Supplementary Information (SI) for Environmental Science: Water Research & Technology.

Supplementary Information

Sorption and Biodegradation of Stormwater Trace Organic Contaminants via Composite Alginate Bead Geomedia with Encapsulated Microorganisms

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14 total pages, **2** Figures, and **7** Tables

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Section S 1: Synthetic Stormwater Recipe.

We prepared our synthetic stormwater (pH: 7±0.2) by dissolving 0.072 mM NH_4Cl, 0.75 mM $CaCl_2$, 0.33 mM Na_2SO_4, 0.072 mM $NaNO_3$, 1 mM $NaHCO_3$, 0.075 mM $MgCl_2$, and 0.016 mM Na_2HPO_4 in deionized water. The pH was adjusted using NaOH and/or HCl.

Section S 2: Analytical Method Details.

We used Agilent 1260 Infinity liquid chromatograph and Agilent 6460 triple quadrupole mass spectrometer to measure imidacloprid and desnitro-imidacloprid concentration for the LC-MS/MS analysis [column: Agilent Zorbax eclipse plus C18 (4.6 mm × 150 mm × 5 μm); guard column: Zorbax eclipse plus C18 (4.6 mm × 12.5 mm × 5 μm)]. We used the following MS/MS parameters— gas temperature (N_2): 300 deg C, gas flow: 5 L/min, nebulizer pressure: 45 psi, sheath gas temperature: 250 deg C, sheath gas flow: 11 L/min, capillary voltage (+)(-): 3500/3500 V, nozzle voltage (+)(-): 500/500 V, injection volume: 20 μL, column temperature: 50 deg C, mobile phase A: 77.5% water with 0.1% formic acid, mobile phase B: 22.5% acetonitrile with 0.1% formic acid, and flow rate: 0.8 mL/min. Parent ion (m/z), quant Ion (m/z) [Collision Energy, V], qual Ion (m/z) [Collision Energy, V], fragment voltage (V), dwell time (ms), polarity, and accelerator voltage (V) for imidacloprid were 256.06, 213 [8], 175.1 [12], 67, 20, positive, 4, respectively. For desnitro-imidacloprid, these parameters were— parent ion (m/z): 211.1, quant Ion (m/z) [Collision Energy, V]: 126 [22], qual Ion (m/z) [Collision Energy, V]: 90.03 [36], fragment voltage (V): 63, dwell time (ms): 200, polarity: positive, and accelerator voltage (V): 4.

We used Agilent 1260 liquid chromatography system with diode array detection (DAD) to measure acetanilide concentration [Column: Higgins Analytical Sprite Targa C18 (40 x 2.1 mm, 5 μm) with a guard column]. The analytical parameters were as follows— peak wavelength: 238.5 nm, column temperature: 50 deg C, injection volume: 10 μL, pump flow: 0.6 mL/min, method length: 10 min, mobile phase A: 15% methanol with 0.1% formic acid, and mobile phase B: 85% water with 0.1% formic acid.

