

Supporting Information

Enhanced sorption performances of natural zeolites modified with pH-fractionated humic acids for methylene blue water removal

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S1. Calibration curve and determination of the dimerization equilibrium constant

Owing to its cationic nature, MB tends to self-associate forming a variety of aggregates including dimers, trimers and tetramers. At MB concentration lower than 70 ppm, the presence of trimeric and tetrameric forms can be neglected [1] and the reaction scheme reduces to:



where $(MB)_2$ is the dimeric form of MB.

Let C_m and C_d represent the concentration (mol L⁻¹ also noted M) of MB in monomeric and dimeric form, respectively. The dimerization equilibrium constant (K) is given by:

$$K = \frac{C_d}{C_m^2} \quad (S2)$$

Moreover, the total concentration of MB (C) can be expressed as:

$$C = C_m + 2C_d = C_m + 2KC_m^2 \quad (S3)$$

The quadratic equation in C_m admits the following positive root:

$$C_m = \frac{-1 + \sqrt{1 + 8KC}}{4K} \quad (\text{S4})$$

According to the Lambert-Beer law, the total absorbance (A) of the solution by MB species can be written as:

$$A = \epsilon_m l C_m + \epsilon_d l C_d = \epsilon_m l C_m + \epsilon_d l \frac{C - C_m}{2} \quad (\text{S5})$$

where ϵ_m and ϵ_d are the molar extinction coefficients ($\text{M}^{-1} \text{cm}^{-1}$) of the monomer and dimer, respectively, whereas l (cm) is the optical length.

Using eq. (S4), we get the absorbance A as a function of the total concentration C :

$$A = \left(\epsilon_m - \frac{\epsilon_d}{2} \right) l \cdot \frac{-1 + \sqrt{1 + 8KC}}{4K} + \frac{\epsilon_d l C}{2} \quad (\text{S6})$$

Note that, due to a typing error, a slightly different equation was published by Spencer and Sutter [2]. This equation cannot be inverted analytically to determine the total MB concentration C from absorbance measurements, but it can be solved with respect to C_m using the definition of K :

$$A = \epsilon_m l C_m + \epsilon_d l K C_m^2 \quad (\text{S7})$$

The quadratic equation in C_m admits the following positive root:

$$C_m = \frac{-\epsilon_m l + \sqrt{(\epsilon_m l)^2 + 4\epsilon_d l K A}}{2\epsilon_d l K} \quad (\text{S8})$$

Equation (S8) allows to calculate C_d and C by means of Equations (S2) and (S5), respectively.

The calibration curve was obtained fitting the A vs C experimental data with Equation (S6) by non-linear regression analysis and the results are graphically displayed in Figure S1. The estimates of ϵ_m , ϵ_d and K at $T = 20^\circ \text{C}$ were found to be $(8.04 \pm 0.01) \times 10^{-4} \text{ M}^{-1} \text{cm}^{-1}$, $(4.0 \pm 0.1) \times 10^{-4} \text{ M}^{-1} \text{cm}^{-1}$ and $(7.38 \pm 0.01) \times 10^{-3} \text{ M}^{-1}$,

respectively; these values are in very good agreement with those reported in recent literature at similar temperature and wavelength [1]. For absorbance measurements at $T \neq 20\text{ }^{\circ}\text{C}$, the calibration curve was corrected taken the values of K from the literature [1].

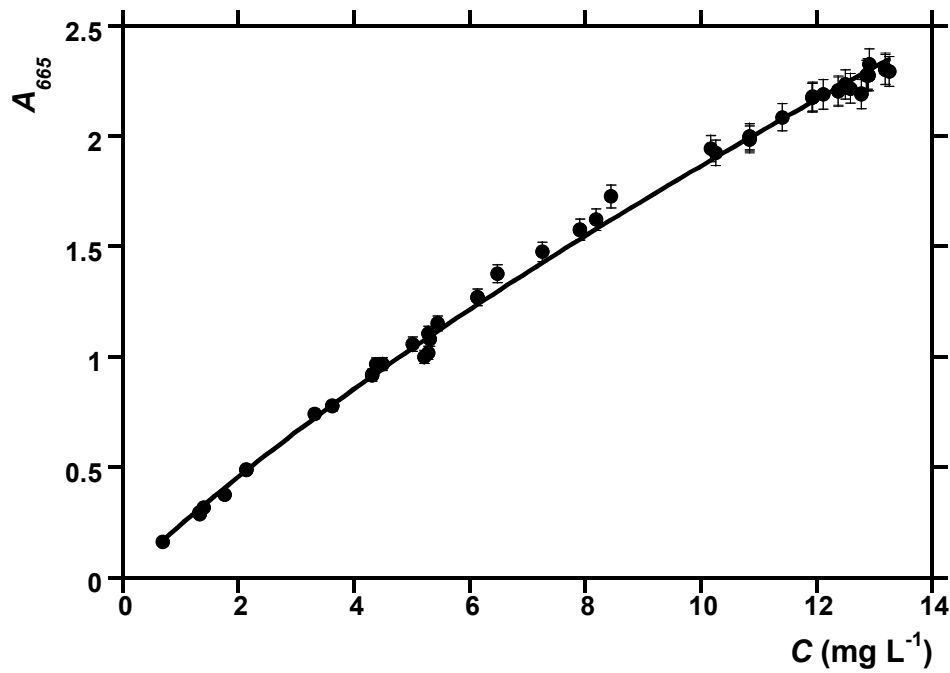


Figure S1. Plot of the absorbance at 665 nm (A_{665}) vs the total MB concentration in solution (C) at $T = 20\text{ }^{\circ}\text{C}$. The curve in figure was obtained via nonlinear curve-fitting using Equation (S6).

