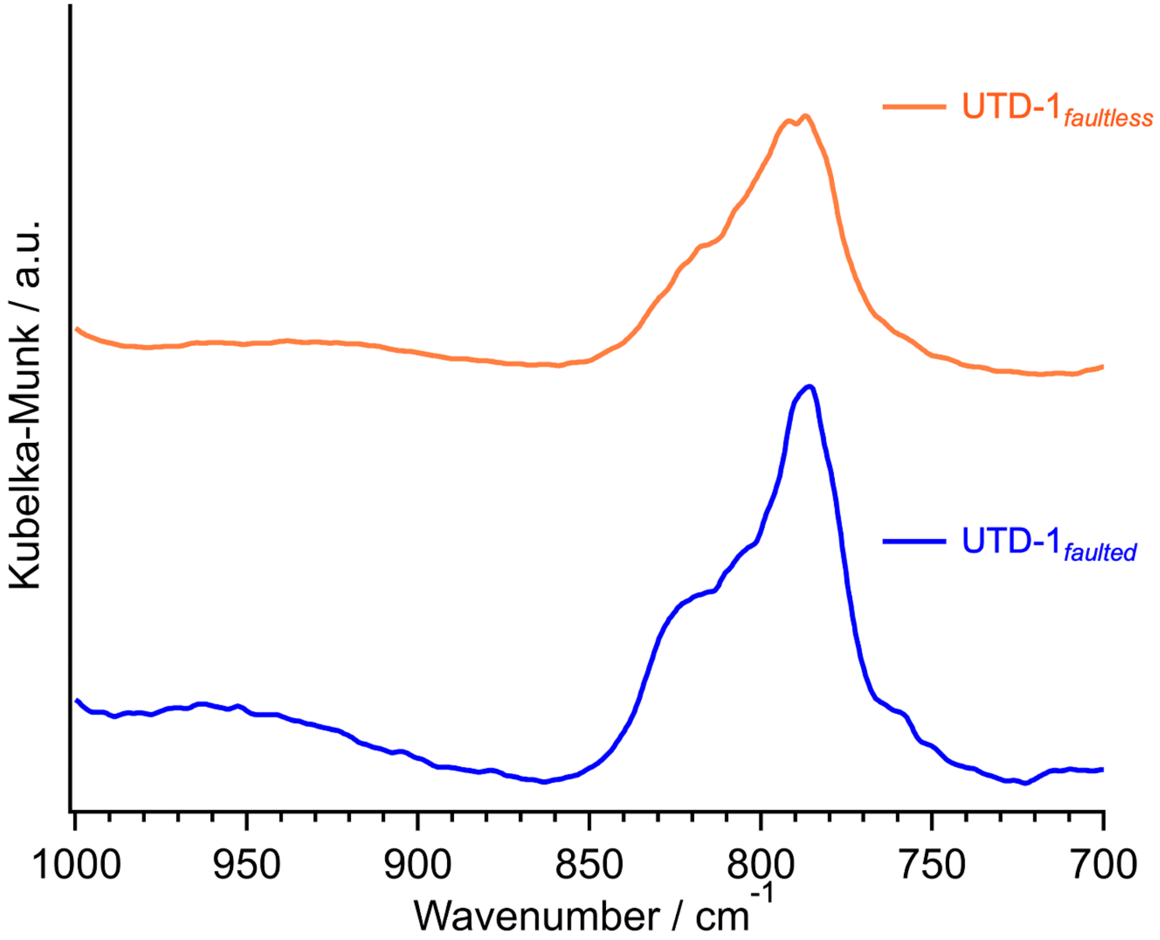

Figure S5. FTIR spectra for fresh UTD-1 variants.

