

Electronic Supplementary Information

Facile synthesis of CeO₂ nanoparticles for enhanced removal of malachite green dye from an aqueous environment

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Characterization techniques

The X-ray diffraction (XRD) study of the dried powder samples was carried out on a PANanalytical EMPYREAN powder X-ray diffractometer using Cu k_{α} radiation with a wavelength of 0.154 nm at an accelerating voltage of 40 kV with 35 mA current. For the scanning electron microscopic (SEM) study, a small amount of the dry powder samples was spread on carbon tape pasted on an aluminium stub, and then sputter-coated with platinum to minimize the charging effect. The micrographs were then recorded in a field emission scanning electron microscope (FESEM) (Zeiss, Sigma VP) at an accelerating voltage of 5.0 kV. For transmission electron microscopic (TEM) studies, a drop of an aqueous suspension of an individual powder sample was cast on a carbon-coated copper grid. The excess solutions were soaked with tissue paper followed by drying in the air. The micrographs were then recorded in a high-resolution electron microscope (Technai, F30 S-Twin) at an accelerating voltage of 200 kV. The nitrogen (N_2) gas adsorption-desorption isotherms of the products were recorded at 77 K (Quantachrome Nova 1000 Instrument) after degassing the powder samples at 110 °C for 4 h in an inert atmosphere. The dye adsorption experiments were monitored in an Agilent Cary60 spectrophotometer. The pH at the point of zero charges (pH_{zpc}) was measured using the pH drift method. For this study, the pH of a solution of 0.01 M NaCl was adjusted between 2 and 10 by adding either HCl or NaOH. The solution was then heated to just boil to remove dissolved CO_2 until the initial pH was stabilized. 0.06 g of the sample was added to 20 mL of the solution and stirred the solution in an airtight container for 24 h. After separating the solid, the final pH of the mixture was recorded. The graphs of final versus initial pH were used to determine the points at which initial pH and final pH values were equal. This was taken as the pH_{zpc} of the sample.

Table S1. Different kinetic models used in this study and their non-linear form of equation^[1]

Entry	Model	Equation
1	Lagergren pseudo-first order	$q_t = q_e(1 - e^{-k_1 t})$
2	Pseudo-second order	$q_t = \frac{q_e^2 k_2 t}{1 + q_e k_2 t}$
3	Elovich	$q_t = \frac{1}{\beta} \ln(1 + \alpha \beta t)$

Here, q_e (mg g^{-1}) and q_t (mg g^{-1}) are the amounts adsorbed per unit mass at equilibrium and at any time, t (min) respectively, k_1 is the first-order rate coefficient (min^{-1}), k_2 is the rate constant of pseudo-second-order ($\text{g mg}^{-1} \text{min}^{-1}$), α is the initial adsorption rate ($\text{g mg}^{-1} \text{min}^{-1}$), β is the desorption constant ($\text{mg g}^{-1} \text{min}^{-1}$).

Table S2. Different isotherm models used in the study with their non-linear form of equation^[2]

Entry	Isotherm	Equation
1	Freundlich isotherm	$q_e = K_F C_e^{1/n}$
2	Langmuir isotherm	$q_e = \frac{q_m b C_e}{1 + b C_e}$
3	D-R isotherm	$q_e = (q_s e^{-k_{ad} \epsilon^2})$
4	Sips isotherm	$q_e = \frac{q_{ms} k_s C_e^{m_s}}{1 + k_s C_e^{m_s}}$

Here, C_e is the equilibrium concentration of the malachite green dye in aqueous solution (mg L^{-1}); q_e is the equilibrium concentration of the malachite green dye in the solid phase (mg g^{-1}). K_f ($\text{mg}^{1-1/n} \text{L}^{1/n} \text{g}^{-1}$) and n are Freundlich coefficients; q_m (monolayer adsorption capacity) and b (equilibrium coefficient) are Langmuir coefficients; q_s is the theoretical saturation capacity (mg g^{-1}); q_{ms} is the maximum adsorption capacity of the Sips model (mg g^{-1}); k_s and m_s are the

Sips equilibrium constant (L mg^{-1}) and exponent respectively. The parameter, k_{ad} is Dubinin–Radushkevich isotherm constant ($\text{mol}^2 \text{k}^{-1} \text{J}^{-2}$). The parameter ε can be correlated as^[3]:

$$\varepsilon = RT \ln \left(1 + \frac{1}{C_e} \right)$$

where, R , T , and C_e represent the gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$), temperature (K) and adsorbate equilibrium concentration (mg L^{-1}), respectively. The mean sorption energy, E , which is the free energy of transfer of 1.0 mole of solute, from infinity (bulk solution) to the surface of adsorbent is given by^[3]–

$$E = \frac{1}{\sqrt{2k_{ad}}}$$

The E (kJ mol^{-1}) value provides valuable information about adsorption characteristics. When the value of E , lies between 8 and 16 kJ mol^{-1} , the adsorption process is considered to be chemical in nature, whereas, if the value is less than 8 kJ mol^{-1} , the interaction is depicted as physical.

