# Comparative study of polymer containing β-cyclodextrin and –COOH for adsorption toward aniline, 1-naphthylamine and methylene blue

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## ARTICLE INFO

## ABSTRACT

Three different polymers P1, P2 and P3 (P1 containing both β-CD and –COOH, P2 containing β-CD and P3 containing –COOH) were synthesized and applied to adsorption toward aniline, 1-naphthylamine and methylene blue. The concentrations ($C$) before and after adsorption were determined and the adsorption capacities ($q$) of P1, P2 and P3 were calculated. The maximum adsorption capacities ($q_{max}$) toward aniline: $q_{max}$ (P1) = 104 μmol g$^{-1}$, $q_{max}$ (P2) = 14.9 μmol g$^{-1}$ and $q_{max}$ (P3) = 53.1 μmol g$^{-1}$; toward 1-naphthylamine: $q_{max}$ (P1) = 184 μmol g$^{-1}$, $q_{max}$ (P2) = 53.8 μmol g$^{-1}$ and $q_{max}$ (P3) = 125 μmol g$^{-1}$; toward methylene blue: $q_{max}$ (P1) = 200 μmol g$^{-1}$, $q_{max}$ (P2) = 12.7 μmol g$^{-1}$ and $q_{max}$ (P3) = 215 μmol g$^{-1}$. P1 exhibited remarkable adsorption toward all the three adsorbates. P2 was almost equal to P1 in adsorption toward methylene blue, but was less efficient than P1 in adsorption toward aniline and 1-naphthylamine. P3 also exhibited considerable adsorption toward aniline and 1-naphthylamine, but was inefficient toward methylene blue. P1 was obtained from nontoxic materials and through environment friendly procedures, so it was potentially an efficient and green adsorbent for water purification.

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## 1. Introduction

Cyclodextrins (CDs) are torus-shaped cyclic oligosaccharides containing 6–12 glucose units. The interior cavity of CDs is hydrophobic and can form inclusion complexes with some molecules through host-guest interactions. The practically important, industrially produced CDs are α-, β- and γ-CDs, which are made up of six, seven and eight α-1,4-linked D-glucopyranose units, respectively. β-CD is the most largely produced cyclodextrin used in many fields including pharmaceuticals, foods, cosmetics, chemical products and technologies [1–7]. The chemical structure of β-CD is shown in Fig. 1.

Widespread contamination of soil and groundwater by organic pollutants and heavy metals has been recognized as an issue of growing seriousness in recent years. β-CD polymer has been reported to be efficient in adsorption toward organic pollutants and heavy metals in water [8–22]. This kind of polymer is usually synthesized by reacting β-CDs with crosslinking agents such as epichlorohydrin [9–13], diisocyanates [14–16], polycarboxylic acids [17–19] and anhydrides [20–22]. Polycarboxylic acids, such as citric acid [23], are generally of low toxicity and friendly to environment. The condensation between β-CD and citric acid can progress at a temperature not higher than 200 °C and without any organic solvent and harmful additive.

It has been found that β-CD polymer crosslinked by citric acid contained carboxyl groups (–COOH) which contributed to adsorption toward metal ions [17–19]. It's not clear yet how β-CD and –COOH will take effects when the polymer is used to adsorb organic molecules. Especially if the target molecules contain both hydrophobic groups (such as phenyl and naphthyl group) and basic groups (such as amino and pyridyl group), the hydrophobic groups should be attracted by β-CD, while the basic groups should be chemically bonded to –COOH, and the adsorption would become more complex and interesting.

Thus, three different polymers containing β-CD and/or –COOH were synthesized and comparatively studied in adsorption toward aniline, 1-naphthylamine and methylene blue. As shown in Fig. 2, aniline is a benzene derivative with one primary amino group, 1-naphthylamine is a naphthalene derivative with one primary amino group and methylene blue is a thiophenylamine derivative with two tertiary amino groups. Aniline and 1-naphthylamine are widely used intermediates which are highly toxic and carcinogenic to human and animal. Methylene blue is a cationic dye which is also toxic and carcinogenic. Various adsorbents and methods have been studied for removal of aniline [24–26], 1-naphthylamine [27,28] and methylene blue [29–31] from water. As has been known, β-CD polymer crosslinked by citric acid, which contains both β-CD and –COOH, is a new adsorbent that has not yet been applied to adsorption toward these organic pollutants.

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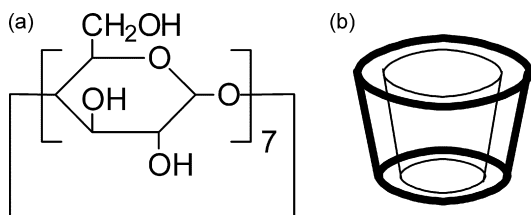E-mail address: gszhaodong@163.com (L. Zhao).

