DEVELOPMENT OF NOVEL ADSORBENTS FOR THE REMOVAL OF EMERGING CONTAMINANTS FROM WATER AND WASTEWATER

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ABSTRACT

There are many reports indicating the presence of various emerging contaminants (ECs) in treated wastewater and other water sources. The detection of such contaminants in the environment and the ability of these contaminants to pose potential threats to the environment at very low concentrations have led to a need for more efficient treatment technologies.

Cyclodextrins (CDs) have gained significant interest as an alternative adsorbent for water and wastewater treatment because of their unique physico-chemical characteristics and excellent selectivity towards organic compounds. The property of CD to form inclusion complexes with various molecules through host-guest interactions has made it a useful compound for the removal of a number of contaminants from water and wastewater.

The overall goal of the study is to identify and develop a novel adsorbent for the removal of ECs of interest. The specific objectives are a) to synthesize various beta-cyclodextrin (BCD) based adsorbents by coating BCD onto different supports such as silica, filter paper, iron oxide, and zeolite, b) to perform batch and column experiments using the developed adsorbents, c) to evaluate the performance of the adsorbents in different water matrices such as MQ water, simulated wastewater in presence of humic acid, and real municipal wastewater, d) to study the regeneration potential of the adsorbents.

In this research, various (BCD) based hybrid adsorbents were synthesized and their performances were evaluated based on the removal of selected ECs. At first, chemically bonded BCD onto silica particles as hybrid adsorbents were synthesized by using crosslinking agents and copolymers. Three different methods were used to synthesize 14 different BCD coated silica adsorbents. The adsorbent prepared by reacting BCD with hexamethylene diisocyanate (HMDI) as crosslinking agent and dimethyl sulfoxide (DMSO) as solvent showed best results in removing the ECs studied. The adsorbent showed more than 95% removal of 17β-estradiol (in single component) and more than 90% of most of the estrogens (mixture of 12), more than 99% of perfluorooctanoic acid (PFOA) (in single component) and more than 90% of most of the PFCs (mixture of 10),

and a maximum of 90% removal in case of bisphenol-A (BPA). The adsorption capacity of the developed adsorbent was observed to be higher for the removal of 17β-estradiol and PFOA than that of commercially available activated carbon (F400) in MQ water. In order to represent the real environmental scenario, further batch experiments were conducted for the removal of two PFCs (PFOA and PFOS (perfluorooctane sulfonic acid)), 17β-estradiol, and BPA at environmentally relevant concentrations from wastewater. The adsorbent was effective in removing the ECs that were spiked in the secondary effluent of a municipal wastewater treatment plant.

Furthermore, the adsorbent was successfully regenerated with methanol over four cycles without significant loss in its adsorption capacity for the removal of PFOA and estrogens. Ozonation as an alternative method of regeneration was also used and the process was also very effective in regenerating the adsorbent over seven successive cycles for the removal of BPA and 17β-estradiol. The characterization of the adsorbents using FTIR, TGA, and TEM confirmed the coating of BCD onto silica particles. The TGA results showed high thermal stability of the adsorbent (upto 300^{o}C).

As an alternative to chemical impregnation, another method of synthesis was developed where various BCD based hybrid adsorbents were synthesized by physically impregnating hydroxypropyl BCD (hpBCD) polymer onto three different supports: iron oxide (Fe_3O_4), zeolite, and filter paper. The hpBCD impregnated filter papers were synthesized by solvent evaporation method and different adsorbents were synthesized by varying the polymer loadings. The polymer loading was optimized based on the performance of the modified (polymer impregnated) filter paper in terms of its filtration capacity as well as adsorption capacity to remove PFOA and BPA. The magnetic adsorbent was prepared by mixing hpBCD polymer with iron oxide particles. It was observed that by increasing the mixing time of the support (Fe_3O_4) with the polymer from 48 to 96 hr, the adsorption capacity of the adsorbent (hpBCD polymer coated Fe_3O_4) could be significantly enhanced. The same approach was also used to synthesize hpBCD polymer coated zeolite adsorbent and both adsorbents (hpBCD/zeolite and hpBCD/Fe_3O_4) were effective in removing the selected ECs from MQ water, simulated water, and wastewater.

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ABBREVIATIONS

AOPs	Advanced oxidation processes
APTES	Aminopropyl triethoxysilane
BCD	Beta-Cyclodextrin
BPA	Bisphenol-A
CDs	Cyclodextrins
CM- BCD	Carboxymethylated beta-cyclodextrin
DCDMS	Dichlorodimethylsilane
DMF	Dimethylformamide
DMSO	Dimethyl sulfoxide
ECs	Emerging contaminants
EDCs	Endocrine disrupting chemicals
EPI	Epichlorohydrin
FTIR	Fourier transform infrared spectroscopy
GPTS	Glycidoxypropyl trimethoxysilane
HMDI	Hexamethylene diisocyanate
hpBCD	Hydroxypropyl beta-cyclodextrin
HRT	Hydraulic retention time
MBRs	Membrane bioreactors
MQ	Milli-Q
NRC	National research council
PBDEs	Polybrominated diphenyl ethers
PFCs	Perfluorinated compounds
PFOA	Perfluorooctanoic acid

PFOS	Perfluorooctane sulfonic acid
PPB	Parts per billion
PPCPs	Pharmaceuticals and personal care products
PPM	Parts per million
SRT	Sludge retention time
TCA	1,1,1-trichloroethane
TEM	Transmission electron microscopy
TGA	Thermogravimetric analysis
US-EPA	United States Environmental Protection Agency

CHAPTER 1
INTRODUCTION

1.1. Background

The continued exponential growth in human population has created a corresponding increase in the demand for the Earth's limited supply of freshwater. Recent decades have brought increasing concerns for potential adverse human and ecological health effects resulting from the production, use, and disposal of numerous chemicals that offer improvements in industry, agriculture, medical treatment, and even common household conveniences (Daughton and Ternes 1999). Surprisingly, little is known about the extent of environmental occurrence, transport, and ultimate fate of many synthetic organic chemicals after their intended use, particularly hormonally active chemicals (NRC 1999), personal care products, and pharmaceuticals that are designed to stimulate a physiological response in humans, plants, and animals (Daughton and Ternes 1999; Jorgensen and Halling-Sorensen 2000). In fact, these contaminants, known as emerging contaminants (ECs), are not new to environment and have existed in the environment for as long as they have been used by various means. It has only become more evident and matter of concern in the last decade because of the introduction of sophisticated methods of analyzing with advanced tools which can be used to detect the concentration of different parameters upto parts per trillion. It suggests that our drinking water still contains some contaminants which might have deleterious effects to human health and aquatic biota.

ECs include pharmaceuticals and personal care products (PPCPs), endocrine disrupting chemicals (EDCs), polybrominated flame retardants (PBDEs), perfluorinated compounds (PFCs), nanomaterials, organisms and nonliving pathogens. PPCPs represent a category of emerging pollutants that are released in the environment through personal activities. Small but cumulative usage of these products by a large number of individuals results in widespread but significant pollution, which is difficult to control. The primary route of pharmaceuticals into the environment is through human excretion, and to limited extent from disposition of unused or expired products, or through agricultural usage in livestock (Fent et al. 2006).

EDCs are pollutants, which interfere with the normal functioning of the endocrine system resulting in adverse effects of reproduction, development, and immune function (Vos et al. 2000). EDCs consist of many classes of chemicals including natural and synthetic hormones and other pharmaceuticals, pesticides, plasticizers, and organometallic compounds.

PBDEs are a group of chemicals that are used as flame retardants in a variety of polymer resins and plastics. They are found in many products such as furniture, televisions, stereos, computers, carpets, and curtains, which are used in homes and businesses. Because of their persistence in the environment, they are ubiquitous, global pollutants which readily bioaccumulate in living organisms (de Wit 2002; Ueno et al. 2004; Ramu et al. 2007). PBDEs can cause neurotoxicity in mammals and can act as thyroid hormone agonists or antagonists in frogs (Veldhoen et al. 2006). PFCs, including the two most common compounds, perfluorooctane sulfonate (PFOS) and prefluorooctanoic acid (PFOA), have been used in industries for over 50 years because of their unique chemical properties such as hydrophobicity, lipophilicity, and moderate solubility. They are found in food packaging, as coatings on cookware, in paints, as surfactants, and also have many other applications. Nanoparticles constitute a very diverse range of compounds. These include those made primarily from carbon, such as the buckminsterfullerene or C60 and carbon nanotubes, to metal based spherical particles. ECs also include organisms and nonliving pathogens such as some infectious agents and invasive species (Poynton and Vulpe 2009).

Potential concerns from the environmental presence of ECs include abnormal physiological processes and reproductive impairment (Purdom 1994; Harrison et al. 1997; Jobling et al. 1998; Panter et al. 2000), increased incidences of cancer (Davis and Bradlow 1995), the development of antibiotic-resistant bacteria (Khachatourians 1998; Gilliver et al. 1999; Smith et al. 1999), and the potential increased toxicity of chemical mixtures (Sumpter and Jobling 1995). For many substances, the potential effects on humans and aquatic ecosystems are not clearly understood (Daughton and Ternes 1999; NRC 1999; Ayscough 2000).

