Supplementary information

Enhancing the photocatalytic activity of TiO_2 nanoparticles using green carbon quantum dots

1. Experimental details

1.1. Kinetic study of MB degradation

The study of the photocatalytic reaction kinetics of the MB was performed using initial MB concentrations of 5 mg/L, 7.5 mg/L, 10 mg/L, 12.5 mg/L, and 15 mg/L in a solution containing 250 mg of TiO_2 NPs. The kinetic order of MB degradation was assessed using Equations (S1) and (S2) [1]:

● Equation of pseudo-first-order kinetics:

$$LnC_t - lnC_0 = -k_1 t \quad \text{(S1)}$$

● Equation of pseudo-second-order can be formulated as displayed by Equation (S2):

$$1/C_t - 1/C_0 = k_2 t \quad \text{(S2)}$$

where C_0 and C_t are the initial and at different times t concentration of MB, respectively. The constants k_1 and k_2 are the velocity constants for pseudo-first-order and pseudo-second-order models, respectively.

The study of the adsorption isotherms of MB on TiO_2 NPs and TiO_2/CQDs was carried out for the following models:

● Langmuir-Hinshelwood model: The Langmuir-Hinshelwood model is widely used to describe experimental results in heterogeneous photocatalysis. This model is expressed by Equation (S1) rewritten as [1]:

$$Ln\left(C_0/C_t\right) = k_1 t \quad \text{(S3)}$$

where C_t is the concentration of MB (mg/L) at irradiation time t, k_1 is the apparent degradation constant (min^{-1}) and t is the irradiation time (min).

● Temkin model: The Temkin isotherm takes into account the fact that the heat of adsorption of all the molecules in the overlying layer decreases linearly with the overlay due to the decrease in adsorbent-adsorbate interactions. Adsorption is characterized by a uniform distribution of binding energies at the surface. The Temkin isotherm is expressed according to Equation (S4) [2]:

$$q_e = (RT/b_t) \cdot Ln(K_t C_e) \quad \text{(S4)}$$

or in the form of Equation (S5):

$$q_e = B_1 \cdot LnK_t + B_1 \cdot LnC_e \quad \text{(S5)}$$

with B_1 is the Temkin's constant for the sorption characteristic, Ce the equilibrium concentration, and K_t ($L.g^{-1}$) the adsorption equilibrium constant corresponding to the maximum binding energy.

1.2. Application

In order to study the applicability of the synthesized TiO_2 NPs and TiO_2/CQDs photocatalytic properties in real samples, wastewater from the University Hospital Center of Cocody (UHCC) was assessed after its contamination with MB. After sampling, the collected water was transferred to a 1 L bottle, and quickly closed to avoid any air bubbles and the variation in CO_2 content, carbonate precipitation and oxidation of the mineral elements. The bottle is placed in a cooler containing ice to maintain the temperature at 4°C until it reaches the laboratory. It should be mentioned that the collected water is yellow in color with a temperature of 27.6 °C, pH 8.4, conductivity of 836 µS/cm and water salinity of 1.7. As the electric current is carried by the ions in the solution, this high conductivity suggests that this UHCC wastewater contains higher amount of ions.

2. Photocatalytic study of TiO_2 NPs and TiO_2/CQDs

All experiments were performed in the presence of 250 mg of TiO_2 NPs or TiO_2/CQDs under sunlight exposure at room temperature over time (**Figure S1**). In this figure, it can be observed that the characteristic peak of MB around 664 nm disappears completely after certain times of irradiation, suggesting that TiO_2 NPs and TiO_2/CQDs are efficient photocatalysts for the complete degradation of MB. This degradation is much more important in the case of TiO_2/CQDs. It should be noted that the faster disappearance of MB using TiO_2/CQDs compared to TiO_2 NPs is made possible by the addition of CQDs which leads to the improvement of the photocatalytic properties of TiO_2 NPs.

