

THE SYNTHESIS AND CHARACTERIZATION OF WATER-INSOLUBLE CYCLODEXTRIN POLYMERS FOR THE REMEDIATION OF PERFLUORINATED COMPOUNDS

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ABSTRACT

Perfluorinated compounds (PFCs) are bioaccumulative molecules due to their C-F bonds, and they have proven difficult to remove from wastewater. Inclusion complexes have been observed between PFCs and β -Cyclodextrin (β -CD), a cyclic sugar that can participate in host-guest interactions. These complexes are very stable and are promising for remediation of PFCs. In this study, an environmentally friendly method of polymerization was employed with citric acid as the cross-linker and either polyvinyl alcohol (PVA) or polyethylene glycol (PEG-400) as a backbone. The characterization of the polymers were observed by means of Fourier-transform infrared spectroscopy (FT-IR), UV-Visible spectrophotometer (UV-Vis), and nuclear magnetic resonance (NMR) to verify the completion of the polymerization, quantify the amount of CD available for binding, and determine the ratio between CD and citric acid (CA) in both polymers. In the PEG-400 polymer, the ratio of CD to citric acid was 5:12, whereas the ratio of CD to citric acid was 1:6 in the PVA polymer. Ion Chromatography (IC) was used to observe the β -CD polymers' (β -CDP) absorption capacity of PFCs by measuring the concentration of PFCs in solution with the polymers and comparing to a control.

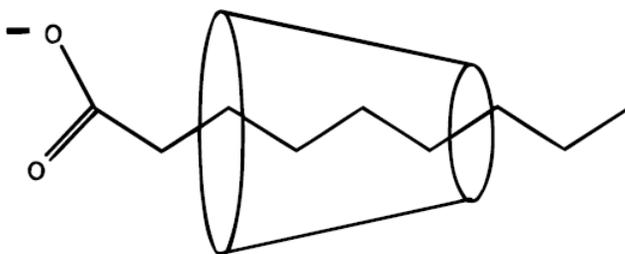


Figure 1. The inclusion complex between perfluorooctanoic acid (PFOA) and β -CD¹

INTRODUCTION

Since 1947, the usage of PFCs as surfactants and aids in polymer synthesis has increased in numerous industries and commercial applications from being a stain repellent in fast food containers to surfactants in fire-fighting foam. Due to this increase, PFCs have been widely detected in the environment, especially water supplies, humans, and wildlife. These persistent compounds bioaccumulate in the food chain and are global pollutants, effecting both the Western and Eastern hemisphere as well as the polar regions. At least 99% of the US population has part per billion (ppb) levels of PFCs in their blood serum, specifically PFOA and/or

perfluorooctanesulfonic acid (PFOS). From lab studies on rat, rabbit and monkey models, PFCs have shown health effects on the liver, bladder, and skeletal bone structure in newborns with delayed ossification and abnormalities². Overexposure to PFCs is known to cause obesity, liver and bladder cancer and infertility in women. PFCs are highly stable and resistant to degradation because of their strong C-F bonds giving them the ability to bypass water treatment processes. Therefore, CDs have been looked at for the remediation of PFCs.

CDs are oligosaccharide cyclic molecules with a hydrophobic cavity and a hydrophilic exterior. The number of glucose monomers range from six to twelve with six, seven and eight monomers, also known as α , β , and γ , being the most important. However, β -CDs have more industrial importance compared to the others as they have been used in applications from pharmaceuticals and cosmetics to food and household products³. Water-insoluble β -Cyclodextrin polymers (β -CDPs) have become a new type of absorbent that assists in filtering out organic pollutants and heavy metals in wastewater. However, most of the β -CDP contain epichlorohydrin (EPI) for cross-linkage between the hydroxyl groups of the CD molecules⁴. EPI is known to pose a potential hazard to human health and the environment⁵. Additionally, a lot of EPI may become waste as high concentrations of sodium hydroxide and temperatures above 200 °C are needed to start the hydrolyzation³.

