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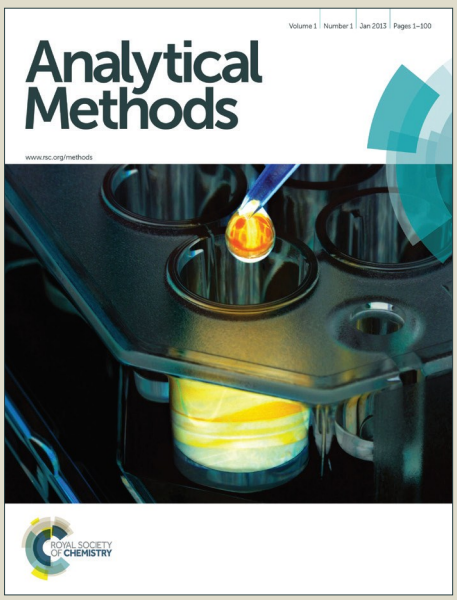

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Facile One-Pot Synthesis of β-Cyclodextrin-Polymer-Modified Fe_3O_4 Microspheres for Stereoselective Absorption of Amino Acids Compounds

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Abstract β-Cyclodextrin-polymer-modified Fe_3O_4 microspheres were synthesized using a one-pot hydrothermal method, with a β-cyclodextrin polymer as the surfactant. Investigation of the effects of the reaction time and amount of β-cyclodextrin polymer on the formation of functionalized microspheres suggested that the main factor affecting the microsphere size was the amount of β-cyclodextrin polymer, rather than the reaction time. The obtained β-cyclodextrin-polymer-modified Fe_3O_4 microspheres were characterized using various methods. The results indicated that the functionalized magnetic microspheres were spherical, dispersible and have high saturation magnetization. The β-cyclodextrin-polymer-modified Fe_3O_4 microspheres were applied for stereoselective absorption of DL-tryptophan enantiomers. The results suggested that the functionalized magnetic microspheres absorb more L-tryptophan and had chiral discrimination ability, and can therefore be used as a stereoselective absorbent for chiral analysis.

Keywords: magnetic microsphere; β-cyclodextrin polymer; stereoselective adsorption

1 Introduction

The two enantiomers of many racemic compounds often have significantly different toxicological, pharmacological, and biological activities as a result of specific stereoselective interactions in biotic environments [1-3]. The separation and analysis of racemic compounds is therefore active research areas in the pharmaceutical, clinical, agricultural, and environmental fields [4-7]. Although a wide range of analytical methods have been used for enantiomer separation, including chromatography [8-11], membrane separation [12], magnetic levitation [13], and crystallization [14, 15], most of these methods are limited to time-consuming and analytical scales. The development of fast and efficient enantioseparation strategies is needed for purity analysis of chiral compounds and control of the quality and safety of enantiomers.

Surface-functionalized nanomaterials such as carbon nanotubes[16], organic polymers [17, 18], metal-organic compounds [5], and mesoporous silica [19, 20] are ideal candidates for the discrimination and separation of chiral compounds [21]. Magnetic nanomaterials with large surface areas and high magnetism have attracted much attention for enantioseparation because they are inexpensive, and their use has the advantages of speed and simplicity [22-24]. Kumar et al. synthesized cellulose tris(3,5-dimethylphenylcarbamate)-modified Fe_3O_4@ZrO_2 magnetic core, and used them to separate racemic chiral drugs [25]. Choi et al. utilize the (S)-chiral selector functionalized magnetic microspheres as a chiral selector to enantioselectively interact with racemic amino acid solutions [26]. Chen et al. reported a simple and convenient

method for the synthesis of β-CD-functionalized silver nanoparticle and β-CD-modified Fe_3O_4 nanoparticle to analyze aromatic isomers and amino acids [27, 28]. In our group's previous work, we successfully prepared magnetic microspheres modified with teicoplanin and human serum albumin, and confirmed enantioselection by magnetic microsphere interactions with racemates [29, 30].

β-Cyclodextrin (β-CD), which is a common chiral selector, is widely used in the separation of aromatic amino acids, chiral pesticides, and chiral drugs, based on combinations of different molecular recognition modes, including host–guest, hydrogen-bonding, dipole–dipole, and electrostatic interactions [31-33]. Recently, β-CD polymers have attracted considerable attention, because they have better stereoselectivities than the parent β-CD as a result of their different structural conformations, rigid structures, and larger numbers of cavities [34-39]. Ahmed et al. prepared new β-CD-functionalized polymer monoliths for enantioseparation of different classes of pharmaceutical racemates. The new β-CD-functionalized polymers provided more points of interaction, significantly increasing their chiral discrimination ability [40]. Singh et al. used a β-CD-glutaraldehyde crosslinked membrane to absorb amino acid enantiomers and obtained 81% enantioselectivity for D-phenylalanine [41].

In the current work, a facile one-pot method for synthesizing β-CD-polymer-modified magnetic microspheres as a stereoselective absorbent for DL-tryptophan solution was developed. The amount of β-CD polymer and the reaction time were varied to investigate the formation mechanism of the functionalized

magnetic microspheres. Various characterization methods confirmed the successful preparation of the β-CD-polymer-modified magnetic microspheres. The adsorption equilibrium time and pH were optimized using stereoselective absorption experiments. The selective absorption capacity of the functionalized microspheres from DL-tryptophan was measured by capillary electrophoresis. A selective absorption mechanism was suggested.

2 Materials and methods

2.1 Materials and reagents

D-Tryptophan and L-tryptophan were supplied by J&K Scientific (Beijing, China). DL-Tryptophan and sodium cyanoborohydride were obtained from Acros Organics (Geel, Belgium). Epichlorohydrin and $FeCl_3 \cdot 6H_2O$ were purchased from the Tianjin Fuchen Chemical Reagent Factory (Tianjin, China). β-CD was purchased from the Tianjin Guangfu Fine Chemical Research Institute (Tianjin, China), and was purified three times using double-distilled water. All other chemical reagents were procured from Beijing Chemical Works (Beijing, China). All the chemicals used were of analytical grade and were used without further purification.

