

## $\beta$ -Cyclodextrin Materials for Water Purification

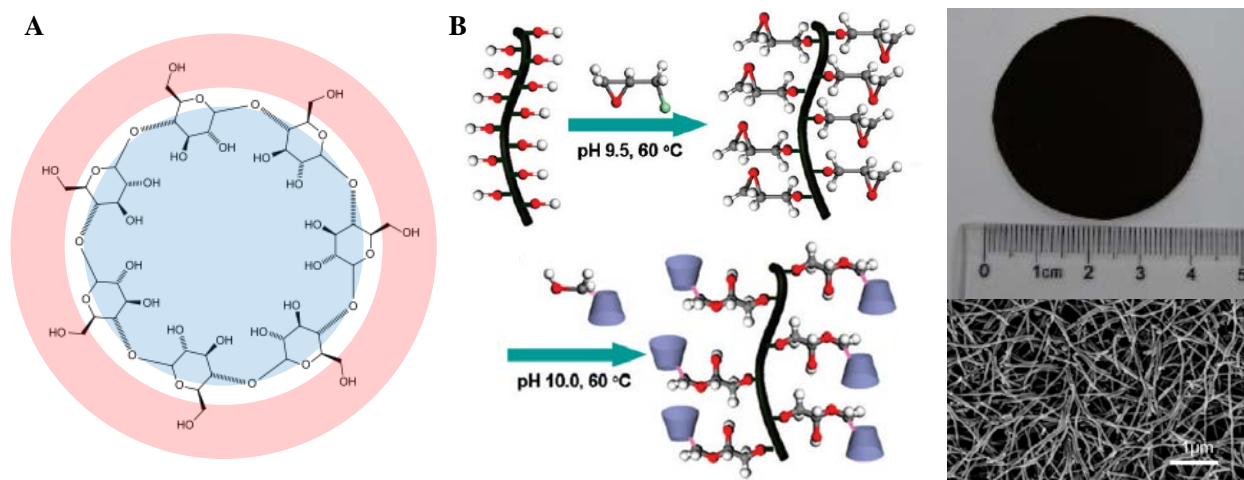
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Literature Seminar

November 16<sup>th</sup>, 2017

Increasing population around the globe brings with it many challenges, including the need for large amounts of clean water. With population increases projected to be higher in urban areas<sup>1</sup>, there is a need to develop water purification systems that can handle large volumes and filter out an increasingly diverse array of small organic molecules from pharmacy and agriculture.<sup>2</sup> Virtually all water purification systems today use activated carbons (ACs) as adsorbents for small organic molecules, due to their high surface area and low cost. However, activated carbons adsorb mainly through physisorption and generally have slow, non-specific uptake. Specifically, standard ACs have poor uptake of amphipathic molecules like propranolol (a beta-blocker)<sup>3</sup>, certain small molecules like 2,4-dichlorophenol (a carcinogen used in herbicide production)<sup>4</sup>, and perfluorinated compounds<sup>5</sup>. Furthermore, ACs require high energy inputs – up to 900 °C heating under inert atmospheres – to regenerate the adsorbent for repeated use.

To solve these issues and improve small molecule sequestration for water purification systems, the chemistry of host-guest complexes can be utilized. In such complexes, small molecule guests are trapped in pores of a larger host (macro)molecule via chemisorption. One macromolecular host of interest is  $\beta$ -cyclodextrin ( $\beta$ -CD), a 7-unit glucose macrocycle with a hydrophilic exterior and relatively hydrophobic interior (**Figure 1a**). Small hydrophobic molecules can be easily sequestered into this hydrophobic pore, and many commercial technologies exploit this: cyclodextrins are used in the production of cholesterol-free foods, and Febreze® uses aerosolized cyclodextrins to trap and neutralize odors caused by small airborne molecules. Additionally,  $\beta$ -CD has high bioavailability (being derived from starch) and thus is a good candidate for sustainable, inexpensive chemical adsorbents.



