

Supplementary Information
for
DOM removal from surface water
by activated carbon vs. a nanocomposite:
an experimental and modeling approach to optimize treatment

Mario L. Kummel^{1,*}, Itamar A. Shabtai^{2,*,#}, Shlomo Nir¹, Yael G. Mishael¹

¹Department of Soil and Water Sciences, The Robert H. Smith Faculty of Agriculture, Food
and Environment, The Hebrew University of Jerusalem, Rehovot, 7610001, Israel

²Department of Environmental Science and Forestry, The Connecticut Agricultural
Experiment Station, New Haven, CT, 06511, USA

#Corresponding author

*Equally contributing authors

1. Adsorbent and water characterization

Table S1. Physical Properties of the granular activated carbon (GAC), regenerated GAC (rGAC), and granular pDADMAC-montmorillonite composite (PD-MMT) used in this study.

	BET surface area $\text{m}^2 \cdot \text{g}^{-1}$	Zeta potential mV	Iodine number $\text{mg} \cdot \text{g C}^{-1}$
GAC	$1000 \pm 50^*$	-12	800
rGAC	N.D.	-42	810
PD-MT	14.5^{**}	+30	N.D.

* Donau Carbon.¹

**Zusman et al.²

N.D. – Not determined

Table S2. Elemental composition of GAC and rGAC (%w/w).

	C	O	H	N	S
GAC	83.8	2.1	0.6	0.18	0.46
rGAC	81.1	12.8	1.5	0.13	0.15

2. Model parameterization

Examples of extrapolation of a breakthrough curve of HA and FA to determine R_0 are shown in Figure S1 for rGAC and PD-MMT. A logarithmic (\ln) function was used in the case of rGAC and a linear function was used in this case of PD-MMT for both solutions. Based on extrapolation we calculated that in the case of rGA, $C/C_0 = 0.85$ would have been reached after 180 and 1900 pore volumes for HA and FA, respectively, and in the case of PD-MMT, $C/C_0 = 0.85$ would have been reached after 130 and 1090 pore volumes, for HA, and FA, respectively.

After converting UV_{254} to molar removal, R_0 was determined by calculating the area under the curve. R_0 was calculated as follows:

1. Calculation of the adsorbed amount of HA or FA (in moles) in segments (around 17) between sampling, by subtraction of the concentration of organic molecules eluted during the adsorption experiment.
2. Calculation of the extrapolated amount of HM up to $C/C_0 = 0.85$.
3. Summing all HA or FA concentration (in molar) in segments, which included the extrapolated segment.
4. The hydraulic model defines the numbers of HA or FA adsorbed moles in the column as equal to the number of moles of adsorption sites.
5. The molar concentration (M) of adsorption sites (R_0) is calculated from experimental adsorbent pore volume. The R_0 values are shown in table S4.