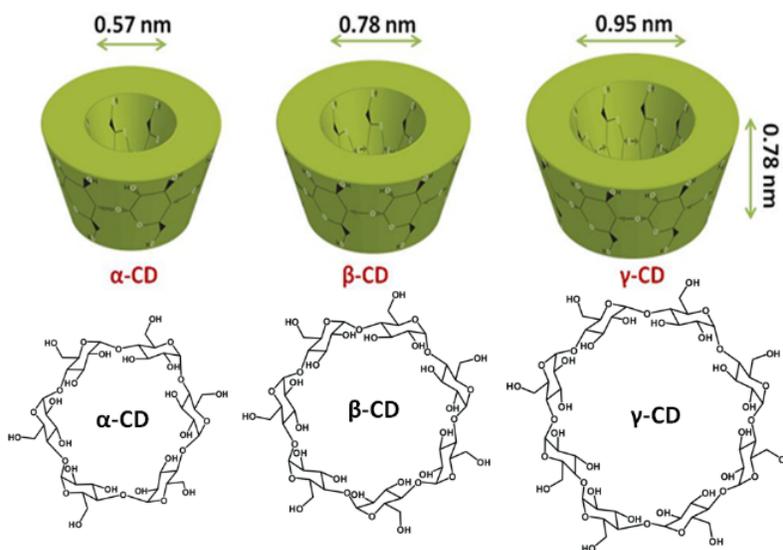


Figure 1. Three smallest versions of CD⁶

From previous studies, binding constants were calculated between PFCs and β -CD to give insight into their association. In this report, an environmentally friendly polymerization of β -CD was employed with CA as the cross linker, monosodium phosphate (MSP) as the catalyst and PEG and PVA as the backbone. The polymers were characterized by FT-IR and NMR spectroscopy at 400MHz. The β -CD content in the polymers was calculated by means of UV-Vis and the IC observed the absorption efficiency of the polymers toward PFOA.

MATERIALS & METHODS

MATERIALS

β -CD (98.0% purity) was purchased from Acros Organics. CA (ACS grade), and PFOA were purchased from Sigma-Aldrich. PEG-400 with a molecular weight of 380-420 and Mowiol® 28-99 (PVA) at molecular weight \sim 145,000 were purchased from Aldrich Chemistry. MSP was purchased from Merck Reagent Company. Both α - and γ -Cyclodextrin (α -CD and γ -CD) were purchased from Tokyo Chemistry Industry.

SYNTHESIS OF CDP

The synthesis of β -CDP followed D. Zhao, et al.^{3,7} and the insoluble fraction was dried overnight until constant weight. An FT-IR spectrum of the dried polymer was taken and the ester peak around 1730 cm^{-1} was used to verify polymerization. The same procedures were performed on α and γ -CD.

β -CD CONTENT IN β -CDP

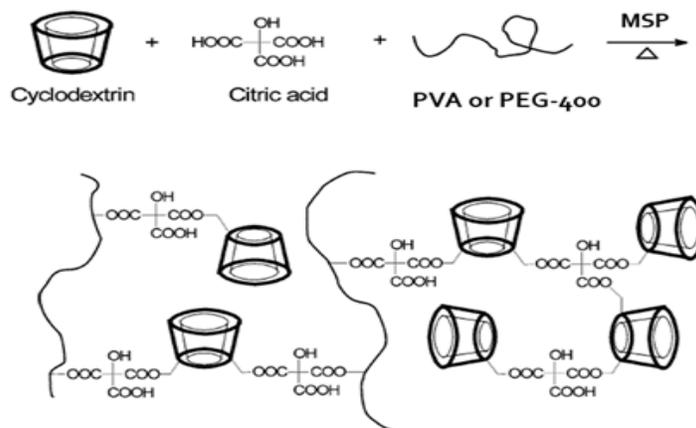
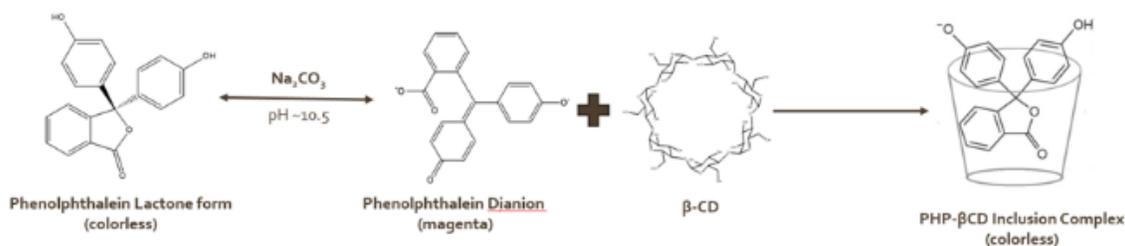


