Adsorption mechanism-based screening of cyclodextrin polymers for adsorption and separation of pesticides from water

Huihui Liu a,b, Xiyun Cai a,b,*, Yu Wang a, Jingwen Chen a

a Key Laboratory of Industrial Ecology and Environmental Engineering (Ministry of Education), School of Environmental Science and Technology, Dalian University of Technology, Dalian 116024, China
b State Key Laboratory of Soil and Sustainable Agriculture, Institute of Soil Science, Chinese Academy of Sciences, Nanjing 210008, China

A R T I C L E   I N F O
Article history:
Received 24 November 2010
Received in revised form 31 March 2011
Accepted 3 April 2011
Available online 12 April 2011

Keywords:
Cyclodextrin polymer
Pesticides
Adsorption
Separation
Screening

A B S T R A C T
A rational screening of cyclodextrin-based polymer (CDP), in terms of the relationship between adsorption potential and adsorbent-adsorbate, was investigated to adsorb and separate pesticides from water. Seven spherical porous CDPs were prepared with onefold or composite cyclodextrin(s) as complex and epichlorohydrin as cross-linking reagent. The adsorption kinetics and isotherms of the polymers toward a mixture of ten distinct pesticides clearly demonstrate that the adsorbents with a homogeneous open network structure can absorb pesticides via multiple adsorption interactions such as CD inclusion, loading into swelling water and physical adsorption on network. The multivariate regression analysis distinguishes the quantitative contributions of polymer properties to its adsorption potential, among which CD content, swelling capacity and pore size appear to be major influencing factors. Consequently, a facile mixture of three CDPs (i.e., β-CDP, RM-CDP and HP-CDP) was screened to obtain above prerequisite properties. The multiplex polymer could superiorly separate the pesticides at environmentally relevant levels from water.

© 2011 Elsevier Ltd. All rights reserved.

1. Introduction
Pesticides, intentionally released into the environment, are ubiquitous in aquatic systems; they are often detected at low levels and commonly occur in the form of complex mixtures (Schwarzenbach et al., 2006; Gilliom, 2007). They have raised serious concerns about aquatic ecosystem and human health because of the long-term accumulation of their single and/or combined toxicological effects (Gasser et al., 2007; Relyea, 2009; Cui et al., 2011). Accordingly, numerous technologies such as biodegradation, fluid extraction, photo-catalysis and adsorption (Robinson et al., 2001; Crini, 2006; Bernhard et al., 2008; Chong et al., 2010), have been developed to remove organic compounds from water. Among them adsorption using cyclodextrin-based polymer as adsorbent, is an efficient technique with the advantages of specific affinity, low cost and simple design (Murai et al., 1998; Crini and Morcellet, 2002; Allabashi et al., 2007; Romo et al., 2008).

Cyclodextrin polymers (CDPs) can be synthesized using cyclodextrin (CD) as complex molecule and polyfunctional substance (e.g., epichlorohydrin (EPI)) as cross-linking agent (Crini and Morcellet, 2002; Gazzio et al., 2008; Daoud-
Mahammed et al., 2009), wherein the CD unit is covalently jointed by repeating glyceryl linkers (Scheme 1). Cyclodextrins have a toroidal shape in geometry with a well-defined hydrophobic cavity, and can accommodate suitably sized organic compounds through host-guest inclusion complexation (Hapiot et al., 2006; Bonenfant et al., 2009). The cross-linking agent (i.e., EPI) leads to a high degree of branching across the CD unit, and the branches themselves have branches. This graft polymerization converts cyclodextrin from water-soluble monomer into insoluble and regenerable network-shaped polymer, the latter has high swelling capacity in water as well as multiple binding sites (Murai et al., 1998; Ozmen et al., 2008). Therefore, the resultant adsorption mechanisms of CDP are believed to involve inclusion complexation, hydrogen bonding and physical sorption on network (Crini et al., 1998; Yilmaz et al., 2010).

Though a number of CDPs with various structures and properties have been developed (Murai et al., 1998; Crini and Morcellet, 2002; Romo et al., 2008), it is still ambiguous how CDP properties affect adsorption affinity toward organic contaminants, particularly mixed pollutants. A higher CD content, generally, is responsible for higher adsorption capacity (Crini, 2003; Yu et al., 2003), whereas less CD loadings, in some cases, favor adsorption (Sawicki and Mercier, 2006; Vélaz et al., 2007). The cross-linking degree, denoting the mean amounts of EPI per CD unit, is opposite to the CD content in stoichiometry; increasing this property can create dense network structures that preclude the accessibility of CD binding sites (Martel et al., 2001), accompanying with a reduction of swelling capacity that is unfavorable for the loading of hydrophilic adsorbate (Thatiparti et al., 2010). In addition, variants of CD and/or cross-linking agent as well as the presence of some modifiers can result in different adsorption capacities of CDP (Shao et al., 1996; Zhao et al., 2009). The fact that most studies are limited to both diversities of adsorbents (i.e., CDPs) and adsorbates (i.e., organic pollutants) hampers the extrapolation of the relationship between adsorption potential and polymer properties. This relationship would allow researchers to predict which polymer would best adsorb and separate the contaminants.

Herein, this study was aimed at distinguishing the roles of CDP properties in its adsorption potential toward pesticides and subsequently screening appropriate CDP(s) for separating them from water. Various CDPs were prepared with onefold or composite cyclodextrin(s) as complex and epichlorohydrin as cross-linking reagent. The adsorption behavior (i.e., kinetics models, controlling step identification and adsorption isotherms) of the CDPs toward a mixture of ten pesticides with distinct properties was analyzed to clarify principal adsorption mechanisms. A multivariate linear regression analysis was used to describe the quantitative contributions of polymer properties to adsorption potential. Finally, a rational screening of CDP(s) was investigated to separate the pesticides at environmentally relevant levels from water.

