Synthesis of Reusable Cyclodextrin Polymers for Removal of Naphthol and Naphthylamine from Water

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Research Article

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Abstract

As one group of important naphthalene derivatives, naphthol and naphthylamine, are diffusely employed as dye intermediates. The presence of naphthol and naphthylamine in water systems may pose risks to the environment and public health due to their carcinogenicity. In this study, four mesoporous polymers prepared by β-cyclodextrin derivatives and tetrafluoroterephthalonitrile were obtained, and applied to deal with 1-naphthylamine, 2-naphthylamine, 1-naphthol, and 2-naphthol from water. The impact of adsorption time, initial concentration of naphthol and naphthylamine, and temperature on the adsorption efficiency of the four polymers were explored separately. The four polymers present fast adsorption kinetics towards naphthol and naphthylamine, attaining 93%~100% of adsorption equilibrium uptake for 1-naphthol, 1-naphthylamine, 2-naphthylamine in 15 min, and 87%~90% of equilibrium uptake for 2-naphthol in 15 min. The kinetics could be depicted well by the pseudo-second-order kinetic model. The adsorption isotherms of the four polymers towards naphthol and naphthylamine accord with Redlich-Peterson or Sips model. The adsorption ratio increases fast with reducing the initial concentration of naphthol and naphthylamine, which suggest that these polymers are applicable to removing low concentration of naphthol and naphthylamine from water. The adsorption ratio of naphthol and naphthylamine in 5 mg/L, can achieve over 95% in 25 ^{o}C. In addition, the four polymers can be effortlessly recovered by a gentle and simple washing procedure with little reduction in performance. The adsorption performance of the four polymers towards the four naphthalene derivatives can be improved by increasing the adsorption temperature. In conclusion, the prepared β-cyclodextrin polymers exhibit rapid water treatment in removing the four low-concentration naphthalene derivatives with convenient regeneration and good reusability.

Introduction

Polycyclic aromatic hydrocarbons (PAHs), released into the environment through natural and anthropogenic activities, are known to have immunotoxicity, genotoxicity, carcinogenicity, and mutagenicity (Haritash and Kaushik. 2009). Naphthalene and its derivatives, a type of PAHs, are frequently present in wastewater produced from dye intermediates (Xu et al. 1997). Naphthylamine and naphthol are one group of important naphthalene derivatives and are diffusely employed as dye intermediates. For example, 1-naphthol, which has hard degradability and high biological toxicity, is a raw material for synthetic dyes, rubber antioxidants, fragrances, and pesticides. (Zhang et al. 1997). 1-naphthol and 1-naphthylamine, among top priority contaminants, are regulated as carcinogens and extensively adopted as industrial intermediates. They are ubiquitous in 1-naphthol production wastewater (Yang et al. 2021; Zhang et al. 2008). 2-naphthylamine, a strong carcinogen, has been banned in the textile industry due to its susceptibility to bladder cancer (Czubacka and Czerczak 2020). Therefore, there is an urgent need to explore an economical, efficient, and green treatment technology to treat naphthol and naphthylamine in water. Compared to other treatment processes, adsorption is generally used as the preferred separation method for removing pollutants from water due to its simpleness, effectivity, and effectivity (Hu et al. 2011; Rebekah et al. 2020). The feasibility and efficiency of the adsorption process

are generally determined by the nature of the adsorbent. The design of new high-performance adsorbents with longer live time are still research interests and technical challenges (Hu et al. 2020; Yang et al. 2020).

Cyclodextrin (CD) has a well-defined cylindrical cavity-essentially a "cage" structure. Both ends of the nano-scale cavity have multiple hydroxyl groups. The central cavity of the cyclodextrin cage is hydrophobic, providing ideal coordination for small organic molecules to form the ”host-guest“ complex compound (Kenneth 1997). High-efficiency crosslinking agents can transform molecular nanocavities into 3D nanoporous polymers. By adjusting the degree of crosslinking, a hydrophobic polymer with a "molecular host" can be obtained, which can capture the target organic compound (Nadia and Grégorio 2013; Zhao et al, 2017). The non-covalent mutual attraction between the guest molecules and the host cavity can effectively remove organic matter even at very low concentrations (Alsbaiee et al, 2016; Hu et al, 2020; Li and Ma 1999; Mhlanga et al, 2007). Using small polyfunctional molecule as the crosslinking agent, such as epichlorohydrin, would result in a weak mechanical strength of the polymer with a gel-like appearance. To synthesize CD polymers with permanent microporosity and high CD content, a multifunctional crosslinking agent with small molecular size and strong structure is needed (Alsbaiee et al. 2016; Gu et al. 2006; Mhlanga et al. 2007). As a new cross-linking agent, rigid tetrafluoroterephthalonitrile is proposed by Alsbaiee et al. (Alsbaiee et al. 2016) and Ling et al. (Ling et al. 2017). Using this new cross-linking agent, an insolubly porous β-cyclodextrin polymer was obtained and applied to removing aromatic organic micro-pollutants effectively from water.

Herein, we explore the cyclodextrin derivatives polymers with tetrafluoroterephthalonitrile (TFPN) as cross-linking agent to deal with the naphthol and naphthylamine in water. The cyclodextrin derivatives include β-cyclodextrin, methylated-β-cyclodextrin, hydroxypropyl-β-cyclodextrin, and hydroxyethyl-β-cyclodextrin. The structures of the synthesized polymers and their adsorption performance for naphthol and naphthylamine removal from water were studied comprehensively.

Materials And Methods

Synthesis of Polymers

All the reagents used were purchased from different vendors and were of analytical grade. The detailed introduction about materials were provided in Supplementary data. Cyclodextrin and its derivative polymers were synthesized according to the reference (Alsbaiee et al. 2016). First, 0.88 mmol of β-CD, HE-β-CD, HP-β-CD and Me-β-CD were separately added into different 500 mL round bottomed flasks, and then 2.5 mmol tetrafluoroterephthalonitrile and 10.93 mmol K_2CO_3 were added into the flasks. 300 mL of mixed solvent containing THF and DMF with volume ratio of 9:1 was added to the flasks under N_2 condition. The mixtures were stirred at 85 ^oC. After 48 hours, the reactions were cooled to room temperature and filtered. The solids in the filter cake were washed with 1 mol/L dilute hydrochloric acid until no bubbles escape. Then, the solids were washed for three times with water for 15 minutes, and soaked in THF for 30 minutes and in dichloromethane for 15 minutes. Finally, the yellow solids for β-CD polymer and Me-β-CD polymer, the light-yellow solid for HP-β-CD polymer, as well as the earthy yellow

solid for HE-β-CD polymer were obtained by filtration and freeze-drying for 24 hours. The solid materials were ground into powder for the next step of analysis and adsorption experiments. The above four polymers were called as β-CDP, HE-β-CDP, HP-β-CDP, and Me-β-CDP, respectively.

