Fractionation of Suwannee River fulvic acid and Aldrich humic acid on α-Al_2O_3: spectroscopic evidences

Supplementary Information

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This section contains 10 pages, 2 tables and 3 figures.

The supplemental information gives: the sorption isotherm expressed as free HS concentration vs. total HS concentration; the kinetic evolution of SUVA and sorption for R_{PAHA} = 10.4; the normalized UV-Vis absorbance spectra of initial SRFA, PAHA, and supernatants after sorption on α-Al_2O_3 at pH 6.1 for different values of available sites ratio RHS; the initial spectrum of HS-covered α-Al_2O_3 sample at RSRFA = 10.9; illustration of the parallel evolution of the intensities of the ET and Bz bands, $A_{0,ET}/A_{0,Bz}$, and of the width ratio Δ_{ET}/Δ_{Bz}, and $^7F_2/^7F_1$ ratios vs. [Eu]/[HS] ($mol_{Eu}.mol_{site}^{-1}$) for original HS samples. The experimental data including pH, actual concentration of α Al_2O_3, SRFA, and PAHA, distribution coefficients are given as well as results of the fits and the fitting parameters and fitting uncertainties. Illustration of the parallel evolution of the intensities of the ET and Bz bands, $A_{0,ET}/A_{0,Bz}$, and of the width ratio Δ_{ET}/Δ_{Bz} are also given.

The expression of a Gaussian peak used is reminded:

$$A_i = A_{0,i} \exp\left(-4 \ln(2)\left(\frac{E_i - E_{0,i}}{\Delta_i}\right)^2\right) \qquad \text{(S1)},$$

where $A_{0,i}$ is the peak maximum, $E_{0,i}$ is the peak position, $E_i(\text{eV}) = \frac{1240}{\lambda_i(\text{nm})}$, and Δ_i is the full width at mid height.

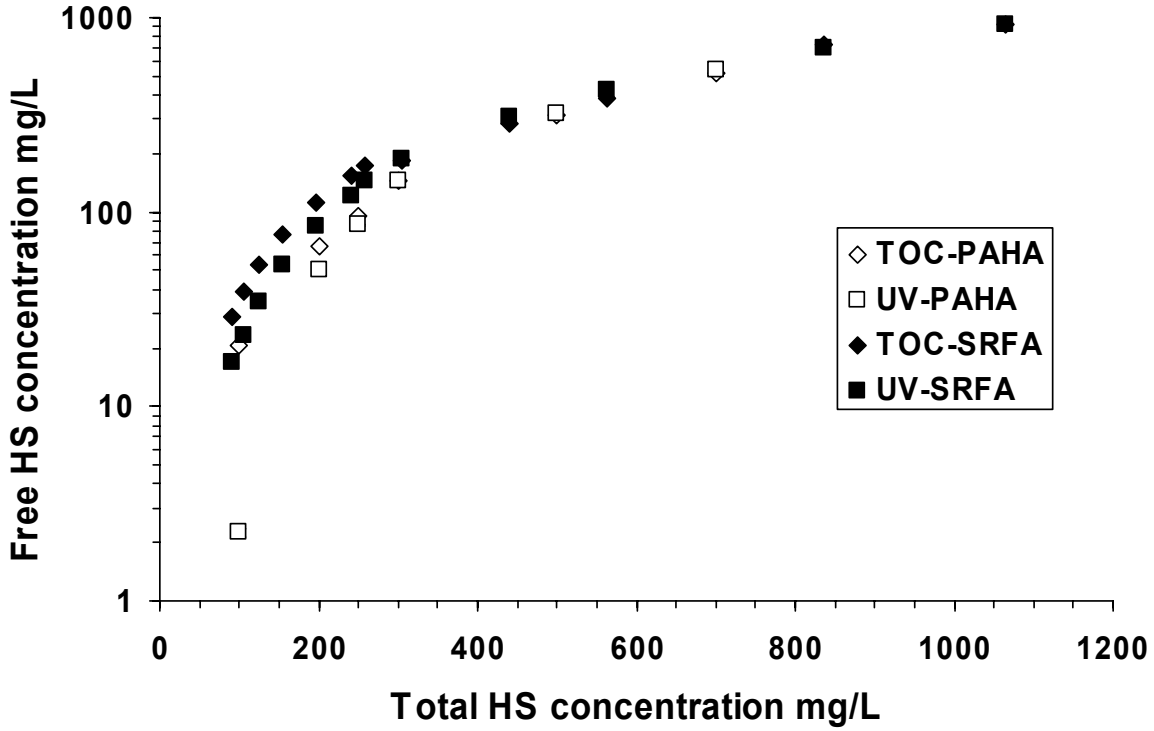
Under our conditions,

$$A_i = A_{0,LE} \exp\left(-4 \ln(2)\left(\frac{E_{LE} - E_{0,LE}}{\Delta_{LE}}\right)^2\right) + A_{0,Bz} \exp\left(-4 \ln(2)\left(\frac{E_{Bz} - E_{0,Bz}}{\Delta_{Bz}}\right)^2\right) +$$