2. Materials and methods

2.1. Synthesis and characterization of CDPs

The related properties and information of cyclodextrins and pesticides were presented in Tables S1, S2 and S3, respectively. Seven CDPs were synthesized according to the method reported by Nussstein et al. (Nussstein et al., 1994), only replacing the dispersing agent “Gafac RM 510” with a mixture of Span80 and Tween20 (75:25 by mass). The polymers included four onefold polymers with single CD as complex (i.e., β-CDP, γ-CDP, HP-CDP and RM-CDP) and three composite polymers with an equimolar mixture of CDs as double complex (i.e., β-γ-CDP, β-HP-CDP and γ-HP-CDP). Their properties were summarized in Table 1.

![Scheme 1](image_url) - Cross-linked structure of cyclodextrin polymer and related adsorption mechanisms.
Table 1 — Related physicochemical properties of cyclodextrin polymers.

<table>
<thead>
<tr>
<th>CDP</th>
<th>Cyclodextrin</th>
<th>Degree of cross-linking</th>
<th>CD Content (%)</th>
<th>Swelling Ratio (g/g)</th>
<th>Particle sizex (μm)</th>
<th>Pore size (nm)</th>
<th>Surface area (m²/g)</th>
<th>Pore volume (10⁻³ cc/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>β-CDP</td>
<td>β-CD</td>
<td>9.02</td>
<td>49.32</td>
<td>7.36</td>
<td>289.92</td>
<td>2.78</td>
<td>3.22</td>
<td>1.31</td>
</tr>
<tr>
<td>γ-CDP</td>
<td>γ-CD</td>
<td>8.32</td>
<td>57.24</td>
<td>6.70</td>
<td>331.83</td>
<td>3.21</td>
<td>6.70</td>
<td>4.60</td>
</tr>
<tr>
<td>HP-CDP</td>
<td>HP-β-CD</td>
<td>4.57</td>
<td>71.91</td>
<td>4.54</td>
<td>275.60</td>
<td>3.12</td>
<td>1.21</td>
<td>5.15</td>
</tr>
<tr>
<td>RM-CDP</td>
<td>RM-β-CD</td>
<td>8.39</td>
<td>57.62</td>
<td>5.14</td>
<td>214.05</td>
<td>5.01</td>
<td>3.92</td>
<td>4.34</td>
</tr>
<tr>
<td>β-γ-CDP</td>
<td>Equimolar mixture of β-CD and γ-CD</td>
<td>19.82</td>
<td>38.62</td>
<td>4.74</td>
<td>245.68</td>
<td>3.08</td>
<td>5.47</td>
<td>3.39</td>
</tr>
<tr>
<td>β-HP-CDP</td>
<td>Equimolar mixture of β-CD and HP-β-CD</td>
<td>10.06</td>
<td>58.49</td>
<td>6.21</td>
<td>197.94</td>
<td>3.10</td>
<td>8.01</td>
<td>5.40</td>
</tr>
<tr>
<td>γ-HP-CDP</td>
<td>Equimolar mixture of γ-CD and HP-β-CD</td>
<td>19.43</td>
<td>43.54</td>
<td>5.40</td>
<td>151.56</td>
<td>3.12</td>
<td>6.14</td>
<td>7.97</td>
</tr>
</tbody>
</table>

a The particle size was determined after swelling in water.

The mass fraction of C and H elements of CDP was measured using Elementar Vario EL III. The CD content (Text S1) was quantified by determining reducing sugars of the polymer on basis of concentrated H₂SO₄ acidolysis and phenol colorimetric analysis (Masuko et al., 2005). The cross-linking degree (Text S2) was calculated from the element analysis coupled with the CD content determination. The swelling capacity in water (Text S3) was determined as the mass loss before and after swelling (Dos Santos et al., 2009).

The surface morphology of dry and swollen CDP was examined by scanning electron microscopy (Hitachi S-4700) and 40× optical microscope (Coic BA100), respectively. Fourier-transform infrared (FTIR) spectrum of CDP was recorded using Shimadzu IR Prestige-21. Differential scanning calorimetry (DSC) was performed on TA Instruments DSC 910S equipped with an aluminum pan, in which the thermogram was obtained at a heating rate 10 °C/min from 30 °C to 400 °C under a dynamic atmosphere of nitrogen. The surface area and porosimetry of CDP was measured by Quadrasorb-SI (USA) that recorded nitrogen adsorption/desorption isotherms at 77 K. The particle size of CDP after swelling in water was determined by Malvern Mastersize 2000 Particle Analyzer.

2.2. Analytical methods

The pesticides were analyzed by a Hitachi L-2000 HPLC system equipped with an L-2130 quat pump, an L-2300 column oven, an L-2200 automated sampler and an L-2455 diode array detector. The stationary phase was a YWG C-18 column (4.6 × 250 mm, 10 μm; Dalian Elite Analytical Instruments Co., Ltd., Dalian, China). A gradient program was performed to elute pesticides, detailed in Table S4. The column oven was maintained at 30 °C. The injection volume was 30 μL. The detection wavelength was set at 275 nm for bromacil, 230 nm for atrazine, 250 nm for fenamiphos and 220 nm for others. Under these conditions, all pesticides were baseline separated (Fig. S1).

2.3. Adsorption kinetics

Adsorption kinetic experiment of pesticides by CDP was performed in 250-ml flasks using 0.400 g CDP and 100 ml of deionized water (pH 6.8) where 0.160 ml pesticide stock solution was added in advance. The level of each pesticide was shown in Table S2. The samples were shaken at 180 rpm and 25 °C. At certain intervals, 1 ml suspension was sampled and filtered through a 0.45 μm Millipore glass fiber membrane. The pesticides in filtrate were measured by HPLC. The amount of pesticides adsorbed by CDP, Qₑ (mg/g), was then calculated by Eq. (1):

\[ Q_e = \frac{V(C_0 - C_i)}{m} \]

where \( C_0 \) (mg/L) and \( C_i \) (mg/L) are the initial and real-time concentrations of pesticide in liquid phase, respectively; \( V \) (L) is the volume of solution; and \( m \) (g) is the mass of CDP used.

