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Supporting information for manuscript

Simultaneous adsorption of ternary mixture of brilliant green, rhodamine B and methyl orange as artificial wastewater onto biochar from cocoa pod husk waste. Quantification of dyes using the derivative spectrophotometry method

Bryan M. Córdova*[a†], Jean P. Santa Cruz [b], Tony V. Ocampo M.[a, b], Ronny G. Huamani-Palomino[a], Angélica María Baena-Moncada*[c†]

[a] *Group of Biomaterials and Polymers, Faculty of Science, National University of Engineering. Av. Túpac Amaru 210, Lima 25, Lima - Peru.*

[b] *Laboratorio de Operaciones Unitarias, Facultad de Ingeniería Química y Textil, Av. Túpac Amaru 210, Rímac, Lima - Perú.*

[c] *Laboratorio de Investigación de Electroquímica Aplicada, Facultad de Ciencias de la Universidad Nacional de Ingeniería, Av. Túpac Amaru 210, Rímac, Lima - Perú.*

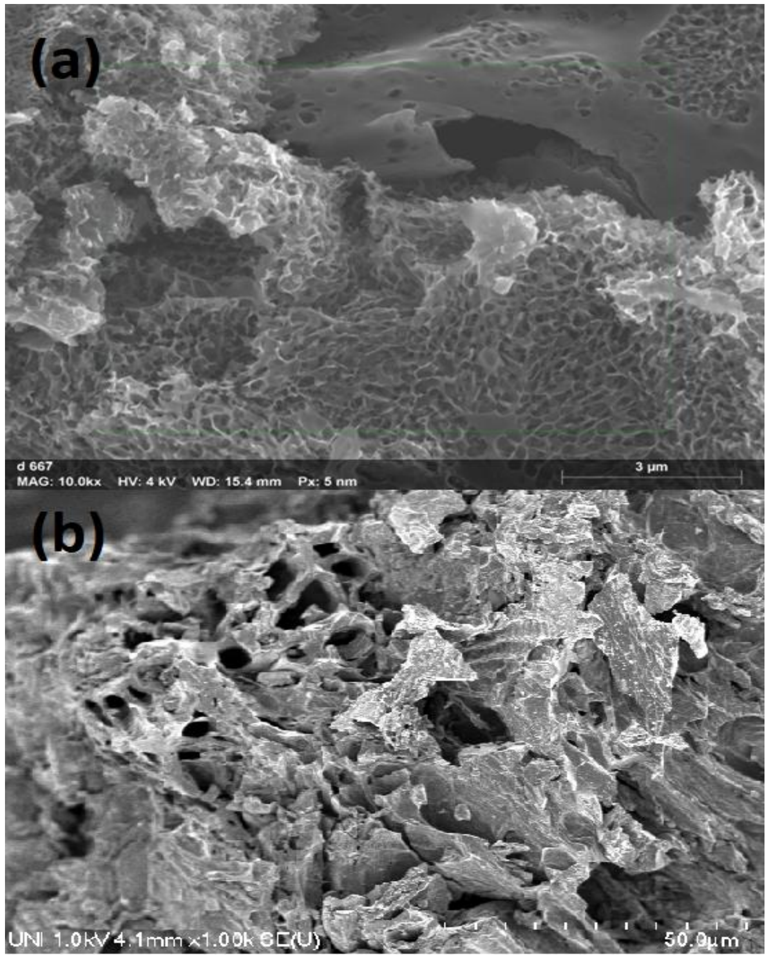

Fig. S1 FESEM image of AQ_1 and b) AQ_2.