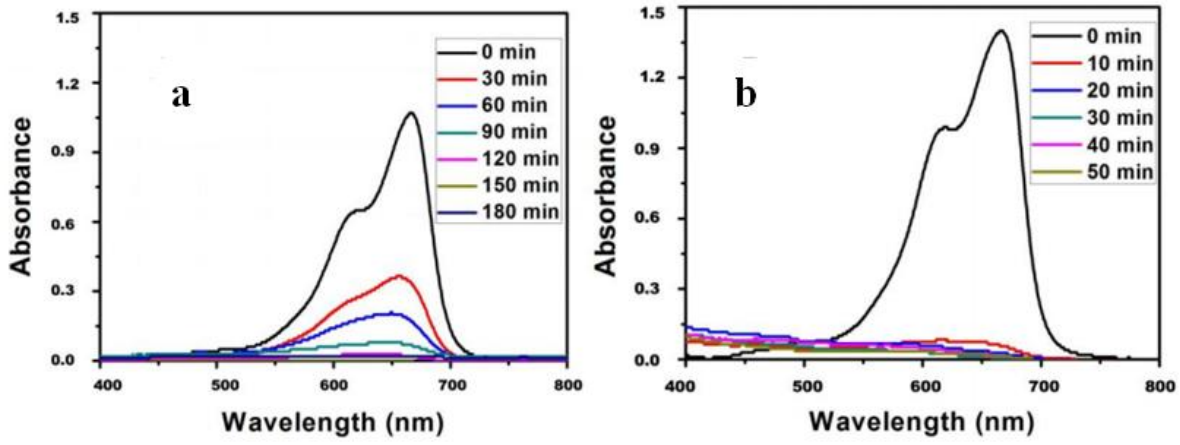

Figure S1: UV-Vis spectra of MB using a) TiO_2 NPs and b) TiO_2/CQDs at different times

3. Kinetics of MB degradation

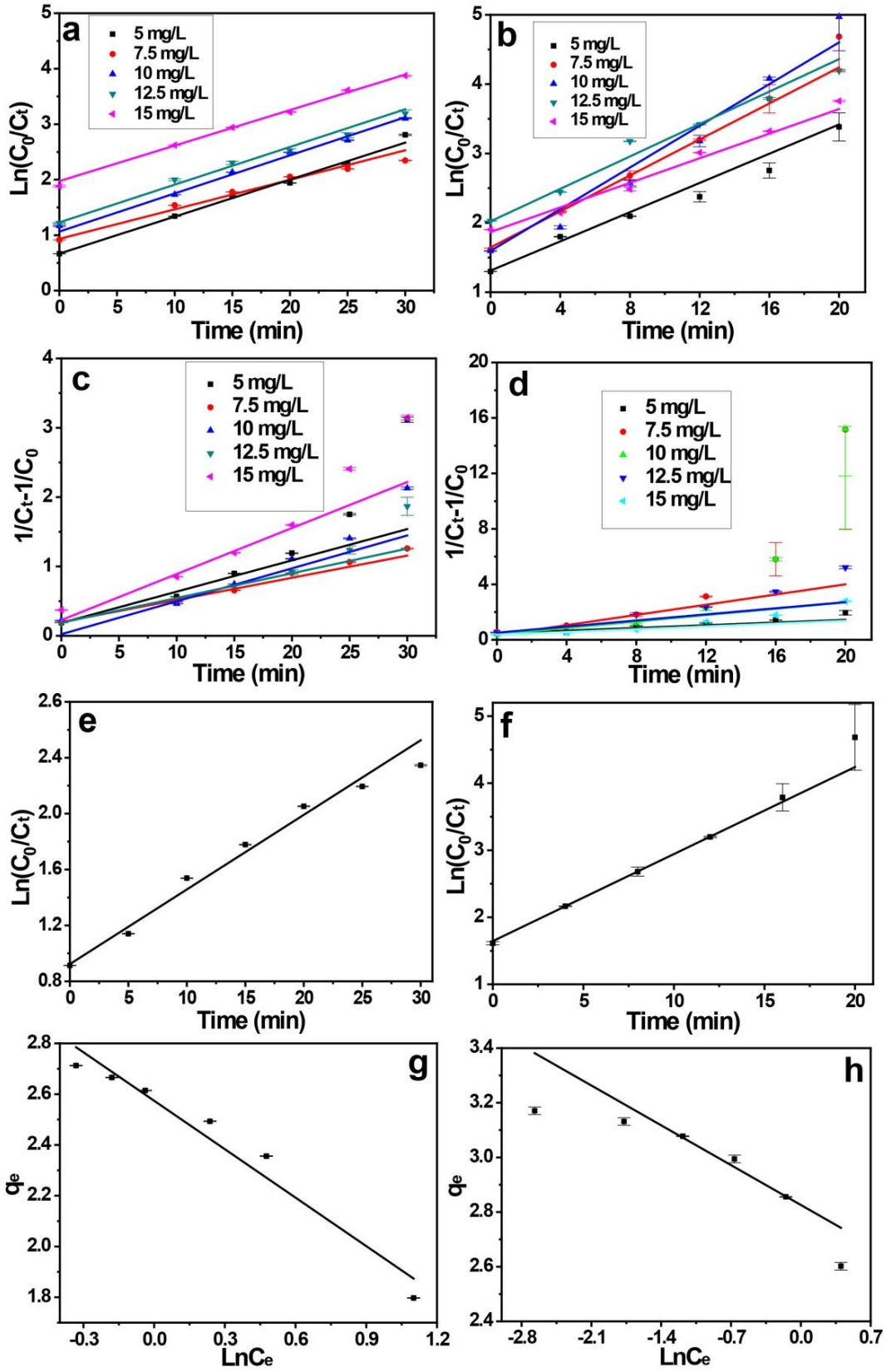

Figure S2: Degradation kinetics of pseudo-first order on a) TiO_2 NPs and b) TiO_2/CQDs, and pseudo-second order on c) TiO_2 NPs and d) TiO_2/CQDs, respectively. Langmuir-Hinshelwood kinetic model using 250 mg of e) TiO_2 NPs and f) TiO_2/CQDs, and Temkin kinetic model using 250 mg of g) TiO_2 NPs and h) TiO_2/CQDs of 7.5 mg/L MB, respectively