Linear pseudo-first and pseudo-second order models corresponded to Eqs. (2) and (3), respectively, and were adopted to investigate kinetic behavior of pesticides by CDP.

\[ \ln(Q_e - Q_{eq}) = \ln Q_e - K_1t \]

\[ \frac{t}{Q_{eq}} = \frac{1}{K_2Q_e^2} \frac{t}{Q_e} \]

where \( Q_e \) (mg/g) and \( Q_{eq} \) (mg/g) are the adsorption amount at equilibrium and time \( t \) (min), respectively; \( K_1 \) (1/min) and \( K_2 \) (g/ (mg min)) are the corresponding rate constants.

Additionally, the moving boundary model (Boyd et al., 1947; Chen et al., 2003; Kadous et al., 2010) was used to distinguish the relative roles of adsorption steps involved to play. If the adsorption process was controlled by liquid film diffusion, intraparticle diffusion or chemical interaction, the rate constant can be expressed by Eqs. (4), (5) and (6), respectively.

\[ k = -\ln(1 - F) \]

\[ k = 1 - 3(1 - F)^{2/3} + 2(1 - F) \]

\[ k = 1 - (1 - F)^{1/3} \]

where \( F \) is the adsorption fraction (\( Q_e/Q_{eq} \)), and \( k \) is the adsorption rate constant. By plotting a linear relationship of \( k \) versus contact time \( t \) (min), the regression coefficients (\( R^2 \)) for three adsorption steps were obtained, of which the one with the highest \( R^2 \) value was assumed to be the rate controlling step.

2.4. Adsorption isotherms

Isothermal adsorption experiment was conducted using a batch equilibration technique in 35-ml glass centrifuge
The adsorbents (0.100 g) were added into 25 ml solution where pesticide stock solutions of 20, 40, 60, 80, 100 and 120 μL were added in advance, respectively. The samples were shaken at 180 rpm and at 25 °C for 24 h to ensure adsorption equilibrium (Fig. S2). The amounts adsorbed by CDP were obtained in the same way as described in 2.3.

The isothermal adsorption of pesticides by CDP was described by linear Langmuir equation (Eq. (7)).

\[
\frac{1}{Q_e} = \frac{1}{Q_{\text{max}}} K_c c_L + \frac{1}{Q_{\text{max}}}
\]  

(7)

where \(C_c\) (mg/L) and \(Q_e\) (mg/g) are the concentration of pesticide in solution and the amount adsorbed at equilibrium, respectively; \(K_c\) (L/mg) is the Langmuir isotherm constant; and \(Q_{\text{max}}\) (mg/g) is the maximum adsorption capacity. The latter two parameters represent adsorption affinity and capacity, respectively. Additionally, the mean value of distribution coefficient \(K_d\) that was denoted as the ratio of \(Q_e\) to \(C_c\) was introduced to assess separation and removal efficiency of pesticides from aqueous solutions. The removal efficiency of pesticides was defined as the ratio of adsorption amounts of pesticides by cyclodextrin polymers to the sum of pesticides.

### 2.5. Relationship between adsorption potential and adsorbent–adsorbate

The multivariate linear regression analysis was performed using a stepwise linear regression model of SPSS Statistics program (SPSS 17.0 version) to investigate how adsorbent–adsorbate properties affect polymer adsorption potential (i.e., kinetic and equilibrium parameters). The dependence of adsorption potential (parameter) on each property of adsorbent and/or adsorbate (factor) was calculated by Eq. (8), in which the factor value was set as independent variable \(x_i\), and the parameter value was set as dependent variable \(y\).

\[
y = k_1 x_1 + k_2 x_2 + k_3 x_3 + k_4 x_4 + \cdots
\]  

(8)

where \(y\) is the adsorption parameter value, \(x_i\) is the adsorbent or adsorbate property value, and \(k_i\) is the standardized coefficient. An independent variable was included only when the probability of F-distribution was less than 0.05. Moreover, the independent variables included were not colinear, as the variance inflation factor was less than 10. In this study, all fitted equations were statistically significant \((p < 0.05)\), in which the property with the largest standardized coefficient was assumed to be the dominating factor.

### 2.6. Separation of pesticides

A physical mixture of β-CDP, RM-CDP and HP-CDP (40:30:30 by mass) was screened as adsorbent to separate the pesticides at environmentally relevant levels (0.063–1.000 mg/L) from deionized and sea waters. The natural water was collected from Dalian Bay (39° 01' N Latitude, 121° 44' E Longitude) and had pH value of 7.2. Appropriate amounts of the multiplex CDP was added into 1 L solution containing the pesticides (Fig. S3), and the solutions were stirred for 2 h. Thereafter, the adsorbent was centrifugally separated and transferred into 40 mL mixed solvents of methanol and water (80:20, v/v). After ultrasonic extraction for 30 min, the solution was centrifuged. The supernatant was concentrated to 2 mL, and pesticides were determined by HPLC. This procedure was conducted twice to ensure complete extraction.

For regeneration, the precipitated CDP with an initial dose of 2.000 g/L was centrifuged, then was washed with water, and finally was dried for 10 h at 60 °C. The reuse experiment of CDP was carried out by repeating above procedure for five times.

### 2.7. Data analysis

All experiments were performed in triplicate, and data for polymer property, pesticide concentration and adsorption amount was represented by mean value \((n = 3)\). Statistical analysis for the significance was performed using One-Way ANOVA in Origin 8.0 (Microcal Software, Inc., USA). The values without overlapping 95% confidence intervals were considered to be significantly different.

