Surface modification of zeolite with β-cyclodextrin for removal of p-nitrophenol from aqueous solution

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ABSTRACT

The surface of zeolite was modified by cationic β-cyclodextrin (CCD), which was synthesized with 2, 3-epoxypropyltrimethylammonium chloride (ETMAC) and β-cyclodextrin (β-CD), to prepare a novel and effective sorbent for removal of p-nitrophenol (p-NP) from aqueous solution. FTIR, SEM and EDS were used to characterize the surface modification. It was found that CCD, which was synthesized at different conditions such as the mole ratio of ETMAC against β-CD and pH, made an impact on sorption capacity of p-NP on CCD-modified zeolite (CCDMZ). Given ETMAC: β-CD = 7:1 and pH = 13, the cationic process of β-CD might be optimum for CCD to bond to zeolite surfaces. In addition, CCD concentration and modification time affected sorption capacity of p-NP on CCDMZ too. The sorption of p-NP on CCDMZ, activated zeolite (AZ) and natural zeolite (NZ) was investigated by contact time, initial p-NP concentration and sorption isotherms with the batch sorption experiments. The results showed that the sorption of p-NP on CCDMZ satisfactorily fitted the known Langmuir model and the sorption capacity of CCDMZ was higher than that of AZ and NZ although the contact time of CCDMZ appeared to be shorter than other two.

Key words | β-cyclodextrin, modification, p-nitrophenol, sorption, zeolite

INTRODUCTION

Aromatic pollutants, in particular phenolic derivatives, belong to a group of organic pollutants because they widely occur in wastewater discharged from industries such as chemical cleaning agents, petroleum refining, resins, plastics, and pesticides (Delval et al. 2006). Due to their toxicity, poor biodegradability and accumulation potential in plant and animal tissues, they have been listed as priority toxic pollutants by U.S. Environmental Protection Agency (Zhou & Lei 2006). Many different methods have been proposed to eliminate phenolic derivatives and other organic contaminants from wastewaters, such as chemical oxidation (Nam & Kukor 2000), electrochemical treatment (Körbahti & Tanyolac 2003), biological methods (Amat et al. 2003), reverse osmosis membranes (Schutte 2005) and sorption (Crini 2003) etc. Among various physicochemical processes sorption is regarded as a promising one for removal of phenol from wastewater when activated carbon (AC) has been widely employed in water and wastewater treatment because of its large specific surface area and adequate pore size distribution. However, AC is relatively expensive and readily saturated, and has less effectiveness to reduce the concentration of the organic pollutants in the presence of dissolved organic matter (Tamara et al. 2005). Therefore, great effort has been exerted to explore new sorbents with high sorption capacity and efficiency, low-cost (Wang et al. 2006), for example, zeolites, clay, organoclay, fly ash, and polymeric sorbents etc. have been taken into account (Aksu & Yener 2001; Li et al. 2002).

Natural zeolites (NZ) have already found many applications as sorbents (Barrer 1978). They are hydrated aluminosilicate materials having permanent negative charges in their crystal structures, making them suitable for surface modification using cationic surfactants, such as hexadecyltrimethyl-ammonium (HDTMA) (Zhou et al. 2007),

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tetramethylammonium (TMA) (Sylvie et al. 2002), benzylidimethyltetradecyl-ammonium (BDTDA) and benzyltrimethylammonium (BTMA) etc. (Sang & Dixon 2001). Unfortunately, the widely used surfactants for modification are still harmful to environment if with high concentrations. Therefore it is also a highlighted problem to look for environmental friendly “save agent” to modify zeolites that are broadly distributed in mountainous and hilly regions of China.

β-Cyclodextrin (β-CD) is a torus-shaped cyclic oligosaccharide consisting of seven α-1,4-linked D-glucopyranose units with an internal hydrophobic cavity. It is well known that this gives rise to a remarkable capacity to form inclusion complexes in solution or in the solid state with organic guest molecules through various interactions involving hydrogen bonding, Van Der Waals forces and hydrophobic interactions. Water molecules are displaced by more hydrophobic guest molecules present in the solution to attain an apolar–apolar association and decrease of cyclodextrin ring strain resulting in a more stable lower energy state (Szejtli 1998). The potential guest list for molecular encapsulation in cyclodextrins is quite varied and includes straight or branched chain aliphatics, aldehydes, ketones, alcohols, organic acids, fatty acids, aromatics, gases, etc. (Martin 2004). Wastewaters containing environmentally unacceptable aromatic compounds such as phenol, p-chlorophenol and benzene after treating with β-CD have considerably reduced levels of these aromatic hydrocarbons from their initial levels (Martin 2004). Hence, β-CD complexation is a procedure of choice for water treatment techniques.