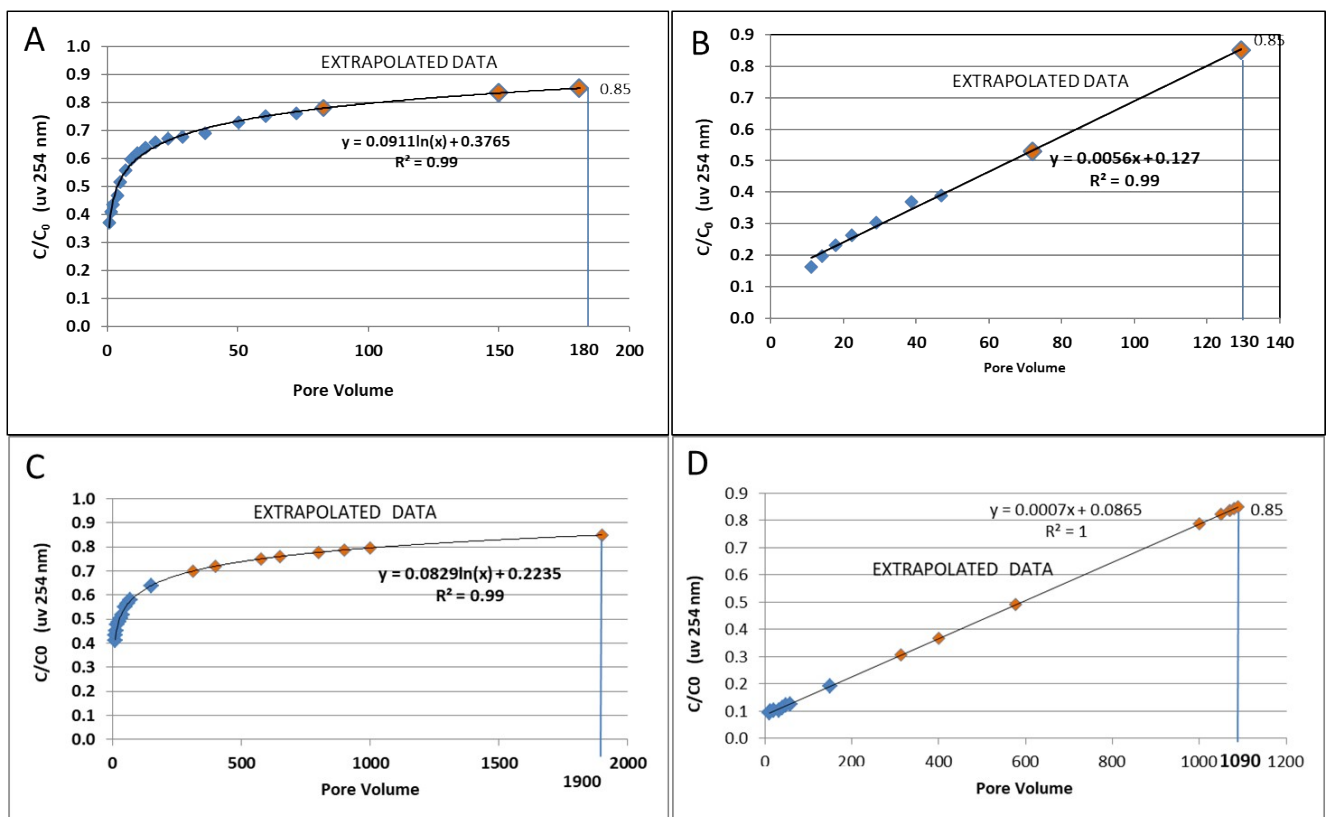


Figure S1. Logarithmic and linear extrapolation for removal of HA (4.5 mg C L^{-1}) by (A) regenerated granular activated carbon (rGAC), (B) PD-MMT, and for FA removal (5 mg C L^{-1}) by (C) regenerated granular activated carbon (rGAC), and (D) PD-MMT.

Table S4. Average extrapolated R_0 values for GAC, rGAC, and PD-MMT for HA and FA solutions.

	GAC		rGAC		PD-MMT	
	HA	FA	HA	FA	HA	FA
Extrapolation shape of curve	ln	ln	ln	ln	linear	linear
R₀ (M)	$7.12 \cdot 10^{-4}$	$4.92 \cdot 10^{-3}$	$6.79 \cdot 10^{-4}$	$6.99 \cdot 10^{-3}$	$1.04 \cdot 10^{-3}$	$8.74 \cdot 10^{-3}$

3. Correlation of HA and FA molar concentrations and absorption at 254 nm

Linear regressions of UV_{254} as a function of the molar concentrations of HA and FA (as single components in a solution) were measured to determine their $SUVA_{254}$ (Figure S2)