Figure 2. The synthesis of water-insoluble CDP

A calibration curve for the concentration of β -CD was formed following the Phenolphthalein (PHP) colorimetric method from Mäkelä, et al.^[8] with $0.055\text{ M Na}_2\text{CO}_3$, $3.732 \times 10^{-4}\text{ M PHP}$ and varying concentration of β -CD in a $5\text{ mL } 1:1\text{ Na}_2\text{CO}_3/\text{PHP}$ solution. The PHP stock solution was prepared with ACS grade PHP and 10% ethanol/water. The solutions were prepped and an absorption reading was taken at 553 nm on a Cary Bio 100 UV-Vis immediately afterwards.



50 mg of the polymers, with PEG-400 and PVA as backbones, were dissolved completely in 25mL of 0.1M NaOH and neutralized with 0.1M HCl. The samples were comprised of 2mL from each of the Na₂CO₃ and PHP stock solutions and 1mL from each polymer. The concentration of Na₂CO₃ and PHP were adjusted for 2mL instead of 2.5mL, 0.0678 M and 4.667x10⁻⁴ M respectively. The concentration of the β-CD in the polymers was determined from the absorption at 553nm and the calibration equation. β-CD concentration was calculated as follows,

Where C is the concentration of β -CDP, V is the total volume of neutralized polymer solution and W is the weight of the polymers ³.

ABSORPTION OF PFOA BY β-CDP

Varying concentrations of PFOA were dissolved in Deionized (DI) H₂O and measured for peak area on a Metrohm 761 Compact IC with a Metrosep A Supp 5 column with a 3.2mM Na₂CO₃/1mM HNaCO₃ buffer as the eluent and 0.1M sulfuric acid as the washing solution. A calibration curve was formulated from the peak area. Afterwards, a series of IC samples were made with 50 mg of the polymers in 2 and 5ppm of PFOA along with a blank sample as the control then ran on the IC an hour after shaking the polymer/PFOA samples at 200 RPM.

RESULTS AND DISCUSSION

SYNTHESIS OF CDP

Polymerization of both the PEG and PVA polymers was successful; however, the yield differed greatly. PVA produced about four times as much of water-insoluble β-CDP compare to the PEG version. The yield between PEG and PVA for α had the smallest gap with 31% difference that increases from γ to β with 40 and 67% respectively. The PVA polymer most likely exhibited a higher degree of polymerization from its greater concentration of hydroxyl groups in PVA compared to PEG, which lead to a higher yield of water-insoluble polymer.

FT-IR CHARACTERIZATION OF CDP

CD	Modifier/Backbone	Yield of Insoluble Polymer (%)
β	PEG	17.8
	PVA	84.7
α	PEG	27.7
	PVA	58.7
γ	PEG	22.1
	PVA	62.3

Table 1. Yield of insoluble polymer

The FT-IR spectra of the CDP were similar to each other and each was compared to their CD

counterparts before polymerization.

In fig. 4 the absorption peak in (b) at 1729 cm^{-1} is absent in (a) due to the formation of the ester group as the crosslinker citric acid reacted with the hydroxyl groups on the CD and formed an water insoluble polymer. At 1643 cm^{-1} , an intense peak appears in both spectra, indicating the vibrations from the water bending. This shows the water was not completely evaporated after polymerizing and the water was present before running the reaction. The broad absorption band at 3400 cm^{-1} appears in (a) from the hydroxyl groups in the CD and a similar band shows up in (b) corresponding to the O-H groups in the backbone and citric acid in addition to the CD. The peaks at 2923 cm^{-1} in (a) and (b) corresponds to the stretching vibration of the $-\text{CH}_2$ asymmetrical bonds. The stretching vibrations of the C-O-C and C-OH groups are responsible for the peaks at 1150 cm^{-1} and 1022 cm^{-1} in (a) and 1149 cm^{-1} and 1024 cm^{-1} in (b). The similarity in peaks indicates the structure was maintained. The spectra of the citric acid and the backbones support this conclusion.

FT-IR spectra of α and γ -CD and CDP had similar readings due to their similar functional groups and structure from their CD to polymer form.

