ZIF-67/CQD Nanohybrids for Combined Adsorptive and Photocatalytic Removal of Tetracycline: Kinetic, Isotherm, and Mechanistic Insights

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S1. Characterization methods

Using a variety of state-of-the-art tools, ZIF-67/CQD and their composites (5ZQ, 10ZQ, and 15ZQ) were carefully examined. X-ray diffraction (XRD) utilizing a Pan Analytical X′Pert-Pro diffractometer (CuKα radiation, λ = 1.5406[1]) revealed information about crystal structures throughout a 2θ range of 5-90°. Field Emission Scanning Electron Microscopy (FESEM-EDS, JEOL) revealed the composites' dimensions, elemental composition, and surface characteristics. X-ray photoelectron spectroscopy (XPS, Omicron ESCA) was used to characterize the chemical states of metal oxides. To guarantee precise binding energy determinations, the XPS spectra were calibrated using the C 1s peak at 284.8 eV as a reference. To precisely resolve overlapping peaks, peak deconvolution was carried out using Gaussian fitting in OriginPro 2018 64Bit. Functional groups were identified using Fourier Transform Infrared (FTIR) spectroscopy (Shimadzu IRTracer-100), which was calibrated using a polystyrene reference standard to guarantee spectral accuracy. OriginPro 2018 64Bit was used for spectral analysis and baseline correction. The volume, surface area, and pore size were assessed using BET and BJH methods employing N_2 adsorption-desorption isotherms on a Microtrac BELSORP MINI II. A UV-Vis spectrophotometer (Shimadzu UV 2600) was used to record the materials' absorption spectra, enabling a comprehensive analysis of their optical characteristics. The photoluminescence spectra were recorded using a spectrofluorometer (Shimadzu RF-6000). The degradation products and possible intermediate byproducts of the degradation process were investigated using High Resolution Mass Spectrometry (HRMS, Alliance 2795, Q-TOF Micromass Mass Spectrometer).

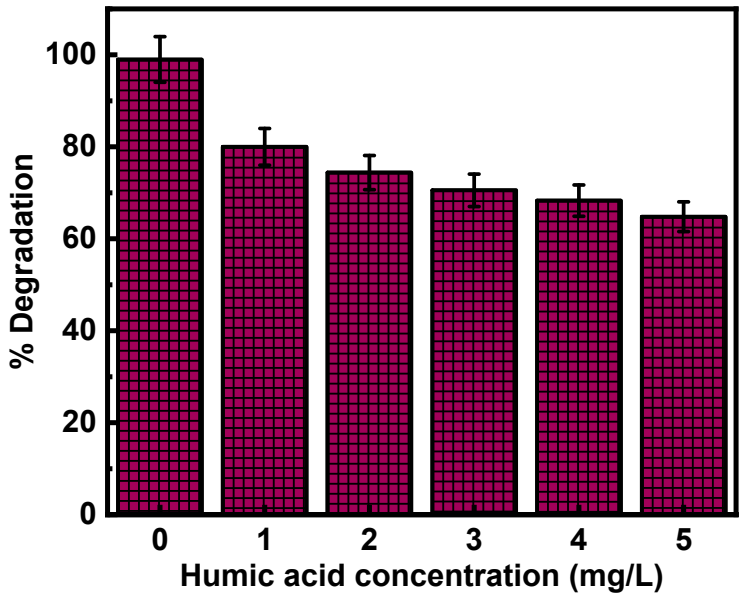

Figure S1: Impact of humic acid concentration on degradation of tetracycline.

S2. Adsorption Isotherms

The binding efficiency of the catalyst with tetracycline molecules is a crucial component of the adsorption process, and the isotherms show how efficient the composite is. By fitting the data to a number of isotherm models, such as Freundlich, Temkin, Harkins-Jura, Halsey, and Dubinin-Radushkevich, the adsorption capacity was evaluated. These isotherms' linear forms are displayed below, and Pearson correlation coefficient (R^2) values were used to assess their correctness.[1]