2.2 Synthesis of water-insoluble β-cyclodextrin-epichlorohydrin polymers

Water-insoluble β-CD-epichlorohydrin polymers (β-CDEP) were synthesized by the reaction of β-CD with epichlorohydrin in alkaline solution. The procedure was a modified version of a previously reported method [42, 43]. In a typical procedure, β-CD (12 g) was dissolved in NaOH solution (20% w/v, 25 mL) in a 100 mL three-necked flask containing $NaCH_3CN$ (30 mg), with mechanical stirring (400 rpm),

for 30 min. Epichlorohydrin (9.1 mL) was slowly added to the solution. During the polymerization procedure, the temperature was kept at 30 °C and the stirring rate was kept at 400 rpm. After 5 h, the polymerization was stopped by neutralizing with 6 M HCl. The obtained β-CDEP was washed three times with distilled water, dried under vacuum at 60 °C, ground, and sieved.

2.3 Fabrication of β-CDEP-modified Fe_3O_4 microspheres

β-CDEP-modified Fe_3O_4 microspheres were synthesized using a one-pot hydrothermal method, with β-CDEP as the surfactant. Typically, $FeCl_3 \cdot 6H_2O$ (2.7 g) and anhydrous sodium acetate (7.2 g) were dissolved by ultrasonication in ethylene glycol (80 mL) to form a yellow solution, followed by addition of the β-CDEP (0.4 g). The mixture was stirred vigorously for 1 h, sealed in a Teflon-lined autoclave of capacity 100 mL, heated in an oven at 200 °C for 8 h, and then cooled to room temperature. The product was collected and washed three times with ethanol, and then dried under vacuum at 60 °C.

2.4 Characterization

The morphologies of the magnetic microspheres were examined using transmission electron microscopy (TEM; Hitachi H-800, Tokyo, Japan) and scanning electron microscopy (SEM; Zeiss Supera55, Germany). The crystal structures of the magnetic microspheres were determined using X-ray diffraction (XRD; Rigaku Ultima3 with Cu Kα radiation, Tokyo, Japan). The functional groups in the magnetic microspheres were identified using Fourier-transform infrared spectroscopy (FT-IR; Thermo Fisher Scientific Nexus 8700, Waltham, CT, USA). The magnetization curves of the

magnetic microspheres were measured using a vibrating sample magnetometer (Lake Shore-7410, Westerville, USA). Thermogravimetric analysis (TGA) of the magnetic microspheres was performed using an HCT-2 thermo-analysis system (Beijing, China), at a heating rate of 10°C min^{-1}, from 25 to 1000°C under a N_2 flow rate of 10 mL min^{-1}. Raman spectroscopy was performed using a confocal laser micro-Raman spectrometer (Renishaw Via-Reflex, London, UK). Energy-dispersive X-ray spectroscopy (EDX) was used to determine the surface composition of the magnetic microspheres (X-Supreme8000, Oxford, UK).

2.5 Optimization of adsorption equilibrium time

The adsorption equilibrium times for D-tryptophan and L-tryptophan were determined by mixing a tryptophan solution and β-CDEP-modified Fe_3O_4 microspheres. The details are as follows: β-CDEP-modified Fe_3O_4 microspheres (100 mg) were dispersed in phosphate buffer (0.2 M, pH = 9.0, 20 mL) and collected using a magnet. The wet functionalized magnetic microspheres were dispersed in 1.5 mg mL^{-1} D-/L-tryptophan (10 mL), with stirring, for various times (0.5, 1, 2, 3, and 4 h). The supernatant was separated and filtered through a 0.22 μm syringe filter. The absorbance of a stock solution (1.5 mg mL^{-1} D-/L-tryptophan) and the supernatant were measured using an ultraviolet (UV) spectrometer. All experiments were repeated three times.

2.6 Optimization of buffer pH

The buffer pH usually affects the amino acid adsorption capacities of microspheres, because of the different charges of amino acids. Detailed experiments were performed

to determine the effect of the buffer pH on the adsorption of D-/L-tryptophan by β-CDEP-modified Fe_3O_4 microspheres. Typically, β-CDEP-modified Fe_3O_4 microspheres (100 mg) were washed with 0.2 M phosphate buffer (10 mL) at pH 4-9 and dispersed in 1.5 mg mL^{-1} D-/L-tryptophan (10 mL) at pH 4-9, with stirring, for 1 h. After separation and filtration through a 0.22 μm syringe filter, the supernatant was examined using UV spectroscopy. All experiments were repeated three times.

2.7 Determination of the enantiomeric excess of DL-tryptophan separated by β-CDEP-modified Fe_3O_4 microspheres

Determination of the enantiomeric excess of DL-tryptophan was examined with capillary electrophoresis (CE) to study the chiral recognition ability of the β-CDEP-modified Fe_3O_4 microspheres. β-CDEP-modified Fe_3O_4 microspheres (100 mg) were washed three times with 0.2 M phosphate buffer (pH 6, 10 mL); the functionalized magnetic microspheres and 0.2 mg mL^{-1} DL-tryptophan (prepared in 0.2 M phosphate buffer, pH 6, 10 mL) were mixed, with mechanical stirring (300 rpm), for 1 h. The supernatant was separated and filtered through a 0.22 μm syringe filter for CE analysis. The enantiomeric excess was evaluated using a calibration curve for D/L-tryptophan, which was constructed by plotting the peak area as a function of the concentration. Quantitative analysis was performed using a Beckman Coulter MDQ system combined with a UV detector at 214 nm (Beckman Coulter Corp., CA, USA). The interactions of various amounts of β-CDEP-modified Fe_3O_4 microspheres with DL-tryptophan were examined.

3 Results and discussion

Typical procedures for the preparation of β-CDEP and β-CDEP-modified Fe_3O_4 microspheres, and the stereoselective absorption experiments, are shown in Figure 1. Epichlorohydrin was used as a crosslinking agent to produce the β-CDEP, and then the β-CDEP was used in a hydrothermal reaction to synthesize β-CDEP-modified Fe_3O_4 microspheres. In this study, the amount of β-CDEP and the reaction time were varied to investigate the formation mechanism of the functionalized magnetic microspheres.

3.1 Characterization of β-CDEP

Epichlorohydrin is a bifunctional crosslinking agent, which can form bonds with β-CD molecules in alkaline media. However, the molar ratio of epichlorohydrin to β-CD affects the rigidity of the polymer. The total amount of β-CD was determined by elemental analysis. The elemental analytical results for β-CDEP were C: 45.58% and H: 6.16%. This indicates that the reaction molar ratio of epichlorohydrin to β-CD was 12:1. The rigidity of β-CDEP is therefore acceptable, based on previously reported results [44]. The broad characteristic absorption in the FT-IR spectrum of β-CD in the range 1200-900 cm^{-1} changed after addition of epichlorohydrin (Figure S1 in the Supporting Information), confirming polymer formation and indicating the presence of basic structural β-CD units in the polymer.

