Electronic Supplementary Material (ESI) for Environmental Science: Water Research & Technology.

The Influence of Natural Organic Matter on the Adsorption of Microcystin-LR by Powdered Activated Carbon

Supporting Information

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Calculating MC-LR Concentration

The concentration of MC-LR was calculated using the calibration curve equation as follows:

$$\frac{A_{\text{unknown MC - LR}}}{A_{\text{nodularin}}} = F\,\frac{C_{\text{unknown MC - LR}}}{C_{\text{nodularin}}}$$

(S1)

where, A is the peak area, C is the concentration, and F is the response factor. The response factor was calculated using the following equation:

$$F = \frac{A_{\text{std MC - LR}} \cdot C_{\text{nodularin}}}{A_{\text{nodularin}} \cdot C_{\text{std MC - LR}}}$$

(S2)

Preliminary QA/QC data showed that on average there is approximately 2 and 16% drift in the nodularin and MC-LR peak area as a function of the sample position in the autosampler in a single batch. Therefore, in this analysis the response factor is considered as a linear function with respect to the sample position in the LC MS/MS autosampler. The linear equation for the response factor is given by $y = mx + b$, where y is the response factor and x is the sample position number.

GLSM extraction method

The GLSM extraction method followed those described by Kim et al. (Kim et al., 2003) and Dittmar et al. (Dittmar et al., 2008). Water samples were collected in acid washed carboys from Grand Lake St. Mary at different locations. The samples were acidified to pH 2.5 using HCl and filtered with a 0.45 μm polycarbonate cartridge filter via a peristatic pump. The styrene–divinylbenzene copolymer (PPL) cartridge was prepared by thorough rinsing with 100 mL of methanol. The filtered water sample was then gravity fed into the PPL cartridge. The PPL cartridge was rinsed with methanol to elute the DOM. The filtrate was transferred into a glass Rotovap flask, which was heated to 50 to 60^0C, until all methanol was evaporated. The dried DOM was re-suspended in Milli-Q water, frozen in a plastic container, and freeze dried using a lypohilizer. The DOM extract was stored at room temperature in the dark until use.

References

Dittmar, T., Koch, B., Hertkorn, N., Kattner, G., 2008. A simple and efficient method for the solid-phase extraction of dissolved organic matter (SPE-DOM) from seawater. Limnol. Oceanogr. Meth. 6, 230-235.

Kim, S., Simpson, A.J., Kujawinski, E.B., Freitas, M.A., Hatcher, P.G., 2003. High resolution electrospray ionization mass spectrometry and 2D solution NMR for the analysis of DOM extracted by C-18 solid phase disk. Organic Geochemistry 34, 1325-1335.

Table S1: Benchmark model water solution composition based on compiled data for Ohio water utility intake water from select surface water sources in Carroll, Clermont, Franklin, Geauga, Mercer, Sandusky and Wood Counties, Ohio.

Component	**Cation/Anion**	**Concentration**
Inorganic	Ca^{2+}	1.5 mM
	Mg^{2+}	1.2 mM
	K^{+}	0.07 mM
	NH_4^{+}	3.24 µM
	Na^{+}	2.9 mM
	Fe^{3+}	7.4 µM
	$CO_3^{2-}{}_{Total}$	2.86 mM
	Cl^{-}	0.36 mM
	SO_4^{4-}	2.6 mM
	NO_3^{-}	3.25 µM
	PO_4^{3-}	4.93 µM
Organic	SRFA/GLSM DOM[b]	5 mg/L[a]
Sodium Azide	-	0.005% by vol.
Milli-Q water	-	-
pH	-	8.4 ± 0.1[a, e]
Alkalinity (as $CaCO_3$)	-	2.93[a] meq/l
Conductivity	-	1.62 ± 0.01[a, c] mS/cm

Note: a) These values are subjected to change in the NOM concentration effect and pH experiments, b) Suwannee river fulvic acid (SRFA) and Grand Lake St. Marys dissolve organic matter (GLSM DOM), c) measured using Orion model 1230 conductivity probe, d) measured using Shimadzu TOC-V CSN and TNM-1 analyzer, and e) measured using Sartorius pH basic benchtop meter.