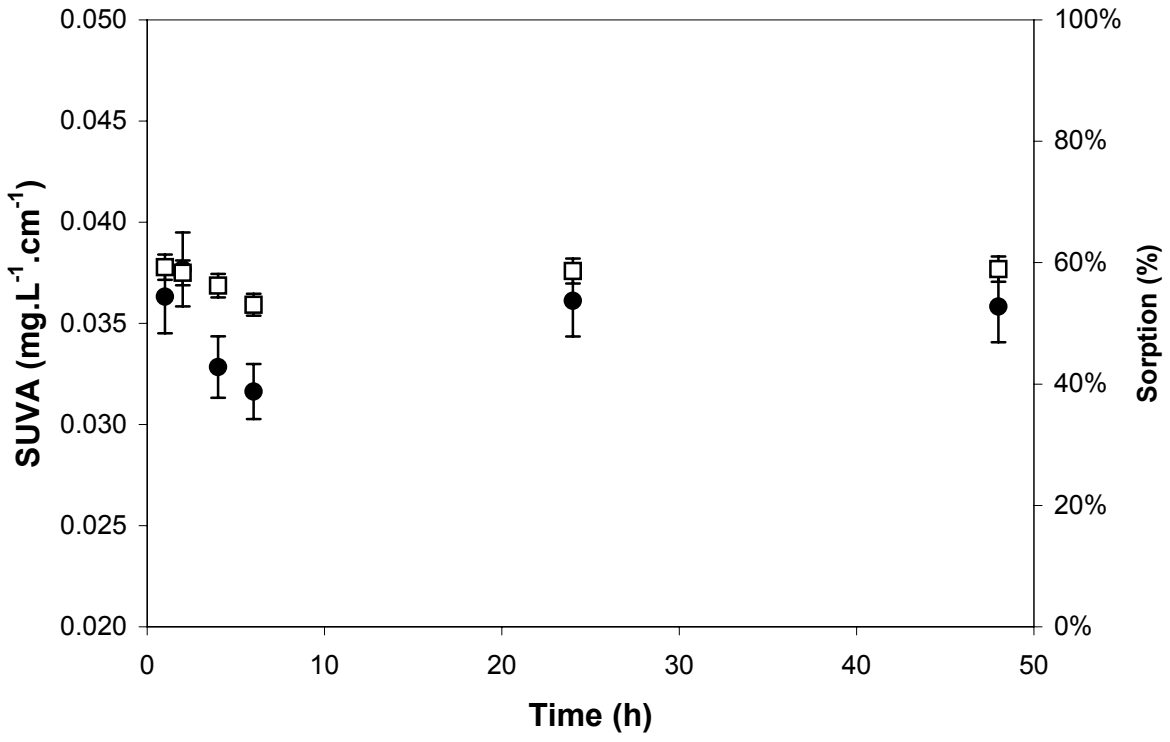
$$A_{0,ET} \exp\left(-4 \ln(2)\left(\frac{E_{ET} - E_{0,ET}}{\Delta_{ET}}\right)^2\right) \qquad \text{(S2)}$$

The adjustments are obtained from a non-linear regression fitting procedure. The uncertainties are obtained from the SolverAid maco in de Levie (How to use Excel in analytical chemistry and in general scientific data analysis; Cambridge University Press: Cambridge, U.K., 2001). The determination coefficient r^2, and the reduced determination coefficient r^2_a, are obtained from:

$$r^2 = \frac{\sum_i (y_i - \bar{y})^2 - \sum_i (y_i - \hat{y}_i)^2}{\sum_i (y_i - \bar{y})^2} \qquad r^2_a = 1 - (1 - r^2)\frac{n-1}{n-p}$$

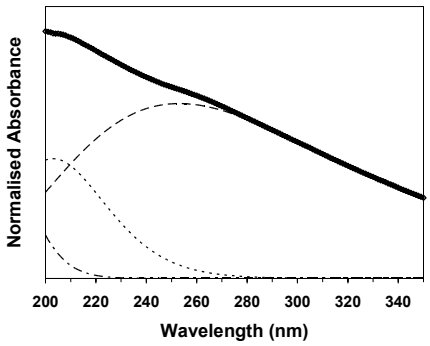


a

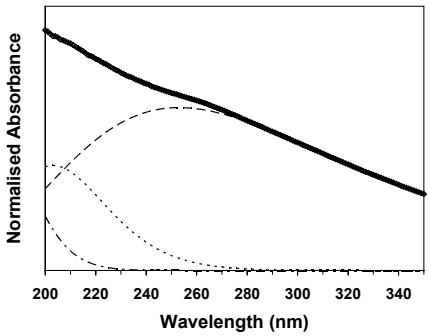


b

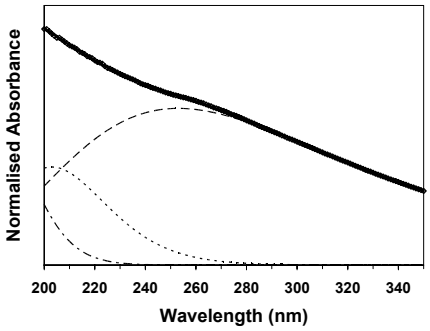
Figure S1: Sorption isotherms of PAHA (open symbols) and SRFA (closed symbols) determined from UV-Vis calibration (square) or TOC calibration (diamonds) (a), and kinetic evolution of SUVA and sorption % for R = 10.4 (b).



