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Synthesis and Characterization of Crosslinked β-Cyclodextrin and Their Sorption Capacities Towards Phenol from Wastewater

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The crosslinked β-cyclodextrin polymer was produced by crosslinker 2,4-toluene diisocyanate (TDI). The influencing factors and optimum synthesis technological conditions were selected *via* orthogonal experimental method and product yield. The results suggest that the mole ratio of *n* (isocyanate): *n* (β-cyclodextrin) is about 1:9, mass ratio of catalyst (dibutyl tin dilaurate and triethylene diamine) equal to 1:1.5, 2,4-toluene diisocyanate is used as diisocyanate, reaction temperature is 70 ºC and reaction time is 9 h. The polymer was characterized by infrared spectrum (FT-IR), scanning electron microscope and thermogravimetric analysis. The result indicates that the crosslinked β-cyclodextrin-2,4-toluene diisocyanate polymer keeps cavity structure of β-cyclodextrin and forms a network structure. The crosslinking reation generates carbamic acid ester base bond. Technological parameters of removal phenol waste water were optimized by adsorption experiments. Regeneration times and adsorptive capacity were study. Controlling limit phenol wastewater pH was 5-7. The maximum amount of polymers was 40 mg/mL. The adsorption rate and adsorbability were low with the increasing of phenol wastewater initial concentration. Regeneration process of adsorbent soaked by methyl alcohol and washed by deionized water. The adsorption efficiency retained more than 88 % after 10 times regeneration.

Key Words: β-Cyclodextrin polymer, Crosslinking reaction, Phenol wastewater, Removal.

INTRODUCTION

Cyclodextrin is a kind of cyclic oligosaccharide linked by D-glucopyranose unit through α-(1→4)-glucosidic bond, of which the most common cyclodextrins are α-, β- and γ-cyclodextrin, with their polymerization containing 6, 7 and 8 1,4- glucosidic bond units respectively[1]. Due to the difference of their physicochemical properties, β-cyclodextrin is most frequently studied. The molecular structure of the cyclodextrin is in a pyramidal cylinder, with the hydrophilic hydroxy distributing on the exterior edge of the molecule, C-H bond and C-O-C bond covering inside the molecule[2]. Such a structure enables the cyclodextrin to have externally hydrophilic and internally hydrophobic characteristics. By making use of its external hydroxy hydrophobic characteristics, in combination with the hydrogen bond and van der Waals, *etc.* formed between hydroxides, the cyclodextrin can make clathrate compound with numerous inorganic and organic compounds[3] and this characteristic is widely applied in the pharmaceuticals industry[4], chemical industry analysis[5] and environmental protection[6], particularly waste water treatment[7], *etc.* (Fig. 1) for the molecular structure of cyclodextrin[1].

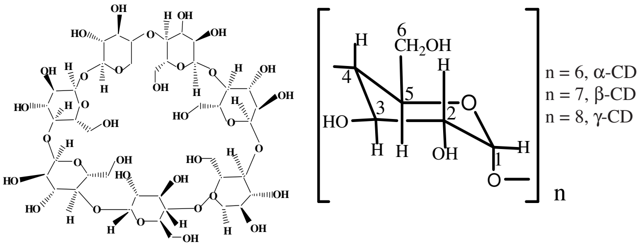


Fig. 1(a). β-Cyclodextrin structure (b) β-Cyclodextrin unit structure

The solubility of β-cyclodextrin in water is 1.64 %. After forming clathrate compound with other substances, it will have a lower water-solubility and is easily separated from the solution by crystallization. If the action of hydrogen bond or van der Waals' force is solely relied on, the clathrate compound can be separated easily. It makes β-cyclodextrin application field greatly limited in treatment of the sewage. To make up the structural deficiency of β-cyclodextrin and enhance its application range, it's required to carry out modification for β-cyclodextrin. The chemical modification method is to obtain the cross-linked polymer by using the chemical reactions such as etherification, esterification, oxidation and crosslinking between the hydroxide in its molecule and other base groups under the condition that the cyclodextrin skeleton is basically kept unchanged. What's most frequently used is hydroxypropyl[8], as well as starch[9,10], chitosan[11] and hexamethylene diisocyanate (HDI)[12]. The modified β-cyclodextrin shows a better efficiency in wastewater treatment.