Table S2: Total MC concentration (μg/L) measured in Lake Erie, State Park beaches, inland lakes, and public water supplies in the State of Ohio. Data retrieved from Harmful algal blooms (HAB): Information for public water systems (http://epa.ohio.gov/ddagw/HAB).

Year	Mean	Max	Total samples
2017	35	194	174
2016	13	171	845
2015	13	3145	1351
2014	42	20000	982
2013	20	220	404
2012	31	1400	248
2011	12	340	171
2010	29	2000	309

Table S3: Summary of kinetic experimental conditions and model fit parameters.

	Water composition						
PAC type	**NOM type**	**[NOM] (mg/L)**	**pH**	**Conductivity (mS/cm)**	**q_e (mg/g)**	**k_{ad}' (hours^{-1})**	**R^2**
Wood	SRFA	0	5.2	NM	10.21	6.56	1
			8.5	1.62	8.835	6.987	0.99
		5	5.2	1.71	7.127	1.401	0.98
			8.5	1.62	8.434	1.643	0.98
				2.92	9.214	2.031	0.99
			9.5	3.12	9.922	3.475	0.99
		10	8.5	1.62	7.777	1.267	0.98
	GLSM	5	8.5	1.62	7.934	0.868	0.98
Coal blend	SRFA	0	5.2	NM	10.72	2.292	0.99
			8.5	1.62	8.810	1.811	0.99
		5	5.2	1.71	5.456	0.227	0.96
			8.5	1.62	5.945	0.393	0.82
				2.92	6.669	0.166	0.88
			9.5	3.12	9.134	0.538	0.96
		10	8.5	1.62	4.759	0.256	0.87
	GLSM	5	8.5	1.62	6.049	0.126	0.92
Bituminous coal	SRFA	0	5.2	NM	9.725	0.851	0.90
			8.5	1.62	8.422	0.474	0.96
		5	5.2	1.71	3.113	0.732	0.76
			8.5	1.62	2.210	0.618	0.83
				2.92	2.779	0.313	0.71
			9.5	3.12	5.674	0.247	0.77
		10	8.5	1.62	1.045	0.117	0.76
	GLSM	5	8.5	1.62	1.232	0.086	0.87
Coconut shell	SRFA	0	5.2	NM	6.482	0.945	0.76
			8.5	1.62	5.657	0.114	0.80
		5	5.2	1.71	2.702	0.536	0.68
			8.5	1.62	n/a	n/a	n/a
				2.92	0.928	1.134	0.49
			9.5	3.12	1.853	1.178	0.92
		10	8.5	1.62	n/a	n/a	n/a
	GLSM	5	8.5	1.62	n/a	n/a	n/a

NM: Not measured

Table S4: The dissolved organic carbon and nitrogen content of 5 mg/L SRFA and GLSM in Milli-Q.

NOM Sample	DOC[a](mg/L)	TDN[b] (mg/L)
SRFA	2.562	0.043
GLSM	2.434	0.135

Note: a) Dissolved carbon (DOC) and b) Total dissolved nitrogen (TDN). As a comparison, the International Humic Substances Society reported % carbon and % nitrogen for SRFA are 52% and 0.7%, respectively.

Table S5: Langmuir isotherm fit parameters for the equilibrium experiments.

PAC type	q_{max} (mg/g)	K (L/µg)	R^2
Wood	63.41	4.226	0.71
Coal blend	40.74	4.659	0.82