### 3. Results and discussion

#### 3.1. Characterizations and properties of CDP

The polymers were obtained to possess characteristic groups of CD monomers, based on the FTIR analysis (Fig. S4) that O–H stretching vibration at 3430 cm\(^{-1}\), C–H asymmetric stretching vibration at 2920 cm\(^{-1}\), O–H bending vibration at 1630 cm\(^{-1}\) and pyranoid sugar ring at 1500–400 cm\(^{-1}\) were identified. The presence of intrinsic groups of CD suggested that the structure of CD unit be essentially maintained in the polymers. Moreover, they had broadening of C\(_{13}\)–H asymmetric stretching vibration at 2920 cm\(^{-1}\) and overlapping of C–OH stretching vibration at 1030 cm\(^{-1}\) and C–O–C stretching vibration at 1159 cm\(^{-1}\) relative to the CD monomers, indicating the introduction of EPI molecule. Thus, the polymers were considered as copolymer (CDP) of CD unit and EPI molecule (Scheme 1).

Dried CDP had coarse surface with hydrogel like material embedded in (Fig. S5) and exhibited the nature of porous material with relatively uniform pore size ranges (2.780 nm (β-CDP) to 5.010 nm (RM-CDP)). The pore sizes of CDP were in the range of mesopores (2–50 nm), which is constructive for completed access to the binding sites of cyclodextrin-based polymers (Huq et al., 2001; Liu et al., 2003). These properties led to high swelling capacity of the polymers (Table 1), and the polymers swelled readily to give a spherical shape in water (Fig. 1). Among them, the ones with onefold CD as complex exhibited higher CD content and lower cross-linking degree than those with composite CDs as complex, and consequently, they were endowed with looser structure and larger particle size.

Additionally, the polymers had good thermostability, as the DSC curves showed (Fig. S6). The curves gave three peaks at ca. 80 °C, 280 °C and 340 °C, which responded to water loss, polymer melting and polymer decomposition, respectively.

#### 3.2. Adsorption kinetics

##### 3.2.1. Pseudo-first and pseudo-second order model

The regression coefficient \((R^2)\) for the pseudo-first order model varied from 0.307 to 0.908 and the \(Q_e\) values calculated from the model deviated tremendously from the experimental values.
(Table S5 and Fig. S7), together indicating the invalidity of the model. However, the pseudo-second order model was greatly applicable for adsorption kinetics of CDP toward the pesticides, represented by high regression coefficients with $R^2 > 0.979$ (Fig. 2) and good consistency between calculated and experimental $Q_e$ values (Table S6). The higher goodness of fitting for the pseudo-second order model could be ascribed to the nature of cyclodextrin-based polymers with multiple adsorption sites, which are responsible for different adsorption steps, respectively.

As generally viewed, an adsorption process composes of several successive kinetic steps, viz. transport in the bulk solution, diffusion across the film surrounding the adsorbent particles, diffusion in the pores of the adsorbent and finally adsorption on the solid surface (Rudzinski and Plazinski, 2007; Kadous et al., 2010). The former three steps are driven mainly by mass balance and/or Fick diffusion (Liu and Shen, 2008; Álvarez-Ramírez et al., 2005), belonging to physical adsorption processes, and reasonably reflects the nature of the first-order kinetic order that it is usually governed by the concept of linear driving force. However, the hindmost step viewed as a kind of chemical reaction would follow the common rate law of chemical reaction (Rudzinski and Plazinski, 2007). As Liu (2008) demonstrates, the rate of adsorption for the chemical adsorption process is usually subject to a second-order rate law primarily with respect to the availability of adsorption sites on the surface of adsorbent, suggesting the applicability of the second-order kinetic model in chemical-dominated adsorption. As well-known, chemical interactions such as accommodation of CD cavity and hydrogen bonding to residual hydroxyl groups of network superiorly enable the polymers to bind adsorbate molecules so that the degree of fitting of the second-order kinetic order model is acceptable.

### 3.2.2. Adsorption controlling step discrimination

As the second-order kinetic model is actually a consequence of cooperation effects of the adsorption steps mentioned above (Rudzinski and Plazinski, 2007; Kadous et al., 2010), extra theoretical adsorption models are usually supplemented to accurately discriminate the adsorption processes. In response to this, the moving boundary model was designated to identify the controlling adsorption step, by distinguishing the roles of liquid film diffusion, intraparticle diffusion and chemical interaction. The fitted linear regression coefficients ($R^2$) for the steps, representing their relative importance, were summarized in Table 2. A remarkable variety of the values clearly revealed varying controlling steps in CDP-pesticide systems, primarily depending on adsorbate molecules.

Fipronil and butenefipronil that belong to very hydrophobic compounds with log $K_{ow}$ values of more than 4 (Lyman et al., 1982) exhibited the highest regression coefficients for Eq. (4), indicating that liquid film diffusion be the rate controlling step. This is probably ascribed to poor solvation potential of the two less-soluble pesticides limiting their mass transport from liquid solutions to adsorbate surface. Concomitant high values for Eq. (6) suggested that chemical interaction should play important roles as well. For moderately hydrophobic pesticides including fomesafen, benalaxyl, pretilachlor and butachlor, their adsorption processes were mainly driven by chemical interaction. This discrimination was in good accordance with strong inclusion interaction between these pesticides and CD monomers, which was manifested by the binding constants (Table S7) from phase-solution experiments (Text S4). In the case of relatively hydrophobic pesticides (e.g., bromacil, atrazine and fenamiphos), their adsorption was mainly controlled by intraparticle diffusion (Eq. (5)). Particularly, it was more obvious for composite polymers (e.g., $\gamma$-HP-CDP) than onefold polymers (e.g., $\gamma$-CDP). In most cases, the former generally had less particle size and pore size but higher CD content and cross-linking degree, and then had the nature of denser network, impeding diffusion of pesticide molecule within the congested intraparticle (Renard et al., 1997; Vélez et al., 2007). Noteworthily, simazine was intraparticle diffusion-dominatedly adsorbed, unlike its hydrophobic analogs (i.e., fipronil and butenefipronil), probably because the herbicide with small molecular size is poorly included by CDs (Table S7).