The objectives of this research was to improve the sorption performance of NZ by coating water soluble β-CD to the zeolite surfaces, considering the capacity of β-CD to form inclusion complexation, especially for enhancing sorption of phenolic derivatives, which would be used for special water purification process matching with the particular water quality to serve pharmaceutical industry according to the favorable characterization of both β-CD and NZ. In a series of experiments, p-nitrophenol (p-NP) was advisedly chosen as a target compound because it could form stable complexes with β-CD; meanwhile it was one of the most challenging classes of priority pollutants to be removed from waste streams and groundwater. In order to attach β-CD onto zeolite surfaces, 2, 3 epoxypropyltrimethylammonium chloride (ETMAC) was selected as a linker. A classical reaction was that the hydroxyl group of β-CD reacted with the epoxy group of ETMAC in the presence of NaOH to form cationic β-CD (CCD), and then CCD was bound to zeolite surfaces by ion exchange between the ammonium cations of CCD and inorganic cations of zeolite. For study on the synthesis process of CCD and modification process of CCDMZ, the effect of contact time and initial p-NP concentration on sorption capacity of CCDMZ were investigated after p-NP solutions were used to interact with CCDMZ, activated zeolite (AZ) and natural zeolite (NZ), respectively. Moreover, the sorption isotherms of p-NP on three sorbents (CCDMZ, AZ and NZ) were also studied so as to explode their sorption performance and mechanisms.

MATERIALS AND EXPERIMENTAL METHODS

Materials and apparatus

β-CD was obtained from Shanpu Chemical Reagent Corp., Shanghai, China. 2, 3-epoxypropyltrimethylammonium chloride (ETMAC) was purchased from Sangong Corp., Yantai, China. P-nitrophenol (p-NP) of 99.9% from Tianxin Chemical Corp., Tianjin, China was used without further purification. The zeolite sieved to yield particles in the range of 20~40 mesh was provided by Baiyin City, Gansu, China. Based on XRD analysis the mineral content of this zeolite was 45% clinoptilolite, 35% quartz, 1% calcite, 6% feldspar, 5% illite, and 5% montmorillonite.

The FTIR spectra of NZ and CCDMZ (KBr pellet) were recorded on a NEXUS 670SX (Nicolet Corp. Madison, WI, USA) in the range of 4,000~400 cm⁻¹. The SEM and EDS of NZ and CCDMZ were measured by JSM-5600LV (Kever Corp. USA) scanning electron microscope and IE 500 X (Kever Corp. USA) energy-dispersive X-ray spectroscopy.

Synthesis of CCD

CCD was prepared using β-CD and ETMAC in the presence of NaOH. The details of the synthesis and reaction process were as follows: 1.5 g β-CD and 10 mL sodium hydroxide
solution were placed in a 50 mL flask equipped with reflux condenser. A known amount of ETMAC was added to this solution. And then the reaction mixture was stirred with a magnetic stirring at 70°C in a water bath for 4 h. After that dilute hydrochloric acid was added to adjust the pH below 7.0 to terminate the cationic reaction process. The final solid product was collected after evaporation under vacuum. The details of synthetic parameters are listed in Table 2.

Preparation of CCDMZ

The modification route of zeolite with CCD was as follows: NZ was activated with 1 mol/L NaCl solution in order to saturate the exchange sites with sodium ions. The activated zeolite (AZ, 15 g) was placed in a 250-mL flask and then 20 g/L CCD solution (100 mL) was added. The mixture was shaken at room temperature by a shaker for 12 h. The supernatants were discarded, and the samples were washed with deionized water three times and air-dried before further use.

Sorption experiments

Sorption of p-NP from water solution was investigated in batch experiments. Air-dried sorbent (1.00 g) was placed in a 50 mL flask with a stopple, and then a known concentration of p-NP solution (25 mL) was added before the flask was sealed. The samples were shaken with 150 rpm at 23°C for sorption equilibrium by a shaker. Then the supernatants were centrifuged at 2,500 rpm for 25 min to yield a clear supernatant for analysis of the equilibrium solution concentrations. The concentrations of p-NP in clear supernatant were measured using an UV-Vis spectrophotometer (UV-2,102C, Unico Instrument Corp.) at 317 nm. The amount of sorption per mass unit of sorbent was calculated using the following expression:

$$q_e = \frac{(C_0 - C_e)V}{m} \times 1000$$  \hspace{1cm} (1)

where \(q_e\) is the amount of adsorbed p-NP per mass unit of sorbent, mg/g; \(C_0\) and \(C_e\) are the concentrations of p-NP in the initial solution and in aqueous phase after treatment for a certain period of time, respectively, mg/L; \(V\) is the volume of p-NP solution, mL; and \(m\) is the amount of sorbent, g.