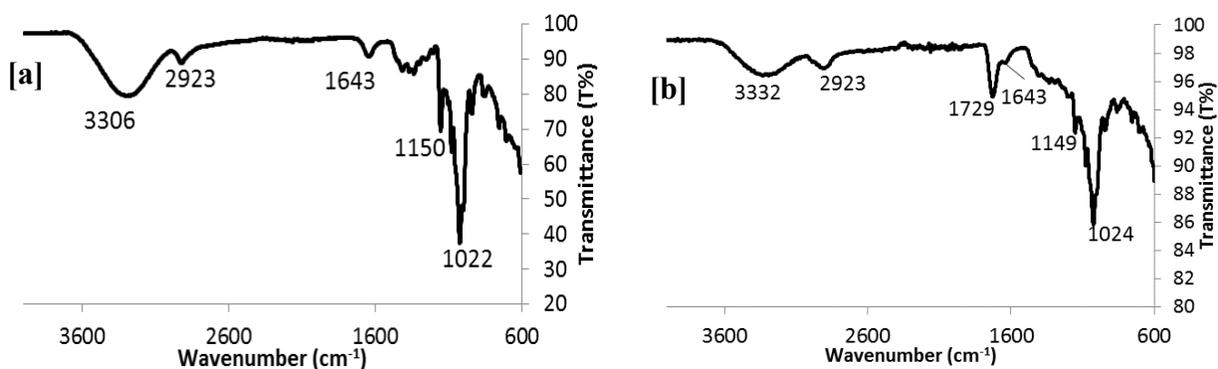


Figure 4. FT-IR spectra of (a) β -CD and (b) β -CDP

β -CD CONTENT IN β -CDP

The CD content in α and γ -CDP were not measured due to phenolphthalein's molecular size (0.6 nm) as it was optimally suited for β -CD with a cavity diameter of 0.78 nm. The α and γ -CD have

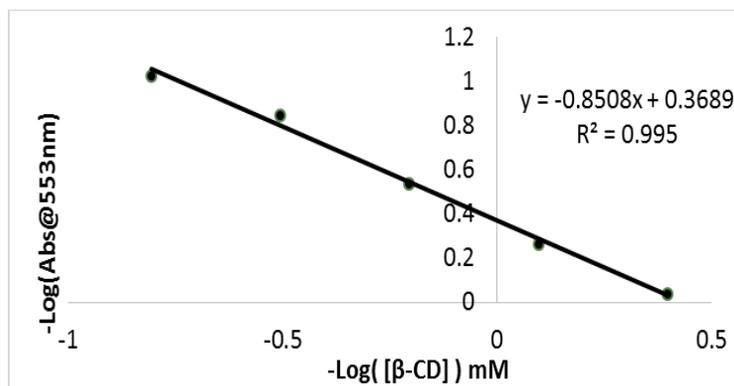


Figure 5. The calibration curve of β -CD

a diameter of 0.57 and 0.92 nm respectively.

Following a modified version of the PHP colorimetric method, the PEG polymer was measured to have a higher concentration of β -CD compare to PVA polymer. This could be due to steric hindrance from the hydroxyl groups in PVA in contrast with the widely spaced hydroxyl groups in PEG.

The reproducibility of the results varied as repeated runs gave significantly different results with the absorption of PVA with PHP fluctuating. When it came to dissolving the dried polymers in 0.1M NaOH for the PHP colorimetric method, the β -CD with PVA did not completely dissolve