The major issues associated with the ECs are a) nonexistence of limiting regulations, especially for new compounds, by-products, pharmaceuticals and PPCPs as related to the water and wastewater treatment industry, b) inability of conventional wastewater treatment plants to remove these compounds effectively, c) quantitation issues in detecting low concentrations of these compounds in various environmental matrices (Bolong et al. 2009).

1.2. Problem statement

The need for effective water and wastewater treatment technologies is driven by water quality as well as water quantity. There are federal and state regulations which require water to be treated to an acceptable level depending on the use. On the other hand, the water scarcity problem in certain parts of US has led to a need for effective technologies which could be used to treat wastewater for potable use. Furthermore, with growing concern over ECs, new and more stringent regulations are likely to be introduced in near future. It would enforce the users, who are currently using conventional technologies, to adopt new technologies or make changes to existing technologies in order to comply with the new regulations. Therefore, advanced treatment technologies are required to remove such contaminants from water and wastewater. Moreover, in arid and semiarid areas where water resources are limited and potable water must be imported at great expense, such advanced technologies are important for reuse of wastewater. Though a number of treatment technologies such as carbon adsorption and chemical oxidation processes have been used to remove the trace organics from water and wastewater, these technologies have their own limitations. Carbon adsorption technology is associated with high usage rate depending on the water matrices which increases the cost of water treatment due to frequent replacement of carbon filters (Sutherland et al. 2004). Therefore, this technology produces waste that needs to be disposed of adding more cost of treating water. On the other hand, chemical oxidation processes such as ozonation is associated with toxic by-products formation such as bromate in treated water (Zimmermann et al. 2011; Gerrity et al. 2011).

The proposed research provides solutions to these limitations by first removing the contaminants efficiently from water and then regenerating the used adsorbent with ozone in order to reuse the adsorbent. The ozone used during regeneration destroys the adsorbed contaminants thereby making the adsorbent reusable. Therefore, there is no waste generated and no issue of presence of toxic by-products in treated water as the regeneration is done offline and using small volume of regeneration water.

1.3. Research Objectives

The broad objective of this project is to identify and develop novel adsorbents for the removal of ECs of interest. The specific objectives are

a. Synthesis of BCD based adsorbents:
   i. Synthesis and optimization of coating of BCD polymer onto silica particles
   ii. Synthesis of magnetic adsorbent by impregnating hpBCD polymer onto iron oxides (Fe_3O_4)
   iii. Synthesis of high surface area adsorbent by impregnating hpBCD polymer onto Zeolites
   iv. Synthesis of hpBCD polymer impregnated filter papers

b. Perform batch and column experiments using the developed adsorbent material.

c. Evaluate the performance of the adsorbents in different water matrices such as Milli-Q (MQ) water, simulated wastewater in presence of humic acid, and real municipal wastewater.

d. Comparative study on the efficiency of the developed adsorbents for the removal of target ECs with that of Granular Activated Carbon (GAC) F400.

e. Characterize the developed adsorbents using appropriate techniques such as surface area and porosity analyzer, TGA, FTIR, and TEM/SEM

f. Study the regeneration potential of the adsorbents using methanol and ozone

1.4. Scope and organization of dissertation

Chapter 1 of the dissertation presents a brief background, problem statement, and research objectives. The relevant literature is reviewed in Chapter 2 that provides detailed information on the current issues with ECs, treatment technologies available for ECs, introduction on CDs and their applications in removing various environmental pollutants. Since the focus of the work is on estrogens, BPA, and PFCs, a brief overview on these selected ECs is provided.

In Chapter 3 and 4, synthesis and applications of BCD coated silica (BCD/Silica) adsorbents are discussed. The results described in the Chapter 3 are from the published paper in *Journal of Hazardous Materials* (Bhattarai et al. 2014). This Chapter particularly focuses on the experimental conditions to synthesize various BCD/Silica adsorbents, selection of best adsorbent and further optimization of the polymer loadings onto silica. This chapter also provides information on some preliminary tests done to evaluate the performance of the adsorbents with selected ECs, regeneration studies with methanol, and different characterization techniques used to understand and confirm the coating mechanisms.

Chapter 4 describes the continuation of the application of the best adsorbent selected in Chapter 3 by conducting further experiments with ECs in single component vs in mixture, performance evaluation of adsorbent in removing selected ECs in MQ water, simulated wastewater in presence of HA, and real wastewater. This chapter also discusses an alternative regeneration approach to the methanol (used in Chapter 3) by using ozone to destroy the adsorbed contaminants.

In Chapter 5, various adsorbents were synthesized by physically impregnating hpBCD polymer onto Fe3O4 (magnetic adsorbent), zeolite, and filter paper. The synthesis techniques and application of these adsorbents to remove selected ECs are discussed. The overall findings are summarized in chapter 6 along with suggestions for future work.

CHAPTER 2
LITERATURE REVIEW

2.1. Emerging Contaminants (ECs)

Over the last few decades, the occurrence and frequent detection of ECs in the environment and wastewater effluents have become a serious issue worldwide. ECs are also known as chemicals of emerging concern (CECs) or trace organic compounds (TrOCs) or micropollutants, etc. ECs include pharmaceuticals and personal care products (PPCPs), polybrominated flame retardants (PBDEs), perfluorinated compounds (PFCs), nanomaterials, organisms and nonliving pathogens. PPCPs represent a category of emerging pollutants that are released in the environment through personal activities. Many ECs are endocrine disrupting chemicals (EDCs). EDCs such as BPA and phthalates originate largely from industrial production and product consumption (Fromme et al. 2002; Ying et al. 2002a; Ying et al. 2002b), where as steroid hormones are mostly excretd by humans and animals (Ternes et al. 1999; Andersen et al. 2003). In conventional wastewater treatment system, the removal of ECs, coming from diverse sources, is due to sorption onto suspended solids and sediments, direct and indirect photolysis, volatilization and aerobic degradation (Pal et al. 2010). However, the fate of the chemicals in the aquatic environment is mainly determined by biodegradability of ECs and their propensity (partition coefficients) to get adsorbed onto activated sludge (Venkatesan and Halden 2014). The estimated annual biosolids loads of the most abundant chemicals detected in excess of 1000 µg/kfg-dw (ppm) are shown in Figure 2.1.

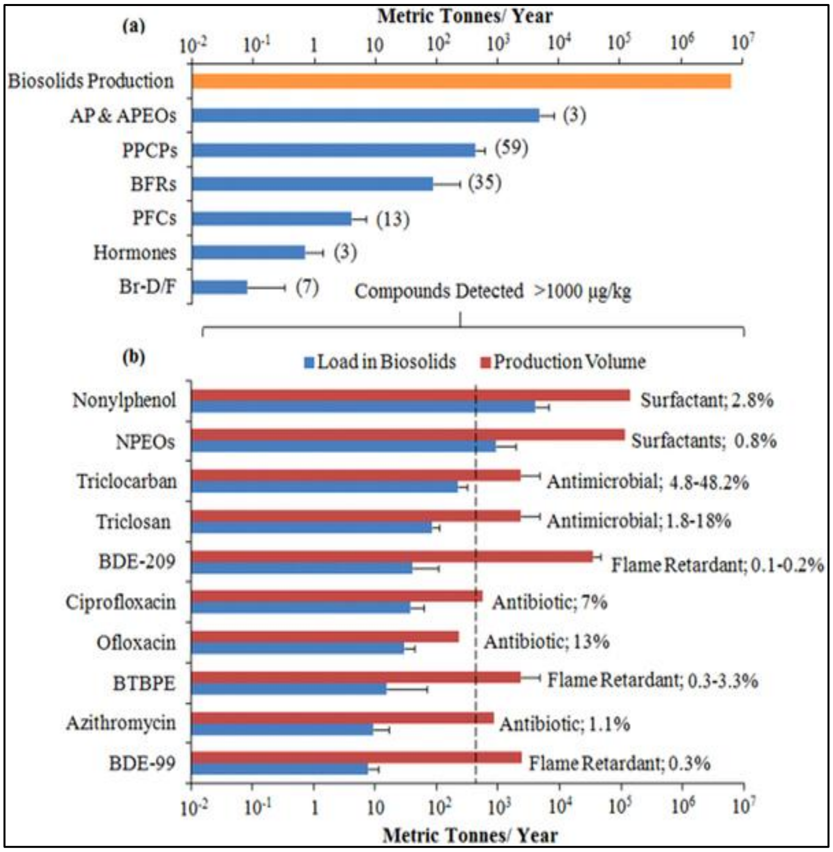


Figure 2.1. (a) Annual mass of US biosolids and of ECs sequestered in biosolids following municipal WW treatment (b) occurrence in biosolids of chemicals detected in excess of 1000 µg/kg-dw and their corresponding annual US production volumes (Venkatesan and Halden 2014)

2.1.1. Estrogen hormones

Various natural estrogens such as estrone, estradiol, and estriol are derived from cholesterol and commonly found in excreta of humans and animals. Other steroid hormones include testosterone and progesterone which are manufactured by a mammal body. There are several non-steroidal chemicals synthetically manufactured which can interact with estrogen receptors such as ethinylestradiol, mestranol, diethyl-stilbestrol (Schafer et al. 2010). These natural as well as synthetic estrogens have been reported in the effluents of wastewater treatment plants (Larsson et al. 1999; Chimchirian et al.