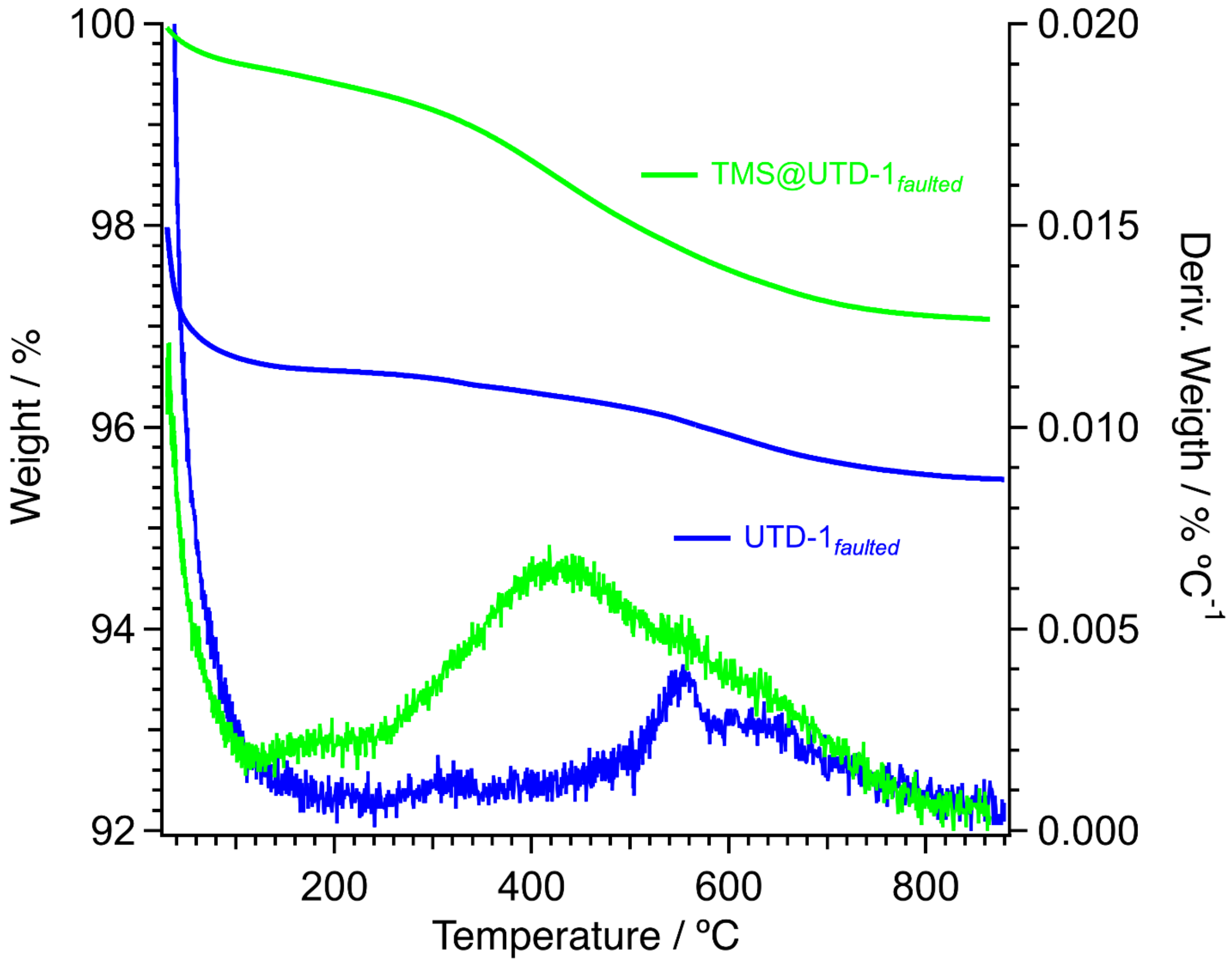

Figure S6. Thermal gravimetric profiles for fresh and spent UTD-1$_{faulted}$. Data gathered under air atmosphere.