Note: Coconut shell based PAC data did not fit any isotherm model

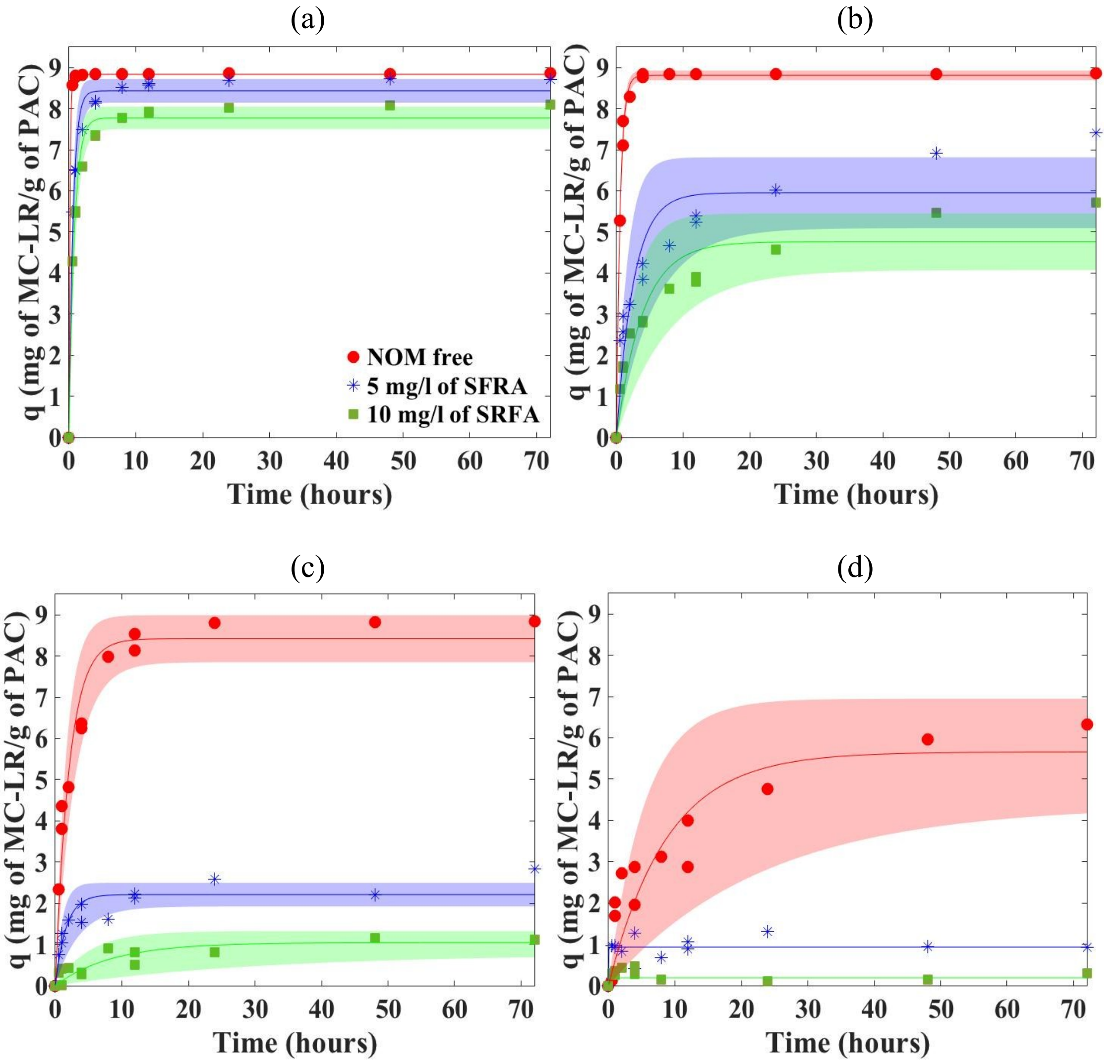

Figure S1: MC-LR adsorption as a function of time to 5 mg/L of (a) wood, (b) coal blend, (c) bituminous coal, and (d) coconut shell based PACs. Samples were at pH 8.5 in model water with 0, 5, and 10 mg/L of SRFA. Lines represent fits to a pseudo first-order kinetic adsorption model and the shaded area represents 95% confidence interval.