**Figure 1.** (a) The hydroxyl-rich macrocycle  $\beta$ -CD has a hydrophilic exterior and hydrophobic interior; (b) Epichlorohydrin can be used to link hydroxyls on a carbonaceous surface to the hydroxyls of  $\beta$ -CD, forming functionalized carbon nanofibers that form a freestanding membrane.

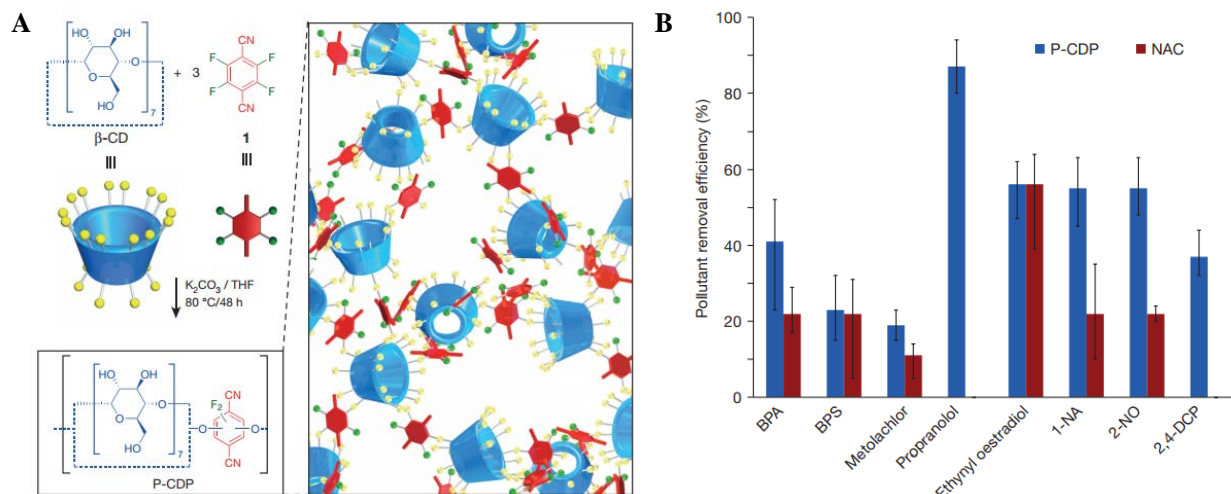
To transform this macrocycle into a usable material for water purification,  $\beta$ -CD must be anchored to some substrate. Two main routes have been explored in the literature: attaching  $\beta$ -CDs to graphitic supports, and crosslinking with other molecules to form  $\beta$ -CD polymers.

In order to covalently bond the hydroxyls of  $\beta$ -CD to a graphitic surface, some functionality needs to be present on the substrate. A simplistic way to prepare large quantities of graphene oxide (graphene sheets with extensively oxidized surface and edge sites) is through the Hummers method.<sup>6</sup> Konkena and Vasudevan<sup>7</sup> functionalized the edge-site carboxylic acid groups of graphene oxide via EDC/NHS chemistry to form amide bonds with aminated  $\beta$ -CD. These bonds were resistant to reduction as the graphene oxide was reduced by hydrazine to restore the  $sp^2$  character of the basal plane. Taking advantage of this  $sp^2$  graphene character, the uptake of azobenzene by the  $\beta$ -CD composite was characterized through fluorescence quenching, which occurs as the azobenzene is brought close to the graphitic plane. Unfortunately, this method only utilizes graphitic plane edges and neglects the majority of the surface area on the basal plane, lowering its overall adsorption efficiency and maximum uptake.

To utilize more area on graphitic surfaces and more easily turn  $\beta$ -CD composites into usable membranes, Chen et al.<sup>8</sup> covalently linked  $\beta$ -CD to carbon nanofibers via epichlorohydrin linkages (**Figure 1b**). The mass loading of  $\beta$ -CD was 20 times higher than the previously mentioned study, showing the importance of utilizing available surface area. The nanofiber composites can form freestanding membranes, which showed a maximum uptake of the dye fuchsin acid four times higher than that of activated carbon. However, the nanofiber membranes showed poor breakthrough capacity and limited recyclability. This may be due to the fabrication of the nanofibers, as the carbon layer is grown around a tellurium nanorod, which is subsequently etched away and leaves behind unfunctionalized pores through which small molecules can flow.