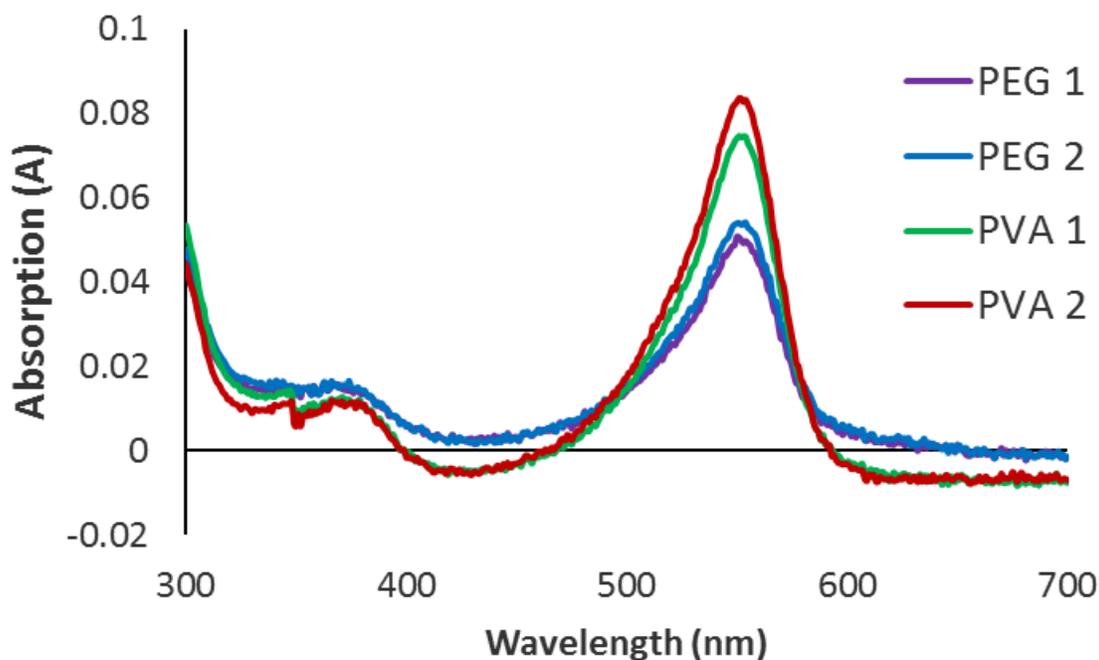


Figure 6. UV-Vis spectra of β -CDP with PHP

after waiting 24 hours. The polymer with PEG backbone dissolved readily after sonication. The solubility of PVA polymer could have skewed the UV-Vis readings as noted in fig.6 the absorption for PVA dips below zero reading. **[b]**

CHARACTERIZATION OF α , β , AND γ -CDP BY NMR

Characterizing the polymers with NMR gave insight into the ratio of binding between citric acid, the backbone, and their CD. In the NMR spectrum of the β -CD/PEG polymer (fig. 9-a) the integration shows seven hydrogens that come from a single β -CD in the polymer and the four peaks at the 2.5 ppm range signifies the four hydrogens from citric acid. There are about 9.56 hydrogens responsible for the CA peaks. By rounding to the nearest integer this shows that five CDs are incorporated for every twelve citric acids within the polymer. For the PVA polymer, the peaks for citric acid (fig.9-b) are bigger than in fig 9-a. and an integration of 23.60 at the same position of 2.5 ppm as the peaks in fig. 9, the number of citric acids bounded to one β -CD is six. The dramatic difference in bonded CA may suggest that the β -CD are more spread out along the PVA backbone compared to the PEG polymer as more citric acid is incorporated into the PVA polymer than the PEG. This is possible due to their differences in where the hydroxyl groups are positioned on the backbone. The more CA bonded to each other, the further the CD is away from the backbone, decreasing any strain the CD would have encountered closer to the backbone. The peaks in the NMR spectra in fig.10 (a) and (b) are in similar positions at 2.5 ppm shift but the heights of them are significantly different where the peaks in (b) appears to be three times as tall as in (a). The incorporation ratio of CD to CA for the PEG version of the α -CDP is 5:18 while the PVA polymer has a 4:53 ratio. As shown in the β -CDP spectra in fig. 7, there seems to be a trend of the PVA polymer having more CAs bonded to the backbone than the PEG polymer. This could indicate the important role of the position of the hydroxyl groups in how CA, CD and the backbone are bonded to one another.