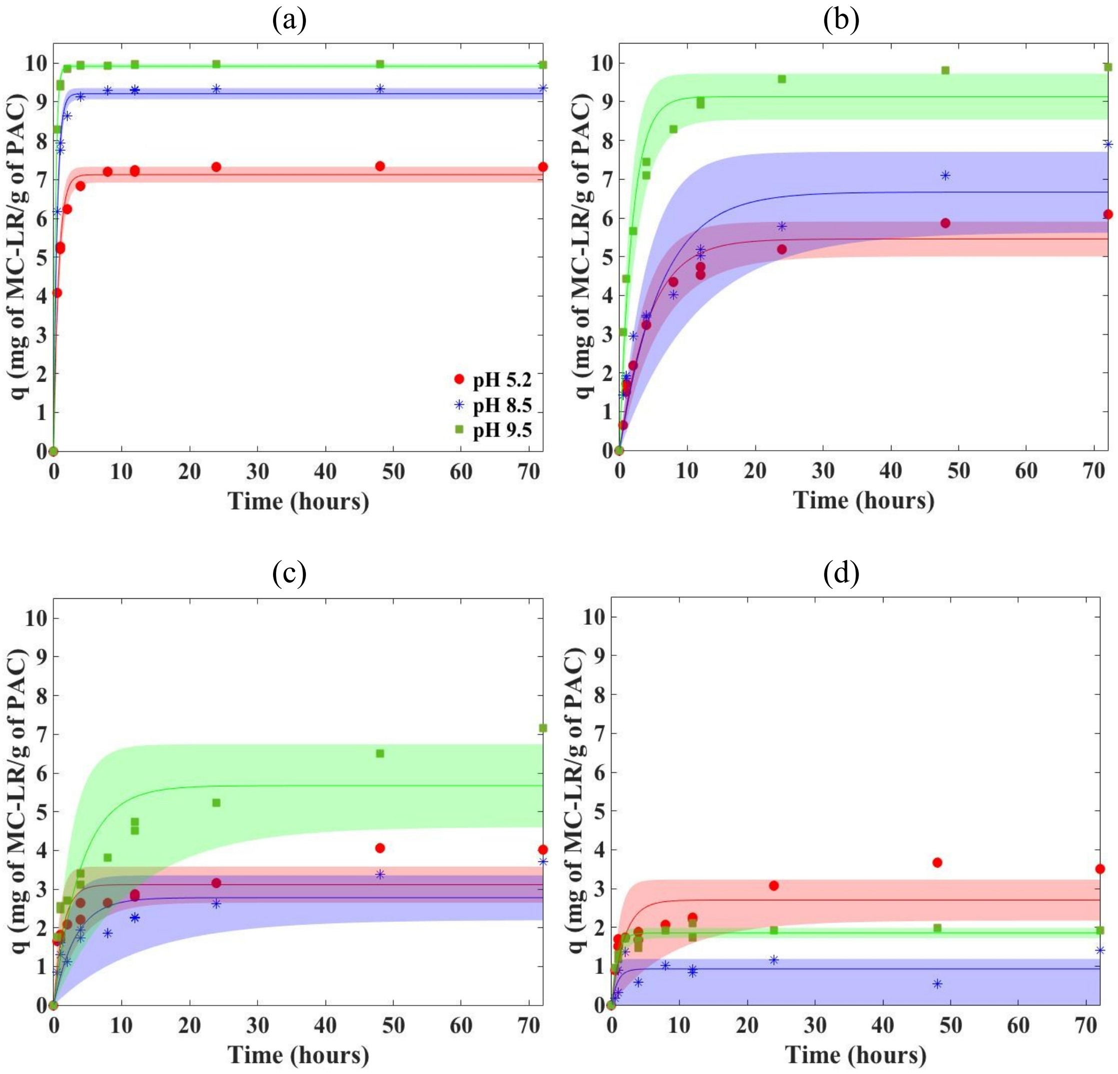

Figure S2: MC-LR adsorption as a function of time to 5 mg/L of (a) wood, (b) coal blend, (c) bituminous coal, and (d) coconut shell based PACs. Samples were at pH 5.2, 8.5, and 9.5 in model water with 5 mg/L of SRFA. Lines represent fits to a pseudo first order kinetic adsorption model and the shaded area represents 95% confidence interval.