2007). Many of these estrogen hormones were observed to be present in surface water of suburban, agricultural and mixed use areas (Velicu and Suri 2009).

Researchers have observed significant concentrations of estrogen hormones in the natural environment. The presence of estrogen hormones in 21 surface water streams located in Eastern Pennsylvania was studied. All the streams sampled showed the presence of at least one hormone compound. Estrone was detected very frequently with concentrations ranging from 0.6 – 2.6 ng/L. Estriol was detected in very high concentrations of 19.7 ng/L (Velicu and Suri 2009).

Many of these estrogens are used as oral contraceptives, management of menopausal and postmenopausal syndrome, and physiological replacement therapy in deficiency states. Some of the estrogen sources are discussed in Table 2.1. The detail structures and properties of estrogens are mentioned in Appendix A.

Table 2.1 Levels of estrogens excreted in μg/day by men and women (Ying et al. 2002b)

Category	17β-estradiol	Estrone	Estriol	17α-ethinylestradiol
Men	1.6	3.9	1.5	-
Menstruating females	3.5	8	4.8	-
Menopausal females	2.3	4	1	-
Pregnant women	259	600	6000	-
Women	-	-	-	35

A major difficulty in removing such contaminants is not only the small concentration in which they occur and are physiologically active, but also their small size or molecular weight. The molecular weight of the hormones is very similar, varying between 268 and 315 g/mol. The hormones that have a phenolic hydroxyl group, dissociate in the same pH range between 10.2 and 10.5 (Appendix A). The log Kow parameter measures the hydrophobicity of the hormones by partitioning between octanol and water. In general, compounds with log Kow>2.5 are expected to accumulate in solid phases instead of being soluble in the aqueous phase. Therefore, these hormones are expected to interact with adsorbents by hydrophobic interactions (Schafer et al. 2010).

2.1.2. Bisphenol-A

Bisphenol A (BPA), which is considered as one of the endocrine disruptors, has less estrogenic effects toward aquatic organisms than natural hormones. However, it has been reported to be able to induce feminization phenomena in various species of animals (Lindholst et al. 2000; Metcalfe et al. 2001). BPA in 1996 was estimated to be 1.62 X 10^9 kg and was primarily produced in three regions: the U.S. (48%), Western Europe (32%), and Japan (20%) (SRI 1998). Most of the BPA produced is used as an intermediate in the production of polycarbonate and expoxy resins, flame retardants, and other specialty products (Staples et al. 2000). During drinking-water production and transport, BPA migration from plastic to water can represent a significant source of human exposure to this micropollutant (Deborde et al. 2008).

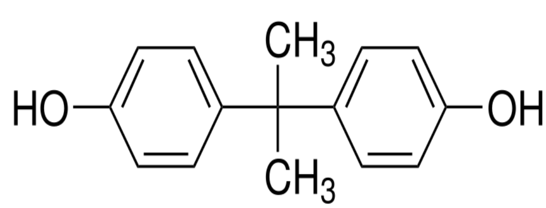


Figure 2.2. Structure of Bisphenol A

Although BPA is detected with a high frequency in surface waters (Kolpin et al. 2002; Stackelberg et al. 2004), its concentration is often lower than the predicted "no effect concentration" of 64 µg/L (Staples et al. 2000; Heemken et al. 2001) because of efficient degradation by microorganisms (Klecka 2001; West et al. 2001). Some physical and chemical properties of BPA are discussed in Table 2.2.

Table 2.2 Physico-chemical properties of Bishpenol A at 25 ^{o}C (Staples 1998)

Parameters	**Value**
Molar mass	228.29 g/mol
Melting point	155 ^{o}C
Water solubility	300 g/m^3
Vapor pressure	5.3 X 10^{-6} Pa
Log K_{ow}	3.40
Henry's law constant	4.03 X 10^{-6} $Pa.m^3/mol$
pKa	9.59-11.30

2.1.3. Perfluorochemicals (PFCs)

PFCs in general consist of carbon chain with different numbers of carbon along with one functional group at the end. The functional groups provide hydrophilic property where as the perfluorinated tails provide the hydrophobic property depending on the chain length. PFCs are persistent, bioaccumulative, and toxic to mammals (Biegel et al. 2001; Butebhoff J 2002). These compounds are believed to be distributed globally in humans (Hansen et al. 2001) as well as wildlife (Kannan et al. 2002). Perfluorooctanoic acid (PFOA) and Perfluorooctane sulfonate (PFOS) are the most common members of PFCs. Eight PFCs were reported in 16 Great Lakes water samples in U.S. (Boulanger et al. 2004) and many surface water in different cities of Japan were also reported to be contaminated by PFOA and PFOS (Saito N 2004).

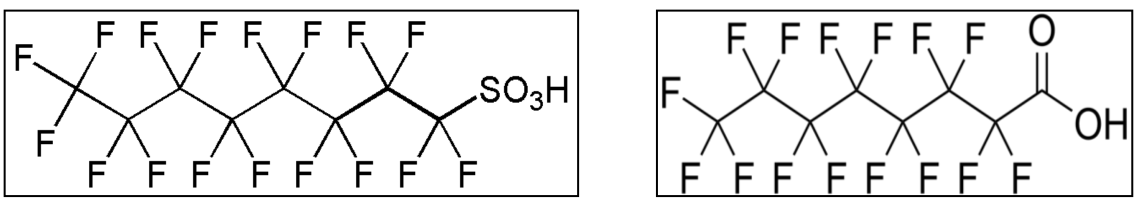


Figure 2.3 Structure of PFOS (left) and PFOA (right)

PFOA and PFOS have eight carbons in the chain and with carboxylic and sulphonic functional groups, respectively. These functional groups can affiliate with water and make PFCs hydrophilic. Different hydrophilic moiety showed diverse behavior in aqueous environment. The perfluorinated tail is covered by the strongest C-F bonds, and surrounded by fluorine atoms which have similar size with carbon atom. This kind of structure protects PFC molecules from breaking down by oxidants such as ·OH radicals. The longer is carbon chain length, the more strongly hydrophobic is PFC molecule. Combination of hydrophobic and hydrophilic moieties, and high stability under extremely thermal and oxidative conditions, make PFCs perfect surfactants which can be applied in extremely critical conditions.

2.2. Treatment technologies

2.2.1. Adsorption

Adsorption is a commonly used technology for the removal of ECs. Although a large number of adsorbents have been reported in the literature such as zeolites (Rossner et al. 2009; Grieco and Ramarao 2013), carbon nanotubes (Joseph et al. 2011; Heo et al. 2012), and magnetic hybrid adsorbents (Ghosh et al. 2013; Huang and Keller 2013), carbon is the most common adsorbent that has been used for the treatment processes due to its low cost and availability. Activated carbon adsorption system is advantageous in terms of its hydrophobic interactions in eliminating most organic compounds, especially nonpolar compounds (compounds with Kow>2) (Ying et al. 2004). This process can be affected by the properties of both adsorbate (Kow, pKa, molecular size, aromaticity versus aliphaticity, and presence of specific functional groups) and adsorbent (surface area, pore size and texture, surface chemistry, and mineral matter content) (Kovalova et al. 2013). With granular activated carbon (GAC) and powedered activated carbon (PAC), more than 90 percent removal of estrogens was observed by Snyder et al. (2007). However, the authors reported a significant reduction in the adsorption capacity of the carbon in removing the estrogens. Such a fouling effect was also observed for the removal of estrone and 17β-estradiol with GAC (Fukuhara et al. 2006) and for the removal of PFOA and PFOS with PAC (Yu et al. 2012).

Bautista-Toledo (2005) studied the removal of BPA from aqueous solution using two commercial activated carbons. They observed that the adsorption capacity of the carbons was dependent on the nature of the carbon surface as well as the solution pH. The most favorable adsorption was observed when the net charge density of the carbon was zero and the BPA was in molecular form. Successful removal of BPA and 17α-ethinyl estradiol with PAC was also observed by Joseph et al. (2011).

2.2.2. Biological treatment

Johnson and Sumpter (2001) reported that the essential sewage treatment system such as activated sludge and biological trickling filters can rapidly convert aqueous organic compounds into biomass that is then separated from the aqueous phase by settlement (clarifiers). Despite its remarkable achievement, unfortunately, not all compounds such as steroid estrogens are completely broken down or converted to biomass. Additionally, although best available technology is adopted, biological treatment removes only a part of a wide range of emerging contaminants, particularly polar ones which are discharged via the final effluent (Petrovic et al. 2003).

