

Supplemental File

Effect of nitric acid oxidation on the surface of hydrochars to sorb methylene blue:

An adsorption mechanism comparison

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Supporting Information consists of 8 pages including this one.

There are four figures and one table.

1. Preparation of Hydrochar Samples: Hydrochars were prepared following a typical HTC process. In brief, approximately 15 g of the precursor (i.e. OP or D-glucose) was added in a 150 mL Teflon-lined autoclave containing 110 mL of DI-water. After a 24 h HTC process at 190 °C with a heating rate of 8 °C/min, the brown precipitate (i.e., hydrochar) was separated by filtration. The obtained hydrochar particles were washed with 0.1 M HCl and then repeatedly rinsed with DI-water until the filtrate reached a neutral pH. The particles were then dried at 105 °C for 24 h, ground and sieved to a size ranging 0.074 to 0.105 mm. The samples were stored in airtight bottles and used as pristine hydrochars without any further treatments. Hereinafter, hydrochars derived from OP and D-glucose were designated as OPH and GH, respectively.

For the production of oxidized-hydrochars, different concentrations of nitric acid (HNO₃) and hydrogen peroxide (H₂O₂) were used as the modification reagents: 1 g of the GH or OPH was added to 30 mL of 30 % (w/w), 50 % (w/w) and 70 % (w/w) of HNO₃ and H₂O₂ solution, respectively, and reacted at room temperature for 4 h; after the oxidation process, the samples were washed with DI-water and dried overnight at 105 °C. The modified samples were referred as mGH and mOPH, respectively (**Fig. S1**).

2. Effect of pH of the MB solution on λ_{\max} values (without adsorbent): The MB concentration in solution was determined using ultraviolet-visible spectrophotometry (Genesys 10S UV-VIS, Thermo Scientific) at maximum wavelength of 665 nm (**Fig. S2**).

3. Result and discussion

Adsorption kinetics

The adsorption kinetics were carried out at 30 °C and pH 7.0 with an initial MB concentration of 620 mg/L. Results of the adsorption kinetics were evaluated based on the non-linearized forms of the pseudo-first-order model (Corbett, 1972) and pseudo-second-order model (Ho and McKay, 1999) as expressed in Equations (1) and (2) respectively,

$$\text{Pseudo-first order: } q_t = q_e(1 - e^{-k_1 t}) \dots\dots\dots (1)$$

$$\text{Pseudo-second order: } q_t = \frac{k_2 q_e^2 t}{1 + k_2 q_e^2 t} \dots\dots\dots (2)$$

where k_1 (min^{-1}) and k_2 ($\text{g mg}^{-1} \text{min}^{-1}$) are the rate constants of the pseudo-first-order and pseudo-second-order models, respectively; q_e and q_t are the adsorbed amounts of MB on the hydrochar samples at equilibrium and at any time t (min), respectively. All experiments were carried out duplicate. The average values were indicated in this study.

Results of kinetic adsorption for all synthetic hydrochars (i.e., GH, mGH, OPH, and mOPH), carried out at pH 7.0 and 30 °C with an initial MB concentration of 620 mg/L, are illustrated in **(Fig. S3-a) and Table S1**. Basically, the adsorption of MB on hydrochars and oxidized-hydrochars exhibited these characteristics: (i) the adsorption phenomenon took place rapidly during the initial 10 to 15 min contact of MB and adsorbents (present in **Fig. S3-b**); (ii) in particular, as high as 68% of MB in solution was removed by mGH within the first 1 min contact, whereas GH only removed 5% of MB from the solution in this short period of time; (iii) the progress of MB-adsorption slowed down after 4 h of the contact interval.

The overall kinetic adsorption behavior can be evaluated by the pseudo-first-order and pseudo-second-order model expressed in Eqs. (1) and (2). As seen in **Table S1**, the pseudo-second-order model well fitted the kinetic data with high correlation coefficients (R^2) when compared with the pseudo-first-order model (i.e., 0.91 vs. 0.80 for GH; 0.96 vs. 0.89 for mGH; 0.92 vs. 0.84 for OPH; 0.94 vs. 0.88 for mOPH); further, the $q_{e,cal}$ values (in mg/g) calculated according to the pseudo-second-order model fitting were significantly close to the $q_{e,exp}$ values. Hence, the pseudo-second-order model is more suitable to describe the sorption kinetics of MB onto hydrochars in this study. The best fit of experimental data with the pseudo-second order model suggested that the adsorption process was highly relative to the concentration of adsorbate and the adsorbent can provide the more active sites (Bulut et al., 2008).