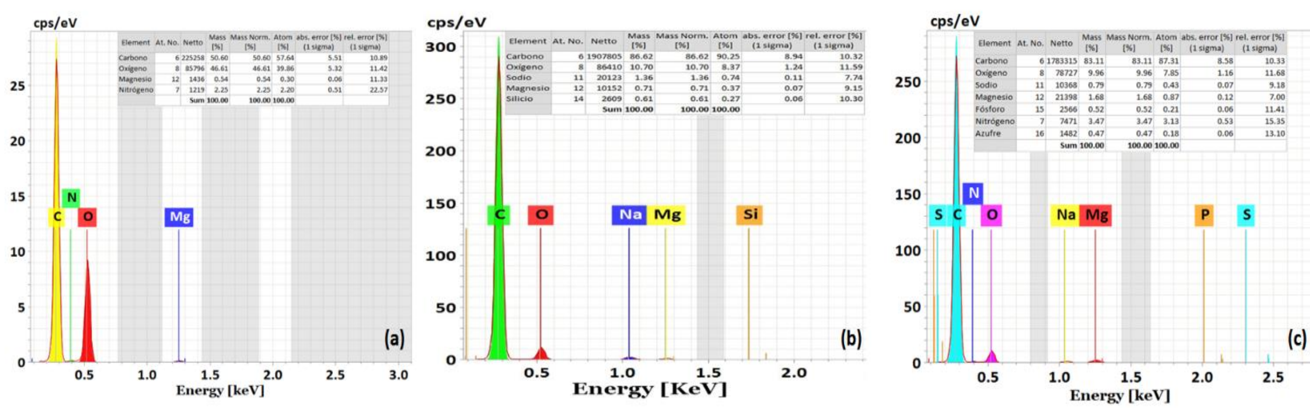

Fig. S2 Elemental composing obtained through EDS-mapping technique. (a) CPH, (b) AQ_1 and (c) AQ_2.

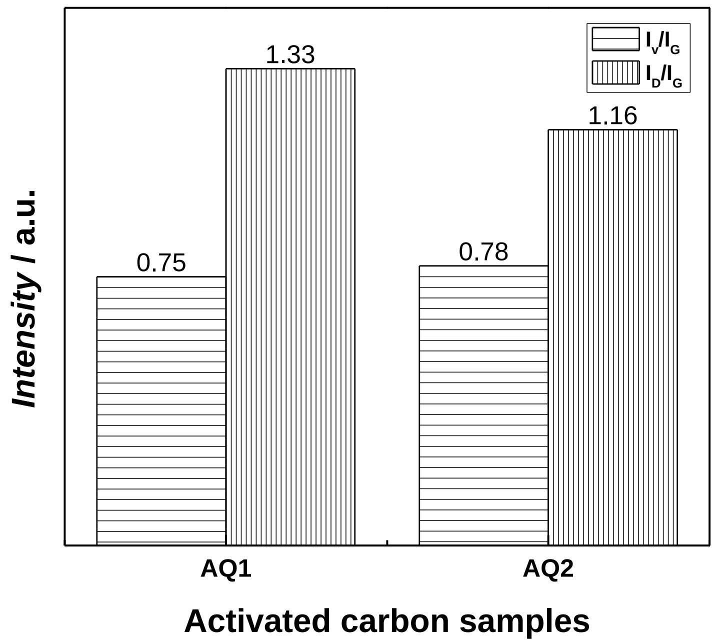

Fig. S3 Relation of ID/IG and IV/IG of AQ_1 (left) and AQ_2 (right).

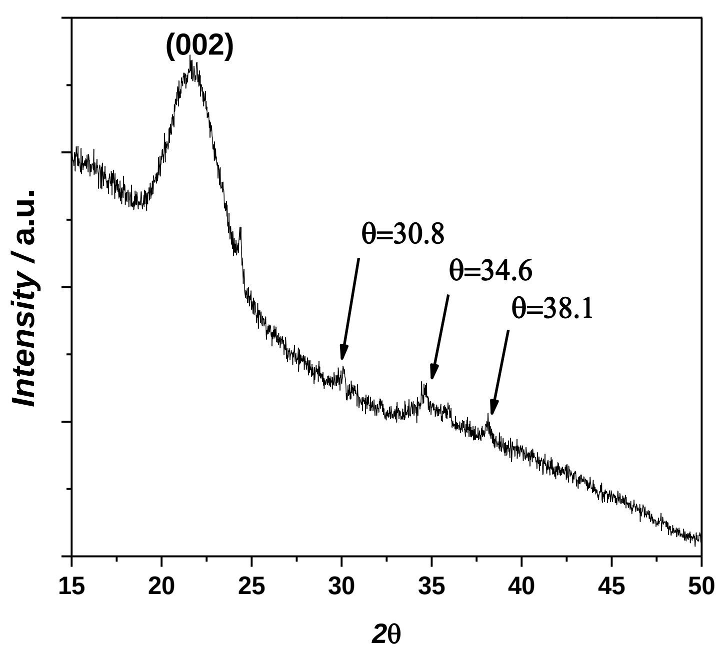

Fig. S4 XRD pattern of cocoa pod husk (CPH).