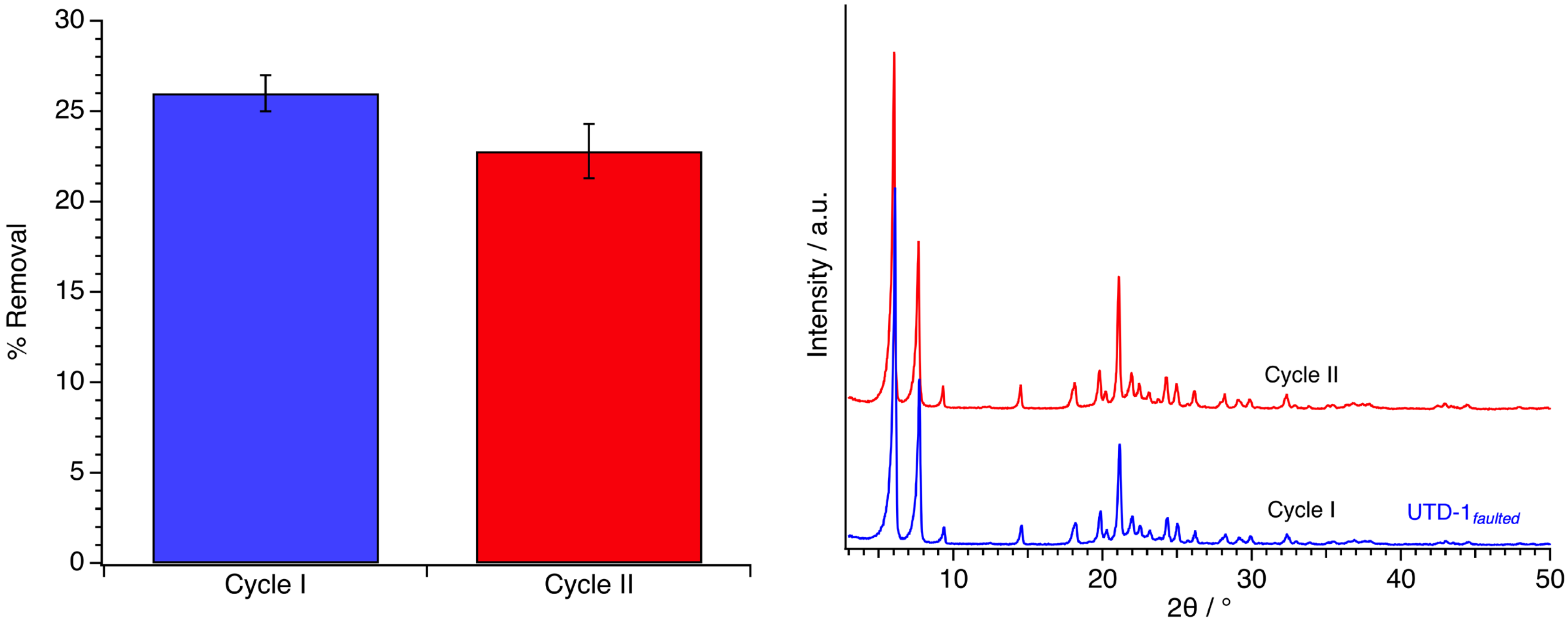

Figure S7. (*left*) Ternary mixture equilibrium uptake (in % removal) for different siloxanes (TMS-DMSD-MMST) onto fresh and regenerated UTD-$1_{faulted}$. (*right*) XRD patterns of UTD-$1_{faulted}$ prior to each adsorption cycle. The initial concentration of each contaminant was 10 mg C L^{-1} (i.e., ppm C), ambient temperature, and pH ~ 7. Adsorbent regeneration was performed through thermal treatment and rehydroxylation.

Table S1. Modified Dubinin Astakhov (MDA) isotherm model parameters for MMST, DMSD, and TMS adsorption onto UTD-1variants.

Adsorbent	**Adsorbate**	***q_0*** **(mg cm^{-3})***	***C*** **(-)**	***K*** **L mg^{-1} (x10^{-4})**	***α*** **(-)**	***n*** **(-)**	**RRMS**
UTD-1$_{faulted}$	**MMST**	620	5.033	1.48	75800	2.19	1.35
	DMSD	590	0.736	5.01	21937	2.56	0.55
	TMS	500	0.455	70.10	100.4	1.74	12.11
UTD-1$_{faultless}$	**MMST**	507	6.491	0.24	131256	2.15	0.02
	DMSD	483	1.265	5.65	14757	2.11	0.90
	TMS	410	1.003	9.27	64.64	1.19	0.17

* Theoretical saturation adsorbed amounts were estimated based on a complete pore-filling and assuming that the corresponding adsorbate molecules behave as hard spheres volumes that are perfectly packed in the available pore voids of each adsorbent.

Table S2. Reported average uptake amounts of DMSD and TMS from water and different adsorbent materials.