Biodegradation processes such as in the trickling filter case studied in Canada (Servos et al. 2005) and Brazil (Ternes et al. 1999) were found to be ineffective to remove estrogens due to their low sludge retention time (SRT) and hydraulic retention time (HRT) properties. Therefore, in order to improve the efficiency of biological treatment, it is important to have longer HRT and SRT, which could increase the extent of the removal of the compounds (Bolong et al. 2009). Membrane bioreactors (MBRs) are considered an alternative to conventional treatment due to the additional features such as (i) they act as a complete barrier to solids onto which many EDCs are adsorbed; (ii) the membrane surface also retains the EDCs; (iii) the longer STR in MBRs may facilitate additional biological transformation of these compounds since bacteria have more time to break down their structure (Spring et al. 2007).

2.2.3. Ozone and advanced oxidation processes

In water treatment processes, ozone is often used as a disinfectant and oxidizer. Oxidation with ozone is effective in degrading EDCs/PPCPs in low dissolved organic carbon (DOC) as DOC has strong influence on the application of the ozonation process (Huber et al. 2005). Ozone reacts with ECs either directly as molecular ozone (O_3) or through the fromation of hydroxyl radicals ($^{\cdot}OH$), which is stronger and less selective than O_3. In AOPs, $^{\cdot}OH$ radicals are generated by the combination of different processes such as O_3/H_2O_2, UV/H_2O_2, and UV/O_3. Both ozonation as well as advanced oxidation processes (AOPs) have been demonstrated to be promising technologies for the treatment of ECs in wastewaters (Esplugas et al. 2007; Bobu et al. 2006; Hollender et al. 2009). Experiments done in pure water showed 100% removal of 17β-estradiol, 17α-ethinylestrdiol, and BPA at initial concentration of 100 nmol/L and ozone dosage of 1.5 mg/L (Alum et al. 2004). Similar results were also observed by Kim et al. (2004) where 99% removal of 17β-estradiol was achieved using ozone dose of 5 mg/L in 15 min or ozone dose of 15 mg/L in 4 min. Huber et al (2003) reported oxidation of 17α-ethinylestrdiol with ozone in MQ water and the by-products of the reaction were idenitified. The ozone doses were varied from 0.5 to 10 mg/L and the estrogenic activity was observed to be removed due to the ozonation. The reduction of the estrogenicity of the treated water was attributed to the cleavage of the phenolic moiety. Efficient degradation of 17β-estradiol and BPA due to ozoantion was also obsercved by Irmak et al. (2005). Ozone and AOPs in general would be expected to be particularly effective in degrading EDC/PPCPs in low DOC matrices such as groundwaters or tertiary treated effluents. Chen et al. (2006a) reported that the combination of UV/H_2O_2 was able to improve the degradation of BPA in MQ water than the UV alone. The degradation of 17β-estradiol, 17α-ethinylestrdiol, and BPA with UV/H_2O_2 was also observed by Rosenfeldt and Linden (2004) where addition of H_2O_2 was observed to enhance the degradation of the contaminants than H_2O_2 alone.

2.2.4. Other treatment processes

In wastewater treatment processes, membrane technology is getting very popular to remove various types of organic as well as dissolved contaminants (Bolong et al. 2009; Snyder et al. 2007). The membrane technology is effective for most of the ECs that range from 150 to 500 Daltons in molecular size. Such contaminants could be removed effectively by reverse osmosis (RO) and tight nanofiltration (NF), but not by ultrafiltration (UF) (Snyder et al. 2007). Schafer et al (2003) reported removal of estrone using NF and RO in aqeous system. The effectiveness of the process was dependent on both size exclusion and adsorptive effects. The deprotonation of estrone resulted in lower retention which was due to the electrostatic repulsion between the negatively charged estrone and the negatively charged membrane surface. Such an effect was also observed by Yoon et al (2002) for the removal of perchlorate with NF and UF.

The use of the combined system for the removal of pharmaceutical compounds such as O_3/activated carbon (Nakada et al. 2007; Sanchez-Polo et al. 2008), ultrasound coupled with H_2O_2 (Flores-Escribano 2007), photo-fenton combined with TiO_2 and MF/RO followed by UV/peroxide (Scruggs 2004) has been effective due to the increased removal efficiency and the reduction in the toxicity of the oxidation by-products (Caliman and Gavrilescu 2009). UV/Fenton reagent is another AOP employed for achieving the oxidation of EDCs in waters. Homogeneous oxidation with Fenton reagent takes place in the system containing ferrous or ferric ions and hydrogen peroxide by free radical chain reactions that produces $^{\cdot}OH$ radicals. The prodcution of $^{\cdot}OH$ radicals is dependent on the solution pH and the ratio of iron and oxidant within the system. The efficiency of the process could be enhanced by the presence of UV light since more $^{\bullet}OH$ radicals are yielded in the system compared to the dark process (Klavarioti et al. 2008). Sonochemical treatment of waters and wastewaters is based on the use of ultrasound at low to medium frequency (20–1000 kHz) and high energy to catalyze the destruction of organic pollutants. Propagation of a pressure wave in aqueous solution results in the occurrence of cavitation phenomenon such as nucleation, growth and collapse of bubbles in the liquid. The last induces localized supercritical conditions, high temperature and pressure electrical discharge and plasma effects. The consequences of these extreme conditions are the cleavage of oxygen and water molecules to produce active species, such as $H^{\bullet}$ and $^{\bullet}OH$ radicals that attack the pollutant molecules present in waters (Augugliaro 2006). The heterogeneous photocatalytic oxidation process consists of illumination of particles of semiconducting materials, such as titanium dioxide, with light energy higher than their band gap energy resulting in the appearance of excited high energy states (electron and holes pairs) that can migrate to the surface of the particles and initiate a wide range of redox reactions (Hoffmann 1995).

2.3. Cyclodextrins

2.3.1. Introduction

Cyclodextrins (CDs) are torus-shaped cyclic oligosaccharides containing six to twelve glucose units. The CD molecules are natural macrocyclic polymers, formed by the action of an enzyme on starch. Although CDs containing as many as twelve glucose units were identified, only the first three homologues were studied in details. The three smallest CDs, α-cyclodextrin, β-cyclodextrin and γ-cyclodextrin which consists of six, seven and eight a-1,4 linked D(C)-glucopyranose units respectively are well known and are available commercially. The most characteristic feature of cyclodextrins is the ability to form inclusion compounds with various molecules, especially aromatics: the interior cavity of the molecule provides a relatively hydrophobic environment into which an apolar pollutant can be trapped (Crini 2005). CDs possess a well-defined geometry. The structure and the molecular dimensions of alpha-, beta-, and gamma-cyclodextrin are shown in Figure 2.4. As a consequence of the C-1 conformation of glucopyranose units (Hedges 1998; Schneiderman and Stalcup 2000), all secondary hydroxyl groups are situated on one of the two edges of the toroidal ring CD molecule, while all primary hydroxyl groups are on the other side.

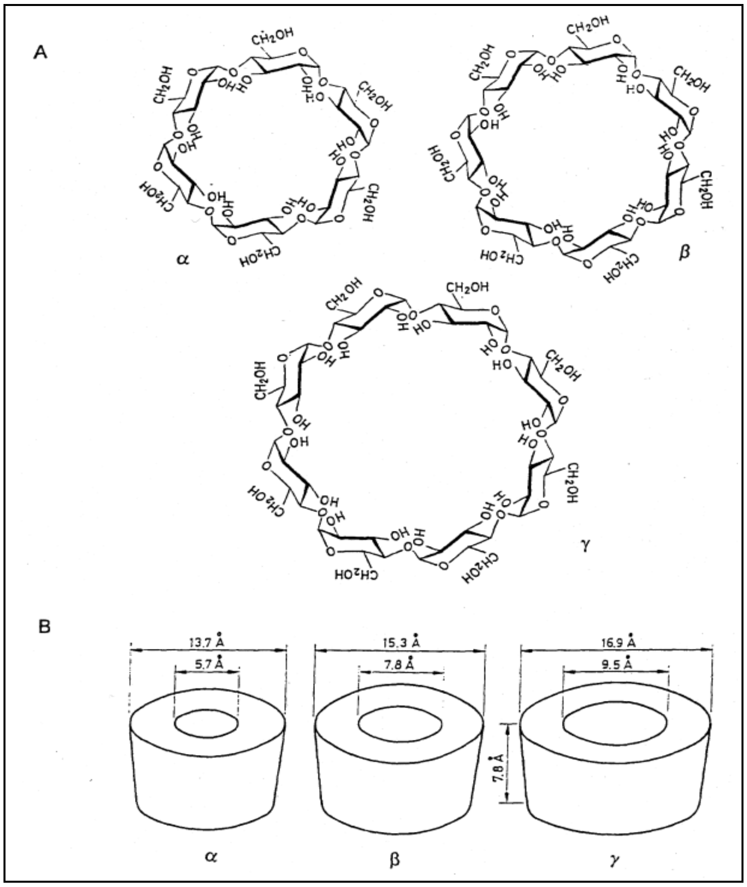


Figure 2.4 a) The three smallest CDs b) their dimensions [Szejtli 1988]

The primary hydroxyl groups attached to C-6 of the glucose unit form a smaller opening. Thus, the CD molecule is shaped like a truncated cone with the secondary hydroxyl side more open than the primary hydroxyl side. While the primary hydroxyl groups can freely rotate to partially block the cavity, the secondary hydroxyl groups are held relatively rigidly (Crini and Morcellet 2002). The interior of the cavity is lined by a ring of hydrogen atoms bonded to the C-5 atom, a ring of glycosidic oxygen atoms, and another ring of hydrogen atoms at position C-3 (Figure 2.5). As a result, the inside of the cavity is relatively hydrophobic (apolar cavity) compared to water. The glycosidic oxygen bridges produce a high electron density (a Lewis character). Since all of the hydroxyl groups are on the outside of the molecule, the external faces are hydrophilic.

