A crosslinked β-cyclodextrin polymer used for rapid removal of a broad-spectrum of organic micropollutants from water

11529024. Zhanghui Wang , Liping Zhu

Department of Polymer Science and Engineering, Zhejiang University, Hangzhou 310027, China

Abstract: **Organic micropollutants in aquatic environment such as plasticizer, pesticide and pharmaceuticals, have posed a serious threat to human health and are emerging as a great challenge to humanity. Here we demonstrate a water-insoluble crosslinked β-cyclodextrin (β-CD) polymer able to remove a broad-spectrum of organic micropollutants from water by rapid adsorption. The β-CDPs were used to adsorb various organic micropollutants in water by static or dynamic adsorption process. It was found that more than 99% micropollutants in water were removed by flowing the feed water through the column of β-CDPs. The results of static adsorption experiments indicated the adsorption process was fast and the adsorption capacity was very high (the maximal value was 113.0 mg of bisphenol A per gram of β-CDP).**

Method

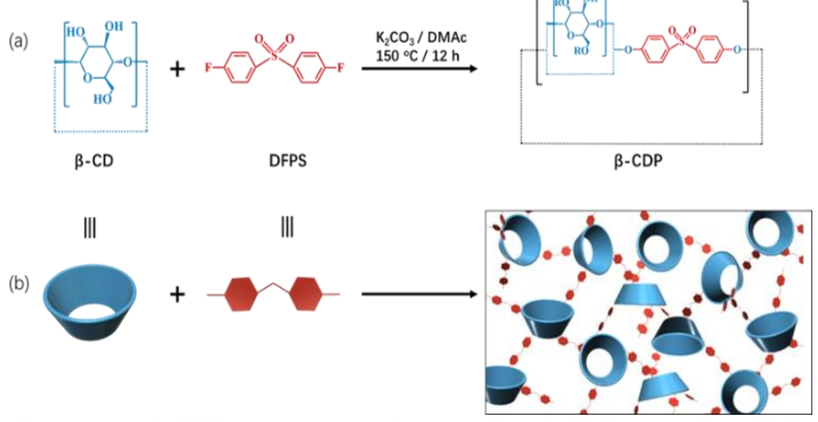

Fig. 1. (a) Synthesis of β-CDP from nucleophilic aromatic substitution reaction. (b) Schematic of β-CDP structure.

Results and discussions

1. Characterization of β-CDP.

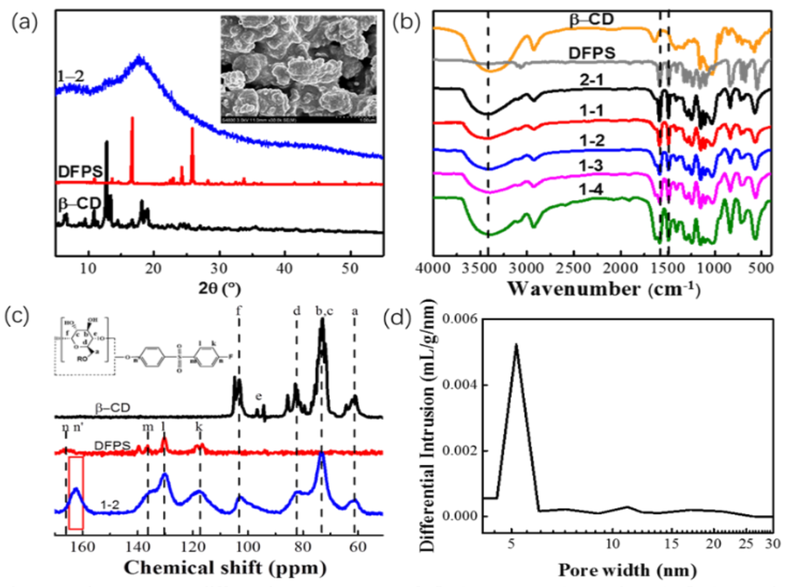

Fig. 2. (a) Powder X-ray diffraction pattern of β-CD, DFPS and 1-2 β-CDP (Inset displays scanning electron microscopy image of 1-2 β-CDP), (b) FTIR spectra of β-CD, DFPS and various β-CDPs, (c) Solid-state ^{13}C NMR spectra of β-CD, DFPS and 1-2 β-CDP, (d) Pore structure of 1-2 β-CDP calculated by mercury porosimetry method.