PAHA



R = 24.8



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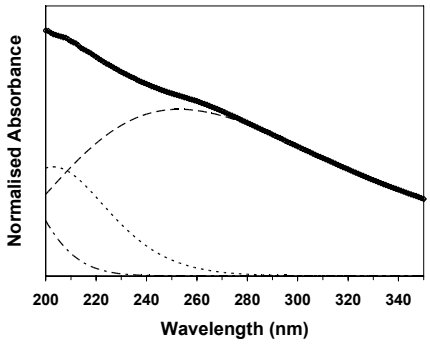

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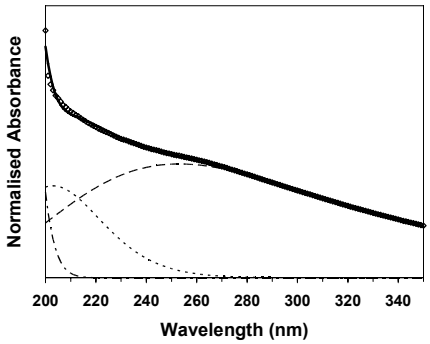
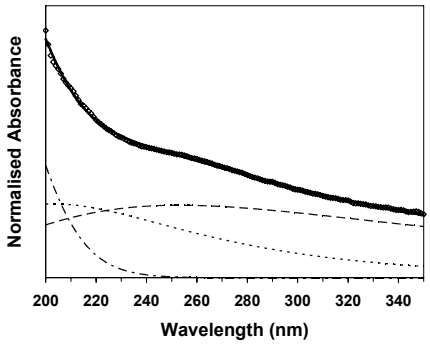


R = 6.9



R = 3.3

Figure S2: Normalized absorption spectra of PAHA and of supernatant after contact with α-Al_2O_3, at pH = 6.1 ± 0.1, for different R_{PAHA} ($mol.g^{-1}_{PAHA}/mol.g^{-1}_{\alpha\text{-}Al_2O_3}$) values, and fitting results using the decomposition in (29).

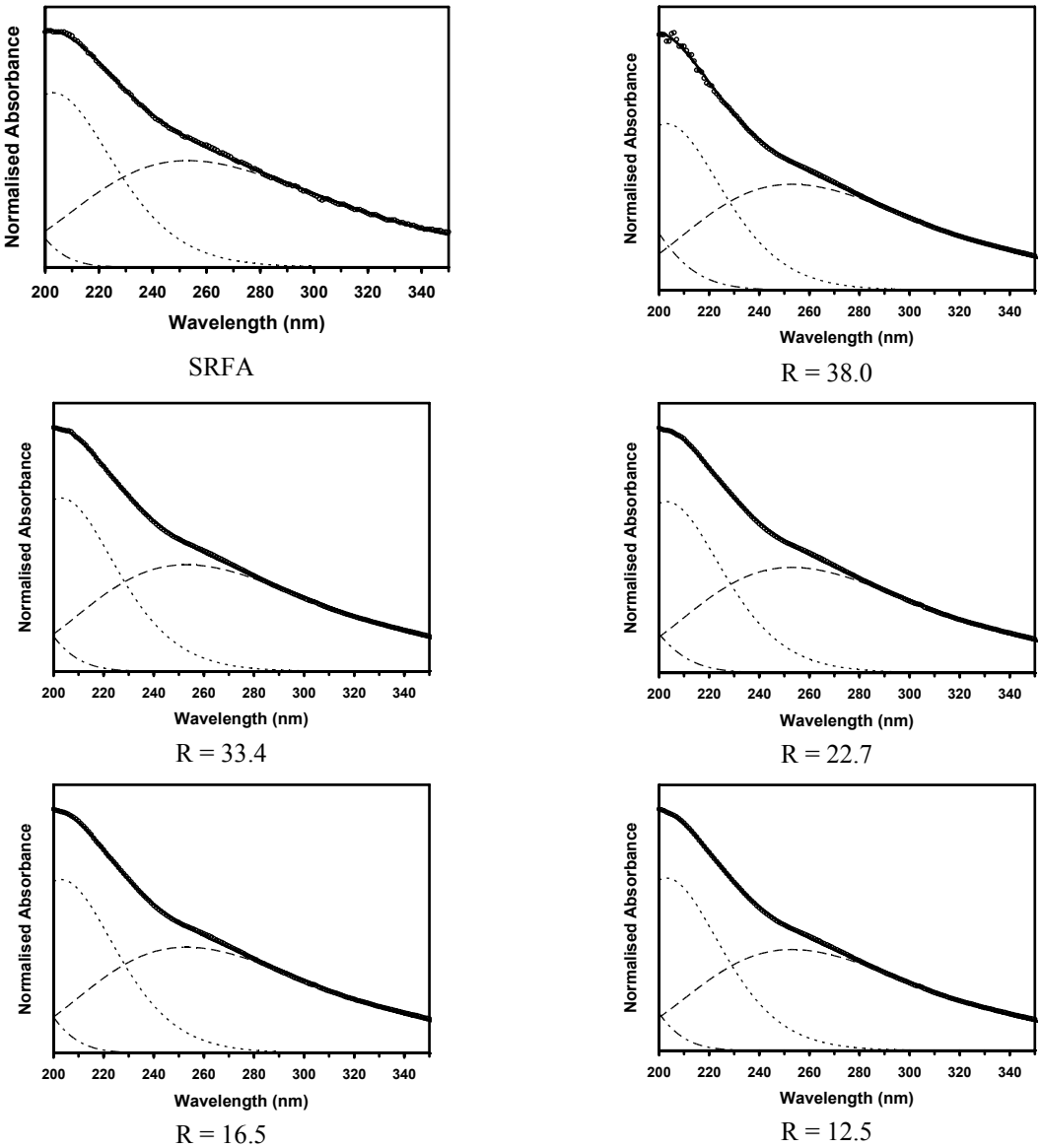
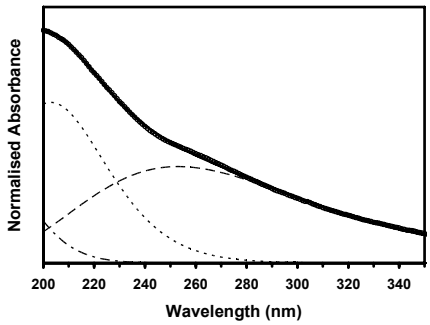
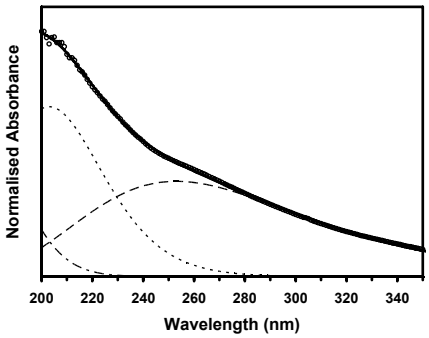