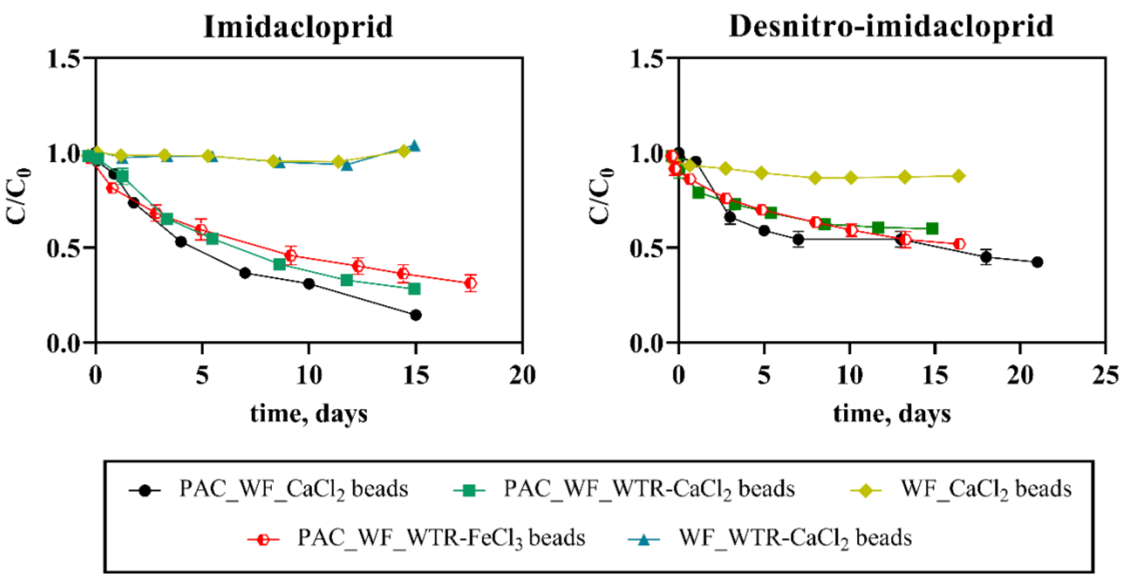

Figure S 1. Neonicotinoid sorption onto different BioSorp Beads. Error bars represent the standard error about the mean (error bars too small to see are obscured by the data points).
*Desnitro-imidacloprid sorption experiment was not conducted with WF_WTR-$CaCl_2$ beads.