Langmuir Isotherm

$$\frac{Ce}{qe} = \frac{1}{QmKL} + \frac{1}{Qm}Ce \quad (1)$$

$$R_L = \frac{1}{1 + K_L C_0}$$

Freundlich Isotherm:

$$logqe = logKf + \frac{logCe}{n} \quad (2)$$

Temkin Isotherm:

$$q_e = BTln\,KT + BTln\,C_e \quad (3)$$

Harkins-Jura isotherm:

$$\frac{1}{q^2e} = \left(\frac{B}{A}\right) - \frac{1}{A}logCe \quad (4)$$

Halsey Isotherm:

$$lnqe = \frac{1}{n}lnK - \frac{1}{n}lnCe \quad (5)$$

Dubinin–Radushkevich model:

$$lnqe = lnQs - B\varepsilon^2 \quad (6)$$

$$\varepsilon = RT\ln\left(1 + \frac{1}{c_e}\right) \quad (7)$$

$$E = \sqrt{1/2B}$$

S3. Adsorption Kinetics

To comprehend the process of tetracycline adsorption, a number of models, including pseudo-first-order, pseudo-second-order, Elovich, intraparticle diffusion, and liquid film models, were used to assess the experimental kinetic data. Lagergren's pseudo-first-order model, which makes the assumption that the adsorption rate is proportional to the number of available adsorption sites, is frequently used to characterize the initial adsorption rate. This rate equation's linear version is given below.

$$-\ln\left(1 - \frac{qt}{qe}\right) = k_1 t \quad (8)$$

The pseudo-first-order rate constant, k_1 (L/min), can be determined from the slope of the linear plot of $-\ln(1 - qt/qe)$ versus time (t). The pseudo-second-order rate equation is presented below.

$$\frac{t}{qt} = \frac{1}{k^2 q_e^2} + \frac{t}{q_e} \quad (9)$$

The slope and intercept of the t/qt versus t plot are used to calculate the pseudo-second-order rate constant, k_2 (g/mg·min). The most appropriate empirical model to describe the

energetically heterogeneous surfaces of the adsorbent is the Elovich kinetic model, which uses Equation (14) to confirm the chemisorption process.

$$qt = \frac{1}{\beta} ln(\alpha\beta) + \frac{1}{\beta} ln(t) \quad (10)$$

Initially, the adsorption rate is represented by α (mg/g·min), while β (g/mg) relates to the desorption and chemisorption amounts.

Weber and Morris' intra-particle diffusion model was used to investigate the rate-limiting phase for tetracycline adsorption.

$$qt = k_1 t^{\frac{1}{2}} + C_1 \quad (11)$$

The intra-particle diffusion rate constant (mg/g·min$^{1/2}$) is represented by k_1 in this context. Its value, along with C_1, is ascertained from the slope and intercept of the qt vs. $t^{1/2}$ plot. The Liquid Film Model helps explain the impact of external mass transfer on the adsorption process by assuming that the diffusion of adsorbate molecules through the boundary layer surrounding the adsorbent is the main factor controlling the adsorption rate.

$$-\ln(1-F) = -K_{fd} \times t \quad (12)$$

Here, K_{fd} stands for the film diffusion constant, and F stands for the proportion of equilibrium reached, which is computed as $F = Q_t/Q_e$. The adsorption process is primarily regulated by diffusion via the liquid layer surrounding the adsorbent, according to a linear plot of -ln(1-F) versus time passing through the origin.

When characterizing adsorption processes on energetically heterogeneous surfaces—where the activation energy of adsorption changes across distinct sites—the Elovich kinetic model is particularly advantageous. The Elovich model is frequently used in systems involving chemisorption—that is, adsorption accompanied by valence forces through sharing or exchange of electrons between adsorbate and adsorbent—because it takes into account the variety of adsorption energies, in contrast to the pseudo-first- and pseudo-second-order models, which assume uniform surface activity. Mathematically, it is expressed as:

$$q_t = \frac{1}{\beta} ln(\alpha\beta) + \frac{1}{\beta} ln(t) \quad (13)$$

Where, $q_t$is the amount of tetracycline adsorbed at time t, α(mg/g·min) represents the initial adsorption rate, and β(g/mg) is related to the extent of surface coverage and activation energy for chemisorption.

A linear plot of $q_t$versus $ln(t)$yields a slope of $1/\beta$and an intercept of $(1/\beta)ln(\alpha\beta)$.

The Elovich model's implementation to tetracycline adsorption implies that heterogeneous chemisorption, as opposed to straightforward physical adsorption, governs the process. This suggests that tetracycline molecules and the active sites may be involved in surface complexation or chemical bonding. Therefore, a strong linear correlation (high R^2) with this model supports the idea that adsorption happens via an active, surface-specific mechanism involving varying energy sites as opposed to uniform adsorption kinetics.[2,3]

S4. Photocatalytic degradation kinetics

The kinetics of tetracycline degradation were analyzed using pseudo-first-order and pseudo-second-order models to determine the most suitable representation of the degradation process.