### 3.3. Adsorption isotherms

Adsorption isotherms of pesticides on the polymers followed Langmuir equation well (Fig. 3), and all the degree of fitting ($R^2$) exceeded 0.99 except simazine-$\gamma$-CDP system (Table S8). These results indicated homogeneous distribution of
adsorption active sites in the polymers. Considering the porous spherical nature, the polymers could have an open structure that makes the adsorption sites easily available to adsorbate molecules (Bibby and Mercier, 2003).

Both adsorption affinity ($K_L$) and the maximum adsorption capacity ($Q_{max}$) of the polymers varied dramatically, depending on both polymers and pesticides (Table S8). The $K_L$ values in this study showed that the polymers appeared to exhibit stronger...
affinity toward neutral pesticides hereof, as compared with dissociable dye molecules (e.g., C.I. Basic Violet 10 and C.I. Basic Blue 3) and surfactants (e.g., dodecylbenzenesulfonic acid) (Crini, 2008; Murai et al., 1997). Moreover, the polymer had distinct potentials to accommodate the pesticides, highlighted by the $Q_{\text{max}}$ values (Table S8). Four of the ten pesticides (i.e., fenamiphos, benalaxyl, pretilachlor and butachlor) were comparable to those for the dye molecules (Crini, 2006, 2008) and surfactants (Murai et al., 1996, 1997). The other six pesticides poorly approached the adsorption sites of the polymers, like some aromatic compounds (Crini et al., 1998; Yu et al., 2003).

3.4. Relationship between adsorption potential and adsorbent–adsorbate

3.4.1. Analysis for adsorption rate constant ($K_2$)

The multivariate regression analysis showed that particle size, pore volume and swelling capacity of polymers contributed positively to the adsorption processes (Table 3). The polymers with higher values of these properties, generally, are prone to have more rapid expansion and looser network structures, which are in favor of liquid film and intraparticle diffusion. As both have negative standardized regression coefficients, higher CD content and/or larger surface area generally resulted in higher numbers and/or more accessibility of strong adsorption sites (i.e., CD cavity and residual hydroxyl groups of network), thereby enhancing the contribution of the chemical interaction involved.

Meanwhile, pesticide molecules played distinct roles in the adsorption processes (Table 3). Hydrophobic molecules (e.g., simazine and fipronil) are in favor of adsorption with high adsorption affinity and less time to reach equilibrium, as demonstrated by a high regression coefficient of $K_{\text{ow}}$ in this study. Pesticide molecules (e.g., benalaxyl and butachlor) involving more H-acceptors and H-donors, could need more time to reach adsorption equilibrium, associated with the chemical adsorption involved (e.g., CD inclusion and hydrogen bonding). In addition, the pesticides with higher molecular weight are adsorbed at lower rates by the polymers. For example, butenefipronil with many nonpolar substituents was very hydrophobic and had poor diffusion potential; and fomesafen with sized-matched structure and relative water solubility, could be included into the cavity of cyclodextrin.