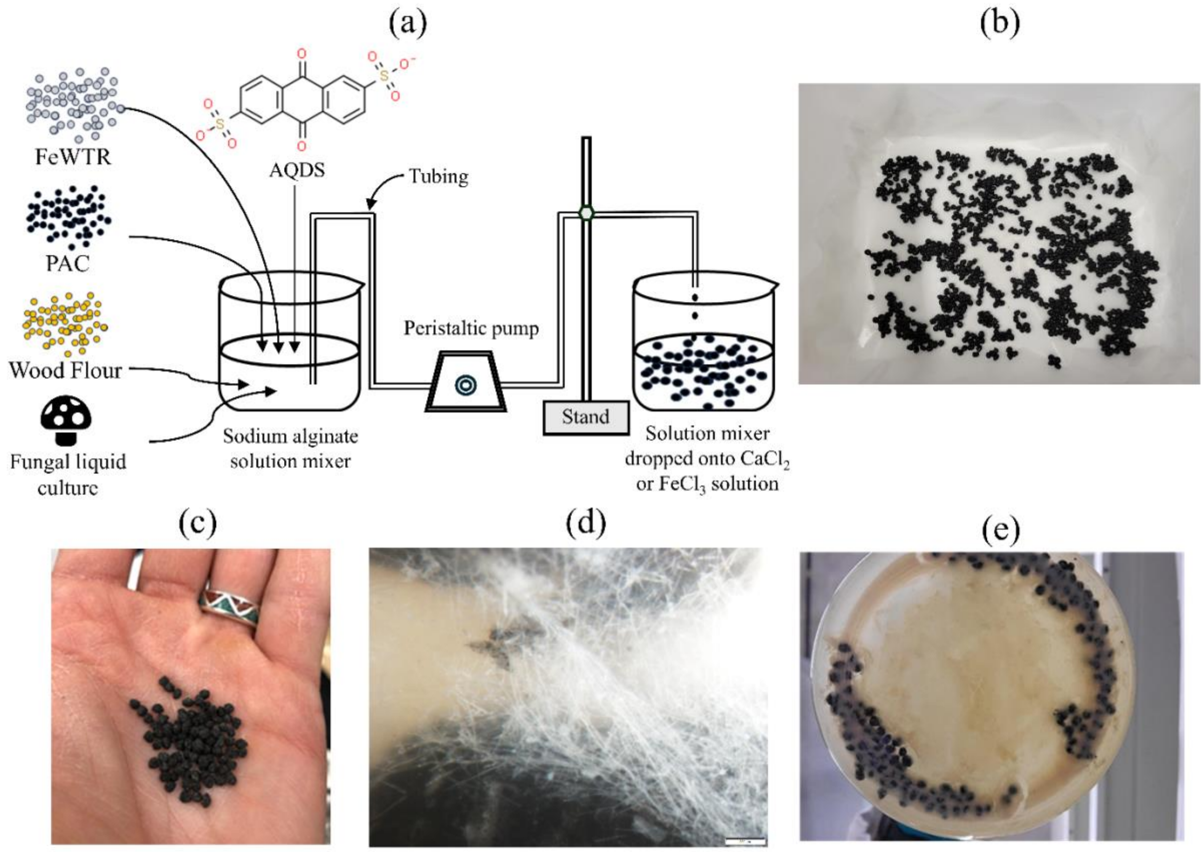

Figure S 2. Overview summary of BioSorp Bead preparation. (a) BioSorp Bead preparation method wherein dry amendments are mixed into dissolved sodium alginate solution that is added dropwise into a polyvalent cation solution via peristaltic pump to instantaneously form beads, (b) Wet beads (freshly prepared) drying on wax paper, (c) Dried BioSorp Beads, (d) Stereoscope image of white rot fungi (*Trametes versicolor*) growing from BioSorp Beads (made with 1% sodium alginate, 1% powder activated carbon, 1% wood flour, and 3% $CaCl_2$), and (e) *Trametes versicolor* grew from the BioSorp beads and spread into malt extract media.

Table S 1. Compositions of different types of BioSorp beads.

Testing conditions		Bead Preparation Recipe							
		Sodium Alginate Concentration	**Crosslinker Concentration**	**Cross-linker Type**	**External Electron Shuttle (AQDS)**	**PAC**	**Wood Flour**	**Fe-WTR**	**Drying Temperature**
1. Varied Alginate Concentration	**Baseline** condition	1%	270.3 mM	$CaCl_2$	-	1%	1%	-	Air dried at room temp
	Other conditions	0.5%, 1.5%	270.3 mM	$CaCl_2$	-	1%	1%	-	Air dried at room temp
2. Varied Cross-linker Concentration	**Baseline** condition	1%	270.3 mM	$CaCl_2$	-	1%	1%	-	Air dried at room temp
	Other conditions	1%	450.5 mM	$CaCl_2$	-	1%	1%	-	Air dried at room temp
3. Varied Cross-linker Type	**Baseline** condition	1%	270.3 mM	**$CaCl_2$**	-	1%	1%	-	Air dried at room temp
	Other conditions	1%	270.3 mM	**$FeCl_3$**	-	1%	1%	-	Air dried at room temp
4. Effects of External Electron Shuttle	**Baseline** condition	1%	270.3 mM	$CaCl_2$	-	1%	1%	1%	Air dried at room temp
	Other conditions	1%	270.3 mM	$CaCl_2$	0.1%	1%	1%	1%	Air dried at room temp
5. Effects of Cross-linker Type on Mechanical	**Baseline** condition	1%	270.3 mM	**$CaCl_2$**	0.1%	1%	1%	1%	Air dried at room temp
	Other conditions	1%	270.3 mM	**$FeCl_3$**	0.1%	1%	1%	1%	Air dried at room temp
6. Drying Temperature	**Baseline** condition	1%	270.3 mM	$CaCl_2$	0.1%	1%	1%	1%	Air dried at room temp
	Other conditions	1%	270.3 mM	$CaCl_2$	0.1%	1%	1%	1%	Oven dried (at 70° C for 8 hours)

Table S 2 (a). Experimental design for abiotic sorption experiments.