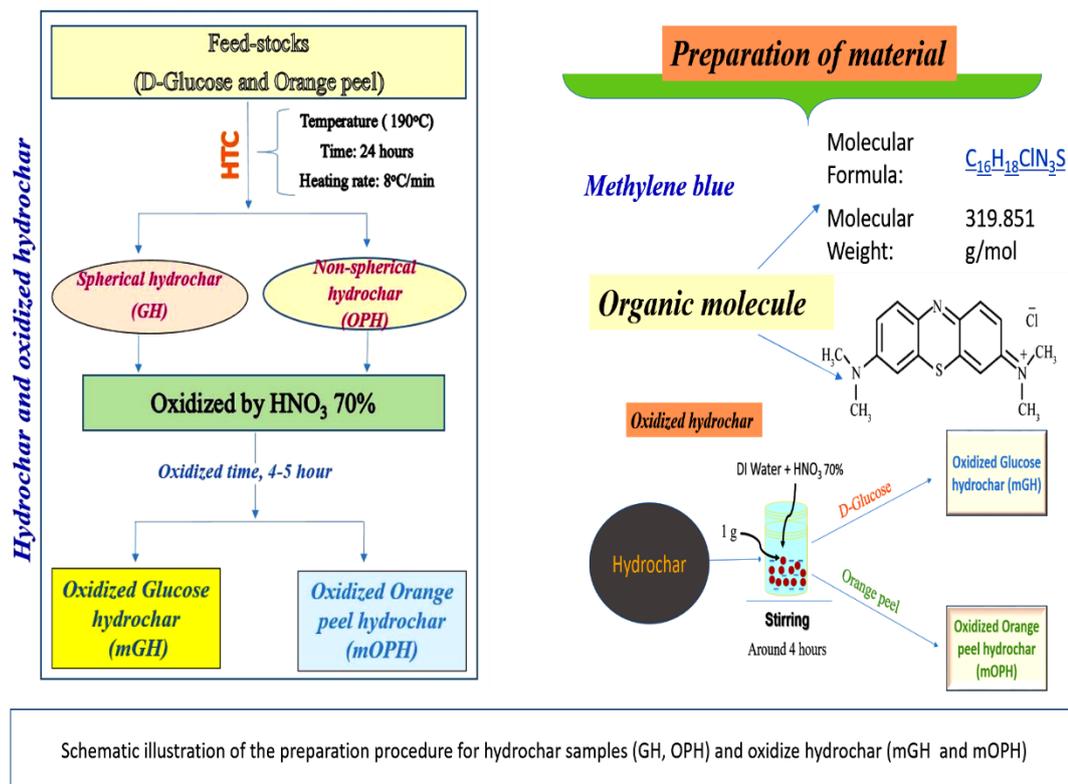


Figure-S1. Schematic illustration of the preparation procedure for hydrochar samples

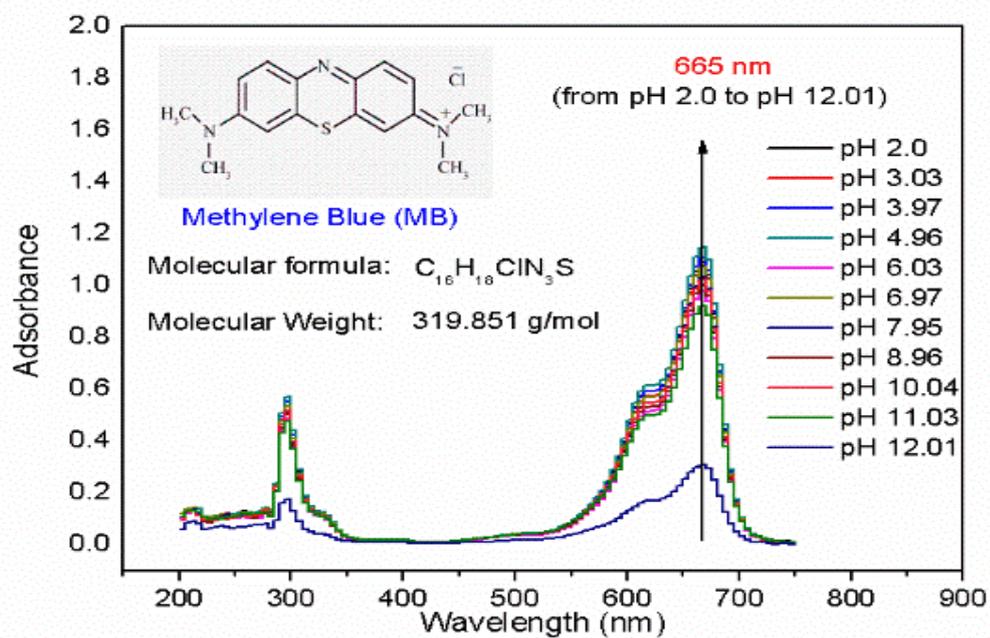


Figure-S2. Effect of pH of the MB solution on λ_{max} values (*without adsorbent*)