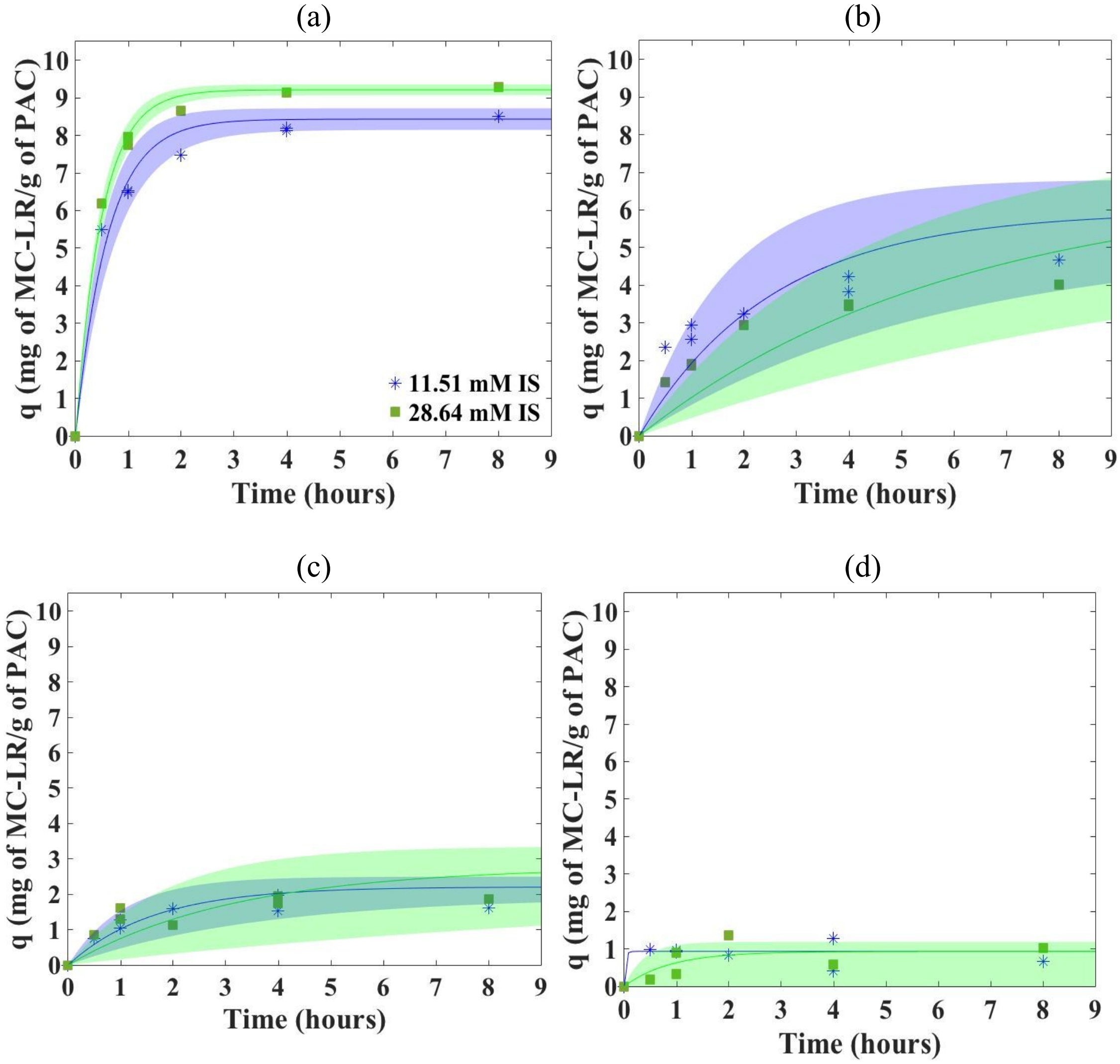

Figure S3: MC-LR adsorption as a function of time to 5 mg/L of (a) wood, (b) coal blend, (c) bituminous coal, and (d) coconut shell based PACs. Samples were at pH 8.5 in model water with 5 mg/L of SRFA at 11.51 and 28.64 mM of ionic strength. Lines represent fits to a pseudo first order kinetic adsorption model and the shaded area represents 95% confidence interval.