Figure S3: Normalized absorption spectra of SRFA and of supernatant after contact with α-Al_2O_3 at pH = 6.10 ± 0.10, for different R_{SRFA} ($mol.g^{-1}_{SRFA}/mol.g^{-1}_{\alpha\text{-}Al_2O_3}$) values, and fitting results using the decomposition in (29).



R = 10.9



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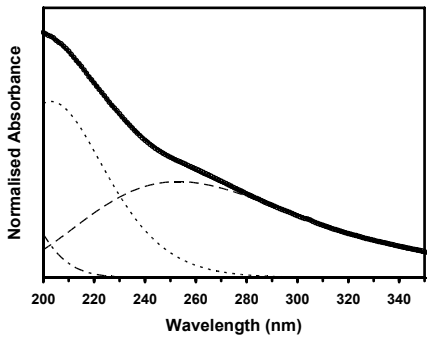

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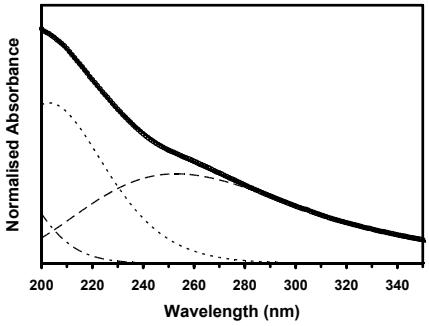
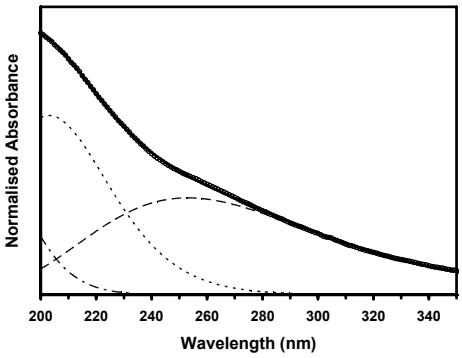
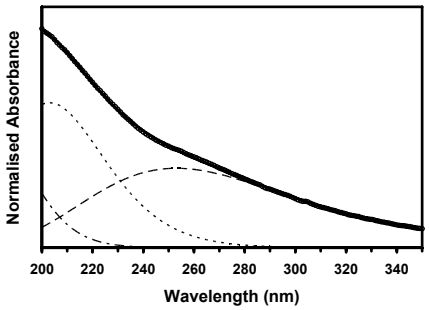


R = 4.0



R = 3.4



R = 2.9

Figure S3-continued: Normalized absorption spectra of SRFA and of supernatant after contact with α-Al_2O_3 at pH 6.1, for different R_{SRFA} ($mol.g^{-1}_{SRFA}/mol.g^{-1}_{\alpha\text{-}Al_2O_3}$) values, and fitting results using the decomposition in (29).