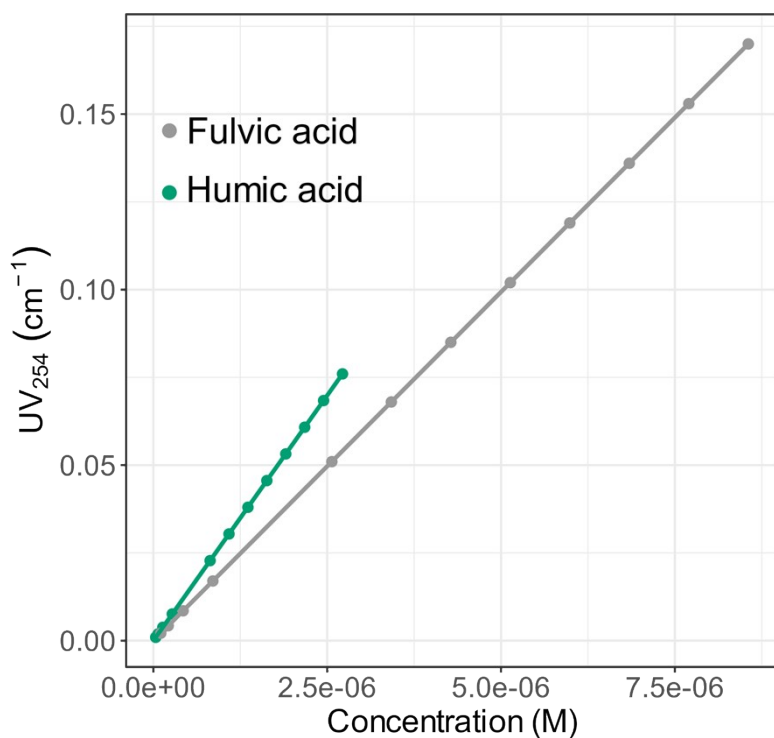


Figure S2. Linear regression of absorption at UV_{254} nm and molar concentration of HA (based on 1 mg C L^{-1}) and FA (based on 4 mg C L^{-1})

4. Validation of determination of HA and FA concentrations by utilizing absorption measurements of solutions of their known mixtures

As stated in Section 2.6, Eqs. 1-3, a Fortran program was written whose input includes the absorption values of the given solution plus preexisting values of absorption at several wavelengths of solutions of HA and FA alone. The unknowns are the concentrations of HA and FA in units of mg L^{-1} at the given solution. The first such validation was obtained for separated solutions of 13.5 mg L^{-1} of HA and 9.6 mg L^{-1} of FA (in both cases 5 mg C L^{-1}) by using absorption values at 10 wavelengths from 240 to 280 nm. The values of HA and FA in mg/L were obtained in this case with relative errors of about 0.1%. We demonstrate here the calculated extraction of (known) concentrations of FA and HA for a solution which included 4 mg C L^{-1} for FA and 1 mg C L^{-1} of HA, which corresponds to 7.69 and 2.70 mg L^{-1} of FA and HA, respectively. We chose 8 wavelengths between 250 and 291 nm, in constructing 6 pairs of linear equations of 2 unknowns.

A recommended starting point is to test whether the absorption of the solution at the given wavelengths satisfies the sum of adsorptions, due to the above concentrations of FA and HA. For wavelengths of 254 and 281 nm, the values of solution absorption were 0.254 and 0.192 cm^{-1} , respectively, whereas the calculated sums of absorptions due to FA and HA were 0.2498 and 0.1872 cm^{-1} , respectively. Thus. the ratios of intensities of absorption amount to 1.017 and 1.026 for the corresponding wavelengths of 254 and 281 nm. During this study, we encountered deviations of up to 6 %, in which case the corresponding wavelengths had to be avoided.

Table S5. Wavelength pairs used in the calculation of FA and HA concentration from a mixture of FA (7.69 mg L^{-1}) and HA (2.70 mg L^{-1}).

wavelength	wavelength	Absorption	Calculated	
pair (#)	nm	cm^{-1}	(mg L^{-1})	
			FA	HA

1	254	0.254	7.17	3.26
	281	0.192		
2	254	0.254	6.51	3.78
	291	0.174		
3	250	0.262	9.35	1.78
	281	0.192		
4	260	0.240	8.48	2.36
	281	0.192		
5	250	0.262	8.16	2.70
	291	0.174		
6	262	0.236	7.91	2.71
	269	0.219		

The average value of FA was 7.93 mg L⁻¹, whereas the value used in the construction of the solution was 7.69 mg L⁻¹, corresponding to 3.1% difference. The average value of HA was 2.76 mg L⁻¹, whereas the value used in the construction of the solution was 2.70 mg L⁻¹, corresponding to 2.2% difference.