<table>
<thead>
<tr>
<th>CDP</th>
<th>Pesticide</th>
<th>Eq. (4)</th>
<th>Eq. (5)</th>
<th>Eq. (6)</th>
<th>CDP</th>
<th>Pesticide</th>
<th>Eq. (4)</th>
<th>Eq. (5)</th>
<th>Eq. (6)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\beta$-CDP</td>
<td>Fomesafen</td>
<td>0.865</td>
<td>0.838</td>
<td>0.952</td>
<td>Bromacil</td>
<td>0.766</td>
<td>0.940</td>
<td>0.878</td>
<td></td>
</tr>
<tr>
<td>$\gamma$-CDP</td>
<td></td>
<td>0.748</td>
<td>0.980</td>
<td>0.951</td>
<td></td>
<td>0.823</td>
<td>0.934</td>
<td>0.903</td>
<td></td>
</tr>
<tr>
<td>HP-CDP</td>
<td></td>
<td>0.979</td>
<td>0.880</td>
<td>0.893</td>
<td></td>
<td>0.973</td>
<td>0.900</td>
<td>0.946</td>
<td></td>
</tr>
<tr>
<td>RM-CDP</td>
<td></td>
<td>0.921</td>
<td>0.957</td>
<td>0.964</td>
<td></td>
<td>0.913</td>
<td>0.926</td>
<td>0.945</td>
<td></td>
</tr>
<tr>
<td>$\beta$-CDP</td>
<td></td>
<td>0.966</td>
<td>0.960</td>
<td>0.967</td>
<td></td>
<td>0.939</td>
<td>0.946</td>
<td>0.924</td>
<td></td>
</tr>
<tr>
<td>$\beta$-HP-CDP</td>
<td></td>
<td>0.880</td>
<td>0.957</td>
<td>0.968</td>
<td></td>
<td>0.922</td>
<td>0.988</td>
<td>0.971</td>
<td></td>
</tr>
<tr>
<td>$\gamma$-HP-CDP</td>
<td></td>
<td>0.979</td>
<td>0.967</td>
<td>0.986</td>
<td></td>
<td>0.823</td>
<td>0.925</td>
<td>0.896</td>
<td></td>
</tr>
<tr>
<td>$\beta$-CDP</td>
<td>Simazine</td>
<td>0.952</td>
<td>0.838</td>
<td>0.865</td>
<td>Atrazine</td>
<td>0.989</td>
<td>0.979</td>
<td>0.992</td>
<td></td>
</tr>
<tr>
<td>$\gamma$-CDP</td>
<td></td>
<td>0.864</td>
<td>0.912</td>
<td>0.895</td>
<td></td>
<td>0.725</td>
<td>0.856</td>
<td>0.811</td>
<td></td>
</tr>
<tr>
<td>HP-CDP</td>
<td></td>
<td>0.656</td>
<td>0.675</td>
<td>0.671</td>
<td></td>
<td>0.754</td>
<td>0.837</td>
<td>0.812</td>
<td></td>
</tr>
<tr>
<td>RM-CDP</td>
<td></td>
<td>0.860</td>
<td>0.887</td>
<td>0.880</td>
<td></td>
<td>0.895</td>
<td>0.968</td>
<td>0.947</td>
<td></td>
</tr>
<tr>
<td>$\beta$-CDP</td>
<td></td>
<td>0.757</td>
<td>0.871</td>
<td>0.834</td>
<td></td>
<td>0.671</td>
<td>0.832</td>
<td>0.776</td>
<td></td>
</tr>
<tr>
<td>$\beta$-HP-CDP</td>
<td></td>
<td>0.672</td>
<td>0.792</td>
<td>0.761</td>
<td></td>
<td>0.822</td>
<td>0.877</td>
<td>0.866</td>
<td></td>
</tr>
<tr>
<td>$\gamma$-HP-CDP</td>
<td></td>
<td>0.789</td>
<td>0.855</td>
<td>0.741</td>
<td></td>
<td>0.823</td>
<td>0.925</td>
<td>0.896</td>
<td></td>
</tr>
<tr>
<td>$\beta$-CDP</td>
<td>Fenamiphos</td>
<td>0.938</td>
<td>0.978</td>
<td>0.972</td>
<td>Fipronil</td>
<td>0.857</td>
<td>0.898</td>
<td>0.936</td>
<td></td>
</tr>
<tr>
<td>$\gamma$-CDP</td>
<td></td>
<td>0.966</td>
<td>0.964</td>
<td>0.978</td>
<td></td>
<td>0.950</td>
<td>0.915</td>
<td>0.918</td>
<td></td>
</tr>
<tr>
<td>HP-CDP</td>
<td></td>
<td>0.948</td>
<td>0.886</td>
<td>0.912</td>
<td></td>
<td>0.941</td>
<td>0.775</td>
<td>0.909</td>
<td></td>
</tr>
<tr>
<td>RM-CDP</td>
<td></td>
<td>0.938</td>
<td>0.971</td>
<td>0.956</td>
<td></td>
<td>0.951</td>
<td>0.614</td>
<td>0.877</td>
<td></td>
</tr>
<tr>
<td>$\beta$-CDP</td>
<td></td>
<td>0.667</td>
<td>0.899</td>
<td>0.772</td>
<td></td>
<td>0.943</td>
<td>0.962</td>
<td>0.966</td>
<td></td>
</tr>
<tr>
<td>$\beta$-HP-CDP</td>
<td></td>
<td>0.921</td>
<td>0.953</td>
<td>0.934</td>
<td></td>
<td>0.884</td>
<td>0.819</td>
<td>0.874</td>
<td></td>
</tr>
<tr>
<td>$\gamma$-HP-CDP</td>
<td></td>
<td>0.898</td>
<td>0.984</td>
<td>0.965</td>
<td></td>
<td>0.922</td>
<td>0.919</td>
<td>0.907</td>
<td></td>
</tr>
<tr>
<td>$\beta$-CDP</td>
<td>Benalaxyl</td>
<td>0.900</td>
<td>0.899</td>
<td>0.961</td>
<td>Butene-fipronil</td>
<td>0.912</td>
<td>0.939</td>
<td>0.966</td>
<td></td>
</tr>
<tr>
<td>$\gamma$-CDP</td>
<td></td>
<td>0.958</td>
<td>0.887</td>
<td>0.926</td>
<td></td>
<td>0.984</td>
<td>0.964</td>
<td>0.951</td>
<td></td>
</tr>
<tr>
<td>HP-CDP</td>
<td></td>
<td>0.753</td>
<td>0.768</td>
<td>0.800</td>
<td></td>
<td>0.980</td>
<td>0.863</td>
<td>0.906</td>
<td></td>
</tr>
<tr>
<td>RM-CDP</td>
<td></td>
<td>0.966</td>
<td>0.915</td>
<td>0.979</td>
<td></td>
<td>0.996</td>
<td>0.954</td>
<td>0.995</td>
<td></td>
</tr>
<tr>
<td>$\beta$-CDP</td>
<td></td>
<td>0.973</td>
<td>0.894</td>
<td>0.945</td>
<td></td>
<td>0.990</td>
<td>0.961</td>
<td>0.970</td>
<td></td>
</tr>
<tr>
<td>$\beta$-HP-CDP</td>
<td></td>
<td>0.791</td>
<td>0.725</td>
<td>0.893</td>
<td></td>
<td>0.995</td>
<td>0.935</td>
<td>0.947</td>
<td></td>
</tr>
<tr>
<td>$\gamma$-HP-CDP</td>
<td></td>
<td>0.919</td>
<td>0.953</td>
<td>0.967</td>
<td></td>
<td>0.970</td>
<td>0.833</td>
<td>0.904</td>
<td></td>
</tr>
<tr>
<td>$\beta$-CDP</td>
<td>Pretilachlor</td>
<td>0.948</td>
<td>0.960</td>
<td>0.969</td>
<td>Butachlor</td>
<td>0.925</td>
<td>0.960</td>
<td>0.983</td>
<td></td>
</tr>
<tr>
<td>$\gamma$-CDP</td>
<td></td>
<td>0.837</td>
<td>0.917</td>
<td>0.816</td>
<td></td>
<td>0.985</td>
<td>0.974</td>
<td>0.954</td>
<td></td>
</tr>
<tr>
<td>HP-CDP</td>
<td></td>
<td>0.955</td>
<td>0.948</td>
<td>0.977</td>
<td></td>
<td>0.841</td>
<td>0.970</td>
<td>0.976</td>
<td></td>
</tr>
<tr>
<td>RM-CDP</td>
<td></td>
<td>0.979</td>
<td>0.944</td>
<td>0.990</td>
<td></td>
<td>0.617</td>
<td>0.830</td>
<td>0.852</td>
<td></td>
</tr>
<tr>
<td>$\beta$-CDP</td>
<td></td>
<td>0.901</td>
<td>0.979</td>
<td>0.923</td>
<td></td>
<td>0.953</td>
<td>0.915</td>
<td>0.912</td>
<td></td>
</tr>
<tr>
<td>$\beta$-HP-CDP</td>
<td></td>
<td>0.786</td>
<td>0.956</td>
<td>0.966</td>
<td></td>
<td>0.892</td>
<td>0.881</td>
<td>0.964</td>
<td></td>
</tr>
<tr>
<td>$\gamma$-HP-CDP</td>
<td></td>
<td>0.955</td>
<td>0.963</td>
<td>0.961</td>
<td></td>
<td>0.898</td>
<td>0.898</td>
<td>0.902</td>
<td></td>
</tr>
</tbody>
</table>