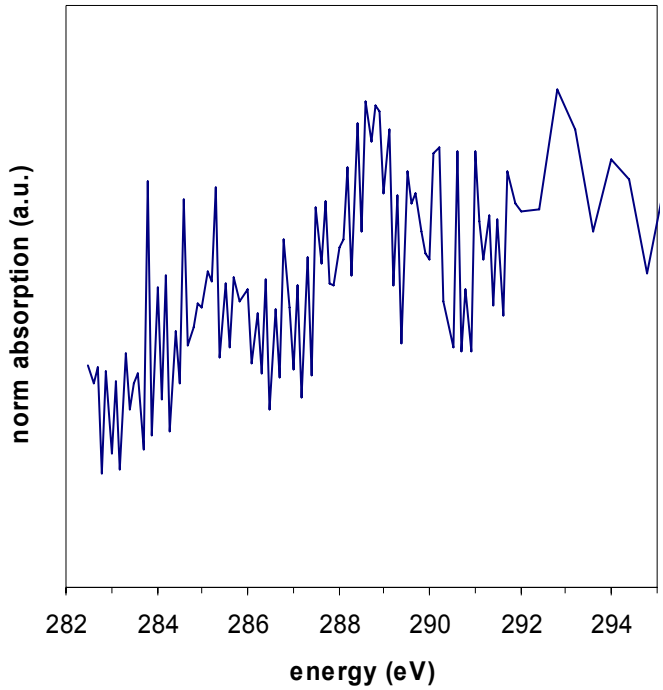


Figure S4: C(1s) NEXAFS spectrum of HS-covered α-Al_2O_3 at R_{SRFA} = 10.9 before smoothing, pH 6.1, *I*=0.1 M

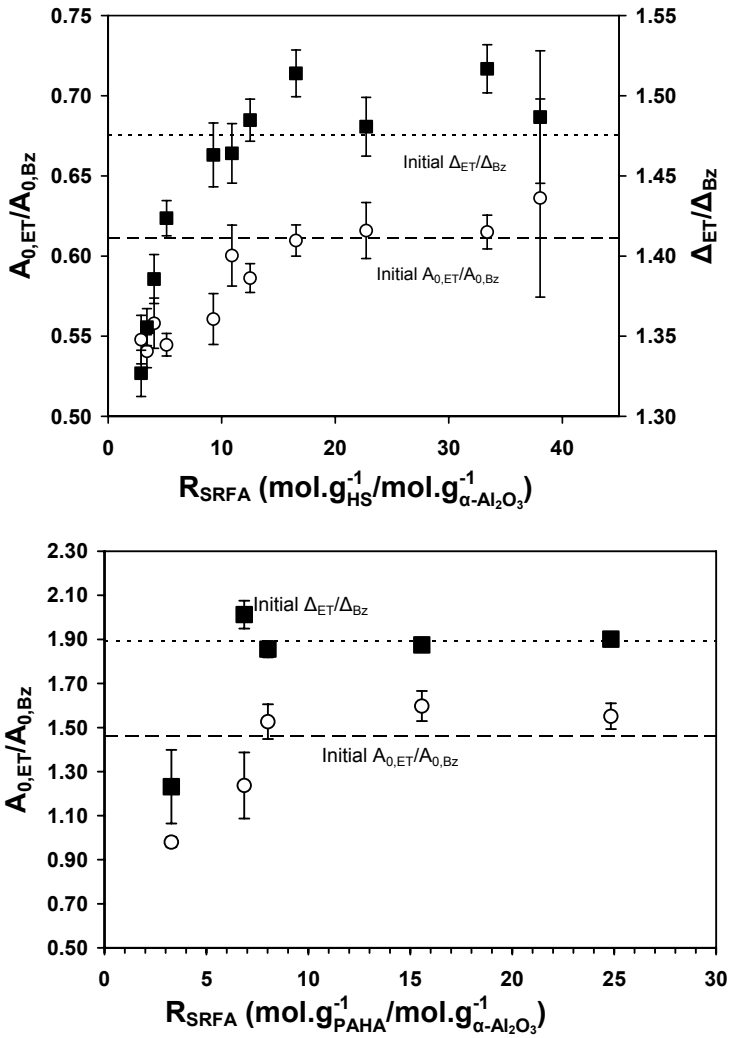


Figure S5: The $A_{0,ET}/A_{0,Bz}$ (○) and Δ_{ET}/Δ_{Bz} (■) values for different R_{HS} at pH 6.1 from Table S3 and S4.