Batch Adsorption And Recycling Experiment

Synthetic contaminant solutions were obtained by dissolving certain amounts of naphthalene derivatives into deionized water. Adsorption tests were carried out as the following procedures. 10 mg of the synthetic adsorbent was added into a 50 mL centrifuge tube, and then 10 mL of contaminant solution with a certain concentration was transferred into the centrifuge tube. The centrifuge tube was fully oscillated in a stable temperature horizontal shaking bath for a period of time. The solution of each batch experiment was filtered using a 0.22 μm membrane filter and the contaminant concentration of the sample was detected by high performance liquid chromatography (HPLC). The initial concentration of contaminant solution was 50 mg/L except for isothermal adsorption experiments. Except for kinetic adsorption experiments, the contact time was 120 min. The adsorption temperature was set at 25 ^{o}C except for specified description. The concentration of the naphthol and naphthylamine in water were determined by HPLC. The adsorption capacity (Q_t, mg·g^{-1}) and adsorption ratio (R%) of CD polymer for naphthol and naphthylamine were used to analyze the adsorption efficiency. Analytical information for all naphthol and naphthylamine is provided in Supplementary data.

After the equilibrium adsorption was reached, the adsorbent was filtered and recovered from the centrifuge, and then dried under vacuum freezing condition. 10 mg of recovered and dried β-CDP was transferred into a centrifuge tube, and regenerated using 10 mL of methanol as desorption solvent at 25 ^{o}C for 120 min. The desorbed adsorbent was dried again overnight in vacuum freeze-drying agent for the next cycle.

Results And Discussion

Characterization

The characterization of the as-synthesized polymers was investigated by thermal gravimetric analyzer, scanning electron microscopy, Fourier transform infrared spectroscopy, and N_2 adsorption-desorption method. The detailed introduction about instruments were provided in Supplementary data. Firstly, the structures of β-CD, β-CDP, HE-β-CD, HE-β-CDP, HP-β-CD, HP-β-CDP, Me-β-CD, Me-β-CDP and TFPN were characterized by FT-IR. As presented in Fig. 1, the characteristic absorption peaks of C ≡ N and C-F vibration are obviously observed at 2252 cm^{-1} and 1260 cm^{-1} in the FT-IR spectrum of TFPN, respectively. The absorption peaks of hydroxyl group at 3386 cm^{-1}, aliphatic C-H stretch at 2929 cm^{-1}, strong C-O stretch at 1033 cm^{-1} are observed in the FT-IR spectrum of β-CD, HE-β-CD, HP-β-CD, and Me-β-CD. All the above characteristic absorption peaks of C ≡ N vibration, C-F vibration, hydroxyl group vibration, aliphatic C-H stretch, and strong C-O stretch are obviously observed in the FT-IR spectra of β-

CDP, HE-β-CDP, HP-β-CDP, and Me-β-CDP, which indicates that the four polymers of β-CD, HE-β-CD, HP-β-CD, and Me-β-CD cross-linked with TFPPN have been successfully prepared.

The surface morphologies of four cyclodextrin polymers were observed by scanning electron microscope. As revealed in Fig. 2, the surface shapes of the four polymers are irregular, and it can be clearly seen that the four cyclodextrin polymers have rough surface morphology and uneven distribution of pores. This structure is conducive to the adsorption of pollutants. The specific surface areas and porosity of β-CDP、HE-β-CDP、HP-β-CDP and Me-β-CDP calculated by BJH method according to N_2 adsorption-desorption isotherms (Fig. 3) were 20.09 $m^2 \cdot g^{-1}$, 19.02 $m^2 \cdot g^{-1}$, 21.37 $m^2 \cdot g^{-1}$ and 23.51 $m^2 \cdot g^{-1}$, respectively. The inset figures in Fig. 3 illustrate the pore size of the four CD polymers ranges from 2 nm to 5 nm, indicating β-CDP、HE-β-CDP、HP-β-CDP and Me-β-CDP have the characteristics of mesoporous materials.

The four cyclodextrin polymers were also characterized by thermogravimetry, exploring the stability of materials at different temperatures. Figure 4 shows that the thermal stability of the four cyclodextrin polymers is similar. The mass loss of water adsorbed on β-CDP, HE-β-CDP, HP-β-CDP and Me-β-CDP are 6.72%, 6.66%, 6.73% and 7.31% respectively in the temperature range of 25 ^oC to 100 ^oC. From 100 ^oC to 245 ^oC, the thermogravimetric analysis curves remain stable, suggesting that the synthetic cyclodextrin polymers are stable in this range of temperature studied. The mass loss of β-CDP, HE-β-CDP, HP-β-CDP and Me-β-CDP was 70.39%, 73.43%, 65.95% and 67.6% respectively in the temperature ranging from 245 ^oC to 325 ^oC, due to the decomposition of materials. When the temperature is higher than 325 ^oC, the carbon chains start to break down, making the decomposition rates slow down. The above results show that the prepared polymers have good thermal stability. **Kinetics study**

To study the adsorption equilibrium time of the four CD polymers for naphthol and naphthylamine, and the kinetics of the adsorption processes, the adsorption time are set from 0.5 to 180 min. As depicted in Fig. 5, the uptake capacities of the four cyclodextrin polymers for 1-naphthylamine, 2-naphthylamine, 1-naphthol and 2-naphthol increase rapidly at first, then increase slowly until to be constant with the increasing of the adsorption time. The adsorption equilibrium can be achieved within 60 min. In addition, the four CD polymers present fast adsorption kinetics towards naphthol and naphthylamine, attaining 93%~100% of adsorption equilibrium uptake for 1-naphthylamine, 2-naphthylamine and 1-naphthol and 87%~90% of equilibrium uptake for 2-naphthol in 15 min, as presented in Table 1.

The kinetics of the adsorption processes were analyzed by the pseudo first-order (PFO) kinetic model (Eq. S(3)) and pseudo second-order (PSO) kinetic model (Eq. S(4)) (Simonin 2016; Ho 2006). As displayed in Fig. S1 and Table S1, the adsorption process of the four cyclodextrin polymers for four naphthalene derivatives can be depicted well by PSO kinetic model, suggesting chemical adsorption may be involved in the above adsorption processes. The adsorption rate constant of HP-β-CDP for 1-naphthol (Table S1) is larger than that of the other three cyclodextrin polymers, while there is no significant difference in the adsorption rate constant (K_2) of the four cyclodextrin polymers for 1-naphthylamine, 2-naphthylamine and 2-naphthol. Additionally, Fig. 5 and Table S1 also show that the equilibrium uptake capacity (Q_e) of the four cyclodextrin polymers for the four substances has certain regularity. For 1-

naphthylamine and 2-naphthylamine, the order of adsorption effect of the four cyclodextrin polymers is as follows: β-CDP > Me-β-CDP > HP-β-CDP > HE-β-CDP. For 1-naphthol and 2-naphthol, the order of adsorption effect of the four cyclodextrin polymers is as follows: Me-β-CDP > HP-β-CDP > β-CDP > HE-β-CDP.