Expected experimental errors and negative solutions for HA or FA concentrations

In the following we present an estimate of the expected errors in the determination of the values of X_1 and X_2 in section 2.6, Eq (3), and estimate the possibility of obtaining a negative value for X_1 or X_2 , for a given pair of equations, which is discarded. Eq (3) for the case of X_{1ij} from the particular pair ij yields:

$X_{1ij} = (S_i * T_4 - S_j * T_2) / D_{ij}$, in which $D_{ij} = T_1 * T_4 - T_2 * T_3$, in which the numerator and denominator are proportional to $1 - S_j * T_2 / (S_i * T_4)$ and $1 - T_2 * T_3 / (T_1 * T_4)$, respectively. A negative value of X_{1ij} can occur if the product of 4 terms in the numerator is larger than 1 and the other product of 4 terms in the denominator is smaller than 1, or vice versa. Let us consider a random numerical example of a set of 2 equations used to determine X_1 and X_2 . The units of absorption are cm⁻¹.

Wavelength= 250 nm; $S_i = 0.262$, $T_1 = S(\text{HA}) = 0.392$; $T_2 = S(\text{FA}) = 0.216$

Wavelength= 260 nm; $S_j = 0.240$, $T_3 = S(\text{HA}) = 0.371$; $T_4 = S(\text{FA}) = 0.198$

The term $S_j \cdot T_2 / (S_i \cdot T_4)$ in the numerator equals 0.999 i.e., the numerator is positive in this case. It is known that for small relative errors the relative error of this term is the sum of the relative errors of the 4 factors in the product. For a typical relative error of 0.01 the total relative error of this term can be 0.04, i.e., the absolute error can be $0.998 \cdot 0.04 = 0.04$, which means that in extreme cases the numerator can be positive or negative.

For solution absorption values below 0.1 cm^{-1} , it is practically impossible to apply this procedure. Hence, in the case of PD-MMT columns, the emerging water could be analyzed by the described procedure only for $PV=62$. It is possible to improve the precision of the procedure, and to apply it for analysis of emerging water from the column by using a longer cell in the measurements of absorption values.