Adsorbate	Adsorbent Material	Adsorbent Description	Siloxane Concentration (mg L^{-1})	Maximum Adsorbed Amount*		Ref.
				mg g^{-1}	mg cm^{-3}	
DMSD	Ambersorb 4652	Graphite based activated carbon	22	0.76	0.30	[8]
	XAD 7HP	porous acrylic	10	0.06	0.06	
	Activated Alumina	Al_2O_3	10	0.04	0.03	
	CSIII	Carbon molecular sieve	22	0.28	0.18	
	C1000	Carbon molecular sieve	22	0.64	0.16	
	C1012	Carbon molecular sieve	22	0.60	0.30	
	SP850	Styrene resin	10	0.06	0.04	
	XAD761	Polymeric adsorbent	10	0.08	0.08	
	MgO	Magnesium oxide	10	0.04	0.02	
	HP2MG	methacrylate	10	0.12	0.08	
	SP 207	Nonionic polystyrene-divinylbenzene polymer resin	10	0.12	0.09	
	Norit RO 0.8X	Activated carbon	10	0.04	0.01	
	Optipore L493	Highly cross-linked styrenic polymer	10	0.12	0.07	
	Ambersorb 572	synthetic carbon	10	0.35	0.18	

Adsorbate	**Adsorbent Material**	**Adsorbent Description**	**Siloxane Concentration (mg L^{-1})**	**Maximum Adsorbed Amount***		**Ref.**
				mg g^{-1}	**mg cm^{-3}**	
DMSD	CFAU	Activated (AC)/Faujasite (FAU) zeolite hierarchical composite	20	0.62	0.75	[9]
	Cu^{2+}-CFAU	AC/FAU hierarchical composite w. Cu(II) cation sites	20	0.47	0.56	
	Ag^{+}-CFAU	AC/FAU hierarchical composite w. Ag(I) cation sites	20	0.72	0.86	
	FAU	Faujasite (FAU) zeolite	20	0.43	0.81	
	Ag^{+}-FAU	FAU with Ag(I) cation sites	20	0.26	0.50	
	AC	Activated carbon	20	0.29	0.09	
	UTD-$1_{faultless}$	Pure silica zeolite	20	3.20	5.50	This work
	UTD-$1_{faulted}$	Pure silica zeolite	20	6.50	11.2	
TMS	Ambersorb 4652	Graphite based activated carbon	8	0.35	0.14	[8]
	CMS 220	Carbon molecular sieve	8	0.02	0.01	
	Optipore L493	Highly cross-linked styrenic polymer	8	0.31	0.19	
	SP 207	Nonionic polystyrene-divinylbenzene polymer resin	8	0.33	0.25	
	XAD 761	Polymeric adsorbent	8	0.32	0.19	
	CFAU	Activated (AC)/Faujasite (FAU) zeolite hierarchical composite	10	1.45	1.74	[9]
	Cu^{2+}-CFAU	AC/FAU hierarchical composite w. Cu(II) cation sites	10	1.22	1.47	

Adsorbate	Adsorbent Material	Adsorbent Description	Siloxane Concentration (mg L^{-1})	Maximum Adsorbed Amount*		Ref.
				mg g^{-1}	mg cm^{-3}	
TMS	Ag^{+}-CFAU	AC/FAU hierarchical composite w. Ag(I) cation sites	10	1.05	1.26	[9]
	FAU	Faujasite (FAU) zeolite	10	0.08	0.16	
	Ag^{+}-FAU	FAU with Ag(I) cation sites	10	1.12	2.14	
	AC	Activated carbon	10	3.29	1.02	
	UTD-1$_{faultless}$	Pure silica zeolite	8	2.98	5.16	This work
	UTD-1$_{faulted}$	Pure silica zeolite	7	18.0	30.6	
MMST	CFAU	Activated (AC)/Faujasite (FAU) zeolite hierarchical composite	10	0.34	0.41	[9]
	Cu^{2+}-CFAU	AC/FAU hierarchical composite w. Cu(II) cation sites	10	0.50	0.6	
	Ag^{+}-CFAU	AC/FAU hierarchical composite w. Ag(I) cation sites	10	0.21	0.25	
	FAU	Faujasite (FAU) zeolite	10	0.013	0.025	
	Ag^{+}-FAU	FAU with Ag(I) cation sites	10	0.25	0.48	
	AC	Activated carbon	10	0.16	0.05	
	UTD-1$_{faultless}$	Pure silica zeolite	10	0.11	0.19	This work
	UTD-1$_{faulted}$	Pure silica zeolite	10	0.75	1.3	

*Maximum adsorbed amounts within the corresponding siloxane concentration range or estimated from isotherm models.

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