Adsorptive removal of methylene blue and crystal violet onto micro-mesoporous Zr_3O/Activated carbon composite: A joint experimental and statistical modeling considerations

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Supporting information

Characterization methods

Differential thermal analyses (DTA) coupled with thermogravimetry (TG) were performed under air between 25 °C and 700 °C with a rate of 10 °C/min using a Shimadzu Instruments DTG-60 equipment. XRD patterns were collected using an Empyrean Panalytical diffractometer operating at 45 kV/35 mA, using CuKα radiation with Ni filter, and working in continuous mode with a step size of 0,013°. The Brunauer–Emmett–Teller (BET) surface area was determined by the nitrogen adsorption and desorption isotherm, pore size distribution and specific surface area were measured using an AUTOSORB-1 surface area and pore size analyzer at 77 K. Scanning electron microscopy (SEM) analyses were performed using FEI Quanta 200 field emission. The determination of chemical compositions was performed using Energy Dispersive Spectroscopy (EDS), in mode of sample surfaces scanning. Raman vibration spectra was performed using a spectrometer NRS-5100 model Jasco Raman spectrometer, using a CCD detector, a laser line of 532 nm and objective lens 100×, with a laser power of 1.6 mW. The Fourier Transform Infrared spectra of the composite was obtained in the region (400-4000 cm^{-1}) using a Shimadzu 4800S. Before analysis, a small amount of sample was dispersed in a matrix of KBr using weight ratio of (sample/KBr) =1/100 and then pressed to form transparent pellet. KBr was previously dried to

avoid interferences due to the presence of water. The spectra were scanned at resolution of 2.0 cm^{-1} and with 20 scanning.

Response surface methodology (RSM)

To examine and optimize the adsorption process of MB and CV onto Zr_3O/AC as a function of three independent variables, namely adsorbent dose (X_1), initial concentration (X_2) and contact time (X_3). Box-Benhken matrix (Bagheri et al., 2017) was used and presented in **Table 1S**. The experimental results were fitted to second-order polynomial regression equation **(Eq. 1)** (Subramaniam and Kumar Ponnusamy, 2015).

$$Y = a_0 + \sum_{i=1}^{n} a_i X_i + \sum_{i=1}^{n} a_{ii} X_i^2 + \sum_{i-1}^{n-1} \sum_{j-1}^{n} a_{ij} X_i X_j \qquad (1)$$

Where y is the predicted response variable; a_0 is the constant coefficient; a_i is the linear coefficients; a_{ii} is the quadratic coefficients; a_{ij} is the linear coefficients for the interaction between independent variables i and j; x_i and x_j are the coded independent parameters.

Table 1S. Independent parameters and response variables of matrix

S. No.	Variable	Name	-1	0	+1
1	X_1	Adsorbent dose (mg)	10.9	13	15.10
2	X_2	Initial dyes concentration (mg/L)	85.9	100	114.10
3	X_3	Contact time (min)	34.4	45	55.60

Run no.	Operating parameters			Rep. variable	
	Adsorbent dose	Initial dyes concentrations	Contact time	MB adsorption% onto Zr_3O/AC	CV adsorption% onto Zr_3O/AC
1	-1.00000	-1.00000	0.00000	99.15	88.83
2	1.00000	-1.00000	0.00000	99.49	97.92
3	-1.00000	1.00000	0.00000	98.62	85.02
4	1.00000	1.00000	0.00000	99.54	96.33
5	-1.00000	0.00000	-1.00000	98.54	85.73
6	1.00000	0.00000	-1.00000	99.50	96.90
7	-1.00000	0.00000	1.00000	98.99	87.12
8	1.00000	0.00000	1.00000	99.80	97.94
9	0.00000	-1.00000	-1.00000	99.52	99.13

10	0.00000	1.00000	-1.00000	99.44	99.09
11	0.00000	-1.00000	1.00000	99.61	97.45
12	0.00000	1.00000	1.00000	99.50	97.40
13	0.00000	0.00000	0.00000	99.45	92.30
14	0.00000	0.00000	0.00000	99.47	92.31
15	0.00000	0.00000	0.00000	99.50	92.19
16	0.00000	0.00000	0.00000	99.51	92.25
17	0.00000	0.00000	0.00000	99.53	92.13
18	0.00000	0.00000	0.00000	99.53	92.34