3.2 Optimization of amount of β-CDEP added and reaction time

It has been reported that the polymer added and reaction times affect the morphologies and structures of functionalized magnetic microspheres [45]. In this study, the amount of β-CDEP added and the reaction time were optimized to explore

the formation mechanism of β-CDEP-modified magnetic microspheres. A series of experiments with different amounts of β-CDEP (0.2, 0.4, 0.6, and 0.8 g) and different reaction times (4, 16, 24, and 32 h) were performed. The experimental results are shown in Figures 2 and 3. When the amount of β-CDEP added was 0.2 g, the average diameter of the microspheres was about 400 nm. The mean diameter of the microspheres decreased significantly to about 220 nm when the amount of β-CDEP was increased to 0.4 g. When the amount of β-CDEP increased to 0.6 g or 0.8 g, the microsphere size was not affected. One explanation is that the β-CDEP becomes saturated in the ethylene glycol, and the excess β-CDEP does not participate in the chemical reaction. In this one-pot synthesis reaction, the β-CDEP is as surfactants against particle agglomeration and plays a role in the assembly of crystalline grains in the microspheres.

Functional magnetic microsphere formation is a very fast process. When the reaction time was 4 h, the prepared microspheres were of similar size; when the reaction time was increased to 32 h, the sizes of the prepared microspheres only increased slightly. These results differed from those in previous reports, which showed that the microsphere diameter increased from 150 to 450 nm for reaction times ranging from 8 to 44 h [46]; therefore a new clarification of the formation mechanism is required to explain the present results. The surface composition of the magnetic microspheres was analyzed using EDX. The results indicated that the weight percentage of iron and carbon elements was 11.8% and 10.7%, respectively (Figure S2 in the Supporting Information). It is suggested that the surfaces of the

functionalized magnetic microspheres contain large amounts of β-CDEP resulting in the particle to stop growing; therefore the microsphere diameter is unchanged.

3.3 Characterization of β-CDEP-modified Fe_3O_4 microspheres

The morphologies and sizes of the functionalized magnetic microspheres were examined using TEM and SEM. Fe_3O_4 magnetic microspheres and β-CDEP-modified microspheres synthesized using a reaction time of 8 h was compared. As shown in Figure 4(A) and (C), the mean diameter of the β-CDEP-modified Fe_3O_4 microspheres was smaller than that of the Fe_3O_4 microspheres. The β-CDEP-modified Fe_3O_4 microspheres were spherical, with a narrow size distribution of around 230 nm. Figure 4(D) shows that the surfaces of the β-CDEP-modified Fe_3O_4 microspheres were rough, which suggests that the β-CDEP formed a polymer layer on the surfaces of the microspheres.

The crystal structures of the Fe_3O_4 microspheres and the functionalized Fe_3O_4 microspheres were determined using XRD. As shown in Figure 5(A), all the diffraction peaks of the prepared microspheres were consistent with the standard XRD patterns of Fe_3O_4 (JCPDS, NO.85-1436; not shown). In contrast, based on the intensities of the peaks in the XRD pattern, the β-CDEP-modified Fe_3O_4 microspheres consisted of many large crystalline grains. These results suggest that β-CDEP inhibits the nucleation rate of the crystals, resulting in large crystalline grains.

The FT-IR spectra of the obtained functionalized magnetic microspheres, shown in Figure 5(B), were used to determine the functional groups on the microsphere surfaces. The peaks at 583 and 3400 cm^{-1} indicate the presence of Fe-O groups and

hydroxyl groups, respectively. After β-CDEP addition, peaks appeared at 2926 and 2876 cm^{-1}, assigned to stretching vibrations of $–CH_2$ groups, and the wide absorption peak at 1200 to 900 cm^{-1} was attributed to the characteristic peak of the β-CD cavity, further confirming microsphere modification by β-CDEP.

According to a previous report, surfactant addition may change the structural phases of iron oxides. The XRD patterns did not indicate whether the functionalized microspheres were Fe_3O_4 or γ-Fe_2O_3; therefore Raman spectroscopy was used to determine the crystalline form of the functionalized magnetic microspheres. Figure 5(C) showed a strong peak at 663 cm^{-1}, typical of Fe_3O_4. No characteristic γ-Fe_2O_3 band was observed. These results indicated that the prepared samples were Fe_3O_4, and β-CDEP addition had no effect.

The magnetic behavior of the functionalized magnetic microspheres, which is crucial for practical applications, was measured at room temperature. Figure 5(D) showed that the β-CDEP-modified Fe_3O_4 microspheres had excellent dispersibility in water. The saturation magnetization values for Fe_3O_4 and β-CDEP-modified Fe_3O_4 microspheres were 78.1 and 58.8 emu g^{-1}, respectively. The magnetic response of the β-CDEP-modified Fe_3O_4 microspheres was significantly lower than that of the Fe_3O_4 microspheres because of the nonmagnetic polymer component. However, as shown in the inset in Figure 6(D), the β-CDEP-modified Fe_3O_4 microspheres can be rapidly collected using an external magnet. The β-CDEP-modified Fe_3O_4 microspheres have excellent magnetic responsiveness, which is favorable for separation.

TGA analytical results for the Fe_3O_4 microspheres and β-CDEP-modified Fe_3O_4

microspheres were shown in Figure 6. The TGA curves can be divided into two parts: the first weight loss was explained by dehydration of the microspheres, and the second weight loss is mainly caused by thermal decomposition of organic compounds. For the Fe_3O_4 microspheres, a weight loss of 7.59% was observed over the full temperature range, whereas the weight loss for β-CDEP-modified microspheres was 26.62% at 1000°C. These data showed that the β-CDEP-modified Fe_3O_4 microspheres contained 19.02% β-CDEP. In the one-pot synthetic reactions, the surfaces of the magnetic microspheres were well modified by β-CDEP.

3.4 Evaluation of enantioselective absorption of DL-tryptophan by β-CDEP-modified Fe_3O_4 microspheres

To explore the enantioselective absorption conditions, the adsorption equilibrium time and pH, two of the most important factors, were optimized. The results of the experiments are shown in Figure 7. Figure 7(A) shows that after interaction with the β-CDEP-modified Fe_3O_4 microspheres, the D-/L-tryptophan absorbance decreased significantly. A longer adsorption equilibrium time allows the microspheres to absorb more tryptophan; however, the absorbance only decreased slightly after 1 h. The optimum adsorption equilibrium time was therefore 1 h. The effect of buffer pH on the adsorption of D-/L-tryptophan by the β-CDEP-modified Fe_3O_4 microspheres was also optimized, as shown in Figure 7(B). The results indicate that the optimum pH was 6, near the isoelectric point of D-/L-tryptophan (pH 5.89). The absorption capacity was maximum at this pH. This is probably because of electrostatic interactions between tryptophan and the microspheres, leading to the maximum capacity.

