

Congo Red Dye Adsorption by French Fries-like CeO₂: A Kinetic Study

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Introduction

Since the last few decades, water purification and treatment technologies attracting significant consideration because of the increasing number of various dye effluents such as congo red, methylene blue, methyl orange, methyl red, and acid fuchsin in water sources by several industries viz textile, paper, plastics, and leather tanning.[1,2] This dye effluent is the primary source of water pollution. Further dyes undergo degradation and produce various secondary products, which are water-soluble and highly toxic and lead to cause cancer in the bladder, a disorder in the spleen, liver, and reproductive system, and allergic action to the skin and eyes.[3,4] To remove such impurities from the water system, physical and chemical treatment processes, including biological and chemical coagulation/flocculation, ion exchange, oxidation, electrooxidation, membrane separation, ozonation, and adsorption, are adopted.[5] Amide various processes, the adsorption method is highly significant in environmental sustainability, effortless, easy to perform and observe, and no secondary products formed after treatment.[6] The adsorption method is further classified into chemical adsorption (chemisorption) and physical adsorption (physisorption). The physisorption proceeds through van der Waals forces, and chemisorption proceeds through chemical interaction between the adsorbed and adsorbent molecules. We can say that electrons are shared between adsorbent surface-adsorbed molecules.[7] The dye adsorption mechanism is classified into three stages. (i) Adsorbate molecules migrate from the bulk solution to the adsorbent's outer surface, denoted as film diffusion. (ii) Molecules of the adsorbate migrate within the pores of the adsorbent, which proceed over the outer surface, denoted as intra-

particle diffusion or pore diffusion). (iii) Adsorbate molecules sorption occurs over the pores' internal surface and the adsorbent's capillary space.[8,9]

People use various types of material to remove color impurities. Still, among different materials, CeO₂ is found to be an excellent material owing to having high oxygen storage, environmental sustainability, unique electronic properties, alterable surface, and multiple physiognomies. [10]

Therefore, in this manuscript, I have developed a French fries-like CeO₂ by implementing a synthetic hydrothermal route (a greener approach) using a rate-controlling and a morphology tuning agent. The material was characterized by powder X-ray diffraction and scanning electron microscopy. Further, the dye adsorption experiment was performed using a fixed concentration/amount of dye and CeO₂ for different time scales.

Experimental section

1. Material synthesis

In a usual material synthesis, 5 mmol of analytical grade Ce(NO₃)₃·6H₂O was dissolved in 40 mL of high-purity water. The subsequent solution was stirred for a while to get uniform distribution. To this, a 40 mL solution of cetyltrimethylammonium bromide, CTAB (prepared by dissolving 2.5 mmol of CTAB in 40 mL high-purity water) was added deliberately using a magnetic stirrer. After stirring for half an hour, 20 mmol of solid dimethyl urea was added to this mixture and again stirred the mix for a while. Finally, the complete solution was transferred to a Teflon-lined stainless steel autoclave and heated in a digital hot-air oven at 150 °C for 24 h for hydrothermal reaction. After completing the hydrothermal reaction and cooling to atmospheric temperature, a white-colored CeO₂ precursor material was obtained by washing centrifugally (using water, water-ethanol mixture, and ethanol) and drying at

60 °C overnight. This precursor material is converted into French fries-like CeO₂ by heating in a muffle furnace at 400 °C for 3 h.

2. Characterization techniques

PANalytical XPERT-PRO diffractometer was used to record X-ray diffraction (PXRD) patterns by utilizing Cu-K α ($\lambda=0.1540$ nm) radiation generated at 40 kV and 40 mA with a scan rate of 0.02° s⁻¹ from 10° to 80°. FEI-Nova nano SEM 450 field emission microscope was used to characterize the material's morphology. Perkin-Elmer LAMBDA-750-Uv-Visible-Nir-spectrophotometer used to illustrate the dye adsorption experiment at maximum absorption wavelength (λ_{max}) of congo red (CR) (496 nm).

3. Adsorption kinetic experiment

The kinetic study of the Congo red dye was performed by Batch adsorption experiment using 25 mg/L dye stock solution. To prepare the above stock solution, 25 mg dye was dissolved in 1 liter of high-purity water using a volumetric flask. The batch adsorption experiment was performed in a 20 mL reaction tube with the help of an electrical magnetic stirrer. The reaction tube was filled with 5 mL of dye solution (containing 25 mg/L concentration of dye), and to this, 5 mg of adsorbent (French fries-like CeO₂) was added, and the reaction tube was stirred using a magnetic pellet on a magnetic stirrer for various time interval viz. 5, 10, 20, 40, 80, and 160 minutes.