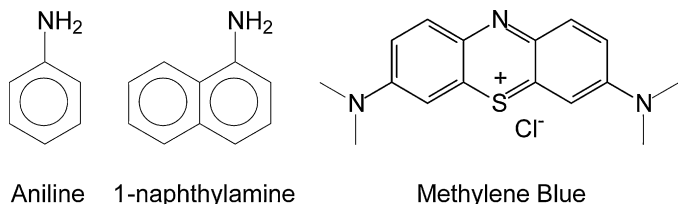**Fig. 1.** Chemical structure (a) and shape (b) of β-cyclodextrin.



Aniline    1-naphthylamine                Methylene Blue

**Fig. 2.** Chemical structures of aniline, 1-naphthylamine and methylene blue.

## 2. Experimental

### 2.1. Materials

β-Cyclodextrin is a biochemical reagent (puritiy ≥99.0%) purchased from Tianjin Bodi Chemical Co., Ltd., China. Citric acid monohydrate, sodium dihydrogen phosphate, aniline, 1-naphthylamine and methylene blue are analytical pure reagents purchased from guaranteed manufacturers. PVA-1799 is a commercial poly (vinyl alcohol), of which the polymerization degree is 1700 and the hydrolysis degree is 99.0%. Potassium bromide (KBr) used for FT-IR is a spectrum pure reagent purchased from Tianjin Guangfu Fine Chemical Research Institute, China.

### 2.2. Synthesis of polymer P1 (containing both β-CD and –COOH)

10 g of β-CD, 5 g of citric acid monohydrate, 0.5 g of sodium dihydrogen phosphate, 1.2 g of PVA-1799 and some deionized water were mixed in a flask and stirred to homogeneous in boiling water bath (preliminary experiments had shown that if PVA-1799 was not

added the yield of P1 would be poor.). The mixture was transferred into a plate and heated in an electric thermostatic oven (DHG-9030A, Shanghai Jinghong Laboratory Instrument Co., Ltd., China) at 135 °C for 4 h. After naturally cooled, the crude product was purified by soaking and washing with deionized water for several times, then suction filtered and dried at 50 °C. The synthesis mechanism of P1 is illustrated in Fig. 3.

### 2.3. Synthesis of polymer P2 (containing β-CD)

10 g of β-CD were dissolved in 20 mL of 20% NaOH aqueous solution. 12 mL of epichlorohydrin was added dropwise into the solution under 50 °C. The solution was stirred thoroughly until it changed into gel, then kept at 50 °C for 5 h to make it crosslinked sufficiently. The product was broken into granulae, soaked and washed for several times with water and acetone respectively, and dried at 50 °C. The synthesis mechanism of P2 is illustrated in Fig. 4.

### 2.4. Synthesis of polymer P3 (containing –COOH)

10 g of PVA-1799, 5 g of citric acid monohydrate, 0.5 g of sodium dihydrogen phosphate and some deionized water were treated by the same method as described for synthesis of polymer P1. The synthesis mechanism of P3 is similar to that of P1.

### 2.5. FT-IR spectra of polymer

Small amount of polymer was mixed and grinded thoroughly with KBr powder in an agate mortar and pressed into thin tablets under 16 MPa pressure using a manual hydraulic press (FW-4A, Tianjin Tuopu Instrument Co., Ltd., China). Fourier-transform Infrared (FT-IR) spectra were measured using the tablets by a FT-IR spectrometer (Thermo Nicolet IR 200, Thermo Electron Corp., USA).

### 2.6. Total acidic groups (TA) of P2 and P3

The amount of total acidic groups (TA) of polymer, including carboxyl groups and ester groups, was determined by titration method. 0.1 g of finely powdered polymer was put into a conical flask containing 20 mL of 0.1 M NaOH solution and stirred for 15 h at 30 °C. Thus, polymer was completely hydrolyzed and dissolved.
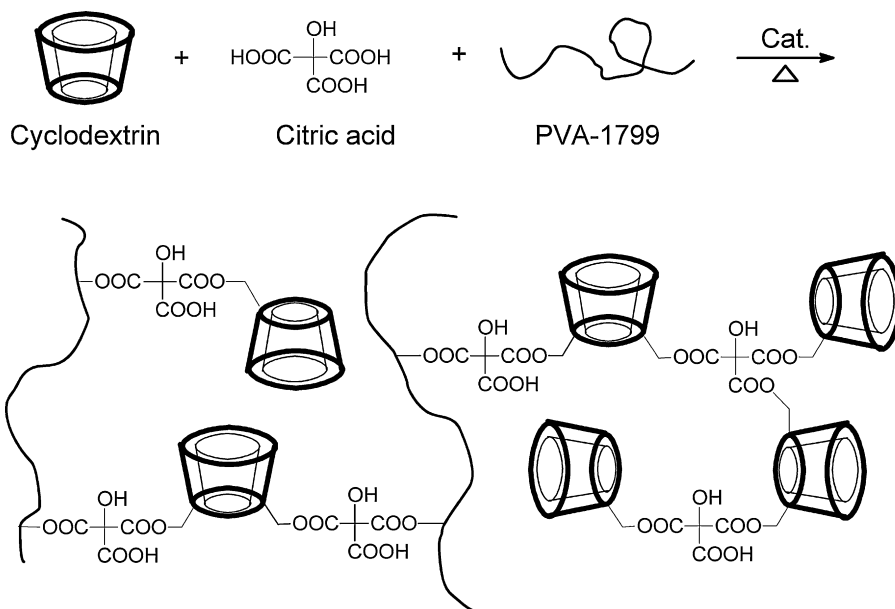