2. Batch adsorption kinetic studies.

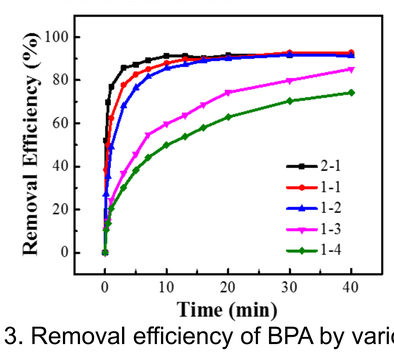

Fig. 3. Removal efficiency of BPA by various β-CDPs.

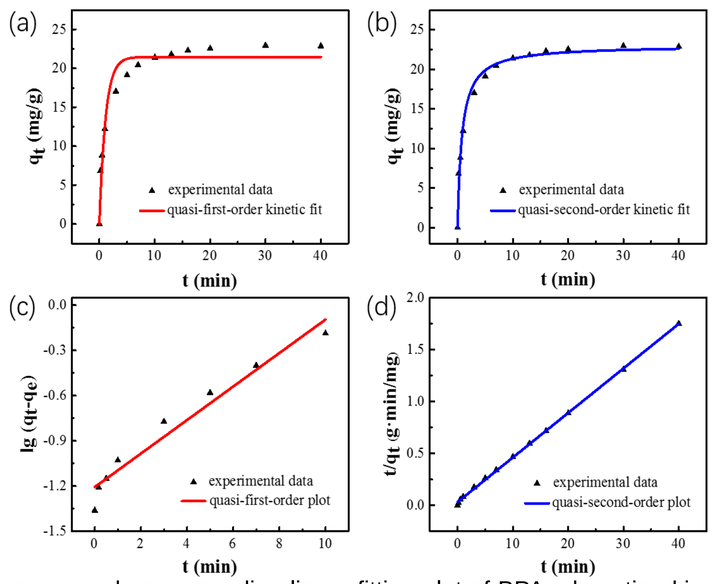

Fig. 4. Fitting curve and corresponding linear fitting plot of BPA adsorption kinetic of quasi-first-order kinetic model (a, c) and quasi-second-order kinetic model (b, d), respectively.

Table 1. Fitting parameters of BPA adsorption kinetic studies

β-CDP	Experimental	quasi-first-order kinetic model			quasi-second-order kinetic model		
	q_e(mg/g)	q_e(mg/g)	k_1(min^{-1})	R^2	q_e(mg/g)	k_2(g/mg·min)	R^2
1-2	22.87	16.08	0.2557	0.9569	23.33	0.0566	0.9994

The pseudo-second-order kinetic model is more suitable for describing the adsorption process than the quasi-first-order kinetics model, indicating that the adsorption behavior between various β-CDPs and BPA is mainly attributed to chemical interaction.

3. Batch adsorption thermodynamic studies.

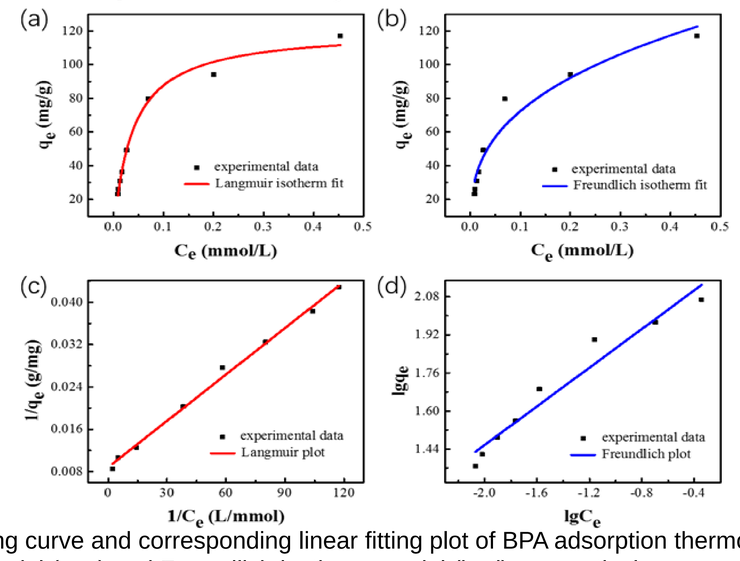

Fig. 5. Fitting curve and corresponding linear fitting plot of BPA adsorption thermodynamic of Langmuir isotherm model (a, c) and Freundlich isotherm model (b, d), respectively.