The amount of dye adsorption q_t (mg/g) at time t on the adsorbent was estimated using the following equation:

$$q_t = \frac{(C_0 - C_t)V}{m} \dots\dots\dots 1$$

in which C_0 and C_t (mg/L) corresponds to the concentration of dye at initial and after time t , V , the volume of the solution (L), and m is the mass of adsorbent used for adsorption (g)

Results and Discussion

Physical characterization

The comprehensive X-ray diffraction profile of the material is presented in Figure 1, which demonstrates diffraction peaks at the two-theta degrees of 28.6, 33.1, 47.5, 56.5, 58.9, and 69.4 corresponding to the (111), (200), (220), (311), (222), and (400) crystal plane of FCC type CeO₂ (JCPDS card no. 81-0792). Besides, no other peaks in the diffraction pattern substantiate the material's phase purity.

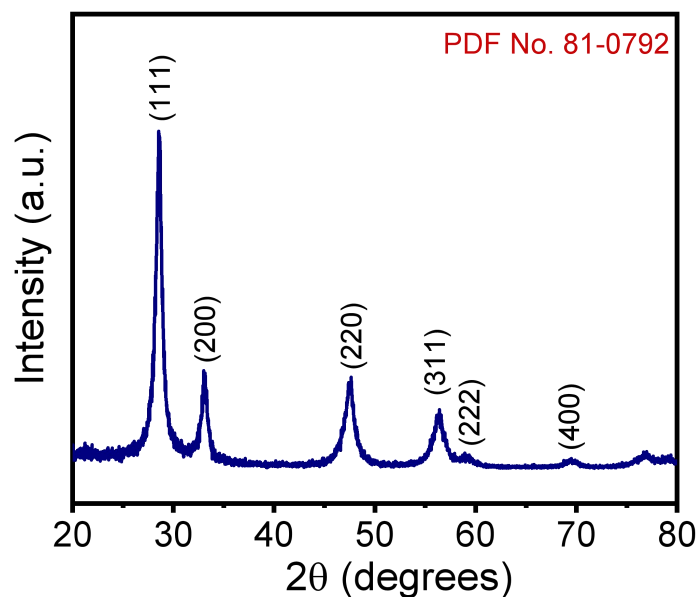
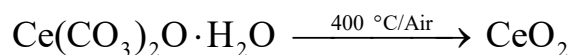
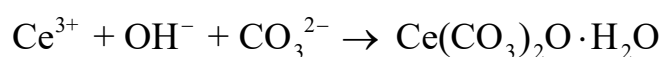
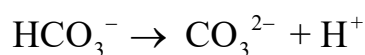
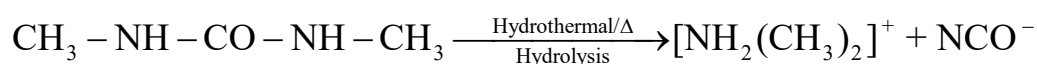


Figure 1. Powder X-ray diffraction pattern of CeO₂.

The following reactions are involved during forming of precursor and French fries-like CeO₂. [11,12]



The approximate crystallite size of the materials was calculated using the Scherrer equation, which is found to be 19 nm. The small crystallite size indicates kinetically controlled precipitation of metal precursor under hydrothermal conditions.

The FESEM images of the material are shown in Figure 2. The low magnification FESEM image of the material in Figure 2A displays French fries-like surface morphology. The high

magnification image in Figure 2B demonstrates that the French fries-like morphology is supposed to form from the controlled aggregation and self-assembly of multiple layers.

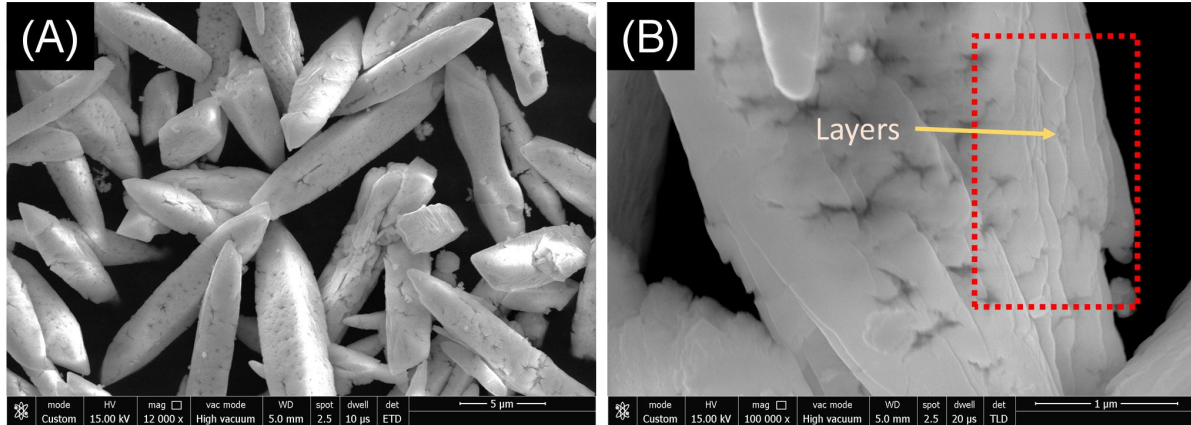


Figure 2. (A) Low magnification and (B) High magnification FESEM images of CeO₂.