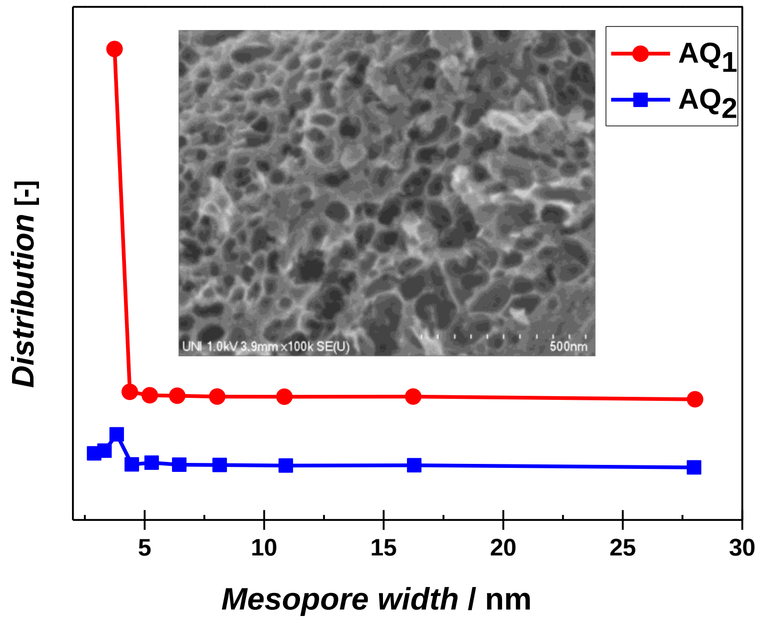

Fig. S5 Pore size distribution of AQ_1 and AQ_2 (honeycomb structure of AQ_1 shown in the inset).

Batch adsorption experiments

Based on the previous results, the biochar selected for the removal of ternary dye mixture composed of RB, BG and MO was AQ_1. In order to provide an ideal adsorbent for this kind of mixture (2 cationic dyes and 1 anionic dye), both biochars were tested in the removal of 10 mg L^{-1} solution of methylene blue (cationic dye) without any adjustment of pH. Probably, the porous structure generated by the one-step NaOH activation process can be directly associated with the production of biochars with high affinity towards cationic dyes since encouraging results were obtained through this activation method (Fig. S6). For this reason, AQ_1 was selected and used throughout the batch experiments in this work. The removal percentage (%R) and adsorption capacity (q_e) were calculated using Eq. (1) and Eq. (2):

$$\%R = \frac{(C_o - C_e)}{C_o} . 100 \qquad (1)$$

$$q_e = \frac{(C_o - C_e)}{m} . V \qquad (2)$$

Where C_o and C_e are the initial and equilibrium concentration (mg L^{-1}) of each dye in the mixture before and after adsorption procedure, respectively; V is the volume (L) and m is the amount of AQ_1 added to the artificial wastewater. All the experiments were performed at room temperature (25 ± 2 °C) using 10 mg of AQ_1, contact time of 24 h and agitation speed of 150 rpm. In certain experiments such as the initial concentration effect and isotherm experiments, concentration of dyes in artificial wastewater was varied, then, throughout the experiments the artificial wastewater contained 10 mg L^{-1} of each dye.

Fig. S6 Effect of AQ_1 (left) and AQ_2 (right) after the removal of 10 ppm methylene blue solution at room temperature (pH 7, agitation time of 24 h and agitation speed of 150 rpm).