a Liquid film diffusion.
b Intraparticle diffusion.
c Chemical interaction.
Fig. 3 – Fitted straight line by Langmuir isothermal equation for the adsorption of each pesticide by CDPs. Solid square (■) β-CDP, solid cycle (○) γ-CDP, solid upward triangle (▲) HP-CDP, solid downward triangle (▼) RM-CDP, hollow square (□) β-γ-CDP, hollow cycle (●) β-HP-CDP, and hollow upward triangle (△) γ-HP-CDP.
3.4.2. Analysis for maximum adsorption capacity (Q_{max})

The maximum adsorption capacity (Q_{max}) could be achieved theoretically when all binding sites of adsorbent are occupied. The Q_{max} value was mainly dependent on adsorbate molecules but not adsorbent material (Table 3). The properties of pesticide molecules appeared to be involved to different extents, when considering a variety of CDPs (Table S9). For adsorbate molecules (e.g., butachlor, pretilachlor, benalaxyl and fenamiphos) with multiple H-acceptors, hydrogen bonding interaction was responsible for high Q_{max} values (Table S10). Interestingly, the contribution of hydrophobicity and water solubility of pesticide molecules was opposite, represented by a positive (0.410) and negative (−0.408) coefficients, respectively. The related interactions can cancel out each other, because CD cavity favorably accommodates hydrophobic and/or low water-soluble molecules (Murai et al., 1998).

3.4.3. Analysis for adsorption constant (K_s)

Adsorption constant (K_{s}) was obtained to depend on both properties of polymer and pesticide. An increase in CD content, swelling capacity, pore size, particle size or pore volume would lead to strong adsorption affinity of polymers toward pesticides, especially hydrophobic compounds (Table 3 and Table S9). This relationship is associated with the intrinsical adsorption mechanisms of the polymers. The increase in these properties can augment the number of binding sites (e.g., CD unit) or facilitate adsorbate molecules to access CD and other adsorption sites.

As the complexes form, guest molecule such as drug and pesticide is partially or entirely accommodated by CD cavity, depending on geometric size of guest molecule. As the cubic fit is essential, the inclusion of CD with guest molecule, generally, is a consequence of the integrated contribution of hydrophobic interaction, van der Waals force, hydrogen bonding and steric effect (Rekharsky and Inoue, 1998; Hapiot et al., 2006; Van de Manakker et al., 2009), enabling cyclodextrin to be good receptor for selectively binding organic compounds. Consequently, the polymer with CD(s) as complex is believed to selectively adsorb organic compounds, as did it in this study (Table 3 and Table S10).

In detail, hydrophobic pesticides (i.e., fomesafen, benalaxyl, pretilachlor and butachlor) were adsorbed on the polymers, primarily related to CD content (Table S10). These compounds are readily included into CD cavity, in terms of the binding constants (Table S7), as they are size-matched and have appropriate hydrophobicity. However, for the very hydrophobic insecticides (i.e., fipronil and butenefipronil) that were poorly accommodated by CDs because of large molecular size, polymer surface area had the highest contribution to adsorption affinity; accordingly, their adsorption was mainly driven by hydrophobic interaction but not CD inclusion. For hydrophilic pesticides (e.g., bromacil and fenamiphos), polymer swelling capacity provided the highest contribution, in accordance with the fact that water-soluble compounds were adsorbed mainly through loading into swelling water (Crini et al., 1998; Thatiparti et al., 2010). It should be emphasized that two triazine herbicides (i.e., simazine and atrazine) could be more readily absorbed by the polymers (e.g., RM-CDP) with larger pore size, rather than those (e.g., β-γ-CDP and β-HP-CDP) with higher CD content and/or larger surface area.