Adsorption Kinetic Study

For the kinetic study of Congo red (CR) dye, 5 mg of CeO₂ and 5 ml of CR dye solution (25 mg/L) were magnetically stirred for different intervals ranging from 5 to 160 minutes. After stirring for a certain period, the supernatant dye solution was subjected to UV-Vis absorption spectroscopy. The resultant UV-Vis absorption spectra and the digital photographs of the dye solution after adsorption at different time intervals are presented in Figure 3A. It is observed from Figure 3A that the corresponding absorption intensity for CR dye decreases rapidly in the initial 5-10 min, and after 10 min, the intensity decreases slowly. The adsorption kinetics of CR dye is studied from the corresponding q_t vs. t graph, presented in Figure 3B. Figure 3B show that the adsorption rate is very fast for CR in the initial 5 minutes, and the equilibrium for CR is achieved within 80 minutes. The high adsorption rate in the initial 5-10 minutes shows better adsorption efficacy of the French fries-like CeO₂. The higher adsorption rate of the CeO₂ at the beginning of the adsorption course is because many active sites are initially vacant on the CeO₂ surface, which decreases with time. Subsequently, the dye molecules

compete to access the vacant adsorption sites.[13-15] The quantity of adsorption at 80 minutes is calculated using equation 2 and is found to be 14.53 mg/L.

$$q_e = \frac{(C_0 - C_e)V}{m} \dots\dots\dots 2$$

To identify the rate of adsorption and type of adsorption mechanism, pseudo-first-order, and pseudo-second-order kinetics were investigated for the material.[16]

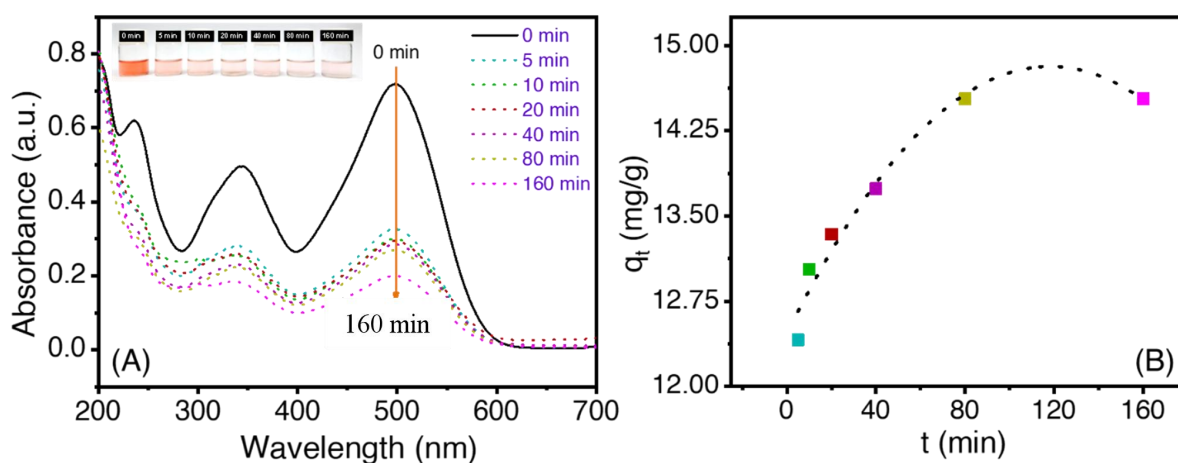


Figure 3. (A) shows the UV-vis absorption spectra, and the inset shows the digital photograph of CR dye solutions after adsorption on CeO₂ for different time intervals. (B) shows the adsorption kinetics of CR on CeO₂.

The pseudo-first-order kinetic model (in which the rate-limiting step is physisorption) was investigated using equation 3.

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \dots\dots\dots 3$$

in which q_e and q_t correspond to the amount (mg/g) of the adsorbed dye at equilibrium and time t (minutes), respectively, and k_1 (min⁻¹) denotes the pseudo-first-order rate constant.