EXPERIMENTAL

N,N-Dimethyl formamide (DMF) (AR, Sinopharm Chemical Reagent Co. Ltd.) is subjected to vacuum distillation before being used; 2,4-toluene diisocynate (TDI) (AR, Shanghai Chemical Reagent Co. Ltd.), which is dewatered and dried with a zeolite molecular sieve before being used; mixed toluene diisocynate (mixed TDI); hexamethylene diisocyanate (HDI) (Adamas Reagent Co. Ltd.); Diphenylmethane diisocyanate (MDI) (GR, New Jersey, USA); β-cyclodextrin (AR, Sinopharm Chemical Reagent Co. Ltd.), which is subject to purification through crystallization before being used; chloroform (CR, Shanghai Zhongshi Chemical Corporation); Dibutyltin dilaurate (BTL) (CR, Shanghai No. 4 Reagent Factory); triethylene diamine (AR, Sinopharm Chemical Reagent Co., Ltd.), which is subject to vacuum drying before being used.

Water bath kettle, vacuum pump, QM-3SP ball mill manufactured by Nanjing University Instrument Plant. Infrared spectrometer FTIR NEXUS670, American Nicolet Company. Chemisorption analyzer, CHEMEBET-3000, Quantachrome Corporation, USA. Scanning electron microscope, S-3400N II, Hitachi Corporation, Japan. Differential thermal/thermogravimetric analyzer, STA 449C/6/F. XRD is D8 Advance automatic X-ray diffractometer manufactured by Bruker Corporation, Germany.

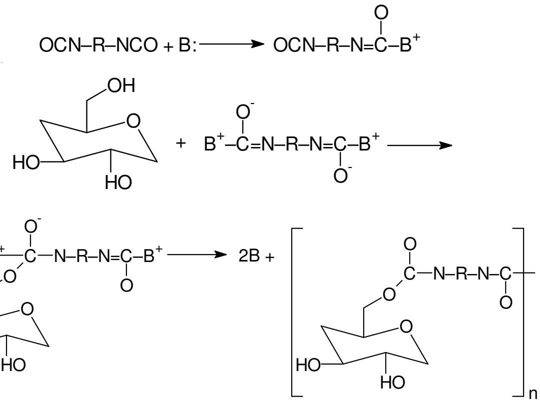
Synthesis of crosslinked β-cyclodextrin-2,4-toluene diisocyanate polymer: Add a proper amount of distilled β-cyclodextrin, catalyst and DMF solvent into a 250 mL three-opening flask. The flask and heater are put in the ultrasonic generator and open N_2 at the same time. After solution reaches an appropriate temperature and add certain proportional diisocyanate into the flask and continue using the ultrasound after it is heated to the reaction temperature. Since the ultrasound releases certain quantity of heat during the reaction, stop the ultrasound after 1 h and then start the ultrasound again 20 min later until the cross-linking reaction is finished[12]. Put in terminator upon complete of the reaction then clean it with lots of water, then put it in the vacuum drying oven until all solvents have been removed. Mill it with a ball mill for future use. Taking the reaction between α-NCO and cyclodextrin as an example, the chemical reaction is as shown in **Scheme-I**.

Absorption of phenol wastewater with polymer: Phenol solutions with different concentrations are prepared by add a certain amount of crosslinked β-cyclodextrin-2,4-toluene diisocyanate polymer into the solutions. The rotate speed of mechanically stir is 150 rpm in 0.5 h put the solution and polymer are centrifugalized in centrifugal separator after the absorption equilibrium. The supernatant liquid is put it into a filter device. The adsorption efficiency is calculated by a spectrophotometer.

Measurement method: The phenol content is measured by ultraviolet spectrophotometry. The wavelength of phenol set as 270 nm. If use the measurement method, it is required to compare the dates of between spectrophotometry and HPLC. Spectrophotometer may be applied if the dates results falls within ± 2.5 %. The calculation formula of absorption efficiency is as follows:

$$\eta = \frac{C_0 - C}{C_0} \times 100\%$$

where, η, absorption efficiency; C_0, the phenol concentration before absorption, mg/L; C, the phenol concentration after absorption, mg/L.



Scheme-I Chemical reaction of 2,4-toluene diisocyanate with β-cyclodextrin

RESULTS AND DISCUSSION

Orthogonal experimental: Five factors of influencing the synthetic rate is selected in experiment. They are the molar ratio (A) of reactant n (cyclodextrin) to n (isocyanate), the type of diisocyanate (B), catalyst ratio (C), reaction temperature (D) and reaction time (E). The experiment adopts the $L_{16}(4^5)$ orthogonal experiment table and takes the synthetic yield ratio (Y) as an evaluation indicator. The experimental results are shown in Table-1.

The dates of range suggest that the effects of the five factors on synthetic yield ratio are different. They influence order are molar ratio of raw materials > type of diisocyanate > catalyst ratio > reaction temperature > reaction time. On the basis of dates of the difference factors and different levels, the optimal technological combination of synthetic reaction is $A_3B_4C_4D_4E_4$. Carrying out experiments based on such combination, the yield ratio is 94.72 %. The optimal technological conditions are equal to 1:9 of the molar ratio of n (cyclodextrin) to n (isocyanate), 2,4-TDI as material isocyanate, catalyst ratio 1:1.5, reaction temperature 70 ºC and reaction time 9 h.

FT-IR spectra: IR of β-cyclodextrin (**1**), β-cyclodextrin-TDI polymer (**2**) and TDI (**3**) is shown as Fig. 2. In this spectra, β-cyclodextrin and β-cyclodextrin-TDI have stretching vibration absorption peaks of an OH bond at 3500-3400 cm^{-1}, which shows that the polyhydroxyl functional group exists in β-cyclodextrin and β-cyclodextrin-TDI polymers. The strength of hydroxyl peak of β-cyclodextrin-TDI polymer is apparently weakened compared with that of β-cyclodextrin. In the IR spectra of β-cyclodextrin-TDI, the characteristic absorption peak of N-H bond appears at 1600-1500 cm^{-1}. β-Cyclodextrin-TDI characteristic absorption peak of carboxylate -C=O

TABLE-1
DATE OF ORTHOGONAL EXPERIMENT

Serial number	Factor A	Factor B	Factor C	Factor D	Factor E	Yield ratio (%)
	Catalyst ratio (wt/wt)	Ratio (mol/mol)	Reaction temperature (ºC)	Reaction time (h)	Diisocyanate kinds	
1	1(1:1.0)	1(1:5)	1(90)	1(3)	1(MTD)	88.57
2	1	2(1:7)	2(80)	2(5)	2(HDI)	87.42
3	1	3(1:9)	3(70)	3(7)	3(2,4-TDI)	90.49
4	1	4 (1:11)	4(60)	4(9)	4(mix TDI)	92.35
5	2(1:2.0)	1	3	3	4	92.79
6	2	2	2	4	3	93.57
7	2	3	1	1	2	91.46
8	2	4	4	2	1	89.53
9	3(1:1.5)	1	3	4	2	92.74
10	3	2	4	3	1	90.12
11	3	3	1	2	4	91.69
12	3	4	2	1	3	93.27
13	4(1:2.5)	1	4	2	3	93.02
14	4	2	3	1	4	91.34
15	4	3	2	4	1	92.58
16	4	4	1	3	2	89.39
K1	358.83	367.35	367.82	366.33		
K2	344.64	362.45	366.22	364.54		
K3	361.11	366.84	367.36	365.02		
K4	364.64	361.66	362.79	371.24		
K5	360.8	361.01	370.35	368.17		
k1	89.71	91.84	91.96	91.58		
k2	86.16	90.61	91.56	91.14		
k3	90.28	91.71	91.84	91.26		
k4	91.16	90.42	90.70	92.81		
k5	90.20	90.25	92.59	92.04		
Range	1.875	4.4525	-0.9775	-2.395	2.3875	
Optimum	A_3	B_3	C_3	D_4	E_3	

appears at about1700 cm^{-1}. The original -NCO peak of TDI at 2200-2300 cm^{-1} disappears in β-cyclodextrin-TDI. It shows that -NCO functional group and hydroxyl react completely and generate urethane group. It mean that cross-linked polymer is generated by synthetic reaction of β-cyclodextrin and TDI.

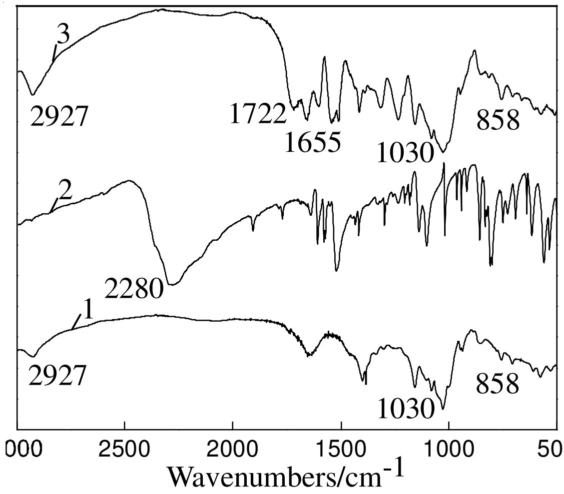
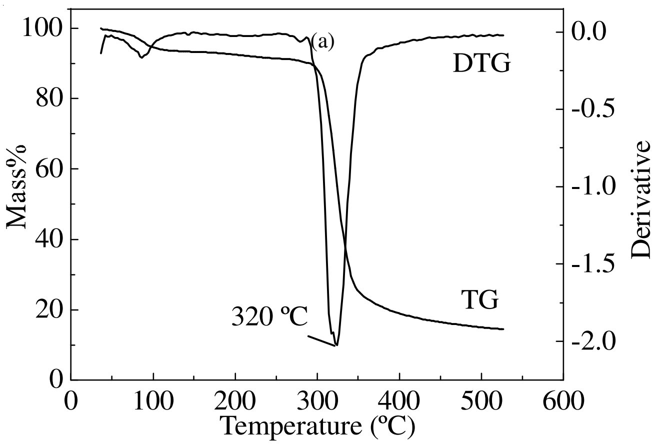


Fig. 2. FTIR spectra of β-cyclodextrin (1), β-cyclodextrin-TDI polymer (2) and TDI (3)

TGA curves: For the characterization and the investigation of the stability of plain, crosskined polymers and β-cyclodextrin thermal (TGA) gravimetric results are obtained. TGA curves of plain and β-cyclodextrin-TDI polymeric powder are given in Fig. 3. Decomposition peak temperatures of β-cyclodextrin-TDI polymeric powder were found to be 340 ºC. But decomposition peak temperatures of plain β-cyclodextrin were found to be 320 ºC. Because β-cyclodextrin is modified covalently onto the polymeric structure, the degradation temperatures are shifted from 320 ºC to 340 ºC. Degradation temperature of β-cyclodextrin is really low compared to the degradation peak temperature of the β-cyclodextrin-TDI polymers. In this way, β-cyclodextrin could be stabilized in the polymeric structure after the modification. Polymers have move molecular weight, density and stability. This is because that the additional carbamic acid ester bonding between β-cyclodextrin and 2,4-TDI is stronger than the hydrogen bonding in the free β-cyclodextrin.



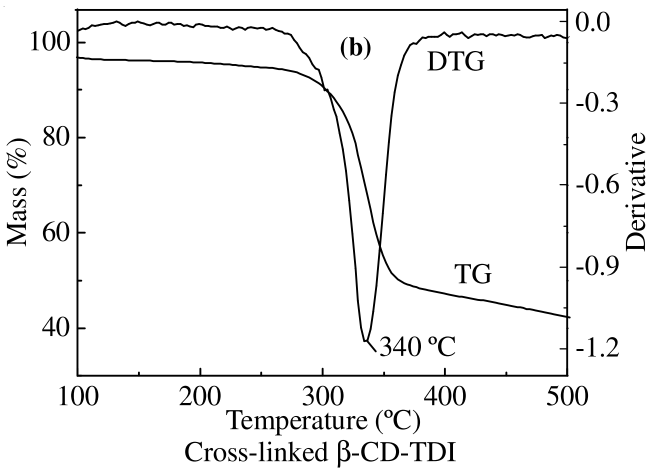


Fig. 3. TG curves of β-cyclodextrin (a) and β-cyclodextrin-TDI polymer (b)

SEM micrographs and XRD diffraction: Fig. 4. is the SEM of β-cyclodextrin (a) and β-cyclodextrin-TDI (b). The surface features of cross-linked polymer can be seen through SEM, as shown in the following pictures.

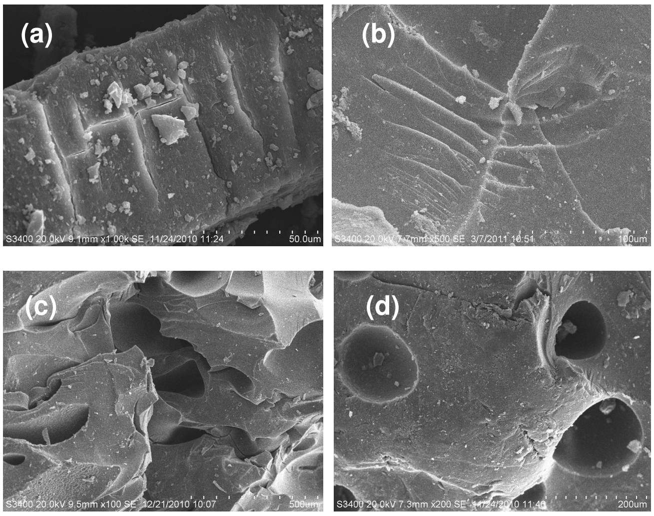


Fig. 4. SEM of β-cyclodextrin (a), β-cyclodextrin-TDI (b-d) polymer

The surface shape of β-cyclodextrin show in Fig. 4(a). The surface shape of β-cyclodextrin shows that surface layer structure and fluorescence. The surface shape of crosslinked β-cyclodextrin polymers show in Fig. 4 (b-d). Crosslinked β-cyclodextrin polymers show distinct network structure in Fig. 4(b) and porosity transverse in Fig. 4(c-d). The β-cyclodextrin fluorescence is completly disappear in crosslinked β-cyclodextrin polymers. These phenomenon suggest that the layer molecular structure of β-cyclodextrin have been modified by crosslinker (TDI). The secondary reaction have produced in synthesis process with bubble. The Fig. 4(c) and (d) shows that the cross-linked polymer has a cavity structure inside, *i.e.* the original cavity structure of β-cyclodextrin is retained. These cavities structure enhances the inclusion complex capacity through host-guest interactions and increases porosity of the adsorbent. The compactness and the lack of pore are solved by this method. Because the lack of pore influences moleculalr diffusivity of guest. The unique structure character of the adsorbent broadens the application range. The polymer may apply drags liberation and wastewater treatment.

Fig. 5 shows that β-cyclodextrin has a strong characteristic diffraction peak in the range of 10º-15º and 20º-25º of 2θ. β-cyclodextrin-TDI polymer has no obvious diffraction peak in the range of 10º-15º and 20º-25º of 2θ (Fig. 6). The phenomenon suggests that the cross-linked polymers are amorphous aggregation and the characteristic diffraction peaks of β-cyclodextrin disappear. The carbamic acid ester bonds are generated by crosslinking reaction of the hydroxyl in β-cyclodextrin with carbonyl in TDI. The reaction weakens the strength of the hydrogen bond and van der Waals' force and results in the reduction of the crystallization ability of polymer.

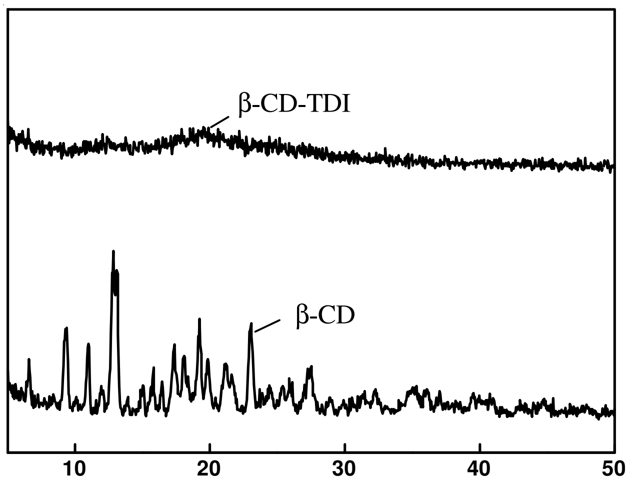


Fig. 5. XRD of β-cyclodextrin and β-cyclodextrin-TDI polymer

Absorption of phenol wastewater: Dilute the prepared phenol solution of 1 g/L to the required concentration in volumetric flask with a precise pipette. All the adsorption tests can be carried out in the following conditions: adsorption temperature 30 ºC, stirring time 0.5 h, stirring speed 150 r/min and adsorption time 2 h.

pH influence: Pour 2 g crosslinked β-cyclodextrin-TDI polymer into the phenol solution. The solution retains initial concentration of 100 mg/L at every turn test. The pH is varied in every experiment. The absorption result is shown in Fig. 6.

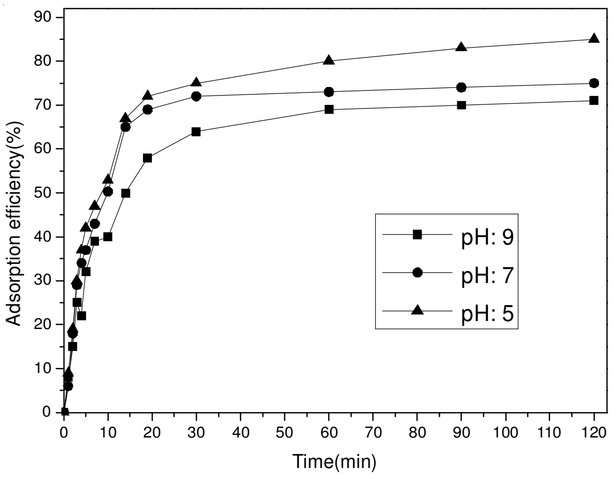


Fig. 6. Sorption efficiency influence of solution pH

Fig. 6 shows that the pH has a great impact on the phenol removal efficiency in effluent. This is possible because the hydrogen bonds between in the polymer and the phenol of contamination is dominated in faintly acid condition. With the acidity attenuates, the impact of hydrogen bond and the Van der Waals' force weakens. But the repulsive force increases by the polarity augment. These conditions affects the adsorption equilibrium process. Considering the acid-base properties of phenol wastewater, pH choose the range 5-7 during every test.

Quantity influence: The β-cyclodextrin-TDI polymers powder of different quantity is added to the above phenol solution. The adsorption efficiency is studied. The results are shown in Fig. 7.

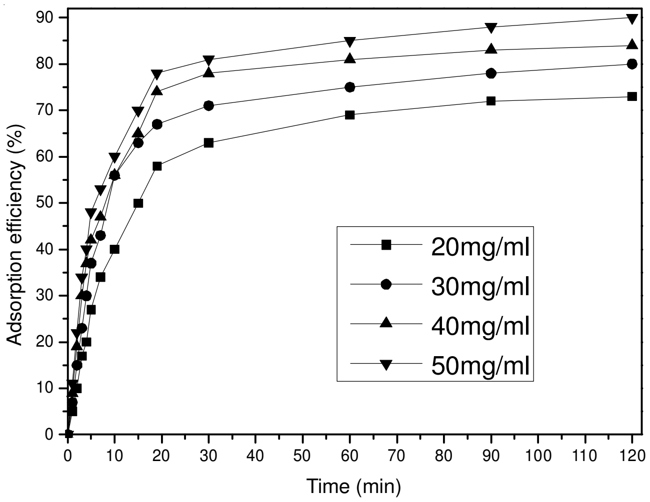


Fig.7. Sorption efficiency influence of different quantity of polymers

Fig. 7 indicates that the absorption efficiency increases with the increase the quantity of polymer. In terms of absorption process, the increasing of adsorbent quantity results in the increasing of active spot and sorption efficiency. However, with the increasing of quantity of polymer, the turbidity of phenol solution is added. The effect directly affects the absorbency of spectrophotometer. In other words, the adsorbent quantity shall be less than the quantity of effect on absorbency. In addition, with the increase of adsorbents quantity, the cost of absorption increases. If the quantity of polymer surpasses 40 mg/mL, the absorbency is affected and the reappearance is poor. So the maximum adsorbent quantity is no more than 40 mg/mL.

Influence of the initial concentration of phenol: Wastewater is diluted to different concentrations at every turn test. The 4 g polymers is added to each solution. The adsorption conditions are shown in Fig. 8.

Fig. 8 suggest that the lower the initial concentration of the phenol solution, is corresponding the higher the adsorption efficiency. The adsorption efficiency decreases with the increase of the initial concentration. The initial concentration of phenol affectes the adsorption efficiency. The adsorption efficiency reaches 70 % in less than 30 min, but after 50 min's adsorption reation reaches equilibrium. The adsorption efficiency is high in reaction begin. The adsorption reation reaches equilibrium in the short time. Adsorption equilibrium includes two reversible processes of adsorption and desorption. After reaching the adsorption equilibrium, the number of phenol absorbed equals to the number desorbed from the active point. Many studies on adsorption kinetic equilibrium are reported[13-16]. The initial concentration influence indicates that the less pollu-tants in the solution has the quicker the absorption rate to the active site on the basis of the fixed the active site. With the increase of the concentration and the pollutants, adsorption rate slows down. This results may be because of the steric effect between polluted molecule and polymer. It leads to the higher the concentration, the lower the adsorption efficiency.

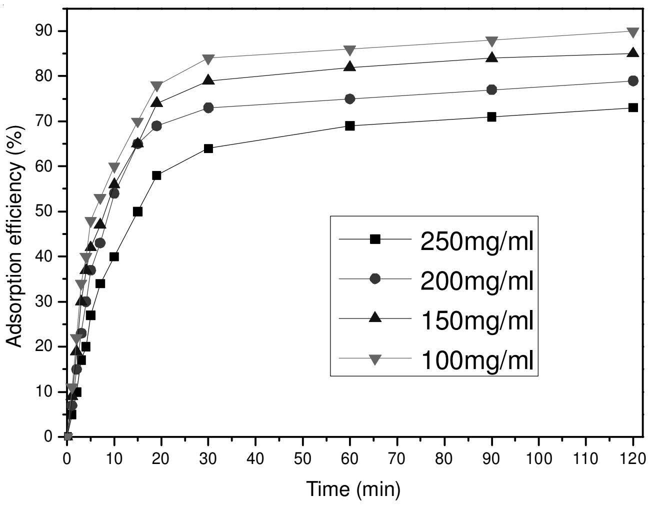


Fig. 8. Sorption efficiency influence of initial concentration

Adsorbent regeneration: The regeneration tests are carried out to reduce the cost of the absorbent. Add 4 g solid to 100 mL phenol solution (100 mg/L) and stir for 0.5 h. Set the adsorption time as 2 h and measure the adsorption rate. Put the polymer into the methanol solution after absorption at room temperature. Adsorbent soak for 24 h and filter. Place adsorbent in the 60 ºC vacuum for 24 h after repeated washing. Repeat the above adsorption test and measure its adsorption rate. The regeneration effect of polymer is shown in Fig. 9.

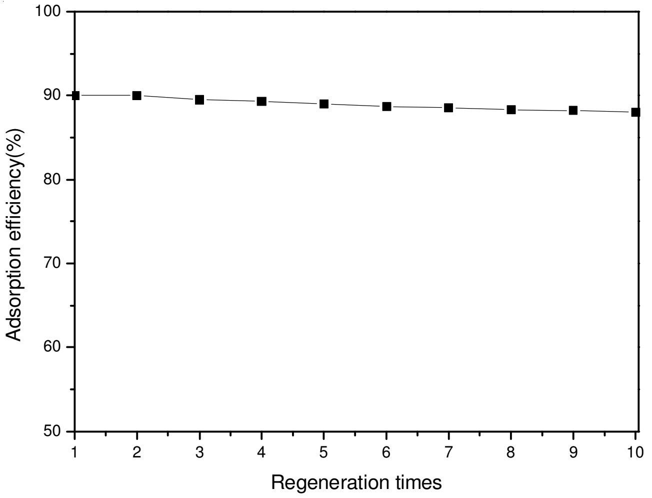


Fig. 9. Regeneration times of cyclodextrin pomers

The adsorptive capacity of the polymer after regeneration declines very little, which can be seen from the data given in

Fig. 9. The adsorption rate of phenol can still reach 88 % after 10 times of regeneration. The conclusion is significant to the industrial application. The desorbed phenol can be returned to the production system in industrial production, which the phenol resources enable a maximum utilization. The reutilization results decrease the cost of adsorbent and waste water treatment. This results is beneficial to application of industrialization.

Conclusion

The optimum technology conditions are found by orthogonality experiment. The results mean that the molar ratio of n (isocyanate) to n (β-cyclodextrin) is equivalent to about 1:9, 2, 4-toluene diisocyanate (TDI) is optimal diisocyanate, mass ratio of catalyst (dibutyl tin dilaurate and triethylene diamine) equal to 1:1.5, reaction temperature is 70 ºC and reaction time is 9 h. Compared with the synthesis reaction without ultrasonic irradiation, the technology parameters obviously change. The β-cyclodextrin-TDI polymer shows a micro-spherical multi-cavity network structure. The results of characterizing the crosslinked polymer show that the crosslinked β-cyclodextrin-TDI polymer possesses of β-cyclodextrin original cavity structure. The crosslinked reaction generates urethane bond. The crosslinked polymer forms the crossing network structure and microballoon surface topography. The microballoon surface topography has larger specific surface area. This structure characteristics provides higher stability and absorption efficiency.

The property facilitate the use of organic waste water treatment. Controlling limit phenol wastewate pH was 5-7. The maximum amount of polymers was 40 mg/mL. The adsorption rate and adsorbability were low with the increasing of phenol wastewate initial concentration. Regeneration process of adsorbent soaked by methyl alcohol and washed by deionized water. The adsorption efficiency retained more than 88 % after 10 times regeneration.

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