RESULTS AND DISCUSSION

Characterization

Figures 1 and 2 show the FTIR spectra of β-CD, NZ and CCDMZ, respectively. In Figure 1, the broad band at 3,412 cm\(^{-1}\) is due to the stretching vibration of O–H groups. The bands at 2,930 cm\(^{-1}\) and 1,155 cm\(^{-1}\) are assigned to C–H stretching vibration and C–O stretching vibration, respectively. The band at 1,641 cm\(^{-1}\) is assigned to the first overtone of the O–H bending vibration and the band at 1,080 cm\(^{-1}\) is attributed to C–O–C stretching vibration. In Figure 2(a), the band at 3,629 cm\(^{-1}\) is for O–H stretching vibration of OH groups bound to Si. The bands at 1,042 cm\(^{-1}\) and 468 cm\(^{-1}\) are assigned to Si–O stretching vibration and bending vibration, respectively. The bands at 797 cm\(^{-1}\) and 778 cm\(^{-1}\) are OH bending vibration of Si–OH groups. A band at 517 cm\(^{-1}\) is due to the Si–O–Al stretching vibration. In Figure 2(b), the band at 2,926 cm\(^{-1}\) corresponds to C–H stretching vibration. The band at 1,483 cm\(^{-1}\) is attributed to C–N scissoring vibration and the band at 1,359 cm\(^{-1}\) is due to the bending vibration of C–N groups. The band detected at 1,082 cm\(^{-1}\) corresponds to C–O–C stretching vibration. Consequently, the appearances of these bands were considered evidence of the modification of zeolite surface by CCD molecules.
Figure 2(c) shows the spectral difference between NZ and CCDMZ.

The SEM microphotographs of CCDMZ and NZ particles are shown in Figure 3. It was evident that the surfaces of CCDMZ were modified to be uniform and coarse with the higher specific surfaces than that of NZ when the morphology of CCDMZ showed the NZ surfaces to be coated with CCD. Therefore, the regular structure of NZ is invisible.

The EDS analyses of CCDMZ and NZ with the relevant percentage of elements are displayed in Table 1. The higher contents of C %, N % and O % on CCDMZ than that on NZ indicated that some CCD molecules were assuredly bound to zeolite surfaces.

**Effect of modification process on sorption capacity of CCDMZ**

**Effect of synthesis of CCD**

In synthesizing process of CCD, the aim was to obtain a series of CCD with different quantity of ETMAC incorporated to β-CD backbone and to evaluate the effect of them on the sorption capacity of p-NP. It can be seen from Table 2
that CCDMZ significantly possessed the higher sorption capacity compared to both β-CD-modified zeolite and ETMAC-modified zeolite. From CCD1 to CCD14, with the increase in the mole ratio of ETMAC to β-CD, the sorption capacity of CCDMZ increased, but the sorption capacity decreased with the further increment after optimum mole ratio (7:1). The results might be explained by the fact that the increase of mole ratio resulted in the rise of the quantity of ETMAC incorporated to β-CD backbone (Pal et al. 2005, 2006), which was defined as the rise of the cationic group of ammonium and the zeta potential (ζ) of CCD (Xiao & Cezar 2005). The initial increase of the mole ratio was favorable for CCD to be firmly bound on zeolite surfaces. However, with the further increase of the mole ratio, the quantity of ETMAC incorporated to β-CD was excessive, as a result, too many reactive sites of zeolite surfaces were occupied by the excessive cationic groups of the same CCD molecules, and finally the actual quantity of CCD molecules bound to zeolite surfaces decreased. The optimum mole ratio of ETMAC to β-CD was 7:1 which might be sufficient to yield the predicted CCD and the optimum CCDMZ.

pH values remarkably influenced the synthesis of CCD, as well as the sorption capacity of CCDMZ. It can be found from Table 2 that the sorption capacity of CCDMZ was gradually improved with the increase of pH values from 9 to 13.6. At a pH range of about 13, the optimal sorption capacity of CCDMZ occurred. Here, quantity of GTA on CCD might be optimized for CCD to modify zeolite. With the further increase of pH, the sorption capacity of CCDMZ decreased. It proved that an available condition to synthesize CCD should be at a correspondingly high pH, at which the sorption capacity of CCDMZ was