4. Calibration for the detection of residual MB after its degradation

In order to quantitatively study the relationship between the concentration of MB before and after the addition of TiO_2 NPs as a function of the irradiation time, the calibration curve is built by plotting the absorbance as a function of the different MB concentrations (0.25 mg/L, 0.5 mg/L, 1 mg/L, 1.5 mg/L, 2 mg/L, 2.5 mg/L, 3 mg/L, 3.5 mg/L, 4 mg/L, 4.5 mg/L, 5 mg/L, 7.5 mg/L, 10 mg/L, 12.5 mg/L and 15 mg/L) (**Figure S3**). The difference in absorbance (ΔA) between the maximum absorbance of MB before (A_0) and after the addition of TiO_2 NPs (A_t) was investigated to evaluate the residual MB. A linear range from 0.25 mg/L to 15 mg/L is obtained, leading to Equation (S6):

$$\Delta A = 0.032 \times C + 0.202 \quad \text{(S6)}$$

with C in mg/L.

This equation is used to assess the MB residual concentration after degradation (0.36 mg/L is the calculated limit of detection).

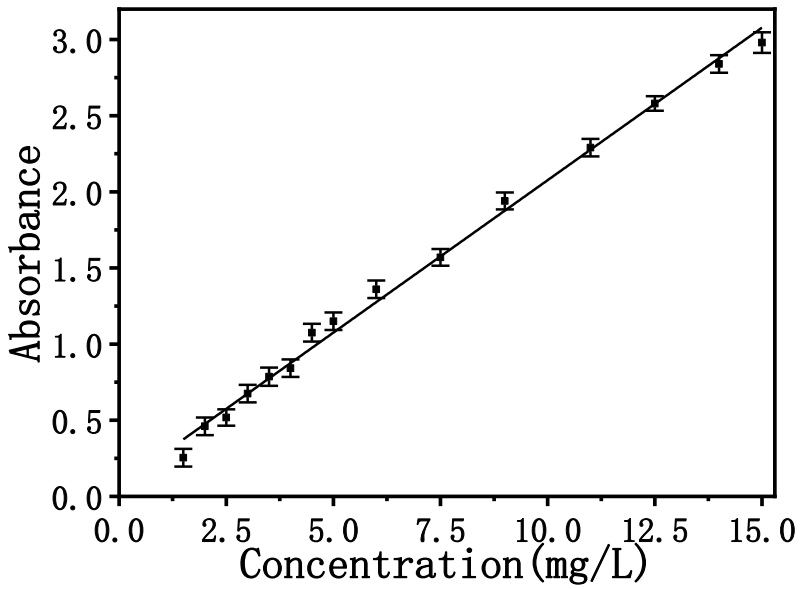

Figure S3: Calibration curve of MB for concentration ranging from 0.25 mg/L to 15 mg/L

5. Application of TiO_2 NPs and TiO_2/CQDs on the degradation of MB in UHCC wastewater

Figure S4 shows the pictures of the different solutions, the UHCC wastewater before and after sun exposure (**Figures S5a&b**) and the MB-contaminated UHCC wastewater before and after 50 min, and 30 min of sun exposure (**Figures S5c&d**) with TiO_2 NPs and TiO_2/CQD as photocatalyst, respectively. Importantly, the synthesized photocatalysts discolor the UHCC wastewater.

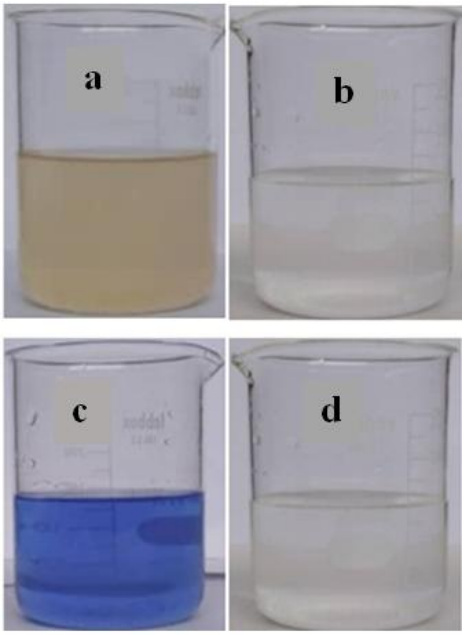

Figure S4: UHCC wastewater a) before and b) after degradation and, the UHCC wastewater contaminated with 7.5 mg/L MB c) before and d) after degradation.