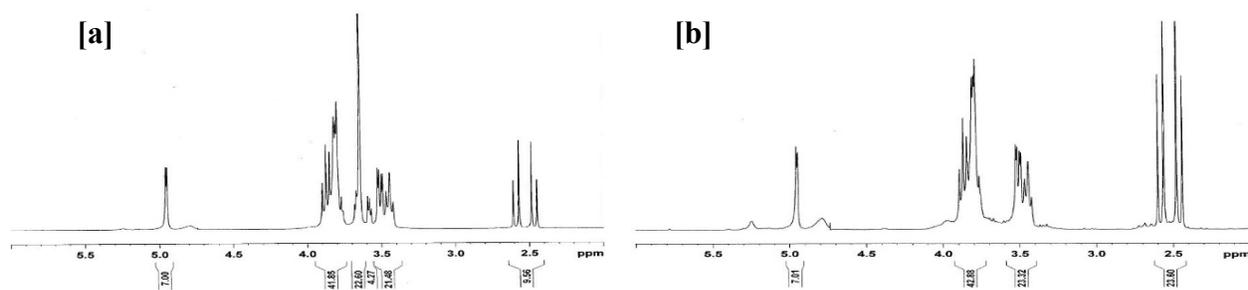


Figure 7. ¹H NMR spectra of β -CD/PEG (a) and β -CDP/PVA (b)

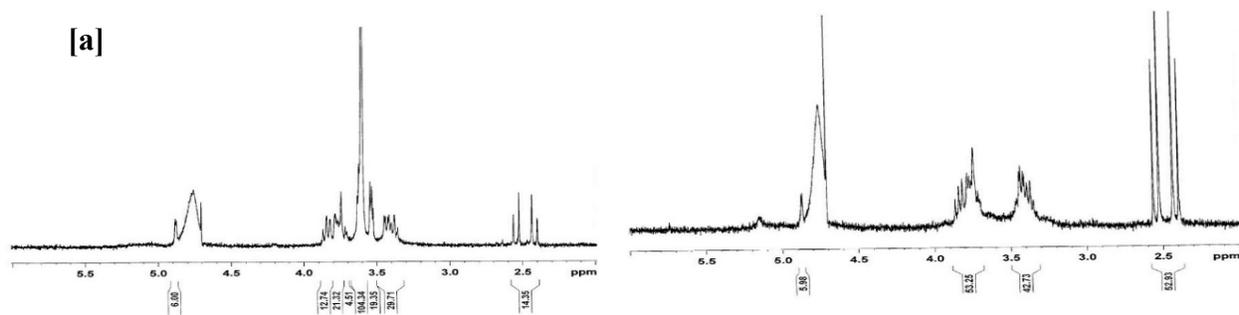


Figure 8. ¹H NMR spectra of α -CDP/PEG (a) and α -CDP/PVA (b)

The same NMR spectra of PFOA (2ppm) and (b) are PFOA (5ppm) are shown in fig. 11(a) and (b) respectively. The furthest right peak in fig. 11(a) and (b) correspond to the hydrogens in CA. The ratio of CD to CA for PEG and PVA polymers are 4:17 and 10:83 respectively. The NMR spectra collectively indicate the proximity of the hydroxyl groups in PVA versus PEG play a part in the number of crosslinkers used to bind the CD to the backbone.

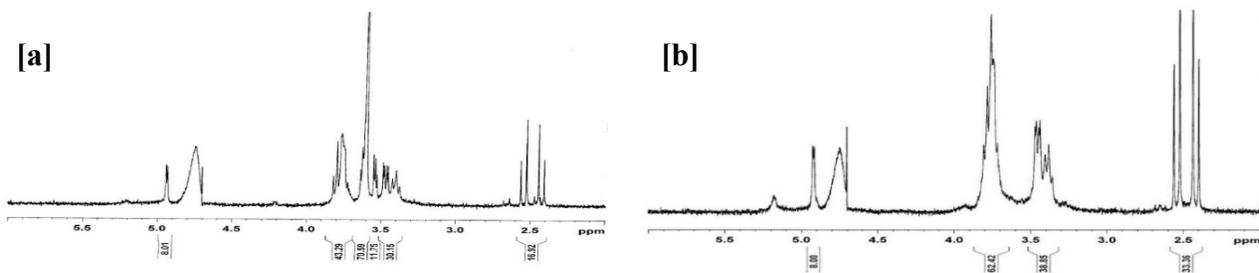


Figure 9. ¹H NMR spectra of γ -CDP/PEG (a) and γ -CDP/PVA (b)