<table>
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<tr>
<th>Table 1</th>
<th>The percentage of elements for NZ and CCDMZ</th>
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<tr>
<td><strong>CCDMZ</strong></td>
<td><strong>Natural zeolite</strong></td>
</tr>
<tr>
<td>Element</td>
<td>Weight %</td>
</tr>
<tr>
<td>C</td>
<td>31.54</td>
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<tr>
<td>N</td>
<td>4.71</td>
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<tr>
<td>O</td>
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<tr>
<td>Mg</td>
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<tr>
<td>Al</td>
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<tr>
<td>Si</td>
<td>44.31</td>
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<tr>
<td>K</td>
<td>2.05</td>
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<tr>
<td>Ca</td>
<td>5.62</td>
</tr>
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<td>Fe</td>
<td>3.25</td>
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<table>
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<tr>
<th>Table 2</th>
<th>Effect of CCD on the sorption capacity of CCDMZ</th>
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<tr>
<td><strong>Modifying agent</strong></td>
<td><strong>Synthetic parameters</strong></td>
</tr>
<tr>
<td>β-CD</td>
<td>–</td>
</tr>
<tr>
<td>GTA</td>
<td>–</td>
</tr>
<tr>
<td>CCD1</td>
<td>1:1</td>
</tr>
<tr>
<td>CCD3</td>
<td>3:1</td>
</tr>
<tr>
<td>CCD5</td>
<td>5:1</td>
</tr>
<tr>
<td>CCD7</td>
<td>7:1</td>
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<tr>
<td>CCD9</td>
<td>9:1</td>
</tr>
<tr>
<td>CCD11</td>
<td>11:1</td>
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<tr>
<td>CCD14</td>
<td>14:1</td>
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<td>CCD21</td>
<td>7:1</td>
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<td>CCD22</td>
<td>7:1</td>
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<td>7:1</td>
</tr>
<tr>
<td>CCD27</td>
<td>7:1</td>
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</table>
enhanced too. It could be coincident with preparation of cationic starch in the presence of sodium hydroxide solution (Zhang et al. 2007).

Effect of CCD concentration and modification time

The effect of CCD concentration on the sorption capacity of CCDMZ is exhibited in Figure 4(a), from which it can be seen that the sorption capacity increases gradually with increasing of CCD concentrations from 5 g/L to 20 g/L. A further increase of CCD concentrations did not observe the remarkable change of sorption capacity. The initial rise in the sorption capacity was due to an enhanced the amount of CCD bound to zeolite. With the concentration of 20 g/L, the surface coverage of CCD molecules on zeolite surfaces could reach the maximum, subsequently, the sorption capacity started to be decreased.

The effect of modification time on the sorption capacity of CCDMZ is shown Figure 4(b), from which it can be found that the sorption capacity achieved the maximum at about 12 h. Thereafter, the sorption capacity basically maintained constant, by which it might be explained that CCD bound to zeolite surfaces through ionic bonding when modification time reached about 12 h although this time was longer than that of linear surfactant modification zeolite by about 8 h (Li et al. 2000).

P-NP sorption

After the modification when the CCD was bound to the surfaces of zeolite, the sorption of CCDMZ, AZ and NZ were systematically studied by investigating contact time, initial p-NP concentration and sorption isotherms.

Effect of contact time

Figure 5 shows the plot of sorption of p-NP against contact time at the initial p-NP concentration of 100 mg/L. The results of batch experiments showed that the sorption equilibrium of CCDMZ was very swift to reach at about 60 min and remained nearly constant $253.6 \times 10^{-3}$ mg/g thereafter. However, an equilibrium time of $80 \sim 100$ min was needed when AZ and NZ were used as sorbents. The amount of p-NP adsorbed on AZ and NZ were $41.07 \times 10^{-3}$ mg/g and $30.26 \times 10^{-3}$ mg/g, respectively. The results suggested that there were stronger interactions between p-NP and CCDMZ than that of AZ and NZ.
Effect of initial p-NP concentration

The plots in Figure 6 show that the sorption capacity of CCDMZ, AZ and NZ increased with the increase of initial p-NP concentrations, especially the sorption capacity of CCDMZ had a remarkably increase. The amount of p-NP adsorbed on CCDMZ, AZ and NZ were $335.01 \times 10^{-3}$ mg/g, $87.09 \times 10^{-3}$ mg/g and $51.87 \times 10^{-3}$ mg/g at the initial p-NP concentration 300 mg/L, respectively. The results suggested that there were stronger interactions between p-NP and CCDMZ than that of AZ and NZ. An increase of the initial p-NP concentration enhanced the mass transfer driving force and therefore the rate at which p-NP molecules passed from the solution to the particle surfaces was multiplied as well. This stimulated the higher sorption of p-NP.