Table 2. Fitting parameters of BPA adsorption thermodynamic studies

β-CDP	Langmuir model			Freundlich model		
	q_{max}(mg/g)	K_L	R^2	K_F	n	R^2
1-2	112.99	30.32	0.9953	186.29	2.46	0.9529

The adsorption data fits better with the Langmuir isotherm model, indicating that the adsorption process is mainly a relatively homogeneous monolayer adsorption. The obtained maximum adsorption capacity (q_m) of 1-2 β-CDP to BPA is 112.99 mg/g, which is probably attributed to the formation of mesoporous structure and superior loading capacity of β-CD.

4. Flow-through adsorption experiments and regeneration experiments.

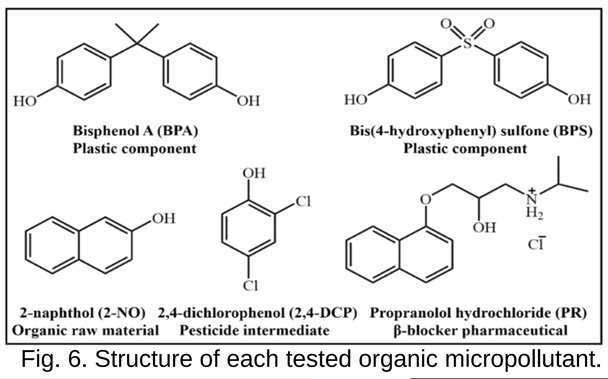

Fig. 6. Structure of each tested organic micropollutant.

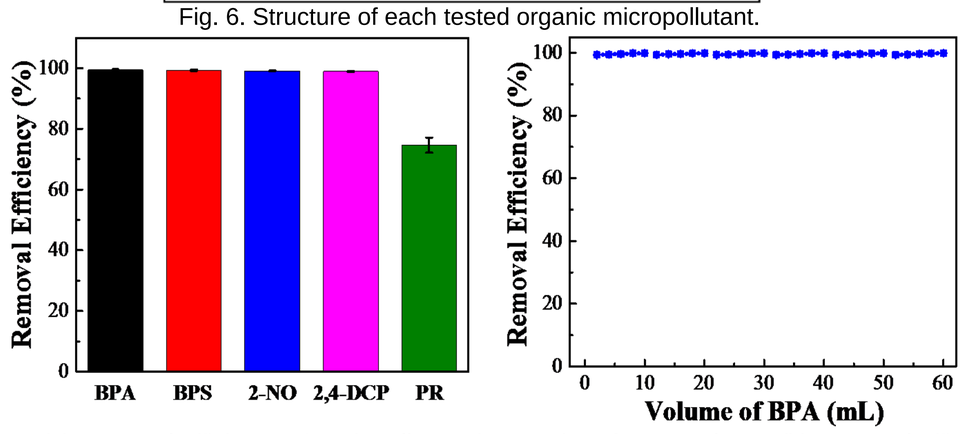

Fig. 7. (a) Removal efficiency of each pollutant (0.1 mM) by β-CDP column, (b) Removal efficiency of BPA after consecutive regeneration cycles.

Conclusions: **Water-insoluble cross-linked β-CDPs were successfully synthesized by nucleophilic aromatic substitution reaction. More than 99% of micropollutants such as plastic components, dye intermediates, pesticide intermediates and pharmaceuticals in water were removed by flowing the feed water through the column of β-CDPs. The adsorption process can be fitted well with the quasi-second-order kinetics and the Langmuir isothermal adsorption model, suggesting that it is mainly a chemical adsorption of monolayer. The adsorption ability of β-CDPs was kept nearly unchanged (99% of removal efficiency) even after five filtration-regeneration cycles.**