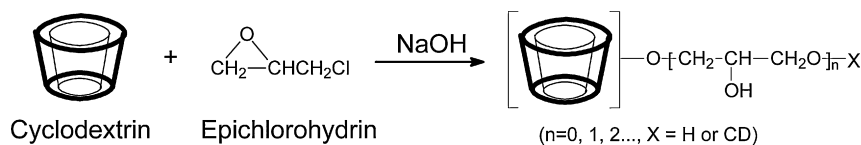**Fig. 3.** Synthesis mechanism of polymer containing both β-CD and –COOH.

**Fig. 4.** Synthesis mechanism of polymer containing β-CD.

The resulted solution was titrated with 0.1 M HCl solution until pH 7, pH measured using a digital pH meter (PHS-3E, Shanghai Precision & Scientific Instrument Co., Ltd.). TA (mmol g$^{-1}$) value was calculated as follows:

$$TA = \frac{C(V_0 - V_1)}{W} \tag{1}$$

where $C$ is the concentration of HCl solution (mmol L$^{-1}$), $V_0$ is the volume of HCl solution consumed by blank solution (L), $V_1$ is the volume of HCl solution consumed by sample solution (L) and $W$ is the weight of polymer (g).

### 2.7. Adsorption of aniline and 1-naphthylamine

0.1 g of polymer was put into a conical flask containing 50 mL of aqueous solution of aniline or 1-naphthylamine. The flask was well covered and shaken in a water bath shaker (SHA-C, Jintan Ronghua Instrument Manufacture Co., Ltd., China) at 30 °C for different time intervals. Total nitrogen (TN, mg L$^{-1}$) of the solution at each time point was determined by a multi N/C 2100 TOC/TN analyzer (Analytik Jena AG, Germany). Standard solutions were determined beforehand to make a calibration curve. Since every aniline or 1-naphthylamine molecule contains one nitrogen atom, the concentration ($C$, μmol L$^{-1}$) and adsorption capacity ($q$, μmol g$^{-1}$) of aniline or 1-naphthylamine were calculated as follows:

$$C = \frac{TN \times 1000}{14} \tag{2}$$

$$q_t = \frac{V(C_0 - C_t)}{W} \tag{3}$$

where "14" is the atomic weight of nitrogen, $q_t$ (μmol g$^{-1}$) is the adsorption capacity per gram of adsorbent at time point $t$, $V$ is the volume of solution (L), $C_0$ is the initial concentration (μmol L$^{-1}$), $C_t$ is the concentration at time point $t$ (μmol L$^{-1}$) and $W$ is the weight of adsorbent (g).

### 2.8. Adsorption of methylene blue

0.05 g of β-CD was put into a conical flask containing 50 mL of methylene blue aqueous solution. The flask was well covered and shaken in the water bath shaker at 30 °C for different time intervals. The absorbance ($\lambda_{max}$ = 665 nm) of the solution at each time point was measured using a spectrophotometer (721 type, Shanghai Analytical Instruments Factory, China). Standard solutions were measured as well to make a calibration curve. The concentration ($C$, μmol L$^{-1}$) corresponded to each absorbance value was calculated according to the calibration curve. The adsorption capacity ($q$, μmol g$^{-1}$) toward methylene blue was calculated according to Eq. (3).

## 3. Results and discussion

### 3.1. Synthesis and characterization of P1, P2 and P3

After purified and dried, P1 (containing both β-CD and –COOH) was obtained as yellowish crisp granulae with a yield of 8.8 g, P2 (containing β-CD) was obtained as white flaky pieces with a yield of 8.1 g, and P3 (containing –COOH) was obtained as white breakable

granulae with a yield of 9.3 g. P2 was flexible and difficult to grind, so it was prepared as thin flakes to provide enough surface for adsorption. Total acidic groups (TA) of P1 and P3 were 4.5 mmol g$^{-1}$ and 4.9 mmol g$^{-1}$, respectively. P1, P2 and P3 were all easily swelled in water because they all had many hydrophilic groups (–OH, –COOH). Thus, adsorbates can easily penetrate into the swelled networks and be adsorbed by the polymers.