Table 1
The Q_t at 15 min vs. the Q_e of the four CD polymers towards the naphthalene derivatives, %

CD polymers	1-naphthylamine	2-naphthylamine	1- naphthol	2- naphthol
β-CDP	94	96	97	89
HE-β-CDP	94	96	93	87
HP-β-CDP	97	97	100	90
Me-β-CDP	96	97	99	90

Adsorption Isotherm Studying

Adsorption isotherms play a significant part in the study of adsorption mechanism and practical application. Figure 6 shows the adsorption isotherms of four cyclodextrin polymers towards the four naphthalene derivatives at 25 ^{o}C. The uptake capacity increases with the increase of adsorption equilibrium concentration as demonstrated in Fig. 6. The nonlinear Langmuir, Freundlich, Redlich Peterson and sips adsorption isotherm models (Foo and Hameed 2010) (Eqs. (S5)-(S8)) were used to fit the above adsorption isotherms. The fitting results are shown in Table S2. Comparing the square of the correlation coefficient (R^2) and chi square coefficient (χ^2) of four adsorption isotherm models, it is found that the three-parameter Redlich Peterson or sips adsorption isotherm model can better fit the experimental data. In addition, Fig. 6 also shows that the order of adsorption effect of the four cyclodextrin polymers for 1-naphthylamine and 2-naphthylamine is as follows: β-CDP > Me-β-CDP > HP-β-CDP > HE-β-CDP, while the order of adsorption effect for 1-naphthol and 2-naphthol is as follows: Me-β-CDP > HP-β-CDP > β-CDP > HE-β-CDP. This is consistent with the results of kinetics studying.

Furthermore, the adsorption ratio of the four CD polymers towards the naphthalene derivatives has a significant increase with the decrease of the initial concentration of pollutants as displayed in Fig. 7. When the initial concentration (C_0) of the pollutant is 10 mg/L, the adsorption ratio is up to 85.3% for the uptake of 1-naphthylamine by β-CDP, 94.8% for the uptake of 2-naphthylamine by Me-β-CDP, 94.0% for the uptake of 1-naphthol by Me-β-CDP, and 90.9% for the uptake of 2-naphthol by Me-β-CDP. When the C_0 of the contaminant is 5 mg/L, the adsorption ratio is increased to 95.6% for the uptake of 1-naphthylamine by β-CDP, 96.6% for the uptake of 2-naphthylamine by Me-β-CDP, 96.3% for the uptake of 1-naphthol by

Me-β-CDP, and 95.2% for the uptake of 2-naphthol by Me-β-CDP. This phenomenon suggests that the four CD polymers are applicable to removal of naphthylamine and naphthol with low concentration, especially for micropollutant.

Study of temperature on naphthalene derivatives removal by CD polymers

The impact of temperature on the adsorption of 1-naphthylamine, 2-naphthylamine, 1-naphthol and 2-naphthol by the four CD polymers were studied ranging from 15 ^{o}C to 35 ^{o}C. Figure 8 shows that high temperature is conducive to the above adsorption process. With the increment of the temperature from 25 ^{o}C to 35 ^{o}C, the adsorption ratio could be improved to 96.5% from 95.6% for the adsorption of 1-naphthylamine in 5 mg/L by β-CDP, to 98.5% from 96.6% for the adsorption of 2-naphthylamine in 5 mg/L by Me-β-CDP, to 98.0% from 96.3% for the adsorption of 1-naphthol in 5 mg/L by Me-β-CDP, and to 97.6% from 95.2% for the adsorption of 2-naphthol in 5 mg/L by Me-β-CDP. In addition, Fig. 8 also shows that the adsorption of four cyclodextrin polymers for the four substances has certain regularity. For 1-naphthylamine and 2-naphthylamine, the order of adsorption effect of the four cyclodextrin polymers is as follows: β-CDP > Me-β-CDP > HP-β-CDP > HE-β-CDP. For 1-naphthol and 2-naphthol, the adsorption effects of β-CDP and HP-β-CDP are similar. Overall, for 1-naphthol and 2-naphthol, the order of adsorption effect of the four cyclodextrin polymers is as follows: Me-β-CDP > HP-β-CDP > β-CDP > HE-β-CDP when the temperature is higher than 25 ^{o}C. This is consistent with the kinetic results.

Reutilization Performance Studying

The adsorbent with excellent reusability will have good practicability. In this study, methanol was selected as the desorption agent to desorb the four cyclodextrin polymers with 1-naphthylamine, 2-naphthylamine, 1-naphthol and 2-naphthol. As depicted in Fig. 9, β-CDP, HE-β-CDP, HP-β-CDP, and Me-β-CDP have a small decrease in the adsorption ratio of four naphthalene derivatives after five adsorption-desorption processes, but not more than 5%. In detail, for 1-naphthylamine, the adsorption ratio of β-CDP, HE-β-CDP, HP-β-CDP, and Me-β-CDP decreased by 3.38%, 2.39%, 3.46% and 2.47% respectively. For 2-naphthylamine, the adsorption ratio of β-CDP, HE-β-CDP, HP-β-CDP, and Me-β-CDP decreased by 2.49%, 3.50%, 3.46% and 2.49%, respectively. For 1-naphthol, the adsorption ratio of β-CDP, HE-β-CDP, HP-β-CDP, and Me-β-CDP decreased by 2.46%, 5.46%, 6.24% and 4.24% respectively. For 2-naphthol, the adsorption ratio of β-CDP, HE-β-CDP, HP-β-CDP, and Me-β-CDP decreased by 4.24%, 3.34%, 2.38% and 3.28%, respectively. The results show that the four cyclodextrin polymers have excellent recycling performance on the adsorption of 1-naphthylamine, 2-naphthylamine, 1-naphthol and 2-naphthol.

Conclusion

β-CD polymer, HE-β-CD polymer, HP-β-CD polymer, and Me-β-CD polymer were successfully prepared by solvothermal method with tetrafluoroterephthalonitrile as crosslinking agent. The four cyclodextrin polymers have rough surface morphology, uneven distribution of pores, similar specific surface area and

similar pore structure. The four cyclodextrin polymers have good thermal stability, and their thermal decomposition temperatures are higher than 200 ^{o}C. The four cyclodextrin polymers have fast adsorption rate for 1-naphthylamine, 2-naphthylamine and 1-naphthol, and could reach more than 93% of the equilibrium adsorption within 15 min. The uptake rate of 2-naphthol is slower, but it could also reach about 90% of the adsorption equilibrium within 15 min. The kinetics of the adsorption processes could be depicted well by the pseudo second-order kinetic model, indicating that chemisorption is involved in the adsorption processes. The adsorption processes of the four cyclodextrin polymers on these four naphthalene compounds are endothermic, and the adsorption isotherms were fitted to three-parameter Redlich Peterson model or sips model. The prepared adsorbent has excellent reusability and is expected to be applied to the removal of naphthylamine and naphthol compounds in industrial wastewater.

Declarations

Funding Information

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Authors' contributions

Weifeng Xu: Conceptualization, Methodology, Project administration, Writing-Review & Editing, Funding acquisition

Xiang Liu: Investigation, Data Curation, Writing-Original Draft

Jianzhe Cai: Investigation, Data Curation, Formal analysis

Tiemeng Xue: Validation

Kewen Tang: Conceptualization, Methodology, Project administration

Data availability

All data generated or analyzed during this study are included in this published article.

Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

Ethics approval and consent to participate Not applicable

Consent to Publish Not applicable

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Figures

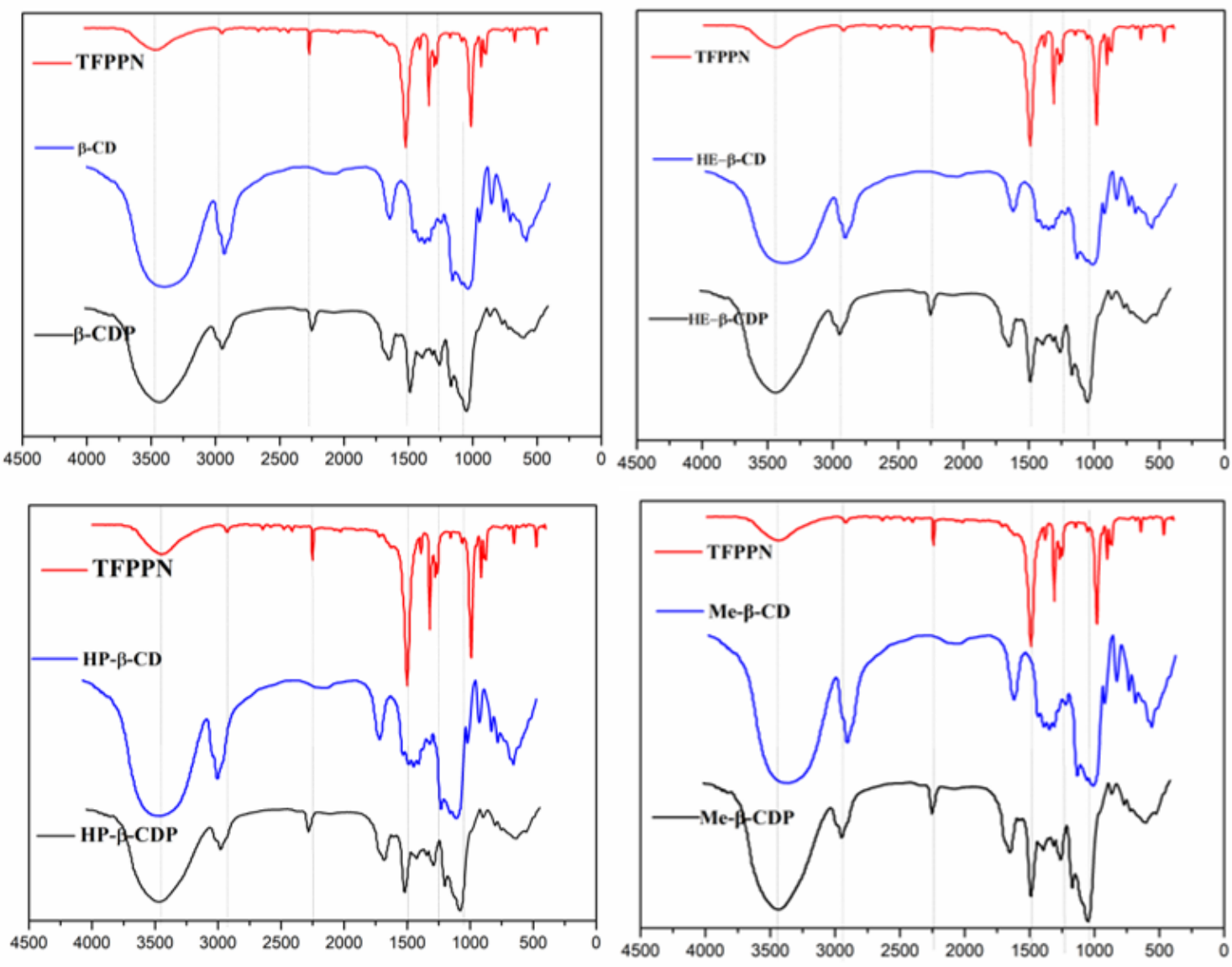

Figure 1

FT-IR images of β-CD, β-CDP, HE-β-CD, HE-β-CDP, HP-β-CD, HP-β-CDP, Me-β-CD, Me-β-CDP and TFPPN.

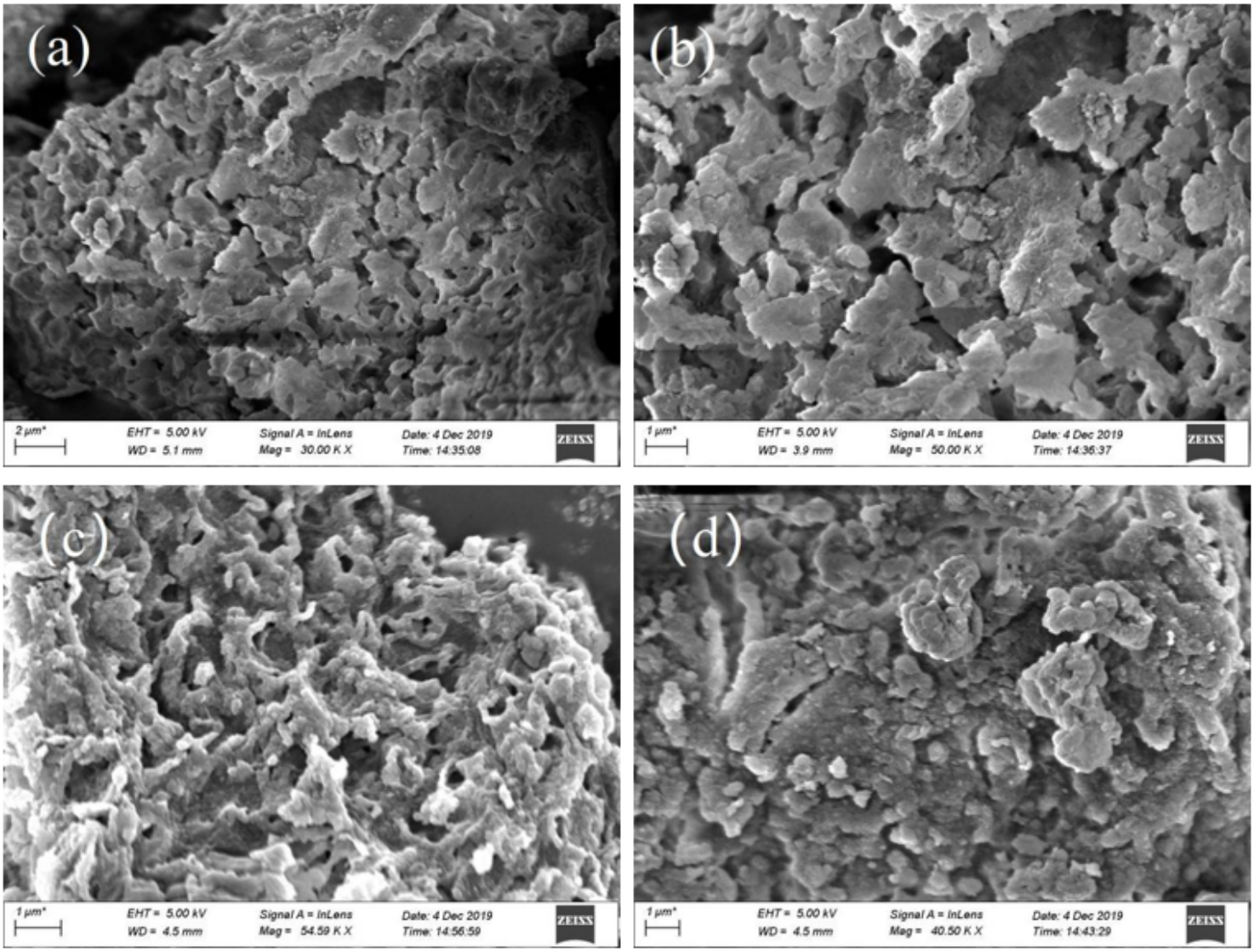

Figure 2

SEM images of CD polymers (a) β-CDP, (b) HE-β-CDP, (c) HP-β-CDP, (d) Me-β-CDP.