Sorption isotherms

Due to the special construction of CCDMZ, the sorption mechanism of CCDMZ also has a big difference from other conventional sorbents. The sorption of p-NP on CCDMZ might occur in the pores of zeolite and internal hydrophobic cavity of CCD, which is the major mode of sorption. Sorption isotherms are fundamental in describing the interactive behavior between solutes and sorbent, and are useful to design of a sorption system (Chiou & Li 2003). The Langmuir and Freundlich sorption isotherms were used to describe the sorption processes of adsorbate. The Langmuir model not only assumed one solute molecule per site, but also assumed a fixed number of sites. As Langmuir Equation is most widely used (Rawajfih & Nsour 2006), it is valid for monolayer sorption onto a surface given by

$$\frac{C_e}{q_e} = \frac{1}{K_{L} q_{\text{max}}} + \frac{1}{q_{\text{max}}} C_e = \frac{1}{K_{L}} + \frac{b_{L}}{K_{L}} C_e$$

where $q_e$ is the amount of adsorbed p-NP per mass unit of sorbent, mg/g; $C_e$ is the equilibrium concentration of p-NP remaining in solution, mg/L; $K_L$ is Langmuir isotherm constant related to the capacity of saturated monolayer, L/g; $b_L$ is Langmuir isotherm constant related to the energy or net enthalpy.

The isotherm parameters $K_L$, $b_L$ and correlation coefficient values ($r^2$) are obtained by linear plots of $C_e/q_e$ against $C_e$ in Figure 7(a), respectively, and they are displayed in Table 3.
The well-known Freundlich equation used for isothermal sorption is a special case for heterogeneous surface given by Chiou & Li (2002) as:

$$\log q_e = \log K_F + \frac{1}{n} \log C_e$$

where $K_F$ is a constant related to the extent of sorption, L/g; $n$ is a constant related to the intensity of sorption or the degree of dependence of sorption on concentration. Likewise, $K_F$, $n$ and $r^2$ are obtained by their linear plots of $\log q_e$ against $\log C_e$ in Figure 7(b).

Based on the correlation coefficient obtained, it can be concluded that the Langmuir model gave a better agreement to the experimental data of CCDMZ ($r^2 = 0.9952$) than the Freundlich. For AZ and NZ, the Freundlich model provided a more consistent fit to the data. In Langmuir equation, coefficient $K_L$ is a measure of the capacity of the sorbent to retain the adsorbed solute. Furthermore, $K_F$, as Freundlich constant, can be considered to be an indicator of sorption capacity. Both the values for $K_L$ and $K_F$ indicated that CCDMZ had the highest sorption capacity of p-NP.

**CONCLUSION**

Modification of the zeolite surfaces with CCD was prepared to render those lots of lipophilic cavities in which appropriately size guest organic molecules could enter to form inclusion complexes when CCDMZ was utilized as sorbent for the removal of p-NP from aqueous solutions. Investigation of FTIR spectrum, SEM and EDS provided a strong proof for successful preparation of CCDMZ. Variation in the synthetic parameters resulted in a series of CCD with varying quantity of ETMAC, as well as different sorption capacity of CCDMZ. At the molar ratio of ETMAC: β-CD = 7:1 and pH 13, the optimal CCD brought on optimal modification processes of CCDMZ. The maximum sorption capacity was obtained when CCD concentration and modified time were 20 g/L and 12 h, respectively. The sorption of CCDMZ, AZ and NZ were investigated regarding with contact time, initial p-NP concentration and sorption isotherms. It was evident that the increase of initial p-NP concentration was favorable to increase sorption although the contact time of CCDMZ was shorter than that of AZ and NZ. Compared sorption isotherms of three sorbents and values of $K_F$ and $K_L$, the results indicated that CCDMZ had the highest sorption capacity of p-NP, and the sorption isotherms of p-NP on CCDMZ followed the known Langmuir model. It was suggested that the low sorption capacity of NZ would be enhanced by surface modification using CCD, which would have a potential to widely use NZ in special water treatment process for removal of organic micro-pollutants.

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