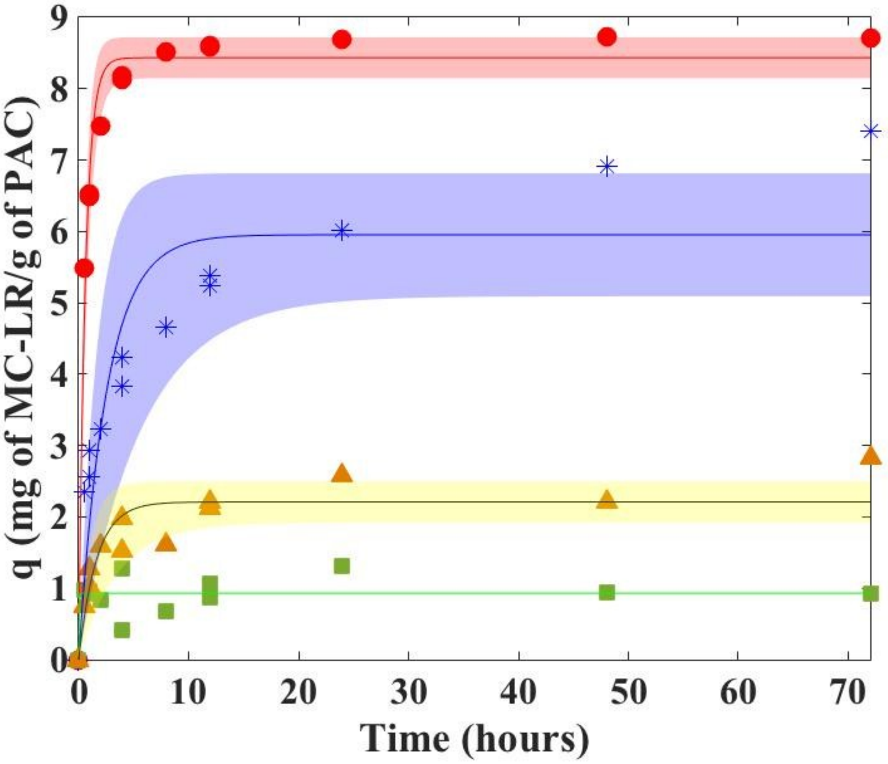

Figure S4: MC-LR adsorption as a function of time to 5 mg/L wood (●), coal blend (✳), bituminous coal (▲), and coconut shell based PACs (🟩). Samples were at pH 8.5 with 5 mg/L of SRFA NOM. Lines represent fits to a pseudo first order kinetic adsorption model and the shaded area represents 95% confidence interval.

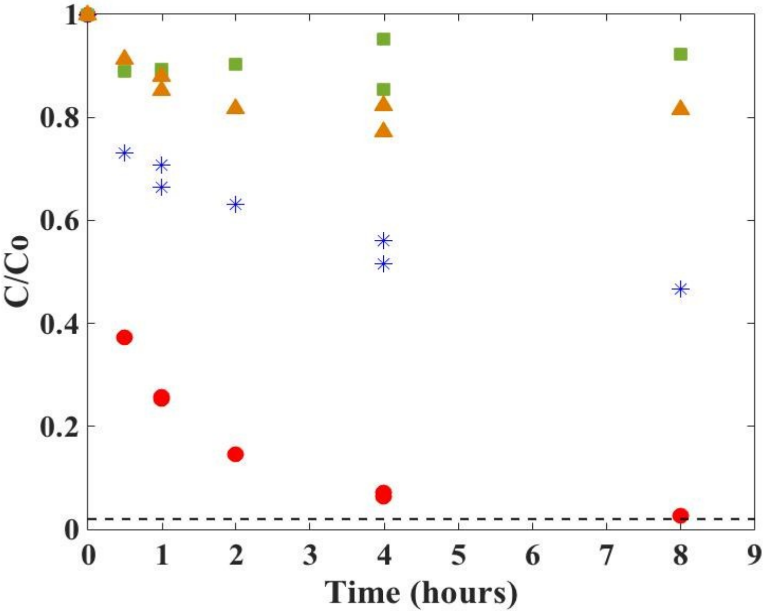

Figure S5: Fraction of MC-LR removed as a function of time to 5 mg/L of a) wood (■), b) coal blend (■), bituminous coal (■), and d) coconut shell based PACs (■). Samples were at pH 8.5 in model water with 5 mg/L of SRFA NOM. The horizontal dash line represents the WHO recommended MC concentration limit (i.e. 1 μg/L) in drinking water.