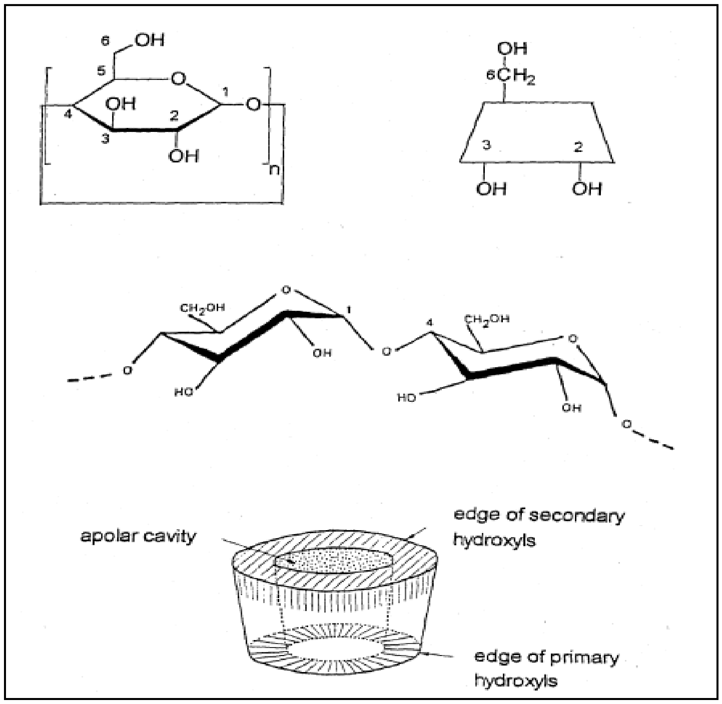


Figure 2.5. Structure of each glucose unit showing primary and secondary hydroxyl groups

The shape of the molecule is stabilized by hydrogen bonds between the secondary hydroxyl groups of adjacent D-glucopyranosyl residues. All these features enable CDs to form inclusion complexes with other molecules. Several important physical and chemical properties (Bender 1978; Szejtli 1982; Duchene 1991) of the three most commonly used CDs are listed in Table 2.3. CDs are soluble in water, and the solubility increases with increasing temperature. BCD has the lowest solubility of all native CDs. The CD solubility decreases in the presence of organic solvents. The α- and BCD are insoluble in methanol, ethanol, isopropanol, acetone, chloroform, and tetrahydrofuran. Dimethylformamide is a good solvent for α- and BCD.

Table 2.3 Chemical and physical properties of the cyclodextrins (Bender 1978; Duchene 1991)

Cyclodextrin	**Number of glucose units**	**Molecular wt. (anhydrous)**	**Cavity diameter, A^o / Cavity Volume, A^{o3}**	**pKa (25^oC)**	**Solubility in water, g/100 ml at 25^oC**
Alpha	6	972	5.7 / 174	12.33	14.5
Beta	7	1135	7.8 / 262	12.20	1.85
Gamma	8	1297	9.5 / 427	12.08	12.08

In order to extend the field of application of native CDs, some modified and derivatized CDs were prepared. The chemical reactivity and the polyfunctionality of the CDs allow preparation of some derivatives whose properties differ from those of the native CDs. The hydroxyl groups at position 2, 3, and 6 in the glucose unit are available for structural modifications without destruction of the cavity. For example, the BCD molecules contain 21 hydroxyl groups, which can be modified chemically (Khan et al. 1998). The C6-OH groups are the more reactive, and the C3-OH the less reactive in given experimental conditions (Bender 1978; Szejtli 1982). This allows the preparation of several groups of CD derivatives by various groups (amino, alkyl, alkoxy, phosphate, sulfonate, tosylate, imidazolyl, ammonium) (Croft and Bartsch 1983). These substitutions and modifications give a number of dimers, polymers, and copolymers in the form of powders, gels, resins, or beads (Bender 1978; Croft and Bartsch 1983; Saenger 1980) and with different solubility.

2.3.2. Inclusion properties

Inclusion complexes are chemical species consisting of two or more associated molecules in which one of the molecules, the host, can admit a guest component into its cavity, resulting in a stable encapsulation without formation of any covalent bonds (Croft and Bartsch 1983; Saenger 1980; Clarke et al. 1988). The structure of CD molecules gives rise to the remarkable ability to form inclusion complexes with inorganic (Bender 1978; Szejtli 1982), organic (benzene and phenol derivatives, amino acids, barbiturates, prostaglandins, pesticides, glycolipids, proteins, tryptophan) (Croft and Bartsch 1983; Mu et al. 2001; Liu et al. 2001) and ionic compounds (Bender 1978; Szejtli 1982), and also with polymers (Hacket et al. 1997; Okumura et al. 2000). The data in the literature (Bender 1978; Szejtli 1982; Croft and Bartsch 1983; Shieh and Hedges 1996) show that several factors play a role in the inclusion complex formation and several interactions were found: a) hydrophobic effects, which induce the apolar group of a molecule to preferentially enter the CD cavity; b) Van der Waals interactions (these interactions involve interactions between permanent and induced dipoles and London dispersion forces); c) hydrogen bonding between the guest molecule and the secondary hydroxyl groups at the rim of the cavity (these contributions increase with polar molecules); d) steric effect, the inclusion process is also influenced by shape, size and polarity of guest molecules; e) solvent effects (release of high-energy water) (Crini and Morcellet 2002).

The formation of an inclusion complex greatly affects the physical chemical properties of the guest; therefore, CDs are used in a number of branches of industry (Hedges 1998). They are used in the pharmaceutical industry to improve the solubility and stability of pharmaceuticals (Loftssona and Jarvinen 1999), as carriers of active substances (Uekama et al. 1994) in biological systems and to retard the release of active substances from the pharmaceutical matrix. The application of CD in research and the preparation of medicinal substances in the pharmaceutical industry has also been summarized in various reviews (Loftssona and Jarvinen 1999; Uekama et al. 1994; Stella and Rajewski 1997; Zhang and Rees 1999). CD have also been used in the food industry (Luong et al. 1997), in the chemical industry to catalyze hydrolytic and oxidation reactions (Chen and Pardue 1993) and in enzymatic processes (Breslow and Dong 1998), in the clothing industry to stabilize the colours of clothing, and in the tobacco and cosmetic industries. CD and their ability to form inclusion complexes are also utilized in agricultural applications (Szejtli 1982).

2.3.3. Literature review on application of CDs to remove environmental pollutants

2.3.3.1. Synthesis and applications of CD bonded to silica as adsorbents

The possibility of the application of cyclodextrin for reducing pollutants in wastewater has long been recognized (Szejtli 1988). Water-insoluble CD derivatives like crosslinked CD polymers (Klein 1997) or CDs immobilized on water-insoluble support (Crini et al. 1998; Martel et al. 2000) can be used for this purpose because of the property of CD to form inclusion complexes with various organic pollutants. Phan et al. (2002) designed two series of supports obtained with a methacryloyl-β-cyclodextrin derivative grafted or coated onto silica to test their ability to sorb aromatic pollutants (para nitro phenol, penta choloro phenol and 2,4-dichlorophenoxy acetic acid) in aqueous solutions. In kinetics studies, the equilibrium adsorption in all cases reached very quickly in approximately 30 mins. Liu et al. (2004) prepared a novel mesoporous organosilica containing microprous BCD for the removal of humic acid from water. The BCD was covalently attached to the mesoporous silica by co-polymerization of a silylated BCD monomer with tetraethoxysilane in the presence of a structure-directing template. It was observed that higher loading of BCD onto slica particles could block the pores of mesoporous silica resulting in lower removal efficiency of humic acid from water.

The application of CD bonded to silica (CDS) was further explored by Faraji (2005) by preparing BCD bonded silica stationary phase as a sorbent for solid-phase extraction (SPE) of selected phenolic compounds. The ability of the CDS for the extraction of a mixture of five phenolic compounds including phenol, 2,4-dimethyl phenol, 4-nitrophenol, 3-chlorophenol and 4-methyl phenol were used as model compounds. The capacity of CDS for retaining phenolic compounds were 50-125 mg g^{-1}, while for phenol was 30 mg g^{-1}.