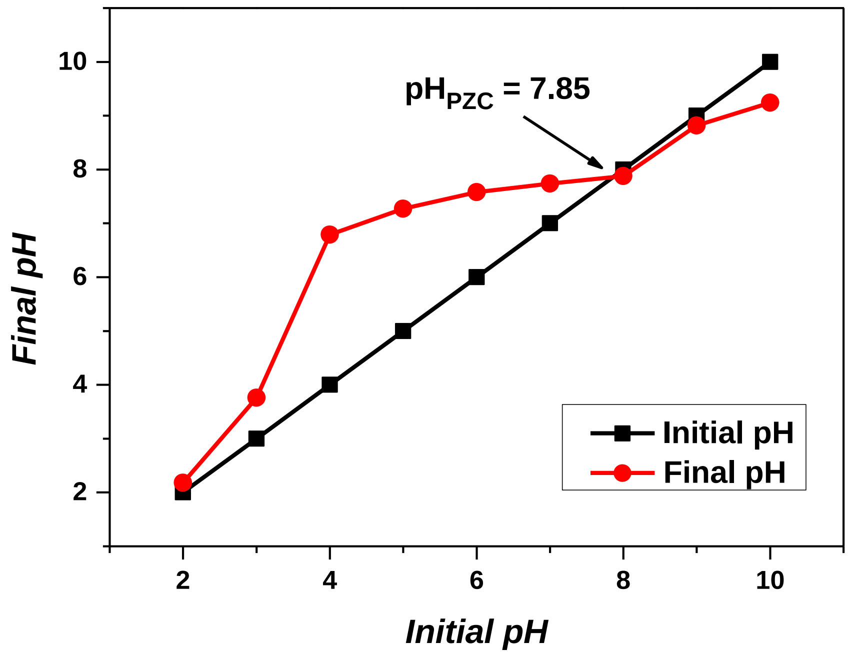

Fig. S7 pH$_{PZC}$ of AQ_1 in NaCl 0.01 mol L^{-1}.