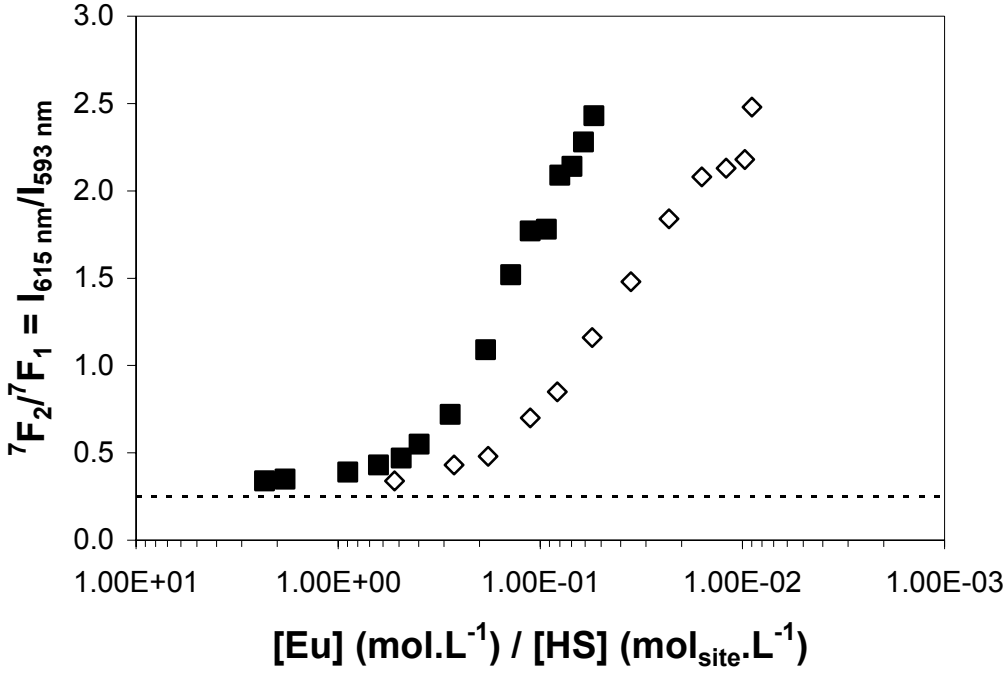


Figure S6: Comparison of $^7F_2/^7F_1$ ratios for PAHA (closed squares) and SRFA (open diamonds).

Table S1: Experimental data for the sorption of PAHA on α-Al_2O_3, at pH 6.1 and I = 0.1 m.

pH	$C_{\alpha\text{-}Al_2O_3}$ $g.L^{-1}$	$Q_{\alpha\text{-}Al_2O_3}$ $\mu mol.g^{-1}_{\alpha\text{-}Al_2O_3}$	[PAHA] $mg.L^{-1}$	Q_{PAHA} $mmol.g^{-1}_{PAHA}$	R_{PAHA} $mol.g^{-1}_{PAHA}$ $/mol.g^{-1}_{\alpha\text{-}Al_2O_3}$
6.09	9.97	10.14	99.3	3.34	3.3
6.13	10.20	9.69	201.5	3.36	6.9
6.07	10.13	10.24	249.5	3.33	8.0
6.11	9.99	9.78	301.0	3.36	10.4
6.04	10.12	10.52	499.1	3.32	15.6
6.16	10.09	9.42	700.5	3.37	24.8
	$[HS_{TOC}]_{free}$ $mg.L^{-1}$	$\log {}^{TOC}R_d$	$[HS_{UV}]_{free}$ $mg.L^{-1}$	$\log {}^{UV}R_d$	
6.09	20.8 ± 0.2	2.58 ± 0.04	2.2 ± 0.1	3.64 ± 0.02	
6.13	66.7 ± 0.6	2.30 ± 0.02	50.4 ± 0.4	2.47 ± 0.01	
6.07	95.3 ± 0.8	2.20 ± 0.02	85.8 ± 0.8	2.28 ± 0.01	
6.11	145.2 ± 1.2	2.03 ± 0.02	145.6 ± 1.0	2.03 ± 0.01	
6.04	318.2 ± 2.7	1.75 ± 0.02	323.3 ± 2.5	1.73 ± 0.02	
6.16	515.9 ± 4.3	1.55 ± 0.02	537.6 ± 4.4	1.48 ± 0.04	

Table S2: Experimental data for the sorption of SRFA on α-$_{Al2O3}$, at pH 6.1 and I = 0.1 m