Under the optimum absorption conditions, the supernatant solution was quantitatively estimated using CE analysis. The results of the experiments are shown in Figure 8. Before the interactions with β-CDEP-modified Fe_3O_4 microspheres, the two enantiomers of DL-tryptophan had equal peak areas. After treatment with 100 mg of β-CDEP-modified microspheres, the peak areas of D-tryptophan and L-tryptophan both decreased sharply. The same results were obtained with 200 or 300 mg of β-CDEP-modified Fe_3O_4 microspheres. However, the peak areas of D-tryptophan were higher than those of L-tryptophan during interactions with β-CDEP-modified Fe_3O_4 microspheres, which suggest that more L-tryptophan was absorbed on the β-CDEP-modified Fe_3O_4 microspheres. In addition, calibration curves for D-tryptophan and L-tryptophan were used to evaluate the supernatant enantiomeric excesses. The calibration curves were $y = (3.91 \times 10^5)\, x + (1.37 \times 10^4)$, $r = 0.9988$ for D-tryptophan, and $y = (3.86 \times 10^5)\, x + (1.56 \times 10^4)$, $r = 0.9986$ for L-tryptophan. The supernatant enantiomeric excess of DL-tryptophan was 8.2%, 10.8%, and 44.2% after interaction with 100, 200, and 300 mg, respectively, of β-CDEP-modified Fe_3O_4 microspheres. These results clearly show that the β-CDEP-modified Fe_3O_4 microspheres have some stereoselective ability for the enantiomers.

4. Conclusions

In this study, a β-CDEP was prepared and used as the surfactant in the one-pot hydrothermal synthesis of β-CDEP-modified Fe_3O_4 microspheres. The size of the functionalized magnetic microspheres was mainly influenced by the amount of β-CDEP. Various characteriation methods were used to confirm β-CDEP modification

of the magnetic microsphere surfaces. The results indicated that the functionalized magnetic microspheres are spherical and have high saturation. Stereoselective absorption experiments using DL-tryptophan as a model indicated that the β-CDEP-modified Fe_3O_4 microspheres showed chiral discrimination, and could be used as a stereoselective absorbent for pharmacological and biomedical research.

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Figures and figure captions

Figure 1 Schematic illustration for synthesis of β-CDEP and β-CDEP-modified Fe_3O_4 microspheres, and its stereoselective absorption of DL-tryptophan

Figure 2 TEM images of β-CDEP-modified Fe_3O_4 microspheres with different amounts of β-CDEP: (A) 0.2, (B) 0.4, (C) 0.6, and (D) 0.8 g; reaction time: 8 h

Figure 3 TEM images of β-CDEP-modified Fe_3O_4 microspheres obtained at different reaction times: (A) 4, (B) 16, (C) 24, and (D) 32 h; amount of β-CDEP added: 0.4 g

Figure 4 TEM and SEM images of (A) and (B) Fe_3O_4 microspheres, and (C) and (D)

β-CDEP-modified Fe_3O_4 microspheres

Figure 5 Properties of (a) Fe_3O_4 microspheres and (b) β-CDEP-modified Fe_3O_4 microspheres: (A) XRD patterns, (B) FT-IR spectra, (C) Raman spectra, and (D) magnetization hysteresis loops

Figure 6 TGA curves of (a) Fe_3O_4 and (b) β-CDEP-modified Fe_3O_4 microspheres

Figure 7 Optimization of (A) adsorption equilibrium time and (B) pH

Figure 8 CE separation (A) and peak area (B) of DL-tryptophan after interaction with different amounts β-CDEP-modified Fe_3O_4 microspheres: (a) 0, (b) 100, (c) 200, and (d) 300 mg. Separation conditions: capillary, 50.2 cm × 50 μm id (40.2 cm to the detector); detection wavelength 214 nm; sample injection, 0.5 psi for 3 s; applied voltage, 25 kV; running buffer, 100 mM H_3PO_4–NaH_2PO_4 (pH 2.5), 40 mM α-CD

Figure S1 FT-IR spectrum of (a) β-CD and (b) β-CDEP

Figure S2 Contents of iron and carbon element in β-CDEP-modified Fe_3O_4 microspheres by EDX spectroscopy analysis

Graphical Abstract

Facile One-Pot Synthesis of β-Cyclodextrin-Polymer-Modified Fe_3O_4 Microspheres for Stereoselective Absorption of Amino Acids Compounds