2.3.3.2. Synthesis and application of CD polymers as adsorbents

Yamasaki et al. (2006) studied the removal of phenolic compounds from a raw industrial wastewater from phenolic resin processing using different CD polymers as adsorbents. A series of adsorbents were prepared by varying the combination of α-CD, β-CD, γ-CD, mix-CD (α-CD:β-CD:γ-CD:dextrin = 30:10:10:50 wt/wt), the crosslinker, hexamethylene diisocyanate (HMDI) or toluene-2,6-diisocyanate, and their molar ratio in the reaction batch. The removal of the phenolic compounds from raw industrial wastewater was an instantaneous process and was completed within about 5 min. The higest removal efficiencies were observed in case of polymers synthesized by crosslinking BCD and mix-CD with HMDI in a 1:8 molar ratio. Similar results were also observed by Yamasaki et al. (2008) with BCD polymer beads, synthesized by crosslinking BCD with HMDi at 1:8 ratio, for the removal of phenol from raw industrial wastewater. Efficient removal of phenols with BCD polymers were also observed by BCD-EPI polymer (Pratt et al. 2010)

A new approach was used by Zhao et al. using ctric acid as a crosslinking agent to synthesize CD polymers. The objective was to replace the commonly used toxic crosslinkers (EPI and HMDI) with an environmentally friendly chemical (citric acid). Thus synthesized water-insoluble BCD polymer was able to remove phenol, methylene blue, aniline and 1-naphthylamine (Zhao et al. 2009a; Zhao et al. 2009b).

Moon et al. (2008) studied the inclusion complexes of 77 steroids with BCD-EPI polymer. Water soluble polymer was obtained when the molar ratio of BCD and EPI was less than 1:10. Therefore, water insoluble polymer (with molar ratio 1:25) was synthesized as an improved SPE sorbent for the steroids. The polymer showed good recovery of the steroids studied showing more than 90% recovery for most of the steroids. It was observed that the hydroxylated estrogens showed an excellent binding capacity (96-116% recovery) to BCD through hydrogen bonding between their phenolic hydroxyl and exterior hydroxyl groups. Successful removal of 17β-estradiol with BCD-EPI polymer was also observed by Oishi and Moriuchi (2010a). Nagy et al. (2014) used commercially available BCD polymer bead (cyclolab, Hungary) for preliminary evaluation as a sorbent for the removal of emerging micropollutants. The BCD adsorbent was combined with sand filter and the similar combination was also used with activated carbon (GAC 830 M). The combination of BCD and sand showed more than 90% removal of BPA, E2, EE2, E3 and 50% removal of cholesterol from simulated wastewater and the values were higher than that of GAC and sand. However, in case of Naproxen, BCD system showed 19% removal whereas the GAC system showed 64% removal.

Kawano et al. (2014) used water insoluble γ-CD polymers for the removal and recovery of polychlorobiphenyl (PCB) contaminants in insulating oil. The polymers were synthesized by using dibasic and dichlorides as crosslinking agents. After adsorption of PCB, acetone was used to recover the contaminant with >99.9% recovery efficiency. It was also observed that the polymer could be recycled at least 10 times for PCB adsorption without any loss in the adsorption capability. Kang et al. (2012) synthesized moleculary imprinted polymers (MIPs) using allylic bromine derived BCD (allyl-BCD) and methacrylic acid (MAA) as the functional monomers. Thus synthesized allyl-BCD-MIPs showed selective adsorption for phthalate from water and was used as selective adsorbents for the solid-phase extraction (SPE) to analyze the phthalates in cow milk.

2.3.3.3. Synthesis and applications of CD based hybrid adsorbents

Chen et al. (2006b) synthesized a novel adsorbent by grafting BCD derivative (carboxymethyl-BCD) onto chitosan for the removal of phenol, meta-cresol, and meta-catechol from industrial wastewater. The effects of pH and temperature on the adsorption capacity of the developed adsorbent were studied. It was observed that the adsorption capacity decreased rapidly as the pH was increased whereas the capacity increased with increasing temperature. Under optimized conditions (pH = 3.0 and temperature = 303 K), best results were obtained by removing 92%, 86%, and >99% of phenol, m-cresol, and m-catechol, respectively.

Arkas et al. (2006) studied the impregnation of BCD on ceramic porous filters to develop a hybrid system of appropriate mechanical strength and high surface area to remove organic pollutants from water. The hybrid filter was developed by impregnating cyclodextrin derivatives in titanium oxide porous ceramic filters. The developed filters were found to be effective in removing more than 95% polycyclic aromatic hydrocarbons and more than 80% of trihalogen methanes, monoaromatic hydrocarbons, and pesticides.

Salipira et al. (2007) synthesized cyclodextrin polyurethanes containing carbon nanotubes for the removal of organic pollutants from water. Water insoluble polymers were prepared first by functionalizing carbon nanotubes and then polymerized with BCD in the presence of HMDI. Thus obtained novel polymers removed 99% of para-nitrophenol from a 10 mg/L spiked water sample whereas granular activated carbon and native cyclodextrin polymer removed only 47 and 58%, respectively. An enhanced adsorption capacity of hybrid adsorbent by grafting BCD on the surface of multiwalled carbon nanotubes was also observed by Shao et al. (2010) for the removal of polychlorinated biphenyls (PCBs) from aqueous solutions.

Pan et al. (2011) prepared BCD/attapulgite composite as support for the selective removal of 2,4-dichlorophenol from aqueous solution. Attapulgite is a hydrated octahedral layered magnesium aluminium silicate material with siloxane groups in the bulk and silanol groups on its surface. The molecularly imprinted polymers (MIP) showed 6 to 11 times greater adsorption capacity towards 2,4-dichlorophenol than non-imprinted polymers. Also, the MIP was successfully regenerated over four cylces without significant loss in adsorption capacity.

Badruddoza et al. (2010) synthesized nano-adsorbent by surface modification of magnetic nanoparticles (Fe_3O_4) with caroxymethyl- BCD (CM-BCD) for the removal of methylene blue (MB) from aqueous solutions. The synthesized adsorbent was also effective in removing copper ions from water (Badruddoza et al. 2011) as well as selective removal of Pb^{2+}, Cd^{2+}, and Ni^{2+} from industrial wastewater (Badruddoza et al. 2013). The presence of CM-BCD was found to enhance the adsorption capacity of the developed nano-adsorbent due to strong abilities of the multiple hydroxyl and carboxyl groups in CM-BCD to adsorb metal ions. The copper ions could be successfully desorbed using citric acid solution and the regenerated adsorbent showed more or less same adsorption capacity over three successive cycles. CM-BCD coated magnetic nanoadsorbent was also synthesized by Chalasani and Vasudevan (2012) which was successful in simulatenous removal of organic pollutants (naphthalene and 2-naphthol) and inorganic pollutnat (As). In this study, no effect of entrapment of organic pollutant on the removal of As was osberved indicating that CDs provide different sites for organic pollutant (hydrophobic cavity) and complexation with metal ions (hydroxyl groups present at the rim of the cavity). Simualtaneous removal of BPA and copper ions was also observed by Wang et al. (2014) with BCD coated magnetic Fe_3O_4 nanoparticles (with poly(glycidyl) methacrylate). A modified approach was used by Yang et al. (2013) where BCD was chemically grafted onto halloysite nanotube/iron oxides showed high-efficient decontamination of U(VI) from aqueous solution.

Ghosh et al. (2013) synthesized magnetic adsorbents by grafting 6-ethlylenediamino-BCD onto thiodiglycolic acid coated Fe_3O_4 nanoparticles. The developed adsorbent successfully removed two pharmaceutically active compounds (naproxen and carbamazepine) and one endocrine disrupting compound (BPA) from water. The formation of inclusion complex of BCD and naproxen was studied by Grandelli et al. (2013) by differential scanning calorimetry in solution phase. The magnitude of the complex formation was found to be dependent upon the composition of the BCD and naproxen mixture with a maximum value of 2:1 molar ratio. Li et al. (2013a) synthesized magnetic cyclodextrin-chitosan/graphene oxide (CCGO) for the removal of chromium from water. The magnetic nanoadsorbents were synthesized by reacting carboxyl group of graphene oxide with the amine group of magnetic BCD-chitosan. The same adsorbent also showed efficient removal of hydroquinone from simulated wastewater (Li et al. 2013b). BCD modified graphene oxide was also synthesized by Song et al. (2013) for the removal of cobalt from aqueous solution.

CHAPTER 3

DEVELOPMENT OF HIGH EFFICIENCY SILICA COATED Β-CYCLODEXTRIN POLYMERIC ADSORBENT FOR THE REMOVAL OF EMERGING CONTAMINANTS OF CONCERN FROM WATER

3.1. Introduction

Cyclodextrins (CDs) are torus-shaped cyclic oligosaccharides containing six to twelve glucose units (Crini 2005). The β-Cyclodextrin (BCD) molecules contain 21 hydroxyl groups, which can be modified chemically (Khan et al. 1998). These substitutions and modifications give a number of dimers, polymers, and copolymers in the form of powders, gels, resins, or beads (Bender 1978; Croft and Bartsch 1983; Saenger 1980) with different solubility. The interior cavity of the CD molecule provides a relatively hydrophobic environment into which an apolar pollutant can be trapped (Crini 2005). It was reported earlier that CDs form inclusion complexes with inorganic compounds (Bender 1978; Szejtli 1982); organic compounds (Croft and Bartsch 1983; Mu et al. 2001; Liu et al. 2001); and with ionic compounds (Bender 1978; Szejtli 1982).