Experiment Type	Experiments	Contaminant	Sorbent			sorbent mass (mg)	Solvent	solvent volume (mL)
Abiotic Sorption Experiment	Dissolved phosphorus sorption kinetics	50 mg/L phosphate	Calcium alginate beads	Baseline condition	PAC_WF_WTR	100	Synthetic stormwater (pH ~7)	100
				Other condition	WF_WTR; PAC_WF; WF			
			Ferric alginate beads	Baseline condition	PAC_WF_WTR			
				Other condition	WF_WTR; WTR; WF; PAC_WF; PAC			
	Acetanilide sorption kinetics	40 mg/L acetanilide	PAC			50	Synthetic stormwater (pH ~7)	100
			Calcium alginate beads	Baseline condition	PAC_WF_WTR	100		
				Other condition	PAC_WF			
			Ferric alginate beads	PAC_WF_WTR				
	Imidacloprid and desnitro-imidacloprid sorption kinetics	30 mg/L imidacloprid and 30mg/L desnitro-imidacloprid	Calcium alginate beads	Baseline condition	PAC_WF_WTR	100	Synthetic stormwater (pH ~7)	100
				Other condition	PAC_WF			
			Ferric alginate beads	PAC_WF_WTR				
	Imidacloprid and desnitro-imidacloprid sorption isotherm	imidacloprid and desnitro-imidacloprid (10, 15, 20, 25, and 30 mg/L)	Calcium alginate beads	PAC_WF		100	Synthetic stormwater (pH ~7)	100
			Ferric alginate beads	PAC_WF				
	Effects of varied alginate concentrations on neonicotinoid sorption kinetics	10 mg/L imidacloprid and 10mg/L desnitro-imidacloprid	Calcium alginate beads (PAC_WF)	Baseline condition	1% (w/v)	100	Synthetic stormwater (pH ~7)	100
				Other condition	0.5% (w/v), 1.5% (w/v)			

Table S 2 (b). Experimental design for abiotic sorption experiments.

Experiment Type	Experiments	Contaminant	Sorbent			sorbent mass (mg)	Solvent	solvent volume (mL)
Abiotic Sorption Experiment	Effects of varied crosslinker concentrations on neonicotinoid sorption kinetics	10 mg/L imidacloprid and 10mg/L desnitro-imidacloprid	Calcium alginate beads (PAC_WF)	Baseline condition	3% (w/v)	100	Synthetic stormwater (pH ~7)	100
				Other condition	5% (w/v)			
	Effects of varied drying temperature on neonicotinoid sorption kinetics	10 mg/L imidacloprid and 10mg/L desnitro-imidacloprid	Calcium alginate beads (PAC_WF)	Baseline condition	air drying at room temp	100	Synthetic stormwater (pH ~7)	100
				Other condition	Oven dried (at 40° C and 70° C for 8 hours)			
	PFAS sorption kinetics	10 mg/L PFOA, PFBA, and PFBS	Calcium alginate beads	Baseline condition	PAC_WF_WTR	30	Synthetic stormwater (pH ~7)	200
				Other condition	PAC_WF; WF_WTR			
			Ferric alginate beads	Baseline condition	PAC_WF_WTR			
				Other condition	WF_WTR			

Table S 3. Experimental design for coupled sorption-biodegradation experiments.

Experiment Type	Contaminant	Fungi	Bead			Bead mass (mg)	Solvent	solvent volume (mL)
Coupled sorption and biodegradation	40 mg/L acetanilide	T. versicolor	Treatment	Baseline condition	PAC_WF_WTR_$CaCl_2$ and PAC_WF_WTR_$FeCl_3$	100	Synthetic stormwater (pH ~7)	100
				Other condition	PAC_WF_WTR_**AQDS**_$CaCl_2$ and PAC_WF_WTR_**AQDS**_$FeCl_3$			
			Autoclaved control	Baseline condition	PAC_WF_WTR_$CaCl_2$ and PAC_WF_WTR_$FeCl_3$			
				Other condition	PAC_WF_WTR_**AQDS**_$CaCl_2$ and PAC_WF_WTR_**AQDS**_$FeCl_3$			
			Azide control	Baseline condition	PAC_WF_WTR_$CaCl_2$ and PAC_WF_WTR_$FeCl_3$			
				Other condition	PAC_WF_WTR_**AQDS**_$CaCl_2$ and PAC_WF_WTR_**AQDS**_$FeCl_3$			
		P. ostreatus	Treatment	Baseline condition	PAC_WF_WTR_$CaCl_2$ and PAC_WF_WTR_$FeCl_3$			
				Other condition	PAC_WF_WTR_**AQDS**_$CaCl_2$ and PAC_WF_WTR_**AQDS**_$FeCl_3$			
			Autoclaved control	Baseline condition	PAC_WF_WTR_$CaCl_2$ and PAC_WF_WTR_$FeCl_3$			
				Other condition	PAC_WF_WTR_**AQDS**_$CaCl_2$ and PAC_WF_WTR_**AQDS**_$FeCl_3$			
			Azide control	Baseline condition	PAC_WF_WTR_$CaCl_2$ and PAC_WF_WTR_$FeCl_3$			
				Other condition	PAC_WF_WTR_**AQDS**_$CaCl_2$ and PAC_WF_WTR_**AQDS**_$FeCl_3$			