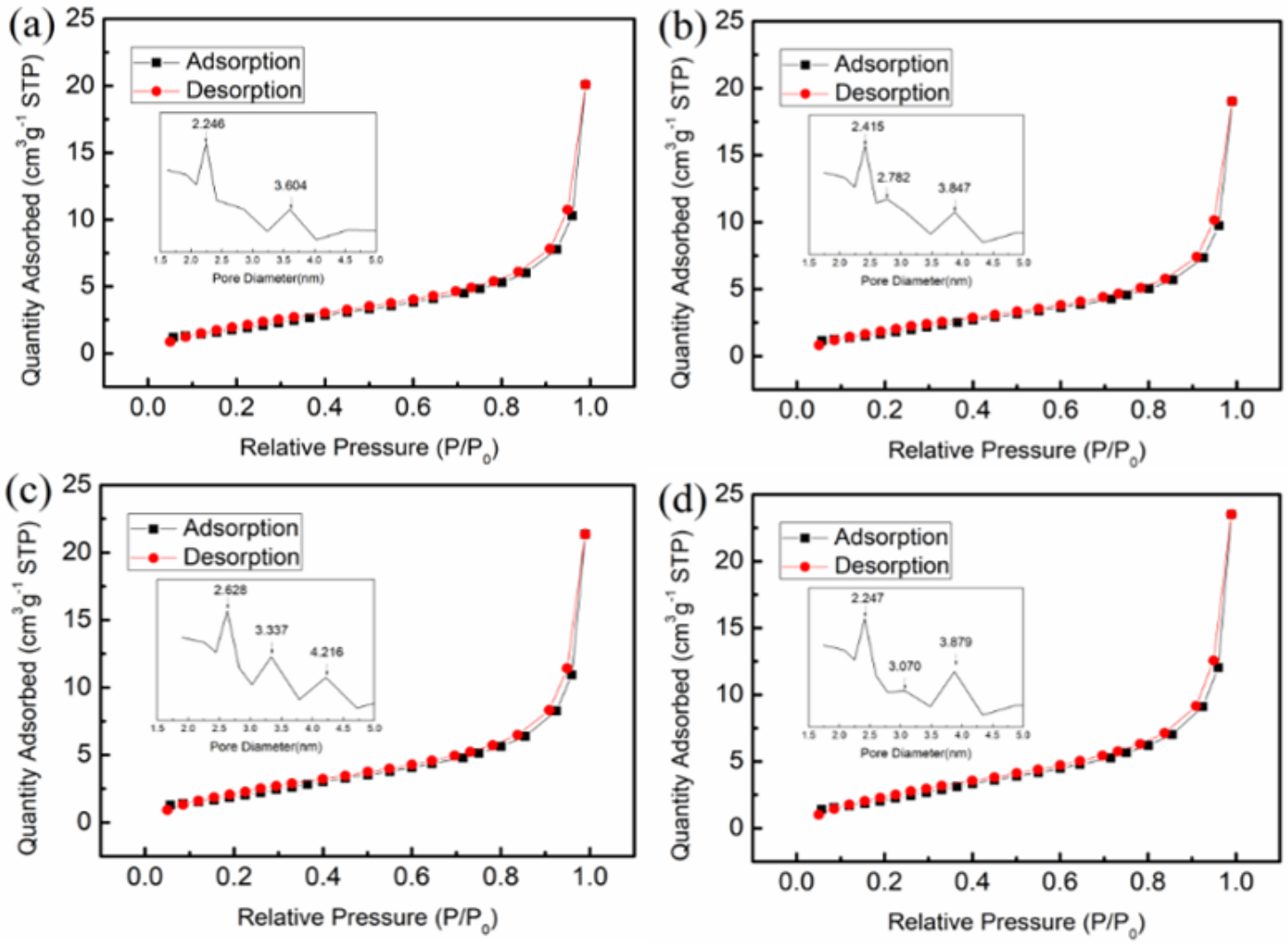

Figure 3

The N2 adsorption-desorption isotherms and pore size distribution maps of CD polymers (a) β-CDP, (b) HE-β-CDP, (c) HP-β-CDP, (d) Me-β-CDP.