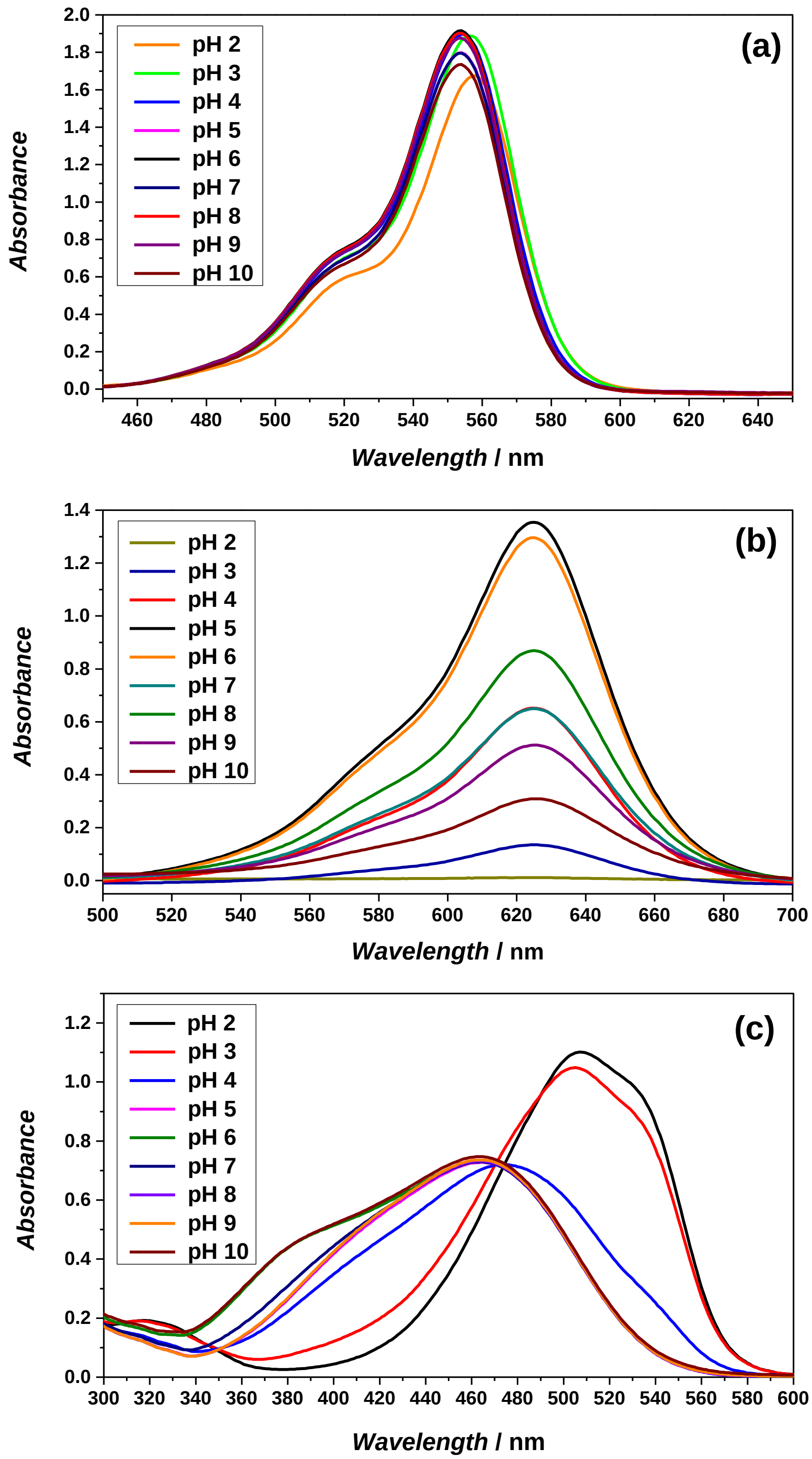

Fig. S8 UV-Vis spectrum (a) rhodamine B, (b) brilliant green and (c) methyl orange.

Fig. S9 Visual effect during decolourization of artificial wastewater varying the amount of AQ_1.

Boehm titration

Traditionally, the Boehm titration has been employed for carbon materials (especially activated carbons) in order to determinate the acidic oxygen functional groups such as carboxylic acids, lactones and phenols. In this work, Boehm titration on AQ_1 was performed according to a standardized procedure reported in the literature.[1] As usual, NaOH, Na_2CO_3 and $NaHCO_3$ were used for the determination of Carbon Surface Functionalities (η_{CSF}) by back titration with HCl 0.1 mol L^{-1} as is shown in Figure S10a-c. Also, 1st and 2nd derivative were acquiered using the potentiometric method aiming to establish the volume in which the equivalence point (V_{eq}) occurs. This method is better than using a colour indicator during titration or by inspection of the potentiometric curve.[1] The η_{CSF} estimated for AQ_1 is reported in Table 1 and is likely to phenols and carboxylic acids play a crucial role on the adsoprtion of MO as it was reported before with modified coffee wastes.[2]