FT-IR spectra of P1, P2, P3 and native β-CD (a) were shown in Fig. 5. The intensive absorption band appeared at 1736 cm$^{-1}$ in (P1), which was absent in (a), was owed to C=O stretching vibration of carboxyl groups and ester groups. The band at 1209 cm$^{-1}$ in (P1), which was also absent in (a), was owed to C–O–C stretching vibration of ester groups. These two bands observed in (P1) indicated that the hydroxyl groups of β-CD had reacted with the carboxyl groups of citric acid. The strong and broad bands at 3400 cm$^{-1}$ in (a) and at 3397 cm$^{-1}$ in (P2) corresponded to the O–H stretching vibration of the hydroxyl groups of β-CD. The similar bands observed at 3435 cm$^{-1}$ in (P1) and at 3425 cm$^{-1}$ in (P3) corresponded to the integrated O–H stretching vibration of hydroxyl groups and carboxyl groups. The bands at 2925 cm$^{-1}$ in (a), 2933 cm$^{-1}$ in (P1), 2927 cm$^{-1}$ in (P2) and 2943 cm$^{-1}$ in (P3) corresponded to the CH$_2$ asymmetric stretching vibration. C–OH stretching vibration at 1030 cm$^{-1}$ and C–O–C stretching vibration at 1159 cm$^{-1}$ of β-CD in (a) also appeared nearly at the same wavenumbers in (P1) and (P2), indicating that the structure characteristics of β-CD were maintained in P1 and P2. C=O stretching vibration at 1734 cm$^{-1}$ and C–O–C stretching vibration at 1213 cm$^{-1}$ in (P3) indicated that the hydroxyl groups of PVA-1799 had reacted with the carboxyl groups of citric acid.

### 3.2. Adsorption of aniline by P1, P2 and P3

P1, P2 and P3 were applied to adsorption toward aniline of which the initial concentration was 590 μmol L$^{-1}$. As shown in
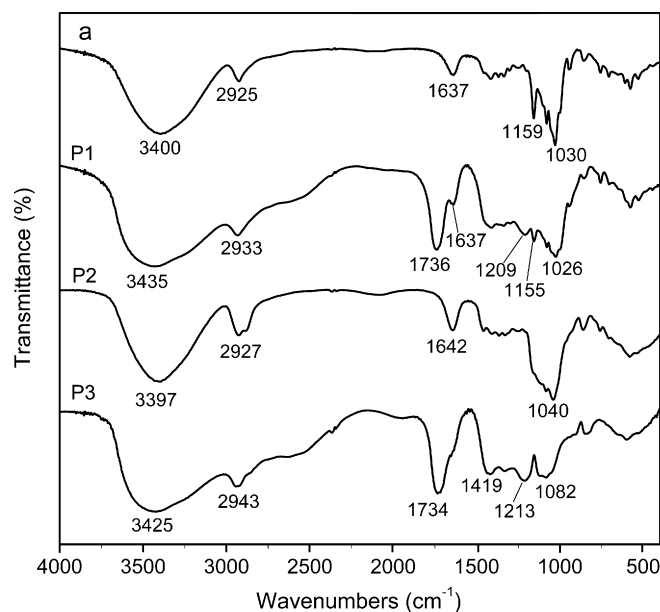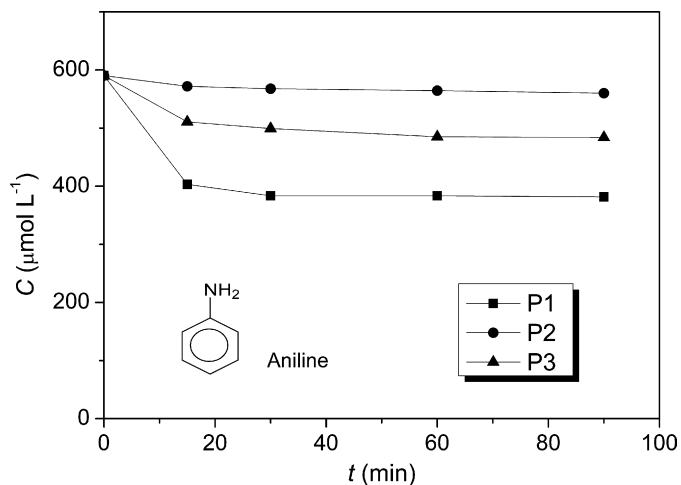


**Fig. 5.** FT-IR spectra of β-CD (a), P1, P2 and P3.

**Fig. 6.** Adsorption of aniline by P1, P2 and P3. Kinetics of concentration. $C_0 = 590\,\mu mol\,L^{-1}$, $V = 0.05\,L$, $W = 0.05\,g$, $T = 30\,°C$.



**Fig. 8.** Adsorption of 1-naphthylamine by P1, P2 and P3. Kinetics of concentration. $C_0 = 829\,\mu mol\,L^{-1}$, $V = 0.05\,L$, $W = 0.05\,g$, $T = 30\,°C$.