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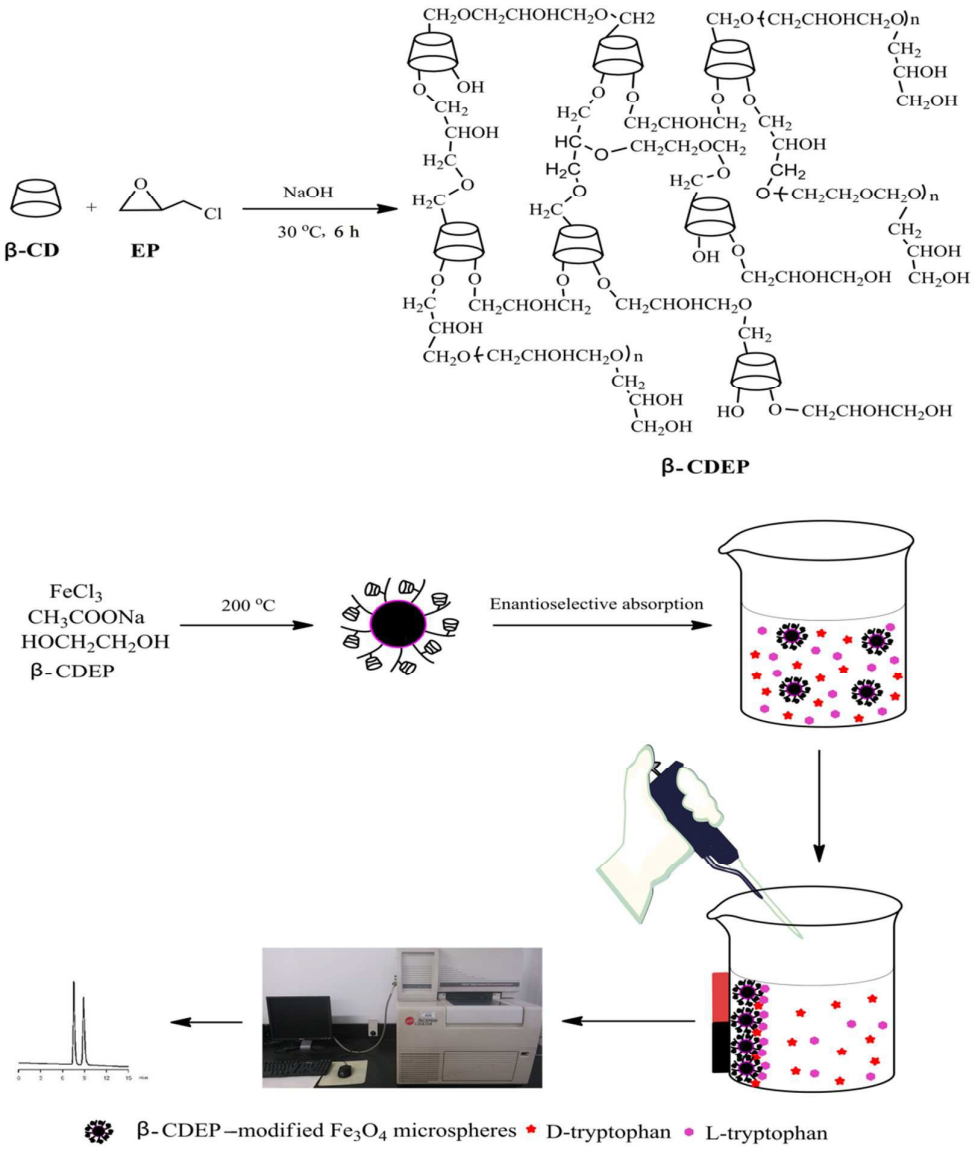
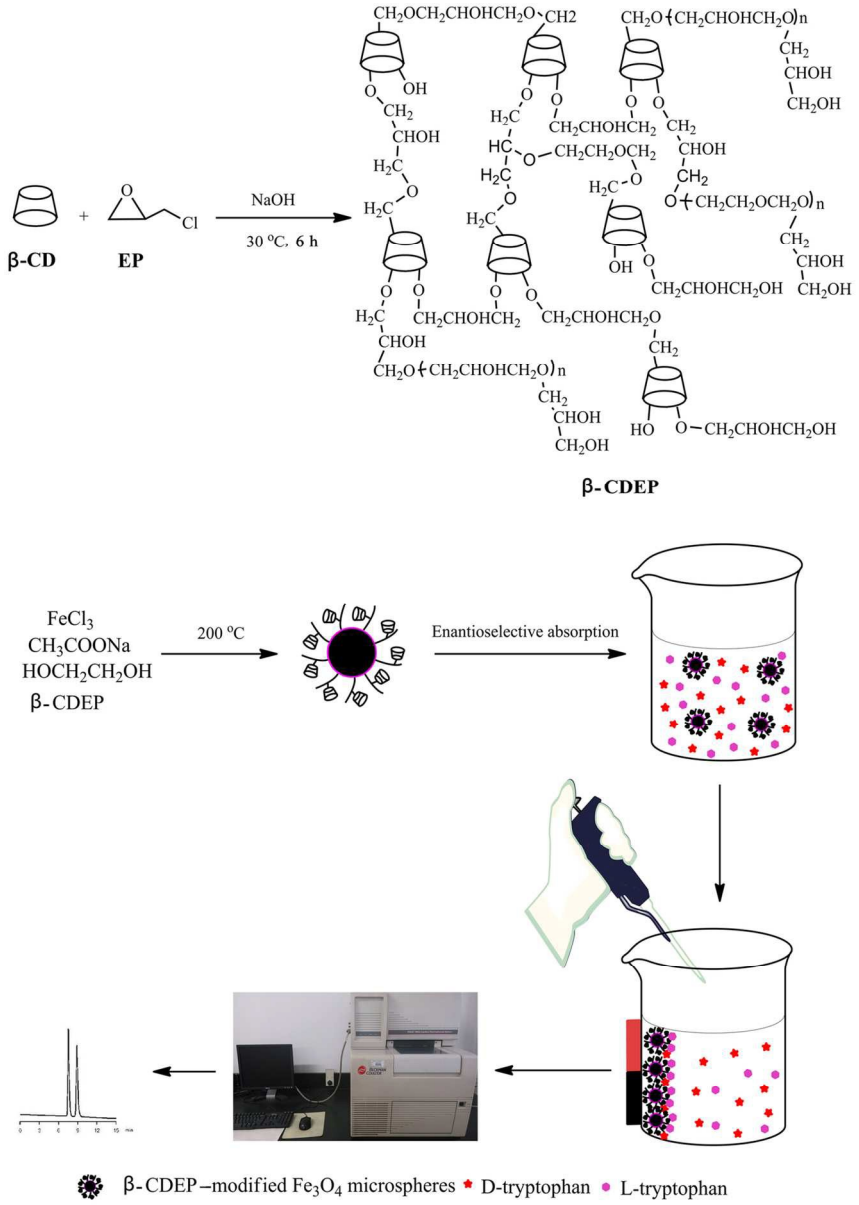


Schematic illustration for synthesis of β-CDEP and β-CDEP-modified Fe_3O_4 microspheres, and its stereoselective absorption of DL-tryptophan



Schematic illustration for synthesis of β-CDEP and β-CDEP-modified Fe3O4 microspheres, and its stereoselective absorption of DL-tryptophan
117x164mm (300 x 300 DPI)