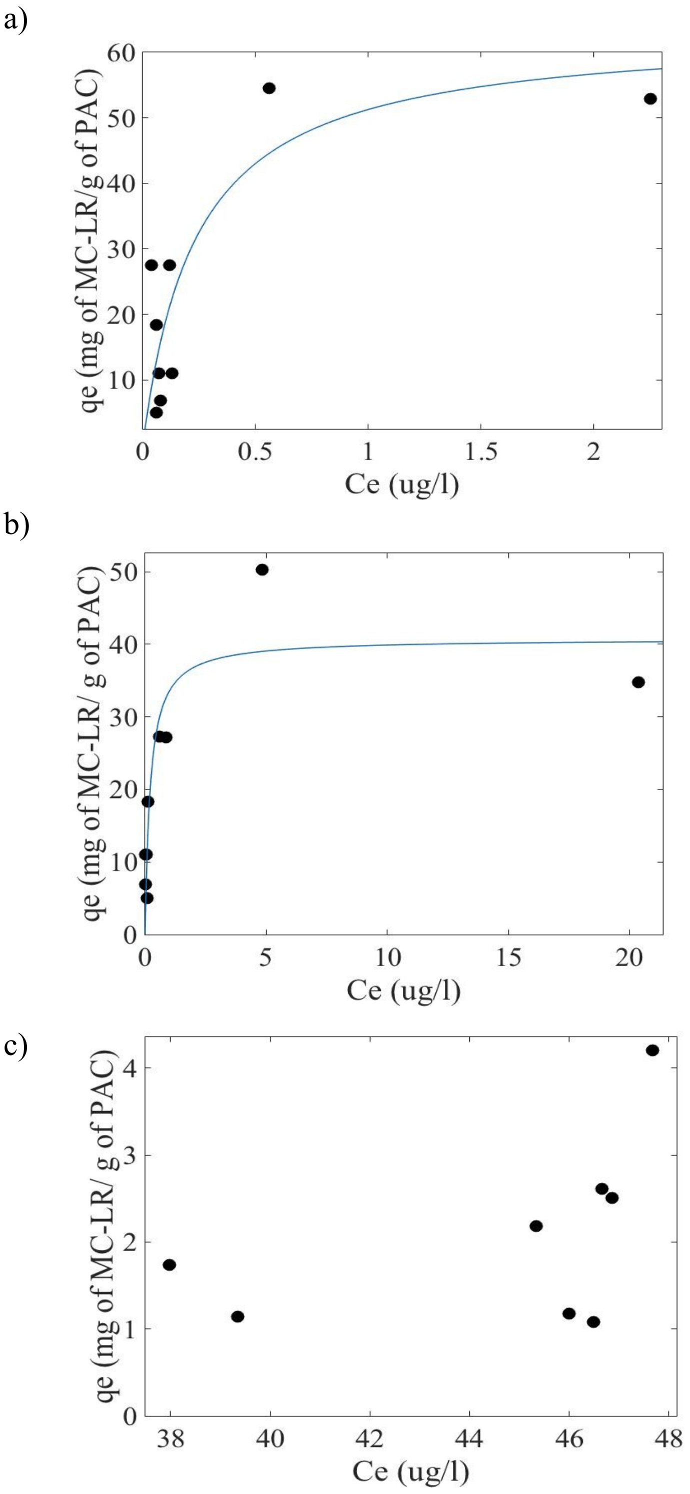

Figure S6: Equilibrium results for (a) wood, (b) coal blend, and (c) coconut shell based PACs fit to the Langmuir isotherm model. Samples were in benchmark model water at pH 8.5 and 5 mg/L of SRFA. The coconut shell based PAC adsorption data did not fit the isotherm equation.