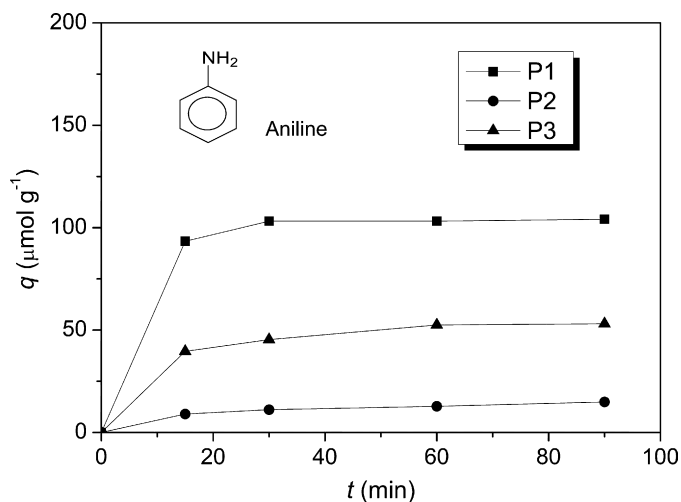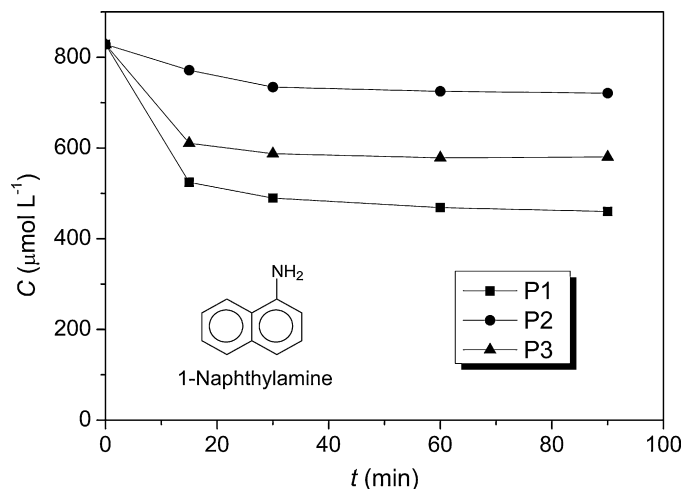**Fig. 7.** Adsorption of aniline by P1, P2 and P3. Kinetics of adsorption capacity. $C_0 = 590\,\mu mol\,L^{-1}$, $V = 0.05\,L$, $W = 0.05\,g$, $T = 30\,°C$.
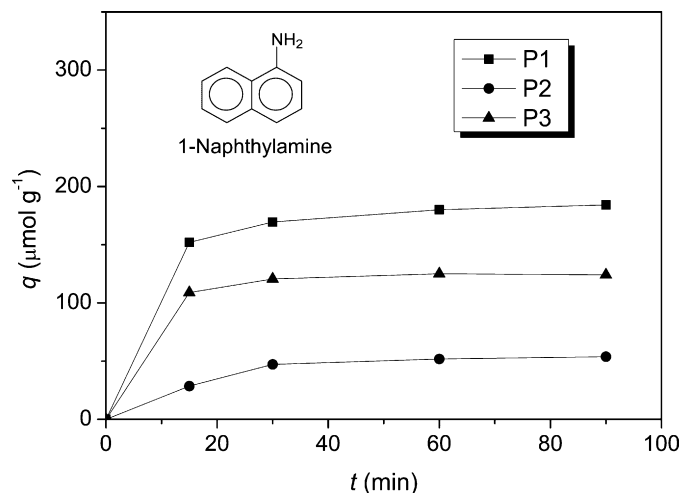


**Fig. 9.** Adsorption of 1-naphthylamine by P1, P2 and P3. Kinetics of adsorption capacity. $C_0 = 829\,\mu mol\,L^{-1}$, $V = 0.05\,L$, $W = 0.05\,g$, $T = 30\,°C$.

Fig. 6, in less than 60 min, the concentration ($C$) of aniline was decreased to 383 $\mu mol\,L^{-1}$ by P1, to 564 $\mu mol\,L^{-1}$ by P2 and to 485 $\mu mol\,L^{-1}$ by P3, respectively. The adsorption capacities ($q$) were calculated according to Eq. (3). As shown in Fig. 7, the maximum adsorption capacities of the three polymers toward aniline: $q_{max}$ (P1) = 104 $\mu mol\,g^{-1}$, $q_{max}$ (P2) = 14.9 $\mu mol\,g^{-1}$ and $q_{max}$ (P3) = 53.1 $\mu mol\,g^{-1}$. $q_{max}$ (P1):$q_{max}$ (P2):$q_{max}$ (P3) = 1:0.15:0.52, indicating that –COOH in P1 and P3 significantly contributed to adsorption toward aniline. P2 also adsorbed aniline considerably, indicating that aniline could be included by the hydrophobic cavity of β-CD in P2. It was exciting that the maximum adsorption capacity of P1 was nearly the twice of P2, implying that β-CD and –COOH in P1 probably cooperated in the adsorption toward aniline so that aniline was in a more stable situation when adsorbed by P1 than P2 or P3.