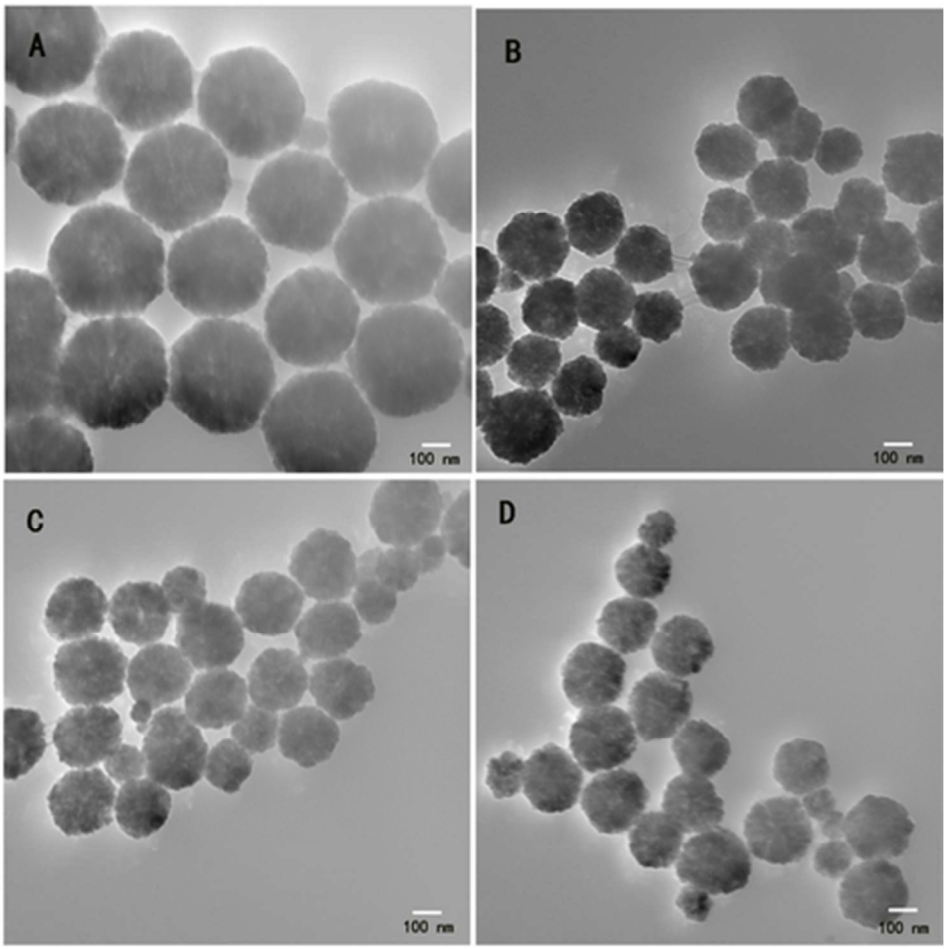


Figure 2 TEM images of β-CDEP-modified Fe3O4 microspheres with different amounts of β-CDEP: (A) 0.2, (B) 0.4, (C) 0.6, and (D) 0.8 g; reaction time: 8 h
39x39mm (300 x 300 DPI)

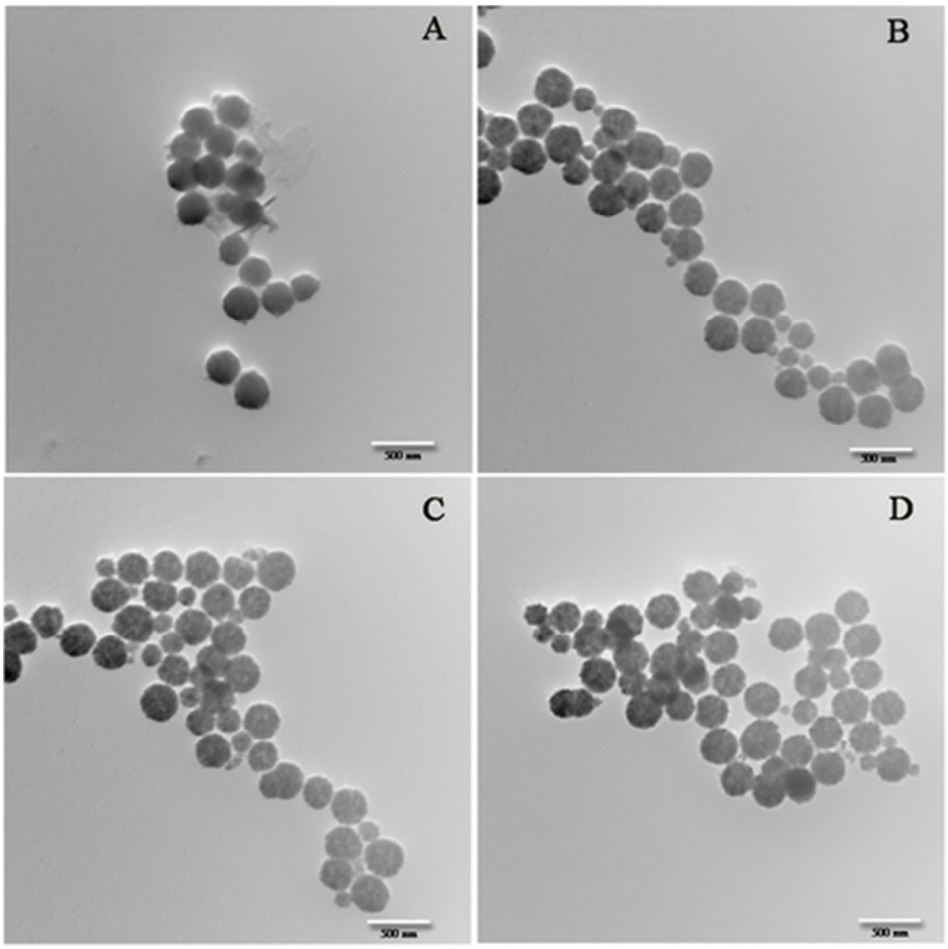


Figure 3 TEM images of β-CDEP-modified Fe3O4 microspheres obtained at different reaction times: (A) 4, (B) 16, (C) 24, and (D) 32 h; amount of β-CDEP added: 0.4 g
39x39mm (300 x 300 DPI)