5. DOM Column adsorption experiment: DOM values in stream water and in water emerging from columns

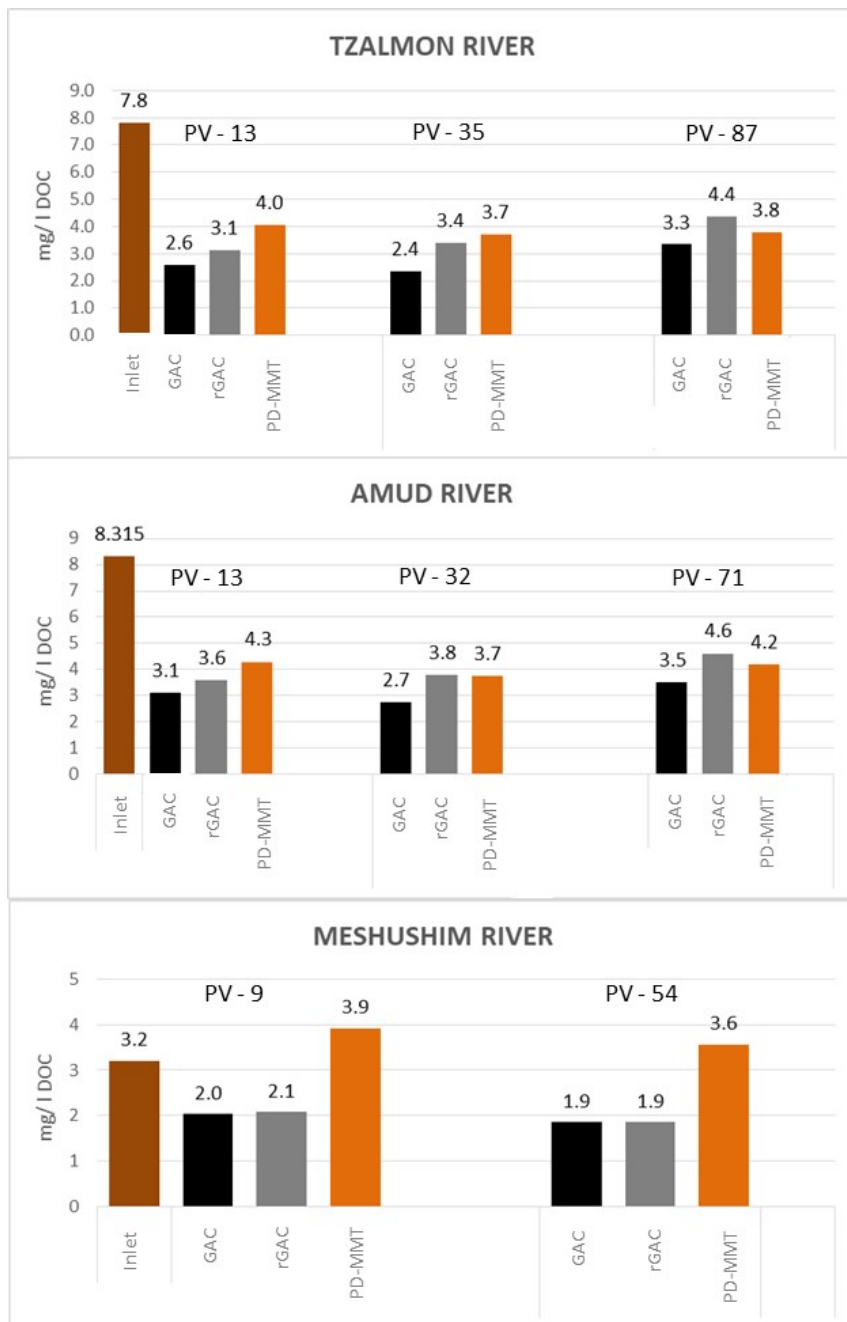


Figure S3. Removal of DOM measured as DOC (mg C L^{-1}) from (a) Tzalmon, (b) Amud, and (c) Meshushim by granular activated carbon (GAC), regenerated GAC (rGAC), and pDADMAC-montmorillonite composite (PD-MMT) at several passed water volumes (denoted as PV) along the adsorption through column experiments. Inlet concentration shows the DOC concentration of the stream water sample.

In all cases, the use of GAC gave the best results for removing DOC, while the use of PD-MMT resulted in lower removal, especially from Meshushim stream, which had DOM with the lowest $SUVA_{254}$ from those tested here. These data are used in Table 1 in the main text.

6. Effect of EBCT on HA removal by PD composite

The effect of empty bed contact time (EBCT) on HA removal by the PD composite was studied. The studied EBCT values (4.5- 9 min) closely match values commonly used in adsorption processes at water treatment plants, and the background electrolyte conditions corresponding to EC 610 $\mu\text{S}/\text{cm}$ represent surface water with intermediate salt content.

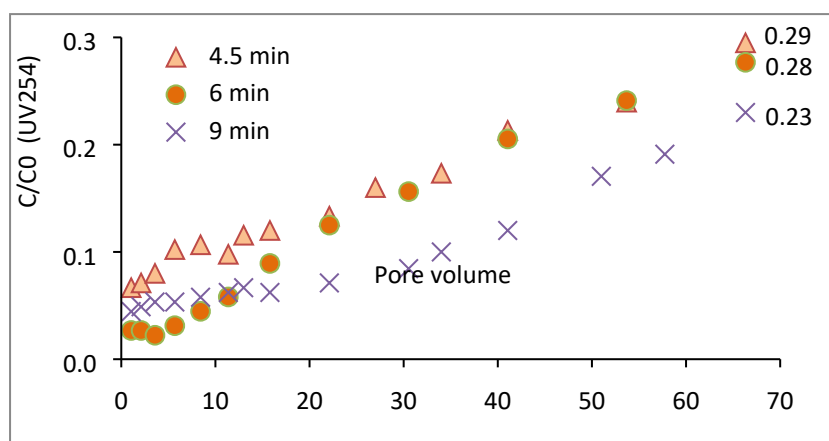


Figure S4. Removal of 8 mg L^{-1} HA (2.9 mg C L^{-1}) by PD-MMT (EC: $610 \mu\text{S}/\text{cm}$ - pH: 7.1) at three different EBCTs.