### 3.3. Adsorption of 1-naphthylamine by P1, P2 and P3

P1, P2 and P3 were applied to adsorption toward 1-naphthylamine of which the initial concentration was 829 $\mu mol\,L^{-1}$. As shown in Fig. 8, in less than 60 min, the concentration of 1-naphthylamine was decreased to 469 $\mu mol\,L^{-1}$ by P1, to 725 $\mu mol\,L^{-1}$ by P2 and to 579 $\mu mol\,L^{-1}$ by P3, respec-

tively. The adsorption capacities ($q$) were calculated according to Eq. (3). As shown in Fig. 9, $q_{max}$ (P1) = 184 $\mu mol\,g^{-1}$, $q_{max}$ (P2) = 53.8 $\mu mol\,g^{-1}$ and $q_{max}$ (P3) = 125 $\mu mol\,g^{-1}$. $q_{max}$ (P1):$q_{max}$ (P2):$q_{max}$ (P3) = 1:0.29:0.67. The three polymers, especially P2 and P3, exhibited notably higher adsorption capacities toward 1-naphthylamine than aniline. As has been known [32], naphthyl group is more easily included by β-CD than phenyl group, because naphthyl group has a more suitable size to the cavity of β-CD. At the same time, the larger hydrophobicity and steric hindrance of naphthyl group could increase the stability of the chemical bond between 1-naphthylamine and –COOH. Thus, P1, P2 and P3 behaved better in adsorption toward 1-naphthylamine than aniline.

### 3.4. Adsorption of methylene blue by P1, P2 and P3

P1, P2 and P3 were applied to adsorption toward methylene blue of which the initial concentration was 267 $\mu mol\,L^{-1}$. As shown in Fig. 10, in less than 60 min, the concentration of methylene blue was decreased to 72 $\mu mol\,L^{-1}$ by P1 and to 61 $\mu mol\,L^{-1}$ by P3, respectively. The adsorption capacities ($q$) were calculated according to Eq. (3). As shown in Fig. 11, $q_{max}$ (P1) = 200 $\mu mol\,g^{-1}$, $q_{max}$ (P2) = 12.7 $\mu mol\,g^{-1}$ and $q_{max}$ (P3) = 215 $\mu mol\,g^{-1}$. P1 and P3 exhib-
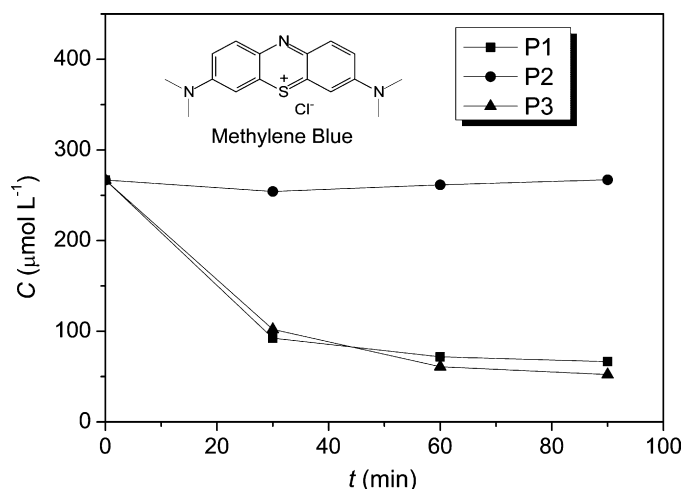
**Fig. 10.** Adsorption of methylene blue by P1, P2 and P3. Kinetics of concentration. $C_0 = 267\ \mu mol\ L^{-1}$, $V = 0.05\ L$, $W = 0.1\ g$, $T = 30\ ^\circ C$.

ited similarly large adsorption capacity, while P2 exhibited very small adsorption capacity. It was inferred that the amino groups of methylene blue were able to react with –COOH and become amine salts, and at the same time, the hydrophobicity and steric hindrance of aromatic rings and methyl groups increased the stability of the amine salts in water. P2 was inefficient in adsorption toward methylene blue, probably because methylene blue was quite hydrophilic and difficult to be included by β-CD. It was particular that methylene blue adsorbed by P2 in the first 30 min gradually went back into the solution. It was probably because when P2 was swelled gradually by water, there would come into polymer networks and β-CD more water molecules which would build hydrogen bonds with the amino groups and the heterocyclic N and S atoms of methylene blue. The hydrogen bonds would counteract the hydrophobic forces of β-CD and bring methylene blue back into the solution.