Table S 4. First order rate constants (with 95% confidence interval level) for imidacloprid and desnitro-imidacloprid sorption onto different PAC-Wood dust beads. [The detailed compositions of these beads are in **Table S 1**]

Bead type	Imidacloprid		Desnitro-imidacloprid	
	1st order rate constant (1/day)	r^2	1st order rate constant (1/day)	r^2
0.5% SA - 3% $CaCl_2$	0.22 (0.19 to 0.25)	0.97	0.21 (0.19 to 0.23)	0.96
1% SA - 3% $CaCl_2$	0.19 (0.15 to 0.23)	0.99	0.18 (0.14 to 0.22)	0.97
1.5% SA - 3% $CaCl_2$	0.13 (0.11 to 0.14)	0.98	0.17 (0.16 to 0.19)	0.95
1% SA - 5% $CaCl_2$	0.16 (0.14 to 0.17)	0.99	0.15 (0.11 to 0.18)	0.95
T40	0.21 (0.20 to 0.22)	0.99	0.18 (0.13 to 0.24)	0.96
T70	0.18 (0.11 to 0.24)	0.97	0.17 (0.16 to 0.19)	0.93

*3% $CaCl_2$= 270.3 mM $CaCl_2$.
**T40= beads oven dried at 40 deg C.
***T70= beads oven dried at 70 deg C.

Table S 5. Phosphate sorption (with 95% confidence interval level) onto various BioSorp beads (Calcium-alginate and iron-alginate beads).

Types of beads	maximum phosphate sorption capacity (mg/g)	adsorption rate constant, k_{ad} (day^{-1})	r^2
WF-WTR-$CaCl_2$	13.01 (11.26 to 15.42)	0.37 (0.20 to 0.72)	0.83
PAC_WF_WTR_$CaCl_2$	8.25 (7.70 to 8.88)	0.27 (0.21 to 0.34)	0.97
WF_$CaCl_2$	2.10 at day 18 (poor model fit)	0.13	-
PAC_WF_$CaCl_2$	0.88 at day 18	* did not follow Langmuir adsorption model	-
WF-WTR-$FeCl_3$	42.12 (38.79 to 45.82)	0.99 (0.53 to 1.89)	0.89
WTR_$FeCl_3$	38.88 (36.96 to 40.82)	1.33 (0.98 to 1.84)	0.96
WF_$FeCl_3$	34.03 (32.09 to 35.99)	1.52 (1.07 to 2.29)	0.95
PAC_WF_$FeCl_3$	29.55 (26.97 to 32.46)	0.37 (0.26 to 0.55)	0.92
PAC_$FeCl_3$	24.98 (21.51 to 30.09)	0.29 (0.16 to 0.61)	0.89
PAC_WF_WTR_$FeCl_3$	17.03 (15.89 to 18.37)	0.20 (0.17 to 0.25)	0.98

Table S 6. Acetanilide, Imidacloprid, and Desnitro-imidacloprid sorption (with 95% confidence interval level) onto various BioSorp beads (Calcium-alginate and iron-alginate beads).

Sorbent	**Maximum sorption capacity (mg/g)**		
	Acetanilide	**Imidacloprid**	**Desnitro-imidacloprid**
PAC	73.77 (70.88 to 76.68)	112 (111.19 to 112.81)	37 (35.4 to 38.6)
PAC_WF_$CaCl_2$ bead	39.43 (36.49 to 42.45)	26.39 (25.35 to 27.54)	14.96 (13.89 to 16.13)
PAC_WF_WTR_$CaCl_2$ bead	38.86 (36.91 to 40.85)	25.52 (23.05 to 29.03)	11.14 (10.52 to 11.83)
PAC_WF_WTR_$FeCl_3$ bead	38.33 (35.77 to 40.96)	18.52 (17.15 to 20.32)	13.04 (11.75 to 14.88)

Table S 7. Sorption of different long and short-chain PFAS onto various BioSorp beads (Calcium-alginate and iron-alginate beads), different black carbon materials, iron-based materials, and aluminum-based materials.