### Table 3 — Multivariate regression analysis between adsorption potential and CDP-Pesticide.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Factor</th>
<th>K_s</th>
<th>Q_{max}</th>
<th>K_L</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Standardized coefficients</td>
<td>Standardized coefficients</td>
<td>Standardized coefficients</td>
</tr>
<tr>
<td>CDP</td>
<td>CD content (%)</td>
<td>−0.131</td>
<td>−0.023</td>
<td>0.618</td>
</tr>
<tr>
<td></td>
<td>Particle size (μm)</td>
<td>0.306</td>
<td>−0.014</td>
<td>0.146</td>
</tr>
<tr>
<td></td>
<td>Swelling ratio (g/g)</td>
<td>0.109</td>
<td>−0.035</td>
<td>0.307</td>
</tr>
<tr>
<td></td>
<td>Surface area (m²/g)</td>
<td>−0.046</td>
<td>−0.055</td>
<td>0.036</td>
</tr>
<tr>
<td></td>
<td>Pore volume (10⁻³cc/g)</td>
<td>0.220</td>
<td>−0.028</td>
<td>0.101</td>
</tr>
<tr>
<td></td>
<td>Pore size (nm)</td>
<td>0.055</td>
<td>0.001</td>
<td>0.261</td>
</tr>
<tr>
<td></td>
<td>log K_{ds}</td>
<td>0.551</td>
<td>0.140</td>
<td>0.735</td>
</tr>
<tr>
<td></td>
<td>Molecular weight (g/mol)</td>
<td>−0.681</td>
<td>0.039</td>
<td>0.010</td>
</tr>
<tr>
<td></td>
<td>Water solubility (mg/L)</td>
<td>0.072</td>
<td>−0.408</td>
<td>−0.264</td>
</tr>
<tr>
<td></td>
<td>Molecular surface area (m²/mol)</td>
<td>−0.005</td>
<td>0.005</td>
<td>−0.068</td>
</tr>
<tr>
<td></td>
<td>Num-H-acceptors</td>
<td>−0.090</td>
<td>0.816</td>
<td>−0.372</td>
</tr>
<tr>
<td></td>
<td>Num-H-donors</td>
<td>−0.220</td>
<td>−0.376</td>
<td>0.230</td>
</tr>
<tr>
<td></td>
<td>R²</td>
<td>0.735</td>
<td>0.830</td>
<td>0.826</td>
</tr>
</tbody>
</table>

3.5. Screening of cyclodextrin polymer

Three cyclodextrin polymers (i.e., β-CDP, HP-CDP and RM-CDP) were physically combined with a mass ratio of 40:30:30 to achieve a multiplex physical mixture, based on the understanding of the quantitative contributions of polymer properties to its adsorption potential. The multiplex polymer was obtained to have appropriate CD content (referring to HP-CDP), swelling capacity (referring to β-CDP) and pore size (referring to RM-CDP). Thus, it could absorb the pesticides more efficiently, verified by higher maximum adsorption capacities (Table S8) and distribution coefficients (Fig. 4).

As a general rule, binding potential of adsorbent would decrease with increasing levels of adsorbrates, as the active sites are occupied until approach saturation (Bibby and Mercier, 2003; Burleigh et al., 2001). The distribution coefficients (K_L) of each pesticide on all CDPs did reduce with an increase in pesticide levels (Fig. 4), whereas the multiplex polymer gave similar or higher K_L values for all pesticides except simazine and butachlor. Accordingly, the multiplex adsorbent exhibited higher average removal efficiency than each component (Fig. 5), particularly for these pesticides (i.e.,
Fig. 4 – Distribution coefficient ($K_d$) of pesticides versus initial concentrations by CDPs. Solid square (■) β-CDP, solid cycle (●) γ-CDP, solid upward triangle (▲) HP-CDP, solid downward triangle (▼) RM-CDP, hollow square (□) β–γ-CDP, hollow cycle (○) β-HP-CDP, hollow upward triangle (△) γ-HP-CDP and hollow pentagon (◇) multiplex CDP.
fomesafen, bromacil, simazine and atrazine) with low hydrophobicity and/or small molecular size.

3.6. Application of the multiplex polymer

The multiplex polymer was used to separate the pesticides at lower levels from deionized and sea waters. Pesticide concentration in liquid phase, denoted as experimental value ($C_{\text{exp}}$, mg/L), was calculated by subtracting the adsorbed amount from the initial level. Meanwhile, it could also be predicted ($C_{\text{pred}}$, mg/L) from respective Langmuir isothermal equation by integrating the adsorbed amount. A significant consistency between both values for deionized ($y = 0.999x, R^2 = 0.999$) and sea waters ($y = 0.976x, R^2 = 0.998$) indicated a good extrapolation of polymer adsorption potential to low levels of contaminants in water (Fig. 6). Moreover, nearly complete overlapping of the values for both waters revealed insignificant effects of water types on adsorption potential of the polymers, similar to other studies (Sawicki and Mercier, 2006) that concurrent metal ions do not interfere with adsorption of CD-based polymers toward organic pollutants. Additionally, the polymer had good stability, as the separation efficiency reduced by less than 10% after 5 times of regeneration (Fig. S8).

4. Conclusions

This study, based on the adsorption behavior recognition of various adsorbent-adsorbate systems, provides evidence that the adsorption mechanisms of the CDPs are primarily inclusion of CD unit, although hydrogen bonding, loading into swelling water and physical adsorption play some roles. The multivariate regression analysis distinguishes the quantitative roles of cyclodextrin-based polymer and organic pesticide. Apparent adsorption potential of the polymer is related mainly to CD content, swelling ratio and pore size. The multiplex polymer screened on basis of the clarified relationship, is obtained to exhibit higher adsorption potential than each component as well as the other four polymers. This work adds a new dimension to screening and design of cyclodextrin-based polymer adsorbents that better bind targeted organic compounds (e.g., micropollutants in natural water and toxic substances in wastewater).

Acknowledgments

This study was supported by the National Natural Science Foundation of China (No. 21077020 and 20707002), the Fok Ying Tung Education Foundation (No. 114042), the China Postdoctoral Science Foundation (No. 20090450103), the Fundamental Research Funds for the Central Universities (No. DUT10LK02), and the Program for Changjiang Scholars, and Innovative Research Team in University (No. IRT0813). We also thank the China Environmental Protection Foundation for the support to Huihui Liu (No. CEPF2008-123-2-13).

Appendix. Supplementary material

Supplementary data related to this article can be found online at doi:10.1016/j.watres.2011.04.004.

References