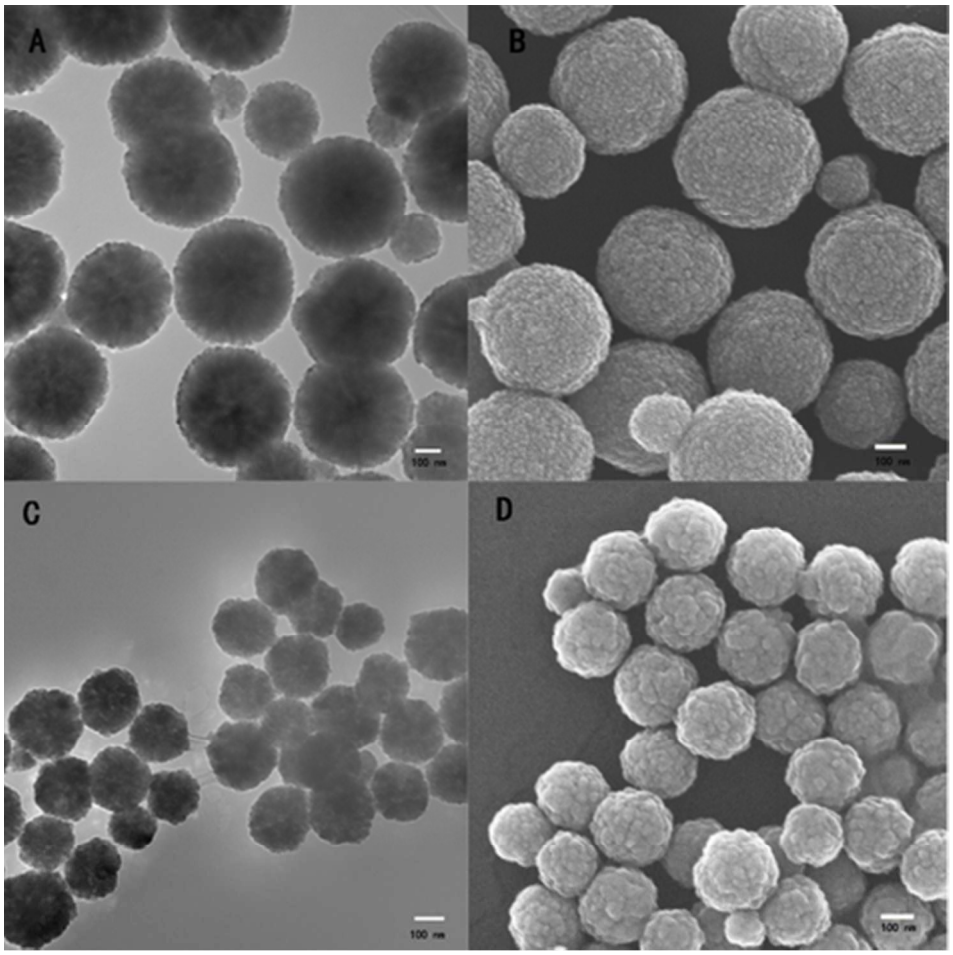


Figure 4 TEM and SEM images of (A) and (B) Fe3O4 microspheres, and (C) and (D) β-CDEP-modified Fe3O4 microspheres
39x39mm (300 x 300 DPI)

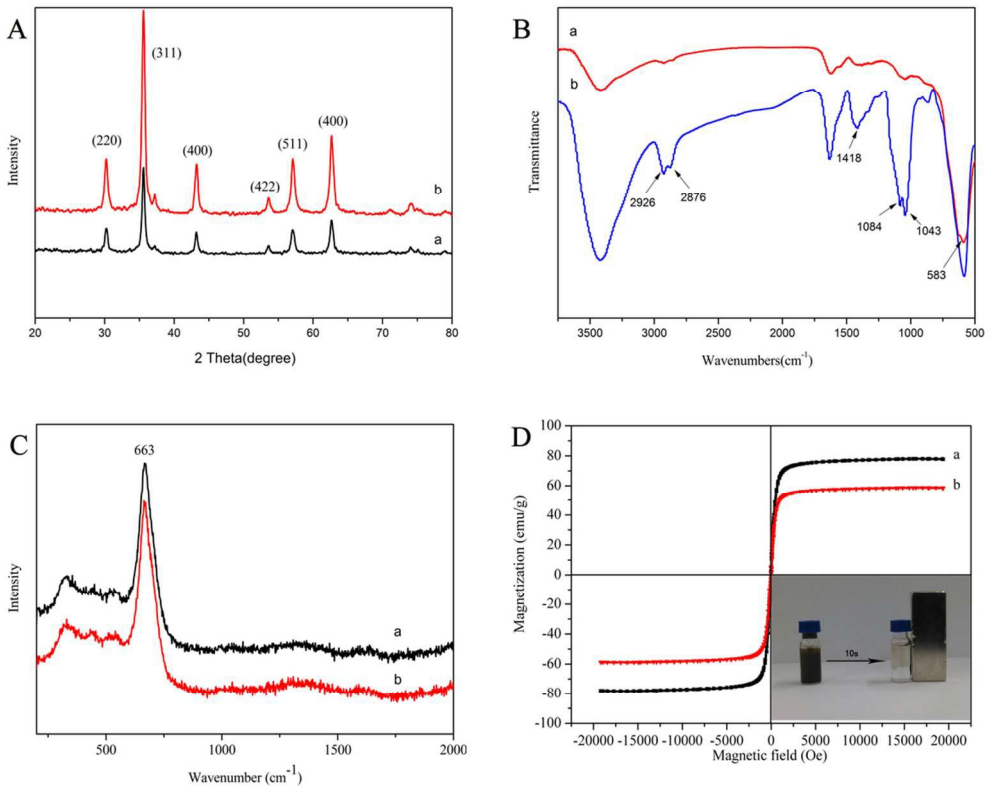


Figure 5 Properties of (a) Fe3O4 microspheres and (b) β-CDEP-modified Fe3O4 microspheres: (A) XRD patterns, (B) FT-IR spectra, (C) Raman spectra, and (D) magnetization hysteresis loops
99x80mm (300 x 300 DPI)

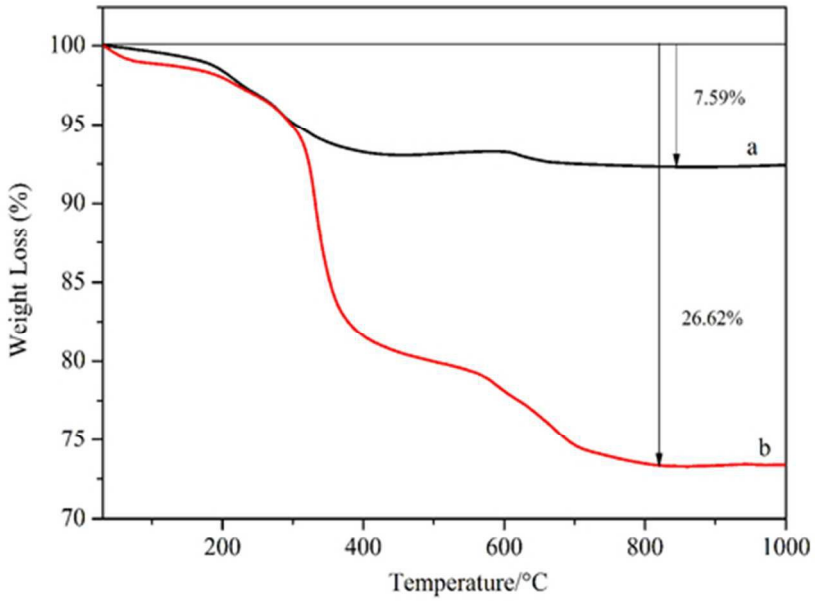


Figure 6 TGA curves of (a) Fe3O4 and (b) β-CDEP-modified Fe3O4 microspheres
49x35mm (300 x 300 DPI)