More recent studies have developed  $\beta$ -CD polymers to increase  $\beta$ -CD mass loading, available surface area, and chemical selectivity. One study copolymerized a  $\beta$ -CD derivative with a secondary host molecule, calixarene, via azide-alkyne click chemistry.<sup>9</sup> The addition of calixarene, a square aromatic macrocycle, helped uptake small aromatic organics like nitrobenzene that are not well adsorbed with  $\beta$ -CD alone. Testing of a wide range of small molecules showed that uptake is sensitive to polymer pore size, solution pH, and guest size and shape.

More recently, the groups of Dichtel and Helbling have developed highly porous, rigid  $\beta$ -CD polymers by crosslinking them via nucleophilic aromatic substitution to an aromatic linker with no pre-functionalization of  $\beta$ -CD.<sup>4</sup> Boasting surface areas ( $263 \text{ m}^2/\text{g}$ ) approaching those of ACs ( $500 \text{ m}^2/\text{g}$ ), these polymers were able to uptake pharmaceutical and pesticide molecules more rapidly and with higher maximum uptake than the best commercially available activated carbons (**Figure 2**). Importantly, the polymers were able to sequester propranolol and 2,4-dichlorophenol in complex pollutant mixtures, demonstrating their advantage over AC systems that do not remove such chemicals. These porous polymers were further developed to make them selective for removal of perfluorooctanoic acid by utilizing a perfluorinated crosslinking molecule.<sup>10</sup> Unlike ACs, such polymer systems do not show fouling and performance loss from natural organic matter.



**Figure 2.** (a) Crosslinking  $\beta$ -CD with a rigid aromatic linker yields high surface area and highly porous polymers; (b) These polymers show more rapid and higher maximum uptake of organic pollutant mixtures than the best activated carbons.

While  $\beta$ -CD can be anchored to graphitic supports,  $\beta$ -CD polymers appear to be the way forward due to greater synthetic control. This allows higher surface areas, greater porosity, and the option for adding secondary hosts or crosslinkers that increase chemical selectivity for specific compounds. While  $\beta$ -CD materials may never totally supplant inexpensive, general filtration systems using ACs, they show promise for augmenting such systems to remove specific hazardous chemicals and can be tailored for specific industrial waste streams to meet those chemical needs.

## References

- <sup>1</sup> *Towards a Water and Food Secure Future*; World Water Council and FAO, Rome, 2015.
- <sup>2</sup> *Pharmaceuticals in Drinking-Water*; World Health Organization, France, 2012.
- <sup>3</sup> Kostich, M.S.; Batt, A.L.; Lazorchak, J.M. *Environ. Pollut.* **2014**, *184*, 354-359.
- <sup>4</sup> Alsbaiee, A.; Smith, B.J.; Xiao, L.; Ling, Y.; Helbling, D.E.; Dichtel, W.R. *Nature* **2016**, *529*, 190-194.
- <sup>5</sup> Qu, Y.; Zhnag, C.; Li, F.; Bo, X.; Liu, G.; Zhou, Q. *J. Hazard. Mat.* **2009**, *169*, 146-152.
- <sup>6</sup> Hummers, W.S.; Offeman, R.E. *J. Am. Chem. Soc.* **1958**, 1339.
- <sup>7</sup> Konkena, B.; Vasudevan, S. *Langmuir* **2012**, *28*, 12432-12437.
- <sup>8</sup> Chen, P.; Liang, H.-W.; Lv, X.-H.; Zhu, H.-Z.; Yao, H.-B.; Yu, S.-H. *ACS Nano* **2011**, *5*, 5928-5935.
- <sup>9</sup> Lo Meo, P.; Lazzara, G.; Liotta, L.; Riela, S.; Noto, R. *Polym. Chem.* **2014**, *5*, 4499-4510.
- <sup>10</sup> Xiao, L.; Ling, Y.; Alsbaiee, A.; Li, C.; Helbling, D.E.; Dichtel, W.R. *J. Am. Chem. Soc.* **2017**, *139*, 7689-7692.