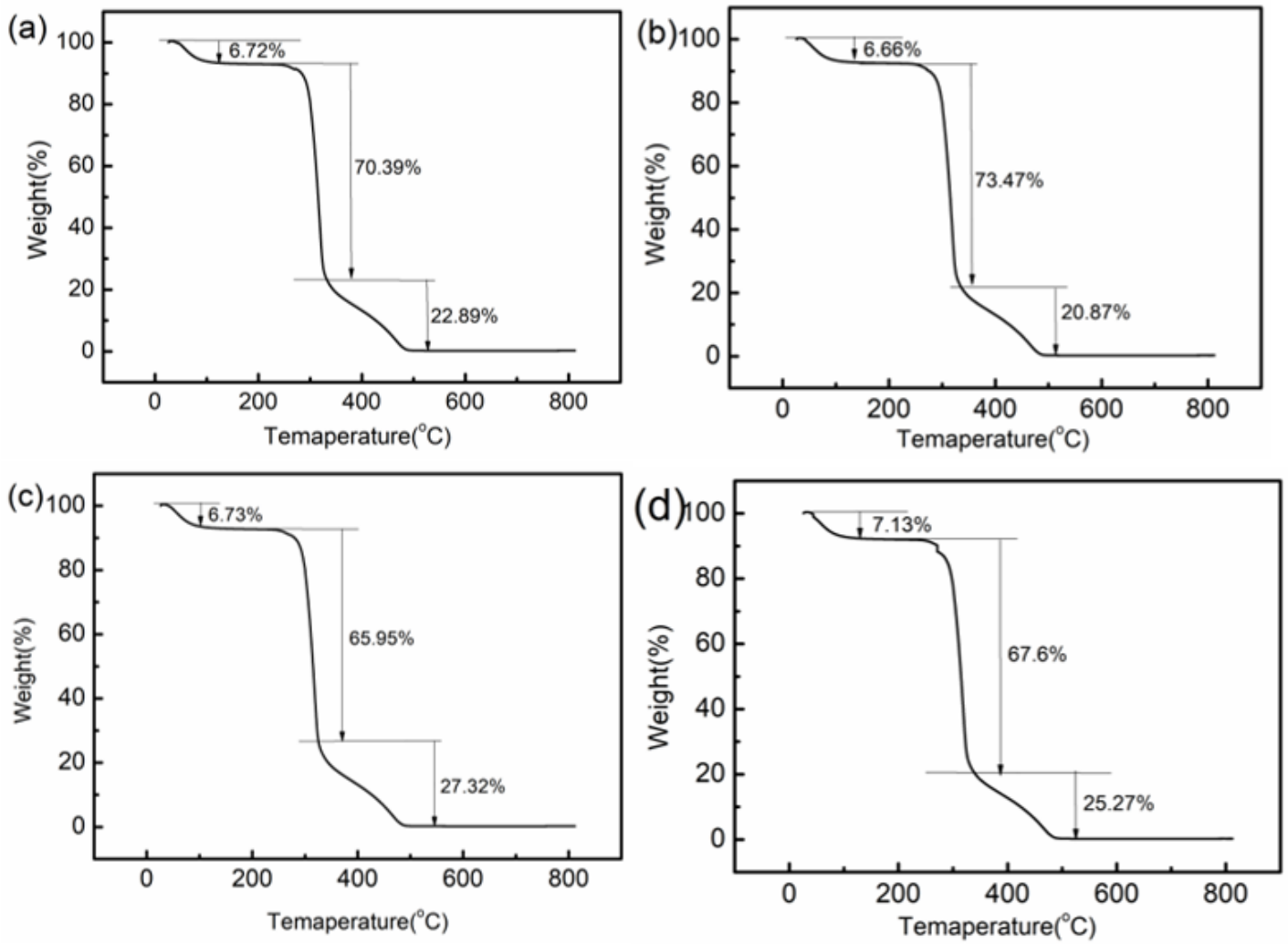

Figure 4

TGA images of CD polymers (a) β-CDP, (b) HE-β-CDP, (c) HP-β-CDP, (d) Me-β-CDP.

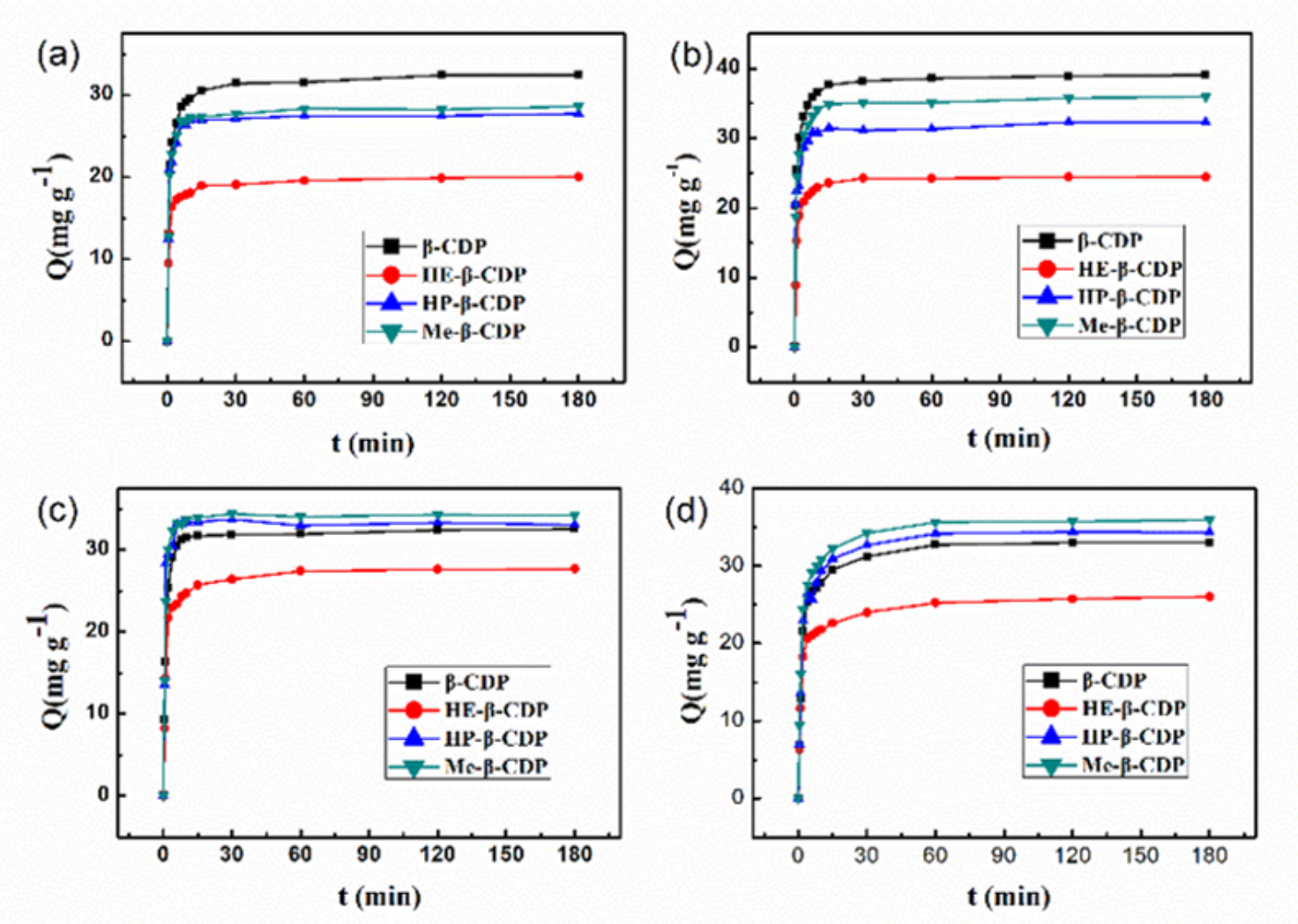

Figure 5

The influence of time on the adsorption of naphthalene derivatives by the four CD polymers (a) 1-naphthylamine, (b) 2-naphthylamine, (c) 1-naphthol, (d) 2-naphthol.