The pseudo-first-order kinetic model assumes that the degradation rate is directly proportional to the concentration of tetracycline, and its linearized form is expressed as:

$$ln(C_t) = ln(C_0) - k_1 t \tag{14}$$

where C_t represents the tetracycline concentration at time t, C_0 is the initial concentration, and k_1 is the pseudo-first-order rate constant. A plot of $\ln C_t$ versus t was used to determine k_1 from the slope $-k_1$, and the intercept gave $\ln C_0$. This model provided insights into the direct proportionality between pollutant concentration and reaction time under this kinetic framework.

The pseudo-second-order kinetic model, however, considers a degradation rate proportional to the square of tetracycline concentration and possibly accounts for interactive processes at the catalyst surface. This model's linearized form is:

$$\frac{t}{C_t} = \frac{1}{k_2 C_0^2} + \frac{t}{C_0} \tag{15}$$

where k_2 is the pseudo-second-order rate constant. By plotting t/C_t against t, the slope $1/C_0$ and intercept $1/k_2C_0^2$ allowed the calculation of k_2 and provided an alternative view of the reaction dynamics.

The tetracycline degradation rate in the zero-order kinetic model is independent of the pollutant concentration and is constant throughout the process. This kind of action often occurs when all of the active sites are constantly occupied and the catalytic surface is saturated with tetracycline molecules. In these circumstances, the catalyst activity and outside variables like light intensity—rather than the pollutant concentration itself—determine the reaction's constant rate. The model can be expressed by the linear equation:

$$C_t = C_0 - k_0 t \tag{16}$$

where $C_t$is the concentration at time t, $C_0$is the initial concentration, and $k_0$represents the zero-order rate constant. When $C_t$is plotted against time, a straight line is obtained, with a slope corresponding to $-k_0$and an intercept equal to C_0.

According to this dependence, the degradation rate stays constant until the tetracycline concentration drops to the point where active site saturation is no longer sustained. It is possible to ascertain if the degradation process is linearly dependent, independent of concentration, or impacted by surface adsorption dynamics by comparing this model with the pseudo-first- and pseudo-second-order models using their corresponding linear regressions (R^2). [4]

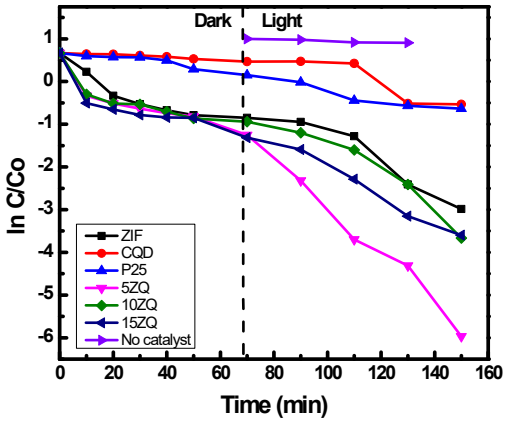

Figure S2: Kinetics plot

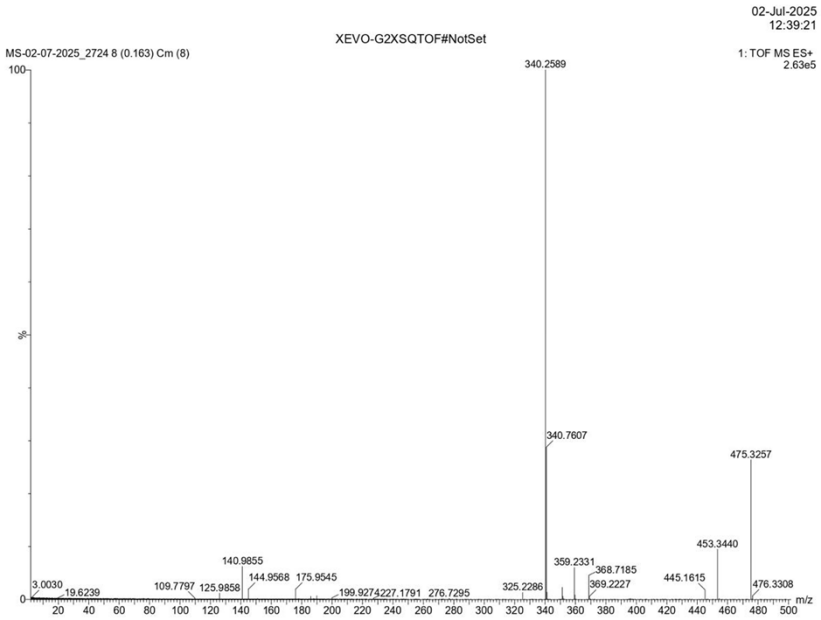

Figure S3: HRMS analysis

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