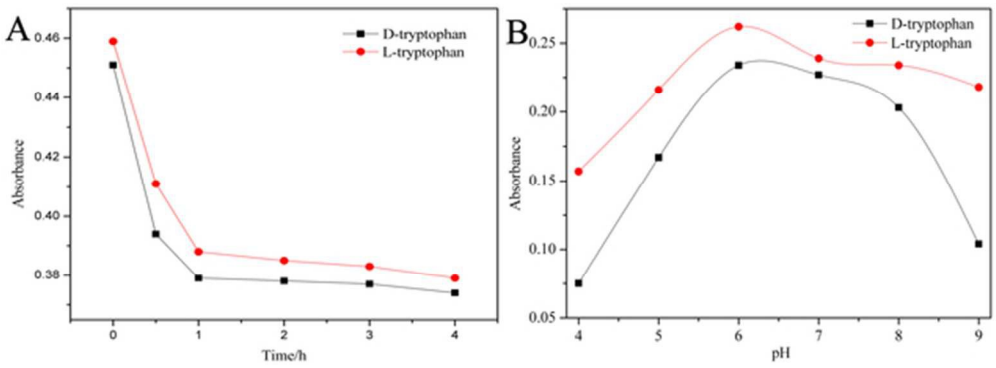


Figure 7 Optimization of (A) adsorption equilibrium time and (B) pH
54x19mm (300 x 300 DPI)

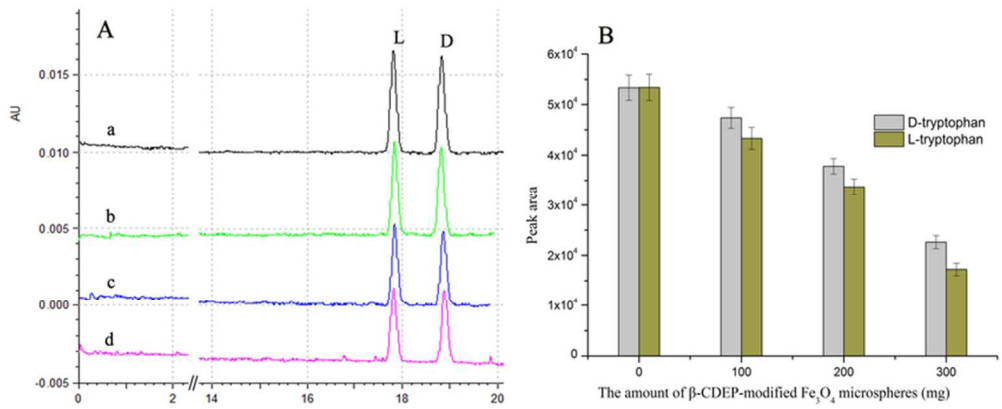


Figure 8 CE separation (A) and peak area (B) of DL-tryptophan after interaction with different amounts β-CDEP-modified Fe3O4 microspheres: (a) 0, (b) 100, (c) 200, and (d) 300 mg. Separation conditions: capillary, 50.2 cm × 50 μm id (40.2 cm to the detector); detection wavelength 214 nm; sample injection, 0.5 psi for 3 s; applied voltage, 25 kV; running buffer, 100 mM H3PO4–NaH2PO4 (pH 2.5), 40 mM α-CD
71x30mm (300 x 300 DPI)

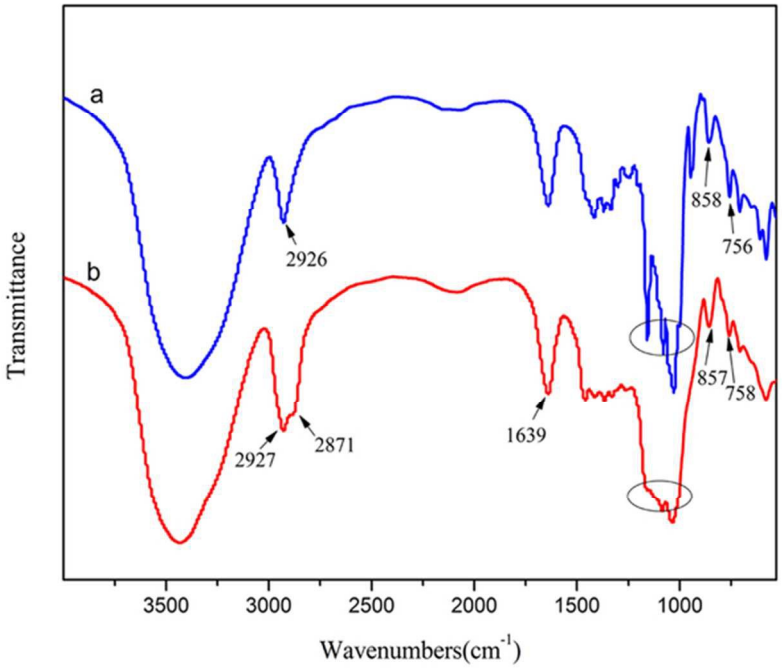


Figure S1 FT-IR spectrum of (a) β-CD and (b) β-CDEP
64x49mm (300 x 300 DPI)

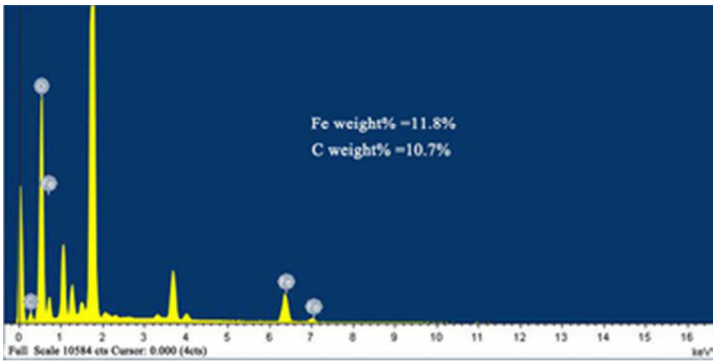


Figure S2 Contents of iron and carbon element in β-CDEP-modified Fe3O4 microspheres by EDX spectroscopy analysis
29x14mm (300 x 300 DPI)