Types	Sorbent Material	PFOA sorption capacity (mg/g)	PFBA sorption capacity (mg/g)	PFBS sorption capacity (mg/g)	Reference
BioSorp beads	1% sodium alginate-1% PAC-1% Wood flour-3% $CaCl_2$ Beads	8.85 *(PAC normalized capacity = 25.67)*	5.17 *(PAC normalized capacity = 14.99)*	3.40 *(PAC normalized capacity = 9.86)*	This study
	1% sodium alginate-1% PAC-1% Wood flour-1% **FeWTR**-3% $CaCl_2$ Beads	6.50 *(PAC normalized capacity = 25.35)*	1.44 *(PAC normalized capacity = 5.62)*	2.20 *(PAC normalized capacity = 8.58)*	This study
	1% sodium alginate-1% Wood flour-1% FeWTR-3% $CaCl_2$ Beads	0	0	0.39	This study
	1% sodium alginate-1% Wood dust-3% $CaCl_2$ Beads	0	0	0	This study
	1% sodium alginate-1% PAC-1% Wood flour-270.3 mM $FeCl_3$ Beads	13.10 *(PAC normalized capacity = 37.78)*	1.20 *(PAC normalized capacity = 3.46)*	5.07 *(PAC normalized capacity = 14.62)*	This study
	1% sodium alginate-1% PAC-1% Wood flour-1% **FeWTR**-270.3 mM $FeCl_3$ Beads	9.27 *(PAC normalized capacity = 35.5)*	0	4.57 *(PAC normalized capacity = 17.5)*	This study
	1% sodium alginate-1% Wood flour-1% FeWTR-270.3 mM $FeCl_3$ Beads	6.91	0	0.84	This study
	2% sodium alginate-3% Biochar-4% $CaCl_2$ beads	n.a.	n.a.	2.895	Militao et al.[1] (2023)
Alginate composite beads	Biochar (made from spent coffee ground)	12.87	n.a.	n.a.	Steigerwald et al.[2] (2023)
Black C materials	GAC	8.54	3.01	n.a.	Riegel et al.[3] (2023)
	Coconut-based GAC	12.2 ± 0.2 (after 10 days)	n.a.	n.a.	Siriwardena et al.[4] (2018)
	Biochar	$16.5*10^{-5}$	n.a.	$8*10^{-5}$	Dalahmeh et al.[5] (2019)

Table S 6. (continued)

Types	Sorbent Material	PFOA sorption capacity (mg/g)	PFBA sorption capacity (mg/g)	PFBS sorption capacity (mg/g)	Reference
Black C materials	Coal based GAC	13.6 ± 0.1 (after 10 days)	n.a.	n.a.	Siriwardena et al.[4] (2018)
	GAC	22.7	n.a.	n.a.	Yao et al.[6] (2014)
	GAC	35.69	6.72	14.49	Zhang et al.[7] (2021)
	GAC	52.8	n.a.	n.a.	Zhang et al.[8] (2016)
	PAC	0.11	n.a.	$7*10^{-4}$	Murray et al.[9] (2019)
	PAC	2.49	n.a.	n.a.	Zhi et al.[10] (2015)
	PAC	16.5	n.a.	n.a.	Qu et al.[11] (2009)
	PAC	484	n.a.	n.a.	Li et al.[12] (2017)
	Different types of activated carbon felts	2.08 to 156	n.a.	n.a.	Saeidi et al.[13] (2020)
Iron based materials	Iron-Filings-based Green Environmental Media (IFGEM)	$7*10^{-9}$	n.a.	n.a.	Ordonez et al.[14] (2022)
AL based materials	Aluminum-based Green Environmental Media (AGEM)	$1.5*10^{-6}$	n.a.	n.a.	Ordonez et al.[14] (2022)
	Aluminum-water treatment residuals	0.094 (at pH 7)	n.a.	n.a.	Zhang et al.[15] (2021)

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