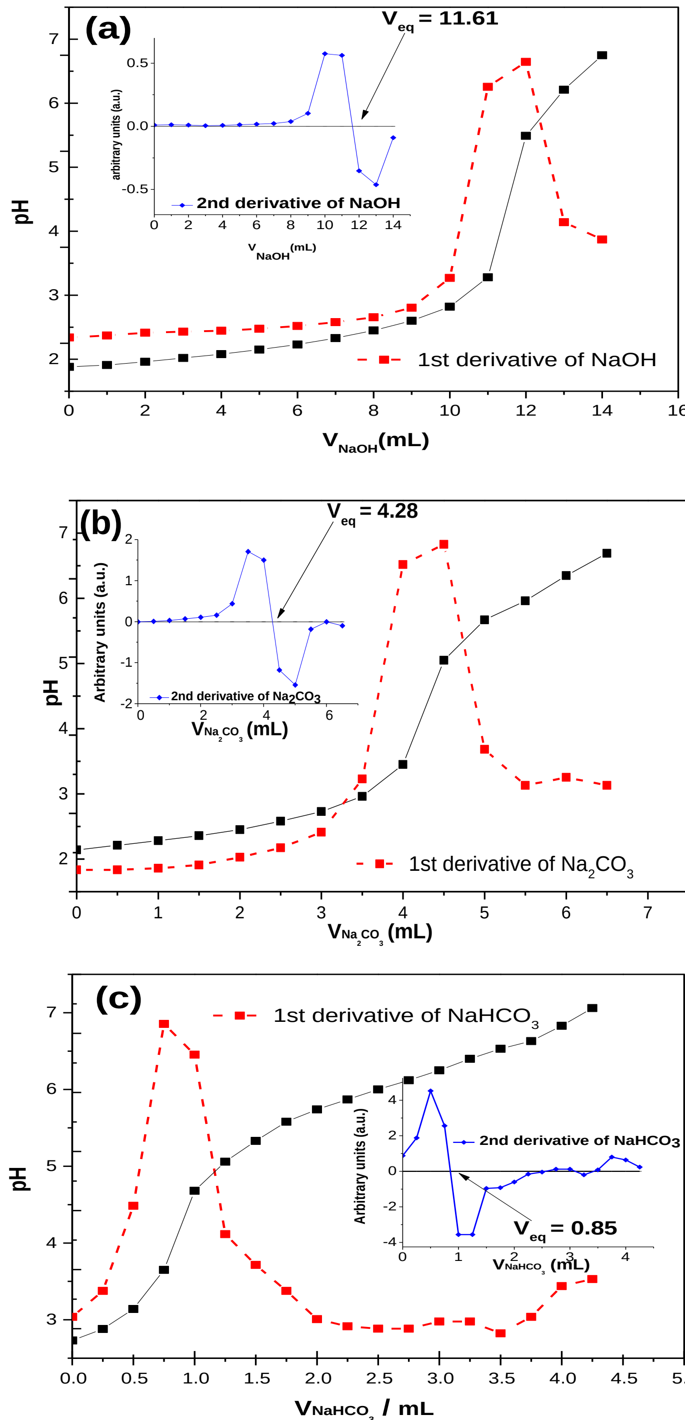

Fig. S10 Boehm titration curve of AQ_1 (a) in 0.05 mol L^{-1} sodium hydroxide solution, (b) in 0.05 mol L^{-1} sodium carbonate solution, (c) 0.05 mol L^{-1} sodium bicarbonate solution.

Table S1. Carbon surface functionalities (η_{CSF}) on AQ_1

Functional groups	η_{CSF} / mmol g^{-1}
Carboxylic	26.9
Lactonic	7.0
Phenolic	20.8

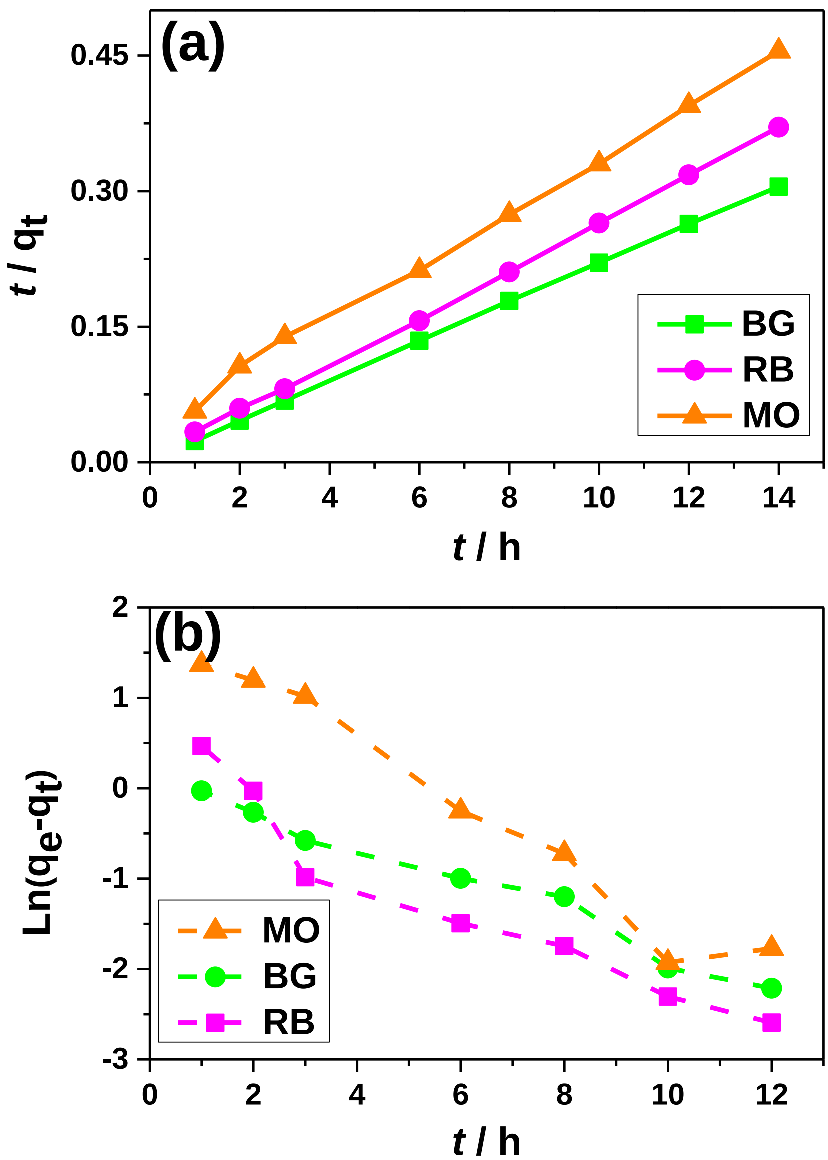

Fig. S11 (a) Pseudo-second order and (b) pseudo-first order adsorption kinetics of each dye in artificial wastewater.