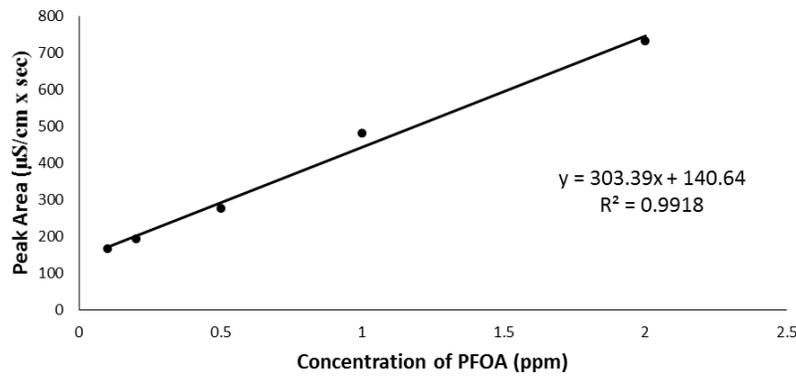


Figure 10. IC calibration curve for PFOA concentration

ABSORPTION OF PFOA BY β -CDP

PFOA peak areas measured with IC varied widely depending on the day the samples were prepared. Carry over from previous samples seemed to have occurred, and the time between making the solutions and testing them appeared to be a factor in how the IC measured the peak area. The consistency of the IC in measuring the samples went down soon after completely cleaning the instrument. However, it appears that the PVA polymer successfully removes PFOA, with a ~85% removal of a 5 ppm solution of PFOA. The PEG polymer was not successful in removing PFOA from solution.

PFOA Conc.	2ppm	5ppm
Blank Peak (μ S/cm x sec)	90.205	1659.213

Table 2. IC peak area of blanks (i.e. no β -CDP)

Table 3. β -CDP removal of PFOA from solution

CONCLUSION

An environmentally friendly polymerization of α , β , and γ -CD was employed with CA as the cross linker, and either PEG or PVA as the backbone to the polymer. After a series of syntheses it was evident that PVA had a higher yield of water-insoluble polymer than PEG; however, from the PHP colorimetric method, PEG had a higher concentration of β -CD incorporated into the polymer. The proximity of the hydroxyl groups could have affected how the cross linker and CD bond. The ^1H NMR spectra of the polymers further verified this conclusion as there is a higher ratio of CD to CA bonded to the PVA backbone compared to the polymers with PEG as a backbone.

The IC experiments showed successful removal of PFOA by the PVA polymer. The opposite of what was expected as PEG had a higher concentration of β -CD. Again, the proximity of the functional groups appears to be a factor into the functionality of the polymers.

Further characterization is needed to determine how the components are bonded to each other and what geometry the polymers take. Future IC experiments would be to change the pH, ionic strength and temperature in order to observe their effects on the water-insoluble polymers' ability to absorb PFOA in solution.

REFERENCES

1. Verrall ER, Wilson DL. 1998. ^{19}F and ^1H NMR Investigation of Cyclodextrin/Fluorocarbon Alkyl Carboxylate Surfactant Inclusion Complexes. *Langmuir*. 14:4710-17.
2. Stahl T, Mattern D, Brunn H. 2011. Toxicology of perfluorinated compounds. *Environmental Sciences Europe*. 23:125-30
3. Zhao D, Zhao L, Zhu C, Tian Z, Shen X. 2009. Synthesis and properties of water-insoluble β -cyclodextrin polymer crosslinked by citric acid with PEG-400 as modifier. *Carbohydrate Polymers*. 78:125-30
4. Crini G, Morcellet M. 2002. Synthesis and applications of adsorbents containing cyclodextrins. *Journal of Separation Science* 25:789-813
5. Crini G. 2005. Recent developments in Polysaccharide-based materials used as adsorbents in wastewater treatment. *Progress in Polymer Science*. 30:88-94.
6. Kayaci F, Umu O, Tekinay T, Uyar T. 2013. Antibacterial Electrospun Poly(lactic acid) (PLA) Nanofibrous webs incorporating triclosan/cyclodextrin inclusion complexes. *Journal of Agriculture food chemistry*. 61(16):3901-08
7. Zhao D, Zhao L, Zhu C, Huang W, Hu J. 2009. Water-insoluble β -cyclodextrin polymer crosslinked by citric acid: synthesis and absorption properties toward phenol and methylene blue. *Journal Inclusion Phenom Macrocycl Chemistry*. 63:195-201
8. Mäkelä M, Korpela T, Laakso. 1987. Colorimetric determination of β -cyclodextrin: two assay modifications based on molecular complexation of phenolphthalein. *Journal of Biochemical of Biophysical Methods*. 14:85-92.