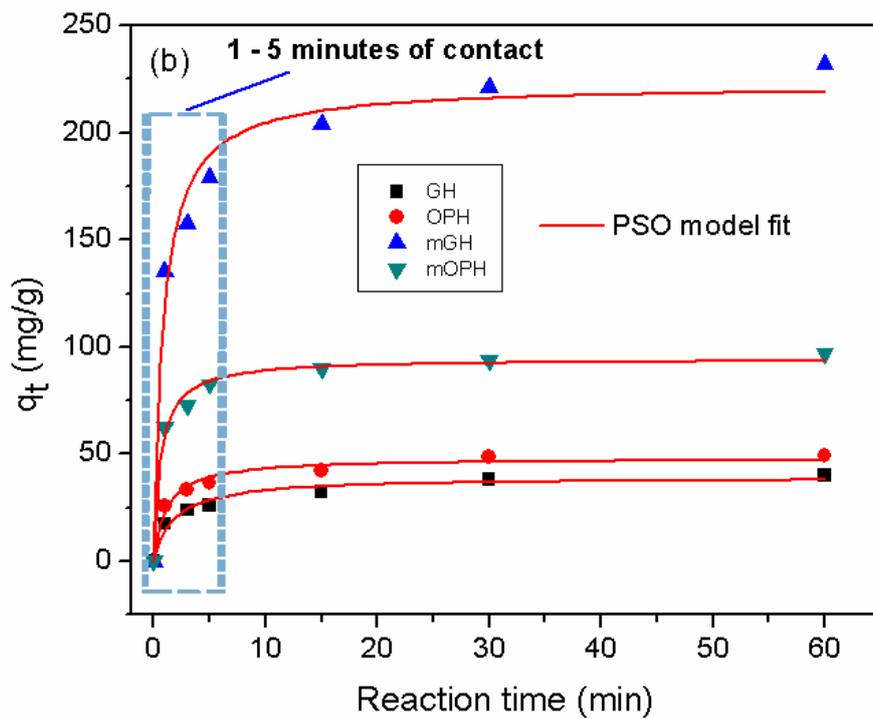
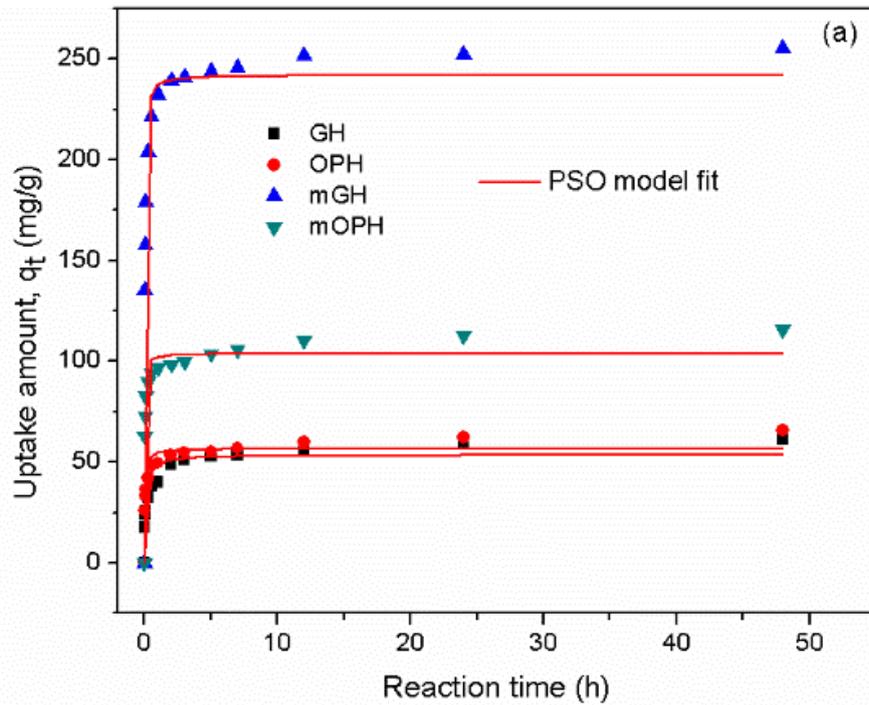


Figure-S3-a,b. Adsorption kinetic of MB dye adsorption onto GH, mGH, OPH and mOPH samples: (initial MB dye concentrations 620 mg/L, initial solution pH 7, temperature at 30 °C). *a-* reaction time calculated by hour, *b-* reaction time calculated by minute (around 60 minutes)

Table-S1. Corresponding kinetic parameters for MB adsorption onto the hydrochar samples.

Kinetic models		Pseudo-First order			Pseudo-Second order		
Sample	q_{e,exp}	q_{e,cal} = q_e(1 - e^{-k₁t})			q_{e,cal} = (k₂ q_e²t)/(1+ k₂ q_e²t)		
		q _{e,cal}	k ₁	R ²	q _{e, cal}	k ₂	R ²
GH	56.01	50.86	0.13	0.80	53.58	0.003	0.91
mGH	243.99	236.23	0.45	0.89	242.03	0.004	0.96
OPH	56.48	54.73	0.31	0.84	56.68	0.008	0.92
mOPH	102.46	101.26	0.60	0.88	103.88	0.010	0.94

References

- Bulut E, Özacar M and Şengil İA. (2008) Adsorption of malachite green onto bentonite: equilibrium and kinetic studies and process design. *Microporous and mesoporous materials* 115: 234-246.
- Corbett JF. (1972) Pseudo first-order kinetics. *Journal of Chemical Education* 49: 663.
- Ho Y-S and McKay G. (1999) Pseudo-second order model for sorption processes. *Process biochemistry* 34: 451-465.