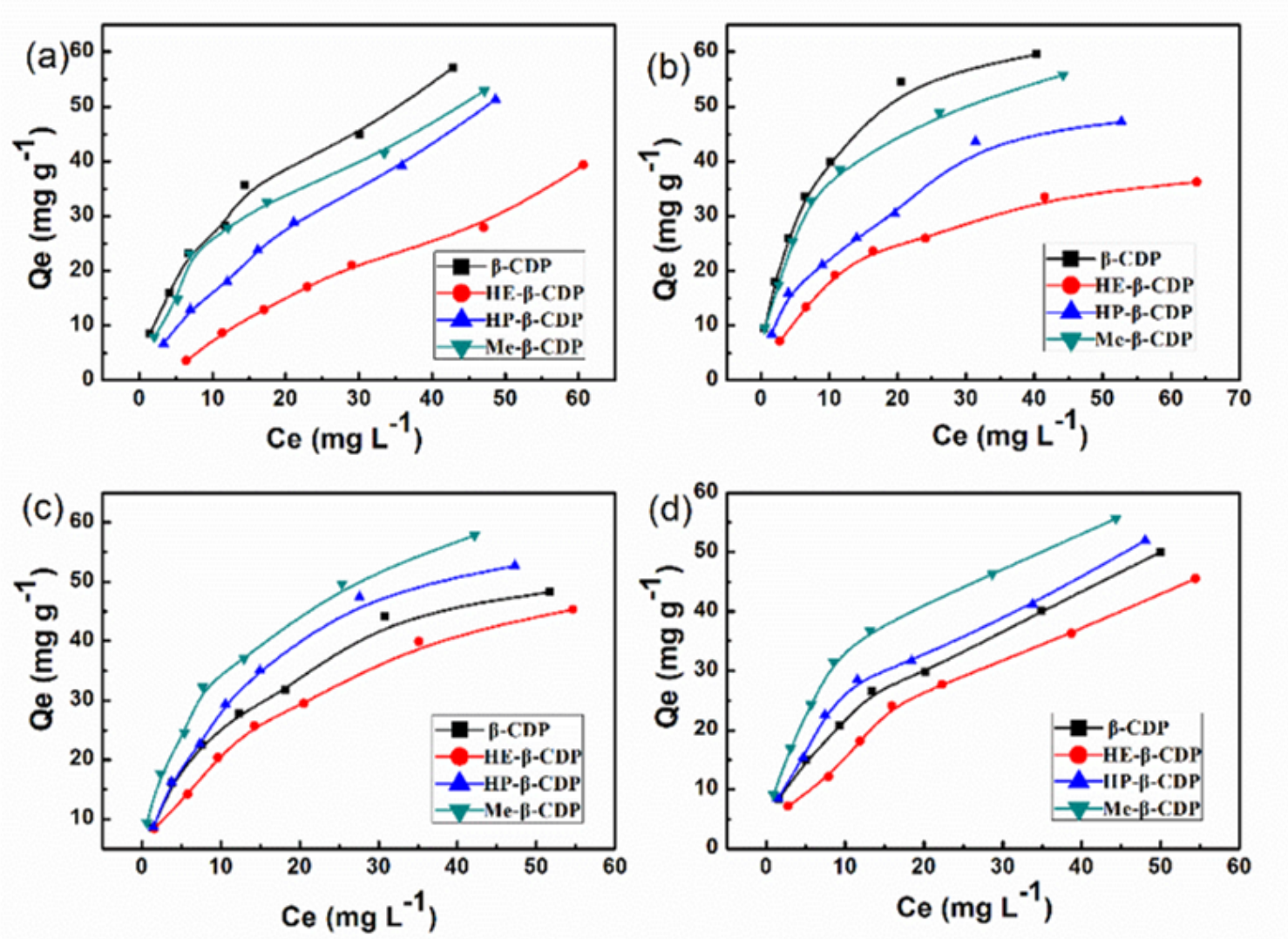

Figure 6

Adsorption isotherms of four cyclodextrin polymers towards four naphthalene derivatives (a) 1-naphthylamine, (b) 2-naphthylamine, (c) 1-naphthol, (d) 2-naphthol.

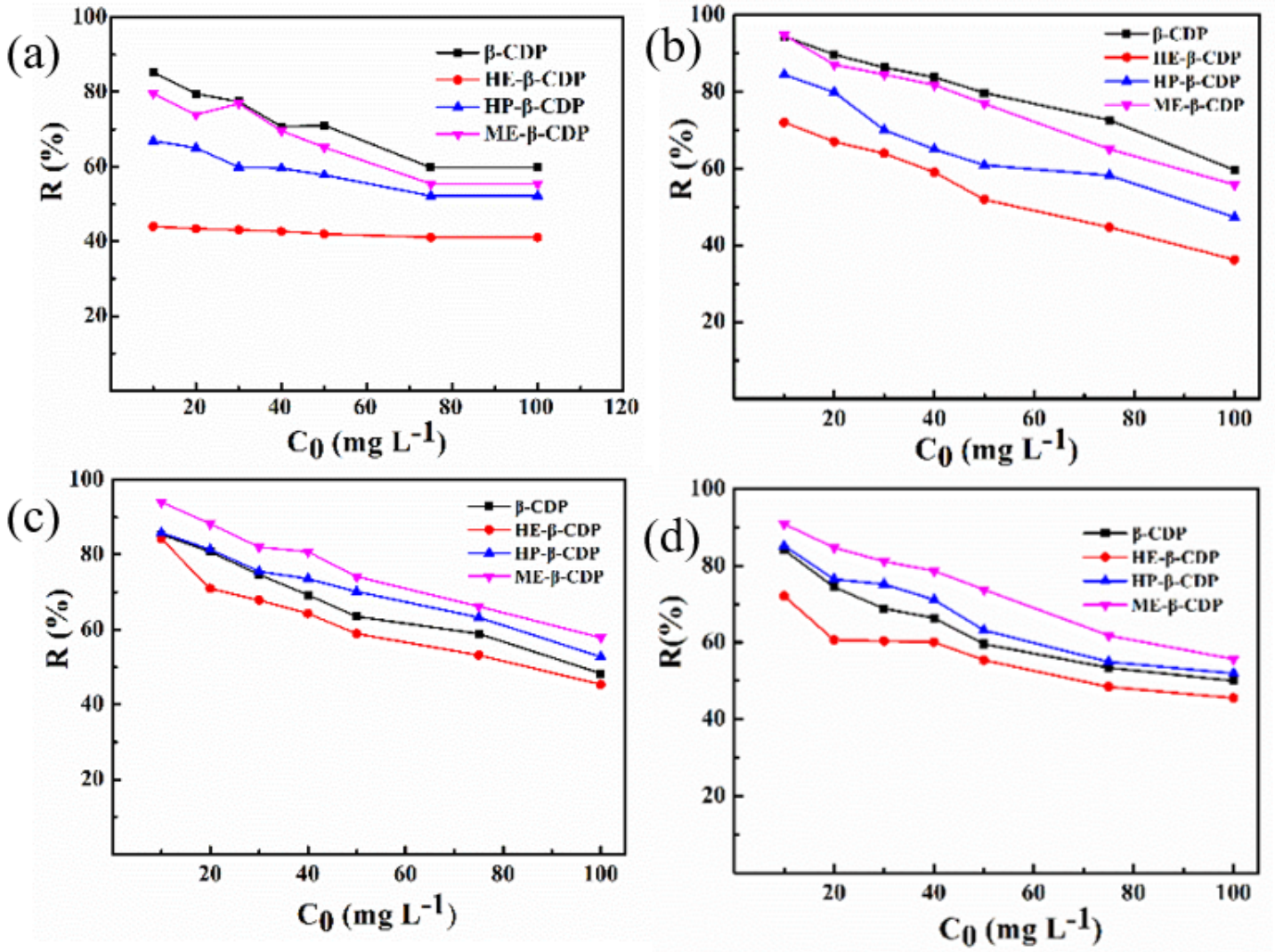

Figure 7

The effect of the initial concentration of naphthalene derivatives on the adsorption of the four CD polymers (a) 1-naphthylamine, (b) 2-naphthylamine, (c) 1-naphthol, (d) 2-naphthol.