Emerging contaminants (ECs) of concern typically refer to contaminants recently detected in the environment such as pharmaceuticals, personal care products (PPCPs), polybrominated flame retardants (PBDEs), perfluorinated compounds (PFCs), nanomaterials, and others (Fent et al. 2006; Andaluri et al. 2012). Some of these ECs may cause adverse effects, for example: estrogens have been reported to cause feminization in fish (Filby et al. 2007), bisphenol-A (BPA) for hormonal effects in humans (Krishnan et al. 1993), and perfluorooctanoic acid (PFOA) for toxic effects in laboratory animals (Butenhoff et al. 2002). Though ECs have been detected at low concentrations ranging from ng/L to low µg/L in surface and ground waters, some studies have reported high concentration of ECs in industrial wastewaters and contaminated sites. For example, wastewater discharges from different industries have shown high concentration of BPA ranging from 1.0 to 125 µg/L (Fuerhacker 2003). Similarly, high concentration of PFOA of up to 105 µg/L (Moody et al. 2003), and estrogens of up to 110 µg/L (Karnjanapiboonwong et al. 2011) have been reported in the literature.

This study examines the removal of steroid hormones, PFOA, and BPA from water using BCD-based adsorbents. Adsorbents composed of water insoluble polymer coated on silica were synthesized and tested for the removal of steroid hormones, PFOA, and BPA. For the synthesis of adsorbents, two different crosslinking agents, two different copolymers, and three solvents were used in order to coat insoluble form of BCD onto silica particles. The influence of adsorbent preparation conditions such as solvent, crosslinking agents, copolymers, and ratio of adsorbent to support on the adsorption capacity was examined. The regenerability of the adsorbent was also examined in four cycles of adsorption and regeneration.

3.2. Materials and methods

3.2.1. Materials

BCD, sodium hydroxide (NaOH), dimethyl-formamide (DMF) and dimethyl sulfoxide (DMSO) were purchased from Fisher Scientific. Hexamethylene diisocyanate (HMDI), epichlorohydrin (EPI), aminopropyl triethoxysilane (APTES), glycidoxypropyl trimethoxysilane (GPTS), and silica (40X100 mesh size) were obtained from Sigma-Aldrich. BPA, PFOA, and all the steroid hormones (17α-estradiol, 17β-estradiol, 17α-dihydroequilin, 17α-ethinyl estradiol, estrone, estriol, equilin, norgestrel, medrogestone, trimegesterone, progesterone, and 3-O-methyl estrone (internal standard)) used for this study were purchased from Sigma-Aldrich.

3.2.2. Methods

3.2.2.1. Preparation of adsorbents

BCD is soluble in water. In order to prepare insoluble form of BCD polymers, it was reacted with crosslinking agents. Depending upon the type of crosslinking agents and the molar ratio of BCD to crosslinking agents, different polymers were obtained. The water insoluble polymers were obtained using a molar ratio of 1:7 with both the crosslinking agents (HMDI and EPI). This ratio was maintained for all further experiments to support BCD onto silica particles. Three different approaches were used to support BCD onto silica. In the first method, BCD was fixed on the silica with crosslinking agents HMDI and EPI. In the second method, BCD was supported on silica with copolymers GPTS and APTES. In the third method, BCD was supported on silica with both crosslinking agents and copolymers.

Different solvents such as NaOH (30% w/w), DMF or DMSO were used to dissolve β-CD. To this solution, silica was added and stirred at 60^{o}C for 15 minutes. The crosslinking agents were added to the mixture drop wise under continuous stirring and the mixture was stirred at 60°C for 4 hours. Then the mixture was transferred to the oven at 60°C for 18 hrs. The final solid adsorbent was crushed, and sieved using mesh size 18 X 35. The adsorbent was washed with MQ water, methanol and dried at 60°C for 24 hours under vacuum.

To obtain two different types of silanized silica, 80 g of silica (preheated at 140°C for 16 hours) was reacted with 150 ml of GPTS or APTES. The reaction was conducted at 70°C under continuous stirring. The obtained product was washed with toluene, acetone and methanol and dried in the oven at 120°C for 18 hrs. The silanized silica was also used as coating support and the details are listed in Table 3.1.

3.2.2.2. Batch adsorption experiments

Batch adsorption isotherm experiments were carried out in 500 ml amber glass bottles, containing 400 mL solution of EC and adsorbent. The bottles were shaken at 140 rpm on a shaker at room temperature until equilibrium was reached. The removal of ECs by the adsorbents was calculated from the differences between the concentrations of the contaminants before and after the treatment (Equation 1).

$$Removal\% = \frac{C_0 - C_e}{C_0} \times 100 \quad \text{...(1)}$$

where C_0 and C_e are the initial and equilibrium concentration of ECs in the solution (μg/L), respectively.

3.2.2.3. Analysis

All samples were analyzed on an Acquity UPLC system equipped with a Xevo TQ MS tandem mass spectrometer equipped with an electrospray ionization source (Waters Co., USA). The Acquity UPLC BEH C18 column (50 X 2.1 mm, 1.7 µm) was used for the LC separation. The column temperature was set to 40 ^oC, and the flow rate of mobile phase was 0.3 mL/min, and the injection volume was 10 µL. Steroid hormones, PFOA, and BPA were analyzed using direct injection and/or solid phase extraction (SPE).

BPA samples were analyzed by direct injection. For direct injection, 4 ml of sample was spiked with internal standard. For SPE, a 200 ml sample was passed through the Bond Elute C-18 SPE column (for estrogens) and Oasis WAX cartridge (for PFOA) at a flow rate of 5 ml/min. Before loading, the SPE cartridges were activated with 6 ml of methanol and then rinsed with 6 ml of milli-Q water. After the sample was passed through the SPE column, the column was rinsed with milli-Q water and then eluted with 6 ml of methanol. The methanol eluent was collected in a test tube (silanized glassware was used in case of estrogens) and a fixed amount of internal standard (3-O-methyl estrone for estrogens and PFOA-C18 for PFOA) was added. The eluent was completely dried in a Genevac vacuum evaporator at 45^o C and 12 mbar. To the dried sample, 1.5 ml of methanol and 1.5 ml of water were added and vortexed. Samples were then transferred into LC vials with no headspace and analyzed on the UPLC/MS/MS instrument.

3.2.2.4. Characterization of the adsorbent

Fourier transform infrared (FTIR) was recorded by using Perkin Elmer Spectrum 100FT-IR Spectrometer. The samples were scanned from 600 to 4000 cm^{-1}. A Perkin Elmer Pyris 6 TGA was used for the thermal analysis. The sample was analyzed at temperature ranging from 30 to 1000^oC with heating rate of 10^oC per minute under air atmosphere. The surface properties of the sample were analyzed by using Micromeritics ASAP 2020 surface area and porosity analyzer. The degassing temperature and time were set to 120^oC and 600 min, respectively. High-resolution transmission electron microscope (HR-TEM) analysis was carried out using a JEOL JEM-1400 and HR-TEM. The samples for HR-TEM analysis were prepared by ultrasonically dispersing the adsorbent in ethanol and then placing a drop of the suspension onto a carbon coated copper grid followed by air-drying. The working voltage of TEM was 120 kV.

3.3. Results and discussion

3.3.1. Synthesis and testing of adsorbents

To evaluate the removal of ECs, a series of adsorbents were prepared under different experimental conditions. 17β-estradiol, PFOA and BPA were chosen as model adsorbates and were tested in batch adsorption tests. Fourteen different adsorbents were synthesized following three different approaches, using different solvents, and by varying the amount of BCD and silica (Table 3.1). In the first approach, the effect of crosslinking agents on the synthesis of adsorbents was studied by keeping the amount of BCD and silica constant. The non-aqueous solvents DMSO and DMF were suitable for the crosslinking agent HMDI, however, both aqueous NaOH and non-aqueous solvents were suitable if EPI was used as crosslinking agent. Six different types of adsorbents were prepared by using the first approach, and are designated as adsorbents A1 to A6, as listed in Table 3.1. In the second approach, adsorbents were synthesized by replacing silica with silanized silica as the precursor, without using crosslinking agents. Two co-polymers (GPTS and APTES) were used for silanization of silica and the co-polymer was used to link BCD molecules with silica as presented in Scheme-2. By using silanized silica, four adsorbents (B1, B2, B3 and B4) were prepared in different solvents by varying the amount solvents and copolymers used for silanization of silica. In order to prepare silanized silica, GPTS and APTES were used as copolymers. This set of experiments provides useful information on how the adsorbent preparation (solvent, crosslinking agent copolymer, nature of silica) influences the adsorption capacity. The third set of adsorbents was prepared by using two types of silanized silica and cross linking agents. Four adsorbents (C1, C2, C3 and C4) were prepared by using HMDI and EPI as crosslinking agent in different solvents as shown in Scheme 3.