Figures

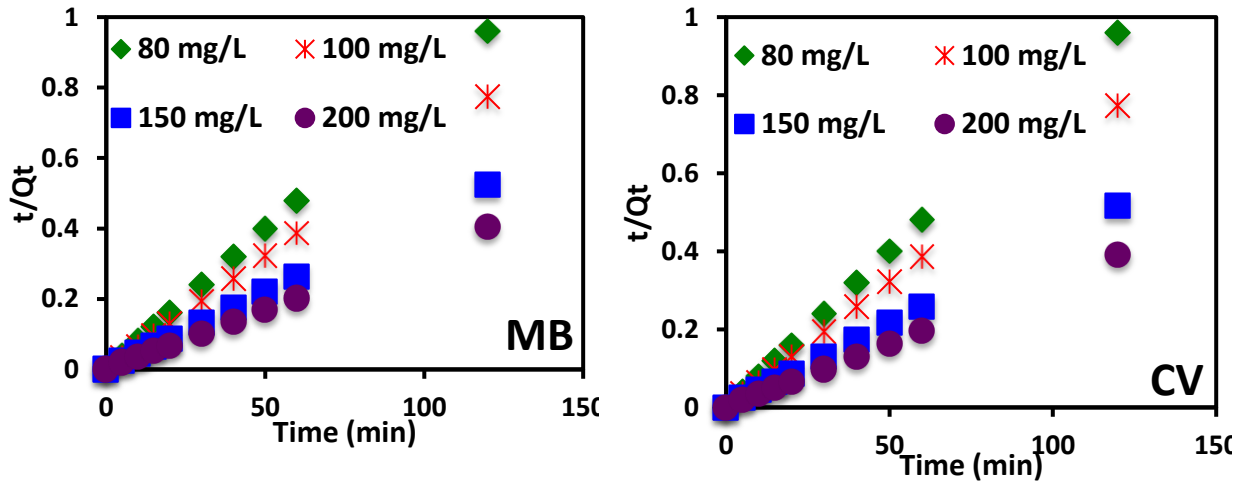

Fig. S1 - Linearized form of pseudo-second-order model for adsorption of both MB and CV dyes at different initial concentrations.

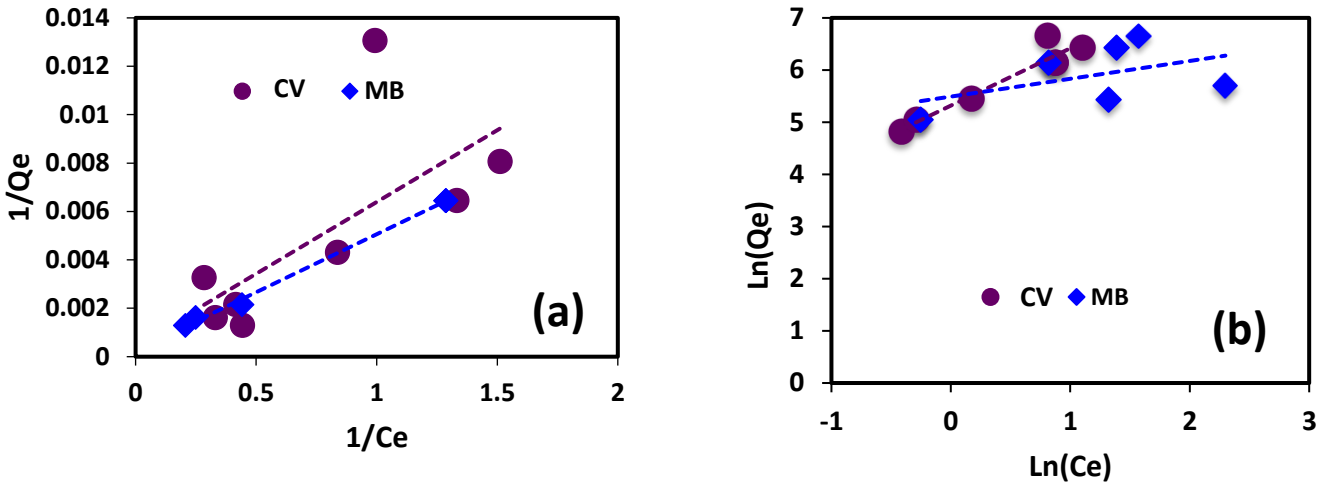

Fig. S2 - Linearized form of Langmuir (a) and Freundlich (b) models.

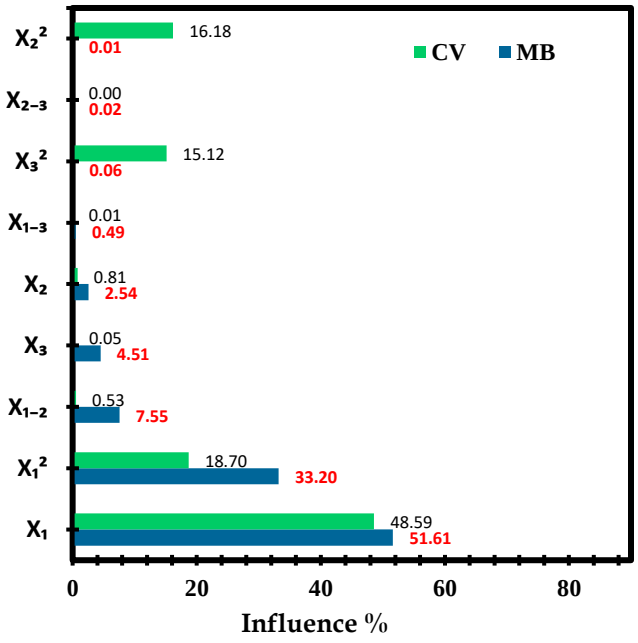

Fig. S3 - Pareto Chart

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Subramaniam, R., Kumar Ponnusamy, S., 2015. Novel adsorbent from agricultural waste (cashew NUT shell) for methylene blue dye removal: Optimization by response surface methodology. Water Resour. Ind. 11, 64–70. https://doi.org/10.1016/j.wri.2015.07.002