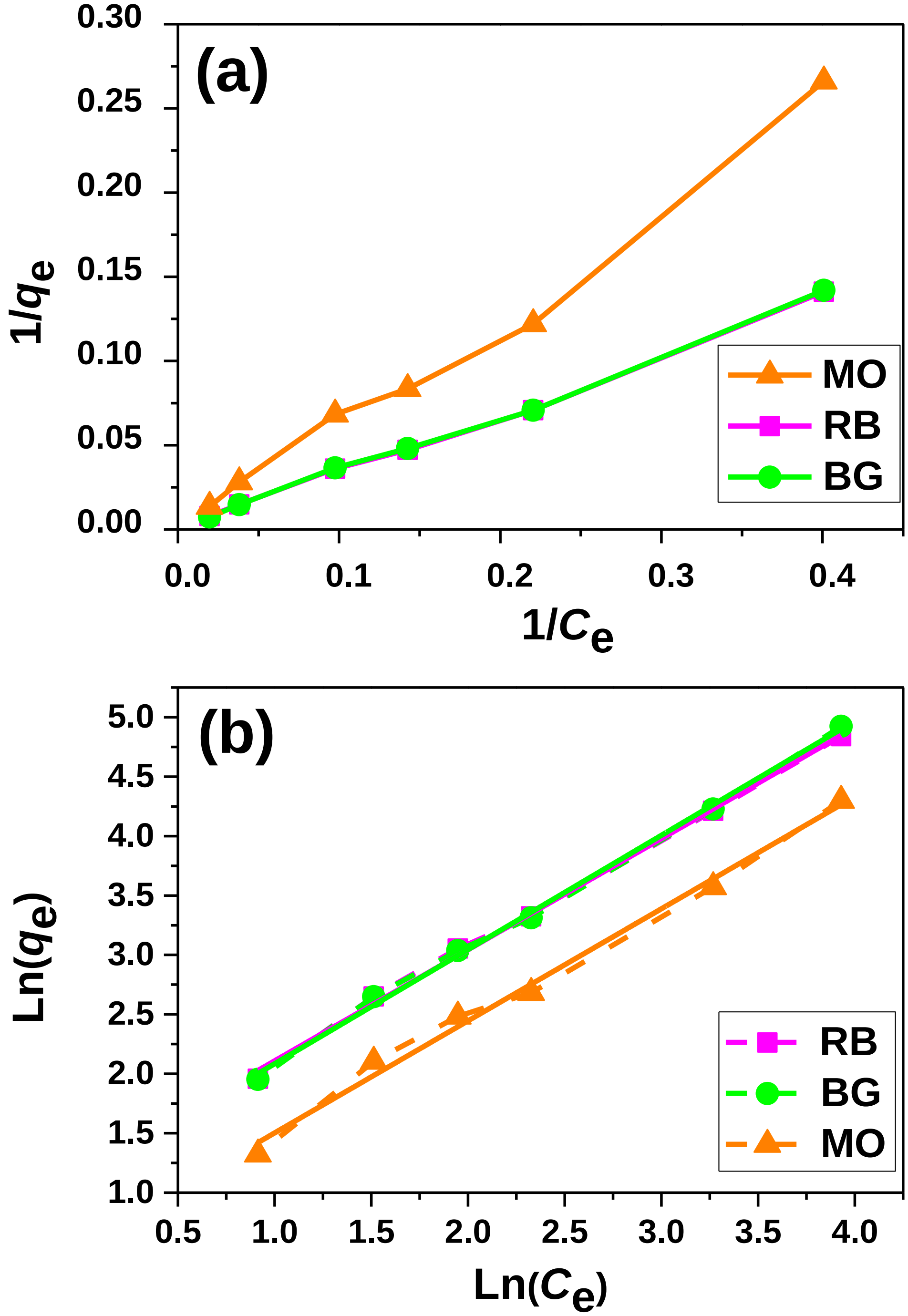

Fig. S12 Linear adsorption isotherms of each dye in the mixture (a) Langmuir model, (b) Freundlich model.

References

1 S. L. Goertzen, K. D. Thériault, A. M. Oickle, A. C. Tarasuk and H. A. Andreas, *Carbon N. Y.*, 2010, **48**, 1252–1261.

2 R. Lafi and A. Hafiane, *J. Taiwan Inst. Chem. Eng.*, 2015, **000**, 1–10.