pH	$C_{\alpha\text{-}Al_2O_3}$ $g.L^{-1}$	$Q_{\alpha\text{-}Al_2O_3}$ $\mu mol.g^{-1}_{\alpha\text{-}Al_2O_3}$	[SRFA] $mg.L^{-1}$	Q_{SRFA} $mmol.g^{-1}_{SRFA}$	R_{SRFA} $mol.g^{-1}_{SRFA}$ $/mol.g^{-1}_{\alpha\text{-}Al_2O_3}$
6.18	18.30	9.25	91.5	5.36	2.9
6.08	16.24	10.14	105.6	5.32	3.4
6.04	15.73	10.52	125.9	5.31	4.0
6.06	15.36	10.33	153.6	5.31	5.1
6.05	15.68	10.42	196.0	5.31	6.4
6.06	16.06	10.33	240.8	5.31	7.7
6.09	14.80	10.05	259.0	5.32	9.3
6.12	15.27	9.78	305.3	5.33	10.9
6.13	14.64	9.69	439.3	5.34	16.5
6.16	14.07	9.42	562.6	5.35	22.7
6.14	13.93	9.60	835.7	5.34	33.4
6.06	14.40	10.33	1065.5	5.31	38.0
pH	$[HS_{TOC}]_{free}$ $mg.L^{-1}$	$\log {}^{TOC}R_d$	$[HS_{UV}]_{free}$ $mg.L^{-1}$	$\log {}^{UV}R_d$	
6.18	29.2 ± 1.7	2.07 ± 0.07	16.8 ± 2.3	2.39 ± 0.16	
6.08	39.1 ± 1.6	2.02 ± 0.05	23.3 ± 2.2	2.34 ± 0.11	
6.04	53.7 ± 1.6	1.93 ± 0.04	34.3 ± 2.0	2.23 ± 0.07	
6.06	76.0 ± 1.6	1.82 ± 0.03	53.1 ± 1.8	2.09 ± 0.04	
6.05	113.0 ± 1.8	1.67 ± 0.02	85.5 ± 1.9	1.92 ± 0.03	
6.06	153.7 ± 2.2	1.55 ± 0.02	121.8 ± 2.5	1.78 ± 0.02	
6.09	175.1 ± 2.5	1.51 ± 0.02	145.5 ± 10.3	1.73 ± 0.09	
6.12	183.8 ± 8.2	1.64 ± 0.05	186.5 ± 9.8	1.62 ± 0.06	
6.13	286.0 ± 7.9	1.56 ± 0.03	311.5 ± 20.4	1.45 ± 0.08	
6.16	387.0 ± 7.9	1.51 ± 0.02	424.1 ± 19.0	1.37 ± 0.05	
6.14	725.4 ± 23.8	1.04 ± 0.04	705.3 ± 18.1	1.12 ± 0.03	
6.06	922.1 ± 23.5	1.03 ± 0.03	917.5 ± 19.9	1.06 ± 0.03	

Table S3: Parameters obtained from the fitting in Figure S2 to Equation S2 for PAHA.

R	$A_{0,LE} \pm \sigma$	$A_{0,Bz} \pm \sigma$	$A_{0,ET} \pm \sigma$	$A_{0,ET}/A_{0,Bz} \pm \sigma$
PAHA	$0.55_6 \pm 0.02_2$	$0.48_5 \pm 0.00_4$	$0.70_8 \pm 0.00_1$	$1.46_0 \pm 0.01_3$
3.3	$0.91_0 \pm 0.00_5$	$0.29_9 \pm 0.00_2$	$0.29_3 \pm 0.00_3$	$0.98_0 \pm 0.01_2$
6.9	$5.92_3 \pm 3.71_4$	$0.37_2 \pm 0.02_2$	$0.46_0 \pm 0.00_9$	$1.23_7 \pm 0.07_7$
8.0	$0.53_1 \pm 0.01_4$	$0.44_5 \pm 0.01_2$	$0.67_9 \pm 0.00_1$	$1.52_7 \pm 0.04_0$
15.6	$0.63_7 \pm 0.00_9$	$0.41_6 \pm 0.00_9$	$0.66_4 \pm 0.00_1$	$1.59_7 \pm 0.03_5$
24.8	$0.60_6 \pm 0.00_9$	$0.43_7 \pm 0.00_8$	$0.67_8 \pm 0.00_1$	$1.55_1 \pm 0.03_0$
	$\Delta_{LE} \pm \sigma$	$\Delta_{Bz} \pm \sigma$	$\Delta_{ET} \pm \sigma$	$r^2_a = 1 - (1 - r^2)\frac{n-1}{n-p}$ [a]
PAHA	$1.06_7 \pm 0.02_5$	$1.35_8 \pm 0.00_7$	$2.57_1 \pm 0.00_3$	0.9999
3.3	$1.37_5 \pm 0.04_2$	$3.11_7 \pm 0.19_8$	$3.83_9 \pm 0.10_5$	0.9986
6.9	$0.68_1 \pm 0.01_8$	$1.25_7 \pm 0.01_8$	$2.53_0 \pm 0.01_7$	0.9968
8.0	$1.23_8 \pm 0.05_0$	$1.38_0 \pm 0.01_4$	$2.56_1 \pm 0.00_5$	0.9998
15.6	$1.20_5 \pm 0.03_3$	$1.39_4 \pm 0.01_2$	$2.61_3 \pm 0.00_4$	0.9999
24.8	$1.15_6 \pm 0._{033}$	$1.369 \pm 0.01_1$	$2.60_3 \pm 0.00_3$	0.9999

[a] n = 151 data points for each spectrum; p = 6 fitting parameters being $A_{0,LE}$, Δ_{LE}, $A_{0,Bz}$, Δ_{Bz}, $A_{0,ET}$, and Δ_{ET}.