P1 and P3 were nearly equal in adsorption toward methylene blue, but P1 was much better than P3 in adsorption toward aniline and 1-naphthylamine. It was probably because phenyl group and naphthyl group were more hydrophobic and more easily adsorbed by P1 which contained β-CD. The adsorption results of P2 also agreed that a molecule containing a more hydrophobic group was more easily adsorbed by polymer containing β-CD.
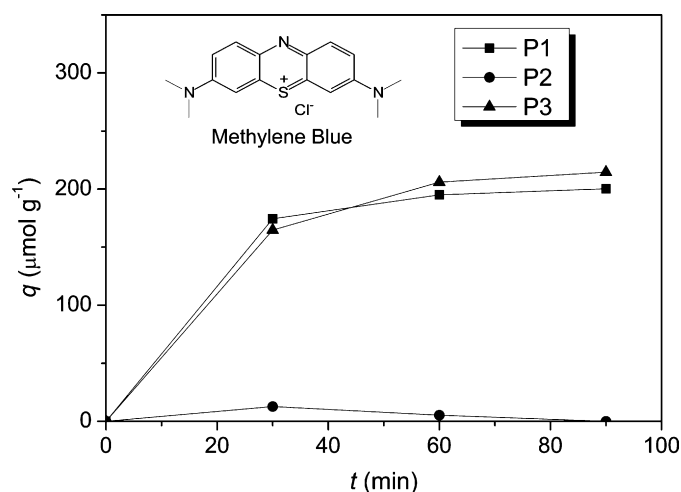


**Fig. 11.** Adsorption of methylene blue by P1, P2 and P3. Kinetics of adsorption capacity. $C_0 = 267\ \mu mol\ L^{-1}$, $V = 0.05\ L$, $W = 0.1\ g$, $T = 30\ ^\circ C$.

## 4. Conclusions

The results showed that the polymer containing both β-CD and –COOH was superior to polymer containing only β-CD or –COOH in adsorption toward aniline and 1-naphthylamine, probably due to synergism of β-CD and –COOH in adsorption. The polymer containing both β-CD and –COOH was obtained from nontoxic materials and through environment friendly procedures, so it was probable to become an efficient and green adsorbent for water purification. It is also attractive to find for this polymer other applications such as microextraction, sustained release and biocompatible materials.

## References

[1] J. Szejtli, Cyclodextrin Technology, 1st edition, Kluwer Academic Publishers, 1988.
[2] S. Li, W.C. Purdy, Cyclodextrins and their applications in analytical chemistry, Chem. Rev. 92 (1992) 1457–1470.
[3] K.H. Fromming, J. Szejtli, Cyclodextrins in Pharmacy, Kluwer Academic Publishers, 1994.
[4] J. Szejtli, Introduction and general overview of cyclodextrin chemistry, Chem. Rev. 98 (1998) 1743–1754.
[5] R. Hedges, Industrial applications of cyclodextrins, Chem. Rev. 98 (1998) 2035–2044.
[6] K. Uekama, F. Hirayama, T. Irie, Cyclodextrin drug carrier systems, Chem. Rev. 98 (1998) 2045–2076.
[7] E.M. Martin Dell Valle, Cyclodextrins and their uses: a review, Process Biochem. 39 (2004) 1033–1046.
[8] G. Crini, Recent developments in polysaccharide-based materials used as adsorbents in wastewater treatment, Prog. Polym. Sci. 30 (2005) 38–70.
[9] Y. Shao, B. Martel, M. Morcellet, M. Weltrowski, G. Crini, Sorption of textile dyes on β-cyclodextrin-epichlorhydrin gels, J. Inclusion Phenom. Macrocyclic Chem. 25 (1996) 209–212.
[10] G. Crini, S. Bertini, G. Torri, A. Naggi, D. Sforzini, C. Vecchi, L. Janus, Y. Lekchiri, M. Morcellet, Sorption of aromatic compounds in water using insoluble cyclodextrin polymers, J. Appl. Polym. Sci. 68 (1998) 1973–1978.
[11] G. Crini, N. Morin, J.-C. Rouland, L. Janus, M. Morcellet, S. Bertini, Adsorption de béta-naphtol sur des gels de cyclodextrine–carboxyméthylcellulose réticulés, Eur. Polym. J. 38 (2002) 1095–1103.
[12] M. Kitaoka, K. Hayashi, Adsorption of bisphenol A by cross-linked β-cyclodextrin polymer, J. Inclusion Phenom. Macrocyclic Chem. 44 (2002) 429–431.
[13] G. Crini, Kinetic and equilibrium studies on the removal of cationic dyes from aqueous solution by adsorption onto a cyclodextrin polymer, Dyes Pigm. 77 (2008) 415–426.
[14] K. Sreenivasan, Synthesis and characterization of poly (vinyl alcohol)-β-cyclodextrin copolymer, Angew. Makromol. Chem. 235 (1996) 15–20.
[15] S. Cadars, M.F. Foray, A. Gadelle, G. Gerbaud, M. Bardet, High-resolution solid-state 13C NMR study of per(3,6-anhydro)-α-cyclodextrin based polymers and of their chromium complexes, Carbohydr. Polym. 61 (2005) 88–94.
[16] E.Y. Ozmen, M. Yilmaz, Use of β-cyclodextrin and starch based polymers for sorption of Congo red from aqueous solutions, J. Hazard. Mater. 148 (2007) 303–310.
[17] B. Martel, P.L. Thuaut, S. Bertini, G. Crini, M. Bacquet, G. Torri, M. Morcellet, Grafting of cyclodextrins onto polypropylene nonwoven fabrics for the manufacture of reactive filters. III. Study of the sorption properties, J. Appl. Polym. Sci. 85 (2002) 1771–1778.
[18] Y. El Ghoul, B. Martel, M. Morcellet, C. Campagne, A. El Achari, S. Roudesli, Mechanical and physico-chemical characterization of cyclodextrin finished polyamide fibers, J. Inclusion Phenom. Macrocyclic Chem. 57 (2007) 47–52.
[19] L. Ducoroy, M. Bacquet, B. Martel, M. Morcellet, Removal of heavy metals from aqueous media by cation exchange nonwoven PET coated with β-cyclodextrin-polycarboxylic moieties, React. Funct. Polym. 68 (2008) 594–600.
[20] S. Berto, M.C. Bruzzoniti, R. Cavalli, D. Perrachon, E. Prenesti, C. Sarzanini, F. Trotta, W. Tumiatti, Synthesis of new ionic β-cyclodextrin polymers and characterization of their heavy metals retention, J. Inclusion Phenom. Macrocyclic Chem. 57 (2007) 631–636.
[21] S. Berto, M.C. Bruzzoniti, R. Cavalli, D. Perrachon, E. Prenesti, C. Sarzanini, F. Trotta, W. Tumiatti, Highly crosslinked ionic β-cyclodextrin polymers and their interaction with heavy metals, J. Inclusion Phenom. Macrocyclic Chem. 57 (2007) 637–643.