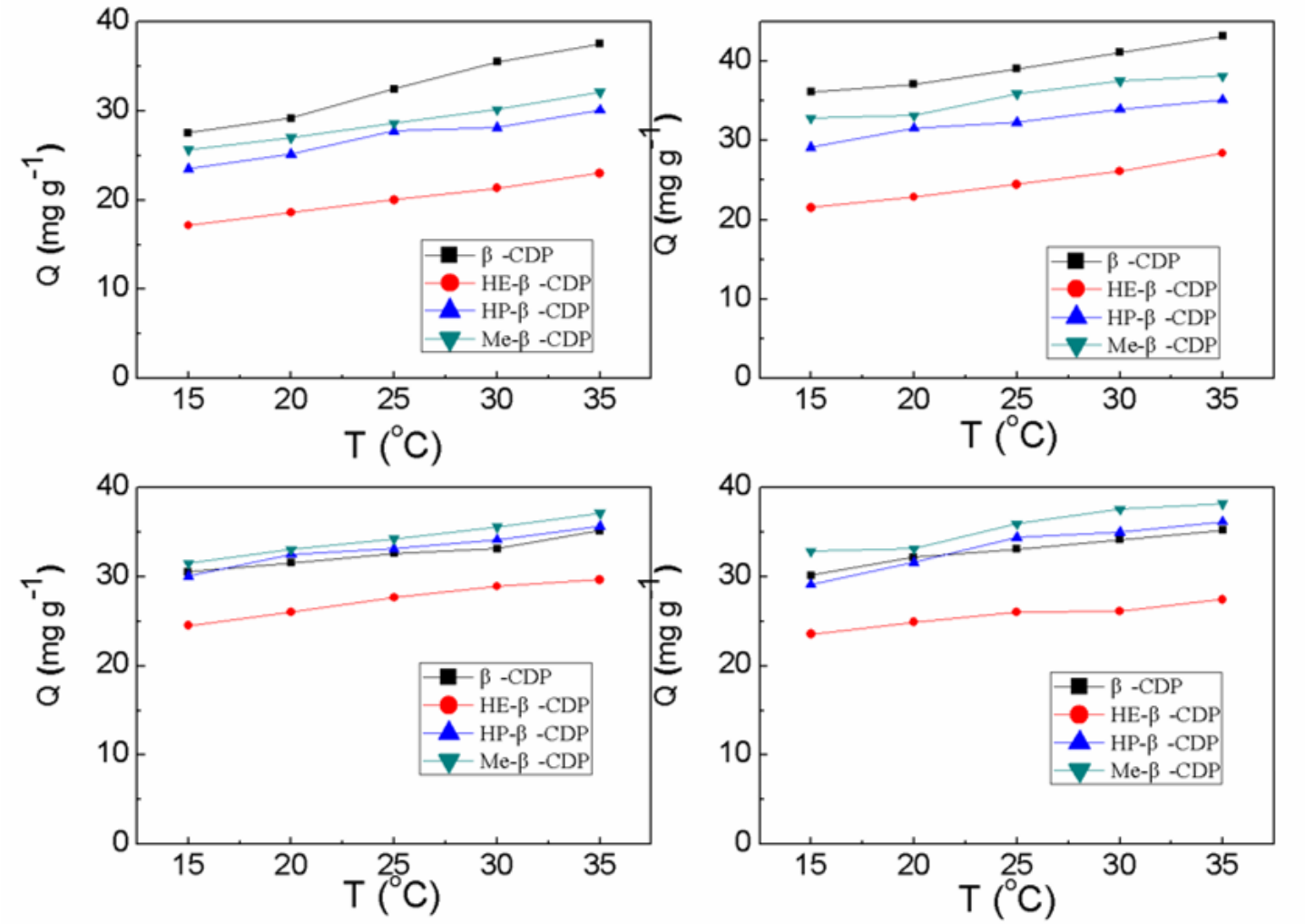

Figure 8

The effect of temperature on the adsorption of the naphthalene derivatives by the four CD polymers (a) 1-naphthylamine, (b) 2-naphthylamine, (c) 1-naphthol, (d) 2-naphthol.

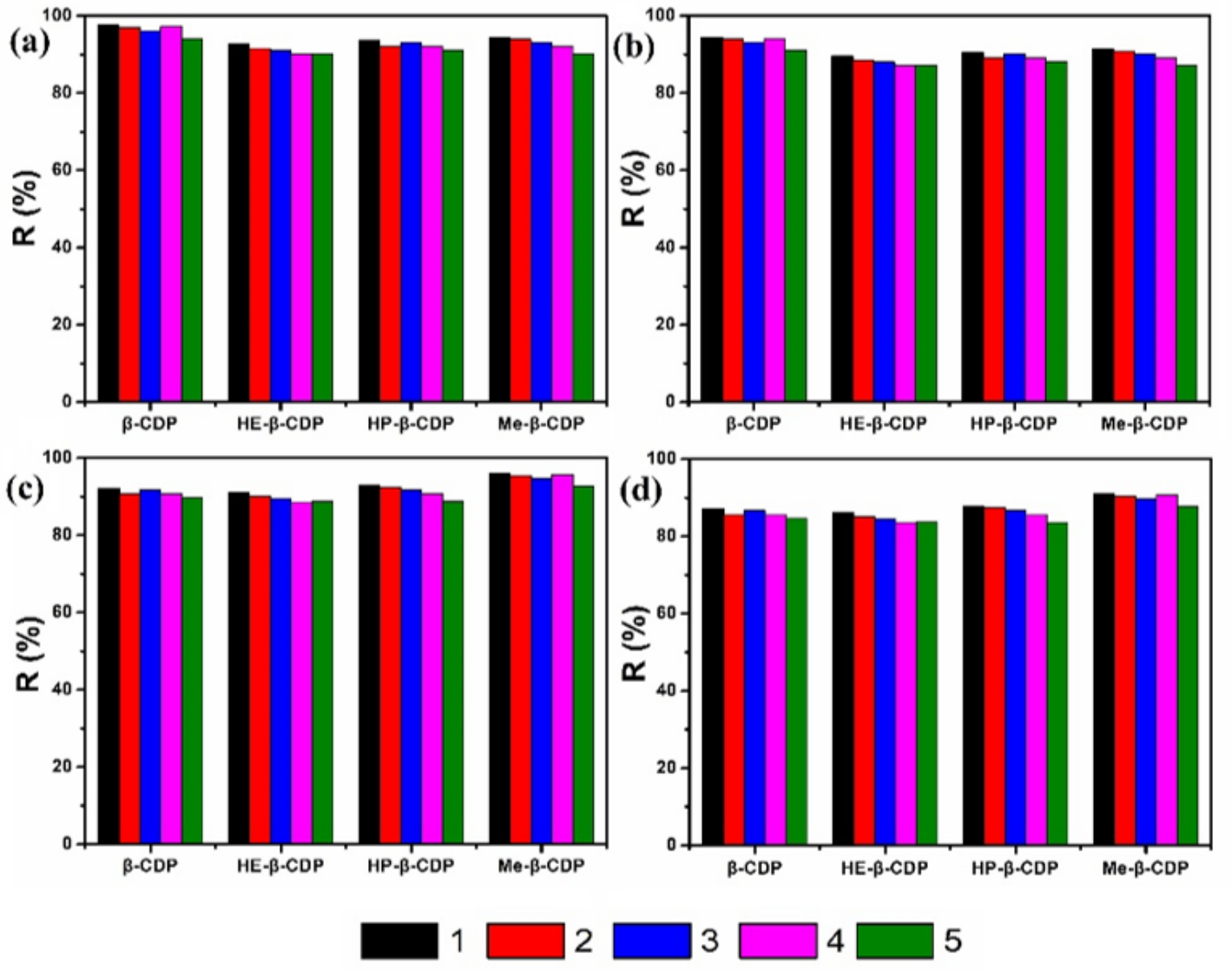

Figure 9

The reusability of the four CD polymers toward naphthalene derivatives (a) 1-naphthylamine, (b) 2-naphthylamine, (c) 1-naphthol, (d) 2-naphthol.

Supplementary Files

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- Supplementarymaterial.doc