

Supporting Information (SI)

Insights into the ligand effect in β -CD@Fe₃O₄ composites to activate peroxymonosulfate for efficient degradation of pharmaceutical contaminants: A study employing density functional theory

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Text S1. The synthesis procedure of β -CD@Fe₃O₄ linked with CIT, PEI, and CTAB

(1) Synthesis of Fe₃O₄@PEI@ β -CD:

Firstly, Fe₃O₄@PEI was synthesized through a hydrothermal coating method. To achieve this, 2 g of FeCl₃·6H₂O was dissolved in 65 mL of ethylene glycol, followed by the addition of 6 g of anhydrous sodium acetate and 3 g of polyethyleneimine (PEI). After stirring for 30 minutes, the mixture was transferred to a polytetrafluoroethylene-lined autoclave and reacted at 200°C for 6 hours. Upon cooling to room temperature, the product was washed with anhydrous ethanol and dried, resulting in Fe₃O₄@PEI, which was then freeze-dried. Subsequently, the synthesized Fe₃O₄@PEI was functionalized with carboxymethylated β -CD to form Fe₃O₄@PEI@ β -CD: 6 g of β -CD and 13 g of maleic anhydride were dissolved in 100 mL of anhydrous DMF. The solution was stirred under nitrogen for 48 hours. Then, 100 mL of ethyl acetate was added, followed by uniform stirring and filtration to yield a viscous white substance. After washing and drying, carboxymethylated β -CD was obtained. A solution containing 0.86 g of carboxymethylated β -CD, 0.1 g of DMAP, and 1.12 g of EDC in 100 mL of deionized water was stirred for 2 hours. Then, 2 g of Fe₃O₄@PEI was added and subjected to ultrasonic treatment for 20 minutes to ensure uniform dispersion of the particles. After stirring for 48 hours, the particles were separated using a magnet. Finally, the Fe₃O₄@PEI@ β -CD was washed and freeze-dried for further use.

(2) Synthesis of Fe₃O₄@CIT@ β -CD:

Synthesis of Fe₃O₄: Magnetite nanoparticles (MNPs) were prepared using the co-precipitation method. Briefly, 2 mmol of FeCl₃·6H₂O (0.54 g) and 1 mmol of FeCl₂·4H₂O (0.198 g) were added to 20 ml of deionized water in a 250 ml round-bottom flask. The mixture was ultrasonicated for 20 minutes at room temperature. The temperature was gradually raised to 60°C, and then 1 M NaOH solution was added dropwise under N₂ atmosphere until the pH of the solution reached 10–11. The mixture was further ultrasonicated for 30 minutes, followed by magnetic separation and washing with deionized water.

Synthesis of CD-CIT: The CD-CIT complex was prepared via an esterification

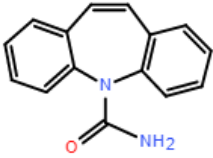
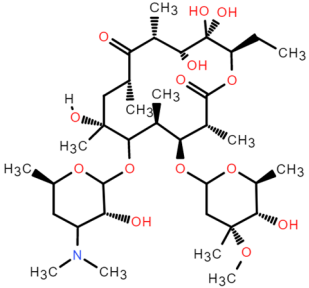
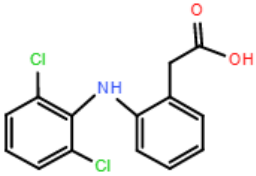
reaction between the -COOH group of citric acid and the primary -OH group of CD, following a previously reported procedure. Citric acid (1 g) and β -CD (3 g) were dissolved in 10 ml of water and stirred at 80°C for 3 hours. The solution became clear and was then treated with isopropanol (15 ml) to precipitate a white solid. The mixture was filtered and thoroughly washed 2–3 times with water (3×10 ml) to remove unreacted components, and then dried at 60°C for 24 hours in a hot air oven to prepare the white solid CD-CIT complex.

Synthesis of $\text{Fe}_3\text{O}_4@\text{CIT}@\beta\text{-CD}$: Fe_3O_4 (0.27g) was redispersed in 100 ml of distilled water, and a CD-CIT complex aqueous solution (10 mL, 0.97 g CD-CIT) was added dropwise. The mixture was stirred at 80°C for 4 hours, yielding a black dispersion of the desired nanocatalyst, which was then separated with an external magnet and thoroughly washed with deionized water ($10 \text{ ml} \times 3$). The product was dried at 70°C for 24 hours in a forced-air drying oven to obtain the desired magnetic nano-phase transfer catalyst.

(3) Synthesis of $\text{Fe}_3\text{O}_4@\text{CTAB}@\beta\text{-CD}$:

Iron oxide nanoparticles were synthesized using the co-precipitation method. In a typical synthesis, $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (21.62 mg) and $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ (11.12 mg) were dissolved in 40 mL of deionized water in a 2:1 ratio. During the reaction process, the solution mixture was heated to 50°C under constant stirring. After 10 minutes, specified amounts of CTAB (7.29 mg) and β -CD (22.7 mg) were added, maintaining a ratio of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ to CTAB to β -CD at 1:0.5:0.5. After stirring with CTAB for 30 minutes, an ammonia solution (25% NH_4OH) was added dropwise to precipitate iron oxide nanoparticles. The final precipitate was thoroughly washed several times with deionized water to remove excess reagents and then freeze-dried.

Table S1. Molecular structures of organic compounds and HPLC settings

Compound	Structure	Detection Wavelength (nm)	Mobile Phase (v/v)	Flow rate (ml/min)
CBZ		285	water: methanol = 35:65	1.0
ERY		215	water (0.01 M K ₂ HPO ₄): acetonitrile = 45:55	1.0
DCF		276	water (0.1% acetic acid): acetonitrile = 15:85	0.5