Table S4: Parameters obtained from the fitting of the experimental points in Figure S3 to Equation S2 for SRFA.

R	$A_{0,LE} \pm \sigma$	$A_{0,Bz} \pm \sigma$	$A_{0,ET} \pm \sigma$	$A_{0,ET}/A_{0,Bz} \pm \sigma$
SRFA	$0.42_1 \pm 0.00_4$	$0.73_7 \pm 0.00_4$	$0.45_1 \pm 0.00_4$	$0.61_1 \pm 0.00_7$
38.0	$0.45_4 \pm 0.01_8$	$0.64_7 \pm 0.06_3$	$0.41_1 \pm 0.00_3$	$0.63_6 \pm 0.06_2$
33.4	$0.40_2 \pm 0.03_7$	$0.71_1 \pm 0.01_2$	$0.43_7 \pm 0.00_2$	$0.61_5 \pm 0.01_1$
22.7	$0.37_5 \pm 0.02_4$	$0.69_9 \pm 0.02_0$	$0.43_0 \pm 0.00_2$	$0.61_6 \pm 0.01_8$
16.5	$0.43_4 \pm 0.04_2$	$0.71_2 \pm 0.01_1$	$0.43_4 \pm 0.00_2$	$0.61_0 \pm 0.01_0$
12.5	$0.44_3 \pm 0.03_5$	$0.71_5 \pm 0.01_1$	$0.41_9 \pm 0.00_2$	$0.58_6 \pm 0.00_9$
10.9	$0.41_7 \pm 0.02_2$	$0.69_0 \pm 0.02_2$	$0.41_4 \pm 0.00_2$	$0.60_0 \pm 0.01_9$
9.3	$0.50_3 \pm 0.04_1$	$0.69_3 \pm 0.01_9$	$0.38_9 \pm 0.00_2$	$0.56_1 \pm 0.01_6$
5.1	$0.52_5 \pm 0.03_3$	$0.71_8 \pm 0.00_9$	$0.39_1 \pm 0.00_1$	$0.54_5 \pm 0.00_7$
4.0	$0.48_5 \pm 0.01_7$	$0.68_4 \pm 0.01_9$	$0.38_2 \pm 0.00_2$	$0.55_8 \pm 0.01_6$
3.4	$0.48_5 \pm 0.01_7$	$0.68_5 \pm 0.01_3$	$0.37_0 \pm 0.00_1$	$0.54_1 \pm 0.01_0$
2.9	$0.54_0 \pm 0.01_8$	$0.66_2 \pm 0.01_8$	$0.36_3 \pm 0.00_2$	$0.54_8 \pm 0.01_5$
	$\Delta_{LE} \pm \sigma$	$\Delta_{Bz} \pm \sigma$	$\Delta_{ET} \pm \sigma$	$r^2_a = 1 - (1 - r^2)\frac{n-1}{n-p}$ [a]
SRFA	$1.02_9 \pm 0.17_8$	$1.40_8 \pm 0.04_0$	$2.07_7 \pm 0.02_9$	0.9996
38.0	$1.35_1 \pm 0.26_4$	$1.40_7 \pm 0.03_8$	$2.09_2 \pm 0.01_4$	0.9993
33.4	$1.13_1 \pm 0.08_3$	$1.39_0 \pm 0.01_3$	$2.10_8 \pm 0.00_8$	0.9997
22.7	$1.23_9 \pm 0.11_9$	$1.40_5 \pm 0.01_6$	$2.08_0 \pm 0.00_8$	0.9997
16.5	$1.10_4 \pm 0.07_6$	$1.37_7 \pm 0.01_2$	$2.08_5 \pm 0.00_8$	0.9997
12.5	$1.12_1 \pm 0.06_9$	$1.37_7 \pm 0.01_1$	$2.04_5 \pm 0.00_7$	0.9998
10.9	$1.25_4 \pm 0.11_4$	$1.39_3 \pm 0.01_7$	$2.03_9 \pm 0.00_8$	0.9998
9.3	$1.16_7 \pm 0.09_7$	$1.35_5 \pm 0.01_7$	$1.98_2 \pm 0.01_0$	0.9996
5.1	$1.10_3 \pm 0.05_0$	$1.36_6 \pm 0.01_0$	$1.94_4 \pm 0.00_6$	0.9998
4.0	$1.25_9 \pm 0.08_5$	$1.39_0 \pm 0.01_5$	$1.92_6 \pm 0.00_6$	0.9998
3.4	$1.21_8 \pm 0.05_5$	$1.38_8 \pm 0.01_1$	$1.88_1 \pm 0.00_5$	0.9999
2.9	$1.26_5 \pm 0.06_8$	$1.39_7 \pm 0.01_5$	$1.85_3 \pm 0._{006}$	0.9999

[a] n = 151 data points for each spectrum; p=6 fitting parameters being $A_{0,LE}$, Δ_{LE}, $A_{0,Bz}$, Δ_{Bz}, $A_{0,ET}$, and Δ_{ET}.