[22] C.A. Kozlowski, T. Girek, W. Walkowiak, J.J. Koziol, Application of hydrophobic β-cyclodextrin polymer in separation of metal ions by plasticized membranes, Sep. Purif. Technol. 46 (2005) 136–144.
[23] Wikipedia (2009). http://en.wikipedia.org/wiki/Citric_acid.
[24] A.A. Gürten, S. Uçan, M.A. Özler, A. Ayar, Removal of aniline from aqueous solution by PVC-CDAE ligand-exchanger, J. Hazard. Mater. 120 (2005) 81–87.
[25] J. Cai, A. Li, H. Shi, Z. Fei, C. Long, Q. Zhang, Adsorption characteristics of aniline and 4-methylaniline onto bifunctional polymeric adsorbent modified by sulfonic groups, J. Hazard. Mater. 124 (2005) 173–180.
[26] C.H. Ko, C. Fan, P.N. Chiang, M.K. Wang, K.C. Lin, p-Nitrophenol, phenol and aniline sorption by organo-clays, J. Hazard. Mater. 149 (2007) 275–282.
[27] W.M. Zhang, C.H. Hong, B.C. Pan, Z.W. Xu, Q.J. Zhang, L. Lv, Cooperative adsorption behaviours of 1-naphthol and 1-naphthylamine onto nonpolar macroreticular adsorbents, J. Hazard. Mater. 66 (2006) 485–493.
[28] W.M. Zhang, C.H. Hong, B.C. Pan, Z.W. Xu, Q.J. Zhang, L. Lv, Removal enhancement of 1-naphthol and 1-naphthylamine in single and binary aqueous phase by acid–basic interactions with polymer adsorbents, J. Hazard. Mater. 158 (2008) 293–299.
[29] G. Muthuraman, T.T. Teng, C.P. Leh, I. Norli, Extraction and recovery of methylene blue from industrial wastewater using benzoic acid as an extractant, J. Hazard. Mater. 163 (2009) 363–369.
[30] E.E. Baldez, N.F. Robaina, R.J. Cassella, Employment of polyurethane foam for the adsorption of methylene blue in aqueous medium, J. Hazard. Mater. 159 (2008) 580–586.
[31] M. Hajjaji, A. Alami, A.E. Bouadili, Removal of methylene blue from aqueous solution by fibrous clay minerals, J. Hazard. Mater. 135 (2006) 188–192.
[32] G. Nelson, G. Patonay, I.M. Warner, Fluorescence lifetime study of cyclodextrin complexes of substituted naphthalenes, Appl. Spectrosc. 41 (1987) 1235–1238.