References

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- [2] Foo, K. Y.; Hameed, B. H., Insights into the modeling of adsorption isotherm systems. *Chem. Eng. J.* **2010**, *156* (1), 2-10.
- [3] Liu, Y.; Liu, Y.-J., Biosorption isotherms, kinetics and thermodynamics. *Sep. Purif. Technol.* **2008**, *61* (3), 229-242.

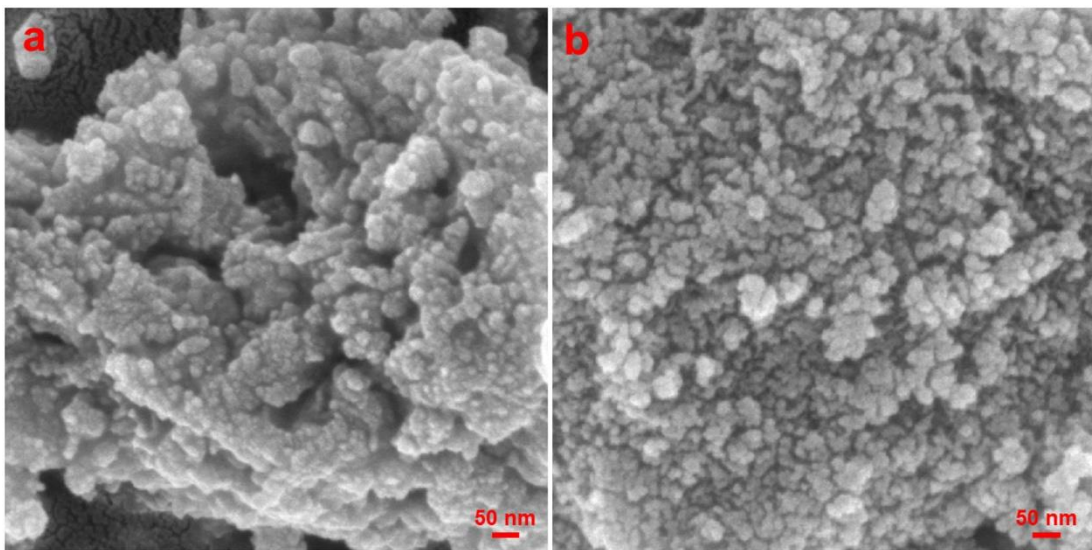


Figure S1. SEM images of samples (a) CeO-1 and (b) CeO-2.

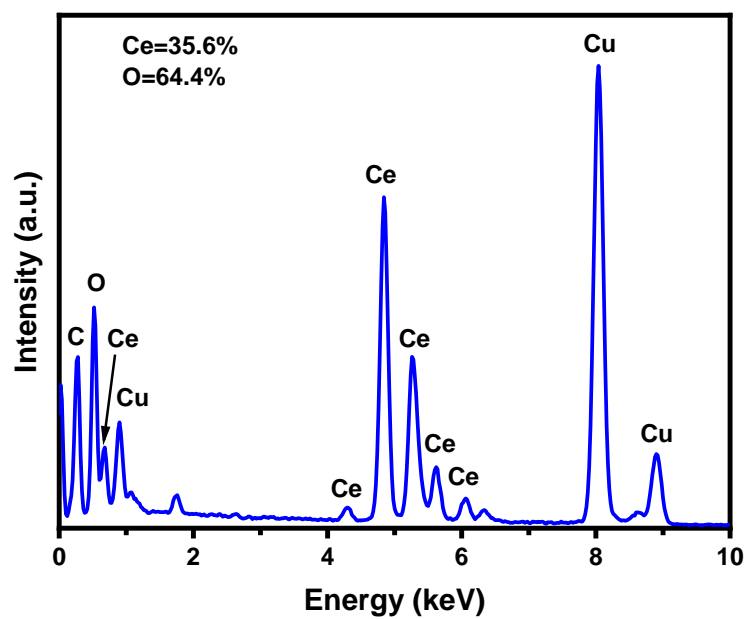


Figure S2. EDX spectrum of CeO₂ NPs (sample CeO-2).