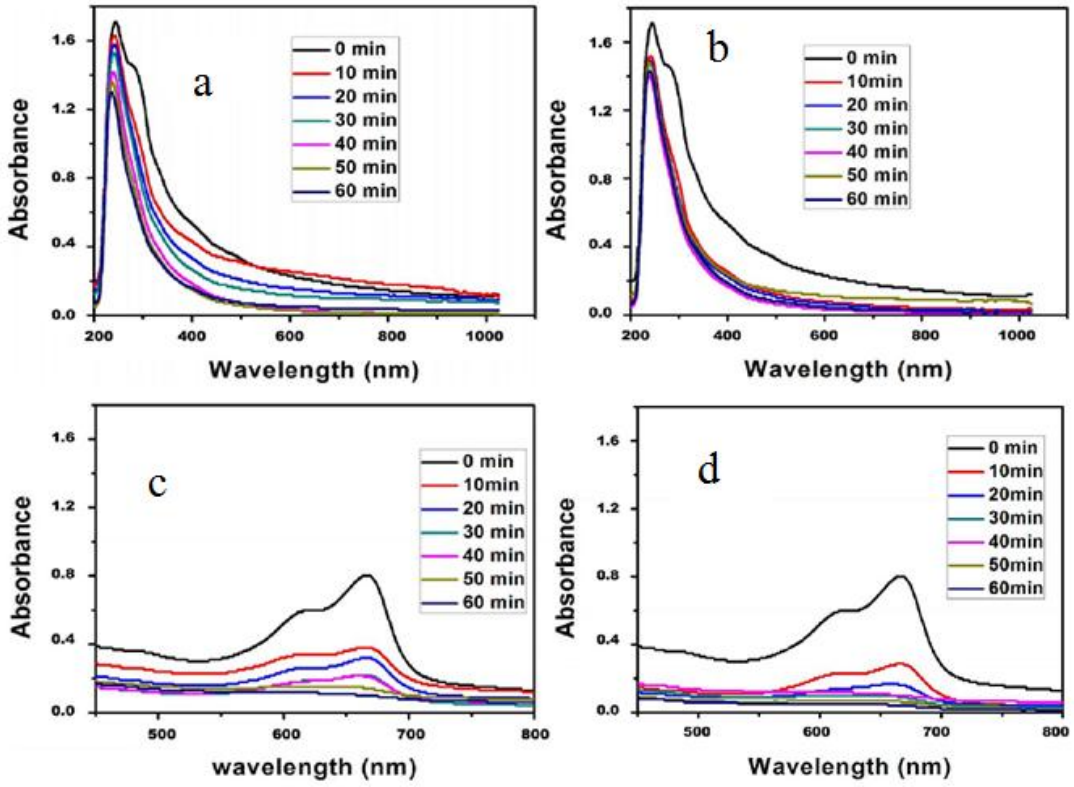

Figure S5: UV-Vis spectra of UHCC wastewater using a) TiO_2 NPs and b) TiO_2/CQDs, and degradation on c) TiO_2 NPs and d) TiO_2/CQDs at different times of UHCC wastewater contaminated with BM. All experiments are done with exposure to sunlight.

Figure S5 shows the UV-Vis spectra of UHCC wastewater (**Figure S5a and Figure S5b**) and UHCC wastewater contaminated with MB (**Figure S5c and Figure S5d**) using 250 mg of TiO_2 NPs or 250 mg of TiO_2/CQDs under sun exposure at room temperature at different times. In **Figure S5a and Figure S5b**, the disappearance of the shoulder of the wastewater spectra during the irradiation time in

the presence of the photocatalysts (TiO_2 NPs and TiO_2/CQDs) is observed. Furthermore, in **Figure S5c and Figure S5d**, it can be observed that the characteristic peak of MB around 664 nm disappears, showing the degradation of MB in the contaminated UHCC wastewater by TiO_2/CQDs.

[1] Urbain, K. Y., Fodjo, E. K., Ardjouma, D., Serge, B. Y., Aimé, E. S., Marc, G. I., & Albert, T., (2017), Removal of imidacloprid using activated carbon produced from ricinodendron heudelotii shells, *Bull. Chem. Soc. Ethiop.*, 31: 397-409.

[2] Kavitha, D., & Namasivayam, C., (2007), Experimental and kinetic studies on methylene blue adsorption by coir pith carbon, *Bioresour. Technol.*, 98: 14-21.