Table 3.1 Preparation and adsorption results of various adsorbents prepared at different experimental conditions [Initial concentration: 25 µg/L (17β-estradiol), 50 µg/L (PFOA), and 100 µg/L (BPA); Adsorbent dosage: 1.5 g/L; initial pH: 6.3-7.1; contact time: 48 hr; temperature: 293 K]

Adsorbent	Reactants used						Removal %		
	BCD (g)	Solvent	Silica (g)	Crosslinking agent (ml)	Silanized silica (g)		PFOA	BPA	17β-estradiol
					GPTS	APTES			
A1	2.27	DMSO	10	HMDI			98.4	89.8	91.3
A2	2.27	DMSO	10	EPI			<5	13.5	19.1
A3	2.27	DMF	10	HMDI			87.6	53.3	67.4
A4	2.27	DMF	10	EPI			98.6	86.8	71.8
A5	2.27	NaOH	10	HMDI			8.4	9.2	13.3
A6	2.27	NaOH	10	EPI			6.9	11.7	18.5
B1	3.0	DMF			10		<5	18.5	46.0
B2	3.0	DMF				10	<5	11.6	43.3
B3	3.0	NaOH			10	10	<5	31.2	12.4
B4	3.0	NaOH					<5	12.3	11.2
C1	2.27	NaOH		EPI	10		<5	23.7	46.9
C2	2.27	NaOH		EPI		10	78.7	32.7	48.4
C3	2.27	DMF		HMDI	10		98.2	61.1	68.8
C4	2.27	DMF		HMDI		10	<5	30.1	58.4

The 14 synthesized adsorbents were tested in batch adsorption experiments. The initial concentrations of 17β-estradiol, PFOA, and BPA used were 25 µg/L, 50 µg/L, and 100 µg/L, respectively. The adsorption results are summarized in Table 3.1. It was observed that some of the synthesized adsorbents were effective in significant removal of 17β-estradiol, PFOA, and BPA. No significant removal of ECs by silica alone was observed in control experiments (data not shown here). The removal efficiency of adsorbents for all the three ECs was in the order as A1 - A6 > C1 - C4 > B1 - B4. These results indicate that crosslinking agents (A and C-series) were important. Use of unsilanized silica (A-series) was better than silanized silica (C-series). Hence, use of crosslinking agents with unsilanized silica provided better adsorbents. The adsorbent A1 showed the highest overall removal of the ECs as compared to adsorbents A2 to A6. However, similar removal of PFOA and BPA with adsorbents A1 and A4 was observed.

It was observed that adsorbents synthesized using the second approach (B1 to B4) were not as efficient in removing ECs as compared to adsorbents A1-A6 and C1-C4. This may be due to low loading of BCD onto silica. To study the amount of BCD loading onto different adsorbents, adsorbents A14, B1, and C3 were characterized using TGA. The thermographs in Figure 3.1 show highest BCD loading on A14 followed by C3 and minimal loading of BCD on adsorbent B1. These results can be directly correlated with their removal efficiencies for the ECs, where A14 and B1 was the most efficient and the least efficient adsorbent, respectively. Therefore, the second methodology of adsorbent preparation was not suitable for BCD loading onto silica.

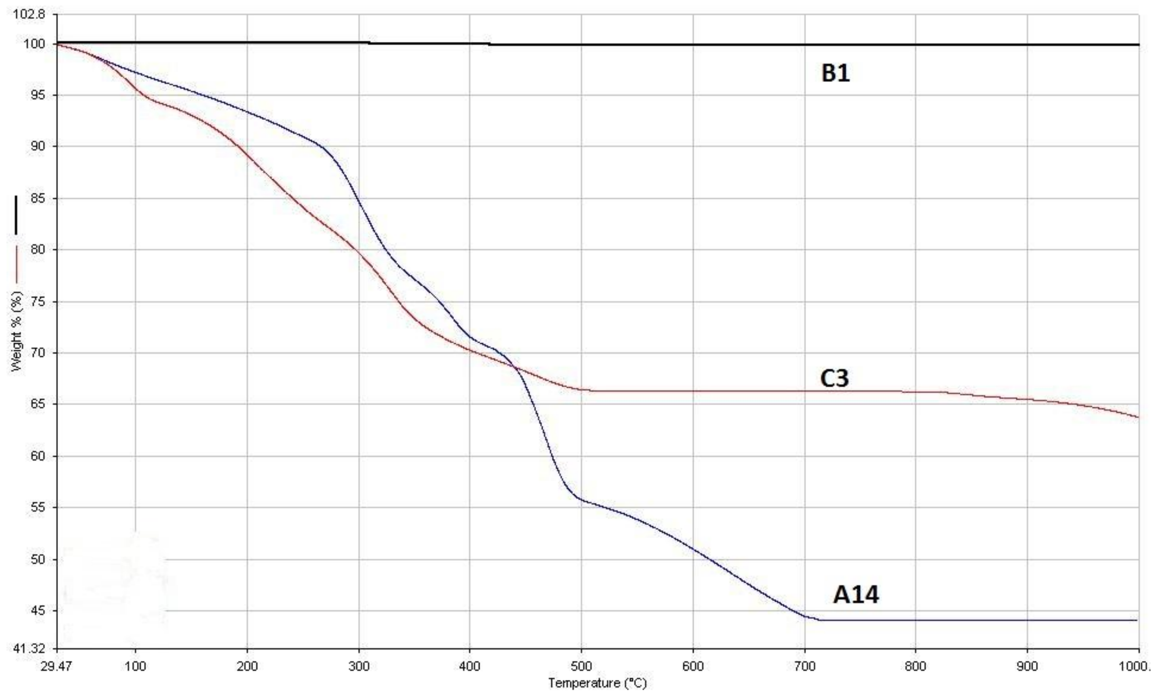


Figure 3.1 Thermographs of adsorbents B1, C3 and A14

It was observed that using HMDI as a crosslinking agent and DMSO as solvent was a better combination in developing efficient adsorbents. In order to study the effects of BCD loadings, different adsorbents were synthesized by varying the loading of BCD on silica and using the above mentioned combination of solvent and crosslinking agent. Four different adsorbents (A11 to A14) were synthesized using BCD theoretical loading of 0.15, 0.23, 0.5, and 0.76 g/g by varying the amount of silica used whereas the molar ratio of BCD and HMDI was kept constant (Table 3.2). These synthesized adsorbents were tested for the removal of ECs in triplicates, and the data is shown in Figure 3.2.

Table 3.2 Experimental conditions for the synthesis of adsorbents with different BCD loading

Adsorbent	BCD (g)	Silica (g)	BCD/Silica (g/g)	Solvent	Crosslinking agent
A11	2.27	15	0.15	DMSO	HMDI
A12	2.27	10	0.23	DMSO	HMDI
A13	2.27	4.5	0.5	DMSO	HMDI
A14	2.27	3.0	0.76	DMSO	HMDI

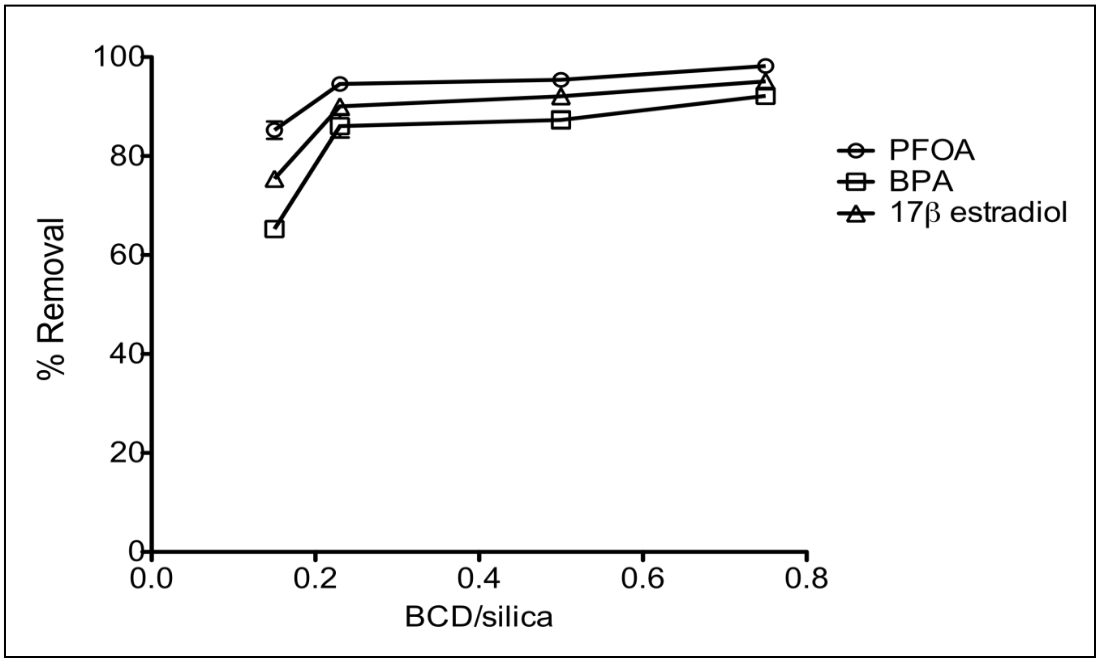


Figure 3.2. Removal of PFOA, BPA and 17β-estradiol with adsorbents of different BCD loading (data shown are triplicates with standard deviation) [Initial concentration: 25 µg