S2. Sorption modelling

Table S1. Kinetic parameters for the MB sorption onto NYT.

Model	k_1 (h^{-1})	k_2 (g mg^{-1} h^{-1})	B (h^{-1})	k_D (h^{-1})	Res. sum of squares	AICc
$C_0=11.9\text{ mg L}^{-1}$						
PFO	0.023 \pm 0.003	-	-	-	1.087	-8.23
PSO	-	0.0027	-	-	0.533	-14.63

			\pm 0.0005			
Boyd	-	-	0.0036	-	0.093	-30.36
			\pm 0.0009			
Vermeulen	-	-	-	0.0048	0.094	-30.25
			\pm 0.0008			
C ₀ =10.3 mg L ⁻¹						
PFO	0.025	-	-	-	1.314	-6.51
	\pm 0.003					
PSO	-	0.0025	-	-	0.438	-16.41
		\pm 0.0003				
Boyd	-	-	0.0061	-	0.056	-34.96
			\pm 0.0007			
Vermeulen	-	-	-	0.0070	0.044	-37.11
			\pm 0.0005			
C ₀ =7.9 mg L ⁻¹						
PFO	0.035	-	-	-	1.977	-2.84
	\pm 0.004					
PSO	-	0.0042	-	-	0.568	-14.06
		\pm 0.0006				
Boyd	-	-	0.0135	-	0.092	-30.42
			\pm 0.0009			
Vermeulen	-	-	-	0.013	0.151	-26.01
			\pm 0.001			
C ₀ =5.9 mg L ⁻¹						
PFO	0.023	-	-	-	1.699	-4.21
	\pm 0.003					
PSO	-	0.0025	-	-	0.901	-9.92
		\pm 0.0006				

Boyd	-	-	0.004 ± 0.001	-	0.164	-25.26
Vermeulen	-	-	-	0.005 ± 0.001	0.192	-23.81
C ₀ =4.1 mg L ⁻¹						
PFO	0.0192 ± 0.0001	-	-	-	0.020	-44.35
PSO	-	0.0013 ± 0.0001	-	-	0.195	-23.69
Boyd	-	-	0.0002 ± 0.0011	-	1.810	-3.64
Vermeulen	-	-	-	0.002 ± 0.002	1.720	-4.09
C ₀ =1.2 mg L ⁻¹						
PFO	0.037 ± 0.005	-	-	-	0.362	-18.11
PSO	-	0.012 ± 0.001	-	-	0.172	-24.84
Boyd	-	-	0.014 ± 0.003	-	0.104	-29.37
Vermeulen	-	-	-	0.013 ± 0.002	0.111	-28.79

Table S2. Kinetic parameters for the MB sorption onto different sorbents; initial aqueous concentration of MB = 11.9 mg L⁻¹; sorbent dosage = 0.29 g L⁻¹; pH = 7.4.

Model	k_1 (h ⁻¹)	k_2 (g mg ⁻¹ h ⁻¹)	B (h ⁻¹)	k_D (h ⁻¹)	Res. sum of squares	AICc
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NYT						
PFO	0.023	-	-	-	0.090	-37.11
	\pm					
	0.003					
PSO	-	0.0027	-	-	0.044	-44.37
		\pm				
		0.0005				
Boyd	-	-	0.0036	-	0.093	-30.36
			\pm			
			0.0009			
Vermeulen	-	-	-	0.0048	0.094	-30.25
				\pm		
				0.0008		
NYT-HA _{ref}						
PFO	0.09	-	-	-	10.543	33.73
	\pm					
	0.02					
PSO	-	0.005	-	-	4.555	29.53
		\pm				
		0.002				
Boyd	-	-	0.05	-	7.988	32.34
			\pm			
			0.02			

Vermeulen	-	-	-	0.05	7.696	32.16
				\pm		
				0.01		
NYT-HA ₃						
PFO	0.07	-	-	-	5.415	30.40
	\pm					
	0.02					
PSO	-	0.009 \pm	-	-	7.796	32.22
		0.008				
Boyd	-	-	0.05	-	6.240	31.11
			\pm			
			0.03			
Vermeulen	-	-	-	0.05	6.348	31.19
				\pm		
				0.02		
NYT-HA ₅						
PFO	0.035	-	-	-	1.016	22.03
	\pm					
	0.003					
PSO	-	0.0017	-	-	2.877	27.24
		\pm				
		0.0005				
Boyd	-	-	0.017	-	5.565	30.54

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\pm						
0.007						
Vermeulen	-	-	-	0.015	4.872	29.87
\pm						
0.006						
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NYT-HA ₇						
<hr/>						
PFO	0.108	-	-	-	1.241	23.03
\pm						
0.008						
PSO	-	0.0066	-	-	0.085	9.65
\pm						
0.0003						
Boyd	-	-	0.077	-	0.728	20.36
\pm						
0.006						
Vermeulen	-	-	-	0.070	0.616	19.53
\pm						
0.005						
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References

1. Fernández-Pérez, A.; Valdés-Solís, T.; Marbán, G. Visible light spectroscopic analysis of Methylene Blue in water; the resonance virtual equilibrium hypothesis. *Dyes Pigments* 2019, 161, 448-456, doi:10.1016/J.DYEPIG.2018.09.083.
2. Spencer, W.; Sutter, J.R. Kinetic study of the monomer-dimer equilibrium of methylene blue in aqueous solution. *J Phys Chem* 1979, 83, 1573–1576, doi: 10.1021/j100475a004