The removal of HA (as UV_{254}) by PD-MMT exhibited a moderate dependence on EBCT, which could indicate a highly kinetic adsorption of HA by PD-MMT or a relative high affinity of HA to PD-MMT.

7. Modeling HA and FA removal by different adsorbents

Figure 3 in the main text shows the predicted and measured adsorption of HA and FA from a mixture containing both. In Figure S5 we show separately the predicted removal of both HA and FA from the same mixture.

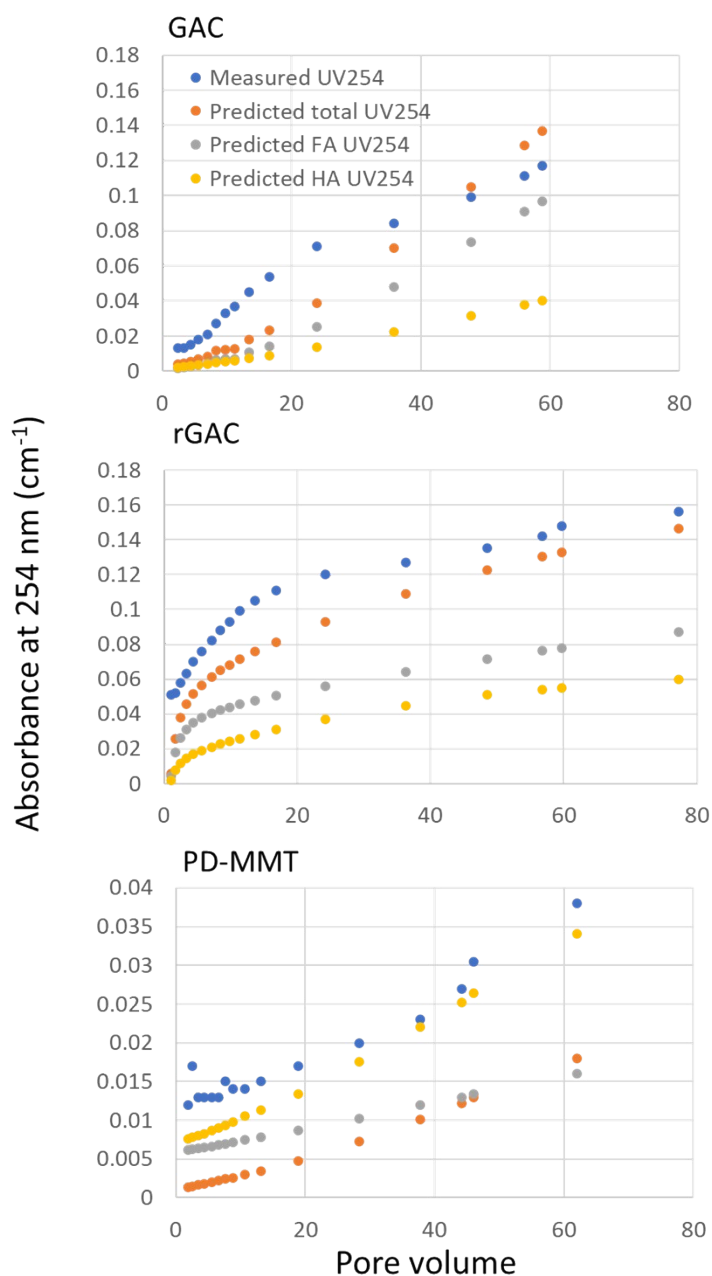


Figure S5: Measured and predicted absorbance at UV_{254} of water eluting from columns packed with GAC (A), rGAC (B) and PD-MMT (C). The solution used comprised of HA and FA (1, and 4 mg C L⁻¹, respectively).

References

- 1 C. Donau, *Donau Carbon*, 2010, **4**, 81–94.
- 2 O. B. Zusman, M. L. Kummel, J. M. De la Rosa and Y. G. Mishael, *Water Res.*, ,
DOI:10.1016/j.watres.2020.115920.