Table 1. Pseudo-first-order kinetic parameters for the adsorption of CR dye on CeO₂

C_0 (mg/L)	$q_{e,exp}$ (mg/g)	k_1 (min ⁻¹)	R^2
25	14.53	0.050	0.96

The value of k_1 for CR on CeO₂ is calculated from the linear fitted $\log (q_e - q_t)$ vs. t plot, as shown in Figure 4A, and the efficiency parameter for pseudo-first-order kinetics is listed in Table 1. The correlation coefficient (R^2) for dye diverges broadly from 1, which recommended that pseudo-first-order kinetics do not follow the rate-determining adsorption step. The adsorption of the dye on CeO₂ does not proceed via the physisorption process.[17]

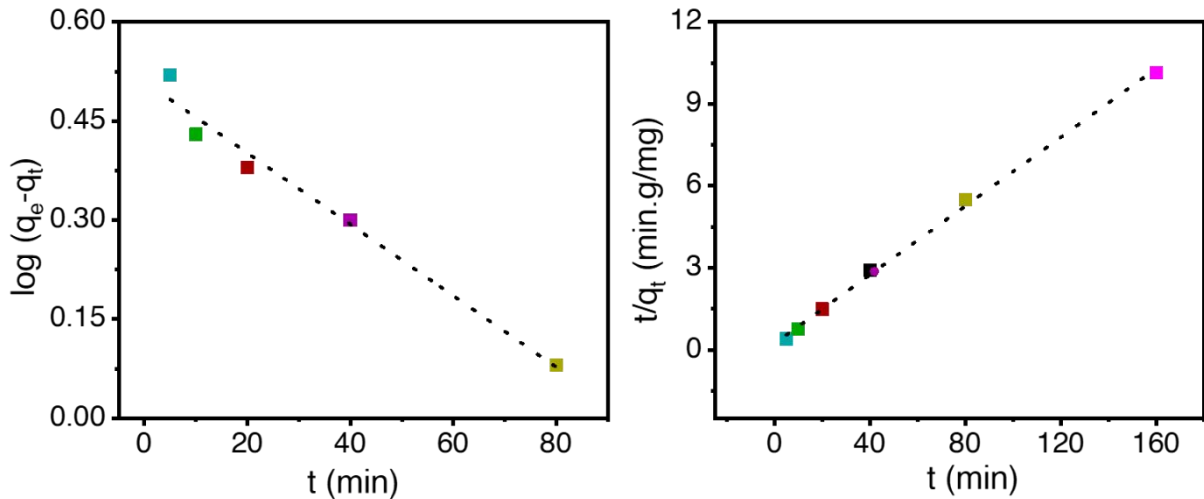


Figure 4. Shows the (A) pseudo-first-order kinetics plot and (B) pseudo-second-order kinetics plot.

Further, the pseudo-second-order kinetic model (in which the rate-limiting step is chemisorption) for dye adsorption is investigated using equation 4.

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} = \frac{1}{q_e} t \dots\dots\dots 4$$

in which k_2 (g/[mg min⁻¹]) is the pseudo-second-order rate constant, q_e and t (min) correspond to the quantity (mg/g) of adsorption at equilibrium and time, respectively. The pseudo-second-order rate constant (k_2) for the adsorption of CR dye on CeO₂ is calculated from the linear fitted t/q_t vs. t plot, presented in Figure 4B. The kinetic parameters of pseudo-second-order kinetics for CR on CeO₂ are listed in Table 2. It is observed from Table 2 that the correlation coefficient (R^2) value for dye is almost equal to 1, which shows that the rate-

determining adsorption step obeys pseudo-second-order kinetics. The adsorption of CR dye on CeO₂ proceeds through the chemisorption process.[18]

Table 2. Pseudo-second-order kinetic parameters for the adsorption of CR dye on CeO₂

C ₀ (mg/L)	q _{e,exp} (mg/g)	k ₂ (g/mg min ⁻¹)	R ²
25	14.53	0.06	0.999

Conclusions

In summary, French fries-like CeO₂ is fabricated by dimethyl urea-mediated synthesis under hydrothermal heating conditions. Broad physical characterizations of the material demonstrate phase purity, low crystallinity, and fries-like morphology developed by aggregation of layers. The CeO₂ shows high adsorption efficiency for CR dye. Thorough kinetic analyses of the dye show that their adsorption follows the pseudo second order kinetics, proving the dye chemisorption on fries-like CeO₂. The excellent adsorption capacity of fries-like CeO₂ is ascribed to a layered structure, which allows full surface access to the dye molecules. Further, the strong electrostatic force of attraction between the anionic CR dye molecules and CeO₂ also plays a vital role in adsorption.

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