Preparation and properties of a cross-linked β-cyclodextrin polymer used for organic micropollutant removal in water

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Introduction

β-Cyclodextrin (β-CD), a nontoxic and inexpensive macrocycle of glucose, can form inclusion complexes with various molecules by the host-guest interactions, which is due to the size/shape match and binding forces between the host CD cavities and guest molecules. So, the insoluble cross-linked β-Cyclodextrin polymer (β-CDP) is a promising absorbent for removing organic micropollutant in water although cross-linked β-CDPs have slow adsorption rate so far.

Here we cross-link β-CD by nucleophilic aromatic substitution of hydroxyl groups of β-CD with 4, 4'-difluorodiphenylsulfone (DFS). The optimal β-CDP can remove 90% of bisphenol A (BPA) equilibrium adsorption amount in 1min.The adsorption process can be well described by quasi-second-order kinetic model and Langmuir or Freundlich isothermal adsorption model, which reveal that it is a chemical adsorption of monolayer.

Method

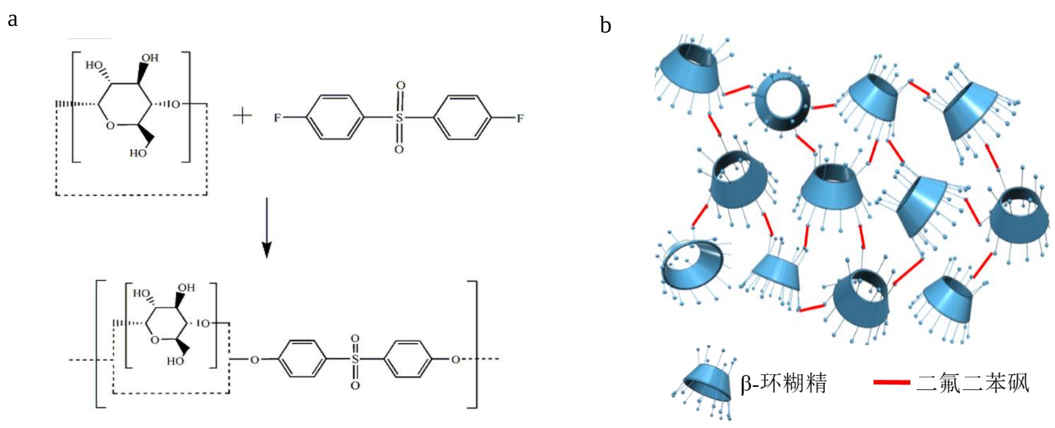

Figure 1. a. Synthesis of β-CDP from nucleophilic aromatic substitution reactions. b. Schematic of β-CDP structure.

Results and Discussions

1. Analysis of chemical compositions

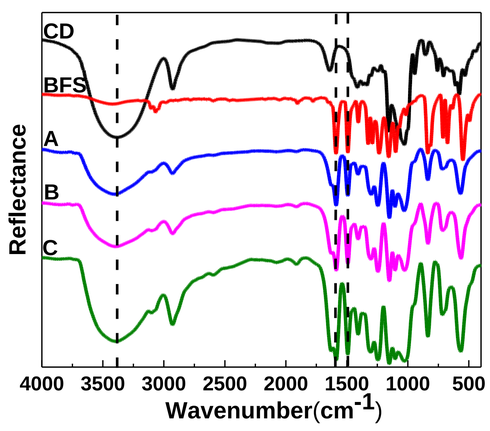

Figure 2. FTIR spectra of β-CD, BFS and CDP with different molar ratio of monomer.

2.Distribution of pore size

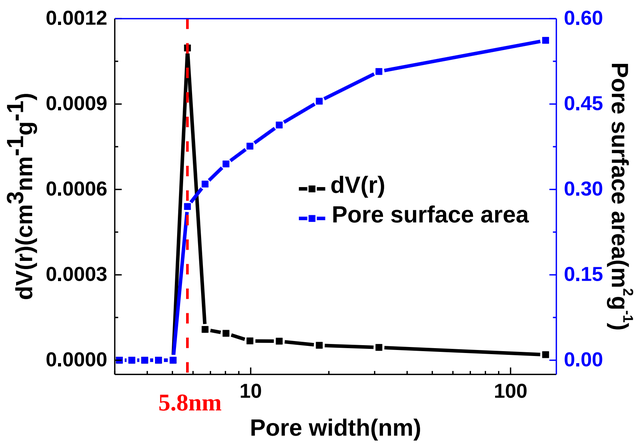

Figure 3. The differential cumulative pore volume of β-CDP obtained by BJH analysis indicates the polymer's mesoporous structure.

3. Removal efficiency of BPA

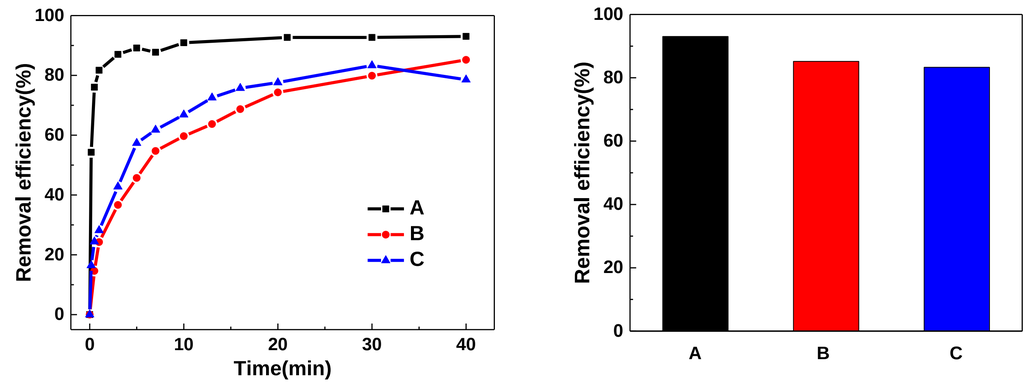

Figure 4. Removal efficiency of BPA by various β-CDP. a, Time-dependent adsorption of BPA by each adsorbent. b, The average percentage of BPA removal efficiency by β-CDP.

The A β-CDP can remove 90% of BPA equilibrium adsorption amount in 1min, which is much more quickly than other adsorbents (Figure 4).

4. Kinetic of BPA adsorption

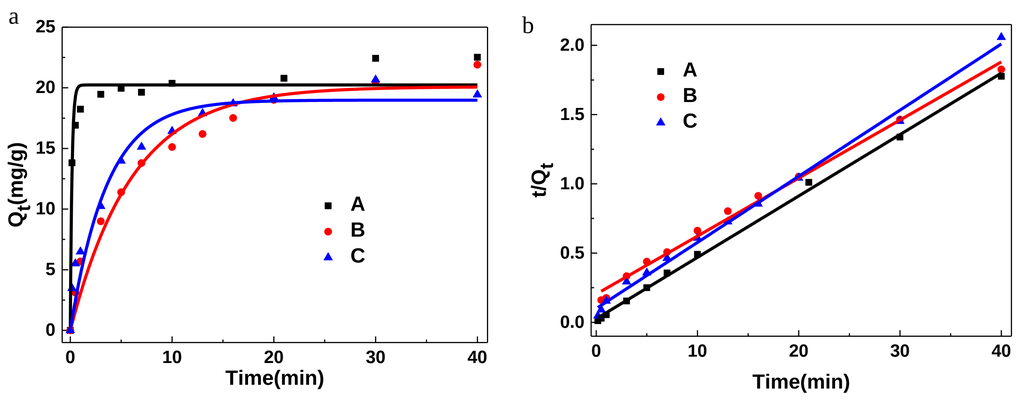

Figure 5. Fitting curve of BPA adsorption kinetic. a. quasi-first-order kinetic model. b. quasi-second-order kinetic model.

Table 1. Fitting parameters of BPA adsorption kinetic

β-CDP	quasi-first-order kinetic model			quasi-second-order kinetic model		
	k_1 (min^{-1})	Q_e (mg/g)	R^2	k_2(g/(mg·min))	Q_e(mg/g)	R^2
A	6.0075	20.24	0.9405	0.0772	22.55	0.9981
B	0.1637	20.09	0.9611	0.0086	23.86	0.9926
C	0.2777	18.98	0.9496	0.0229	20.94	0.9949

The adsorption process can be well described by quasi-second-order kinetic model, which reveals that the adsorption between β-CDP and BPA is attributed to chemical interactions (Figure 5).

5. Fitting curve of BPA isothermal adsorption

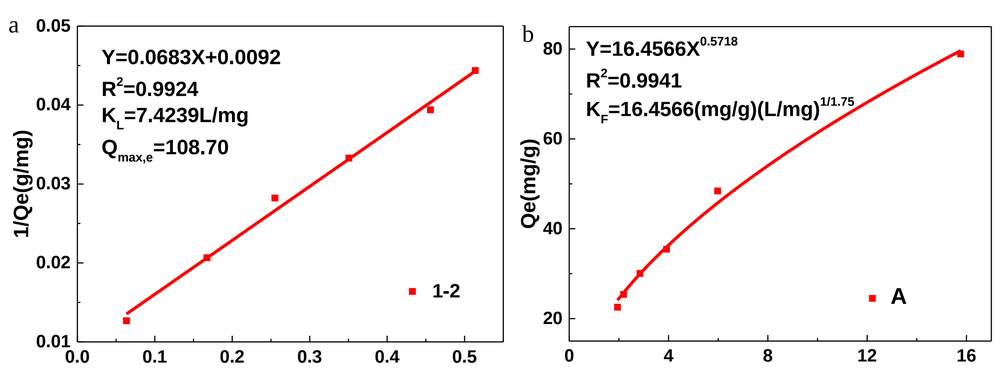

Figure 6. Fitting curve of BPA isothermal adsorption. a. Langmuir isothermal adsorption model. b. Freundlich isothermal adsorption model.

The adsorption process can be well described by Langmuir isothermal adsorption model and Freundlich isothermal adsorption model, which reveal that the adsorption process belongs to monolayer adsorption. What is more, the maximum of the BPA equilibrium adsorption amount can reach 108.70mg/g.

Conclusion

We successfully synthesize cross-linked porous β-CDP, which shows exceptional adsorption performance for organic micropollutant. Further more, the adsorption process can be well described by quasi-second-order kinetic model and Langmuir or Freundlich isothermal adsorption model, which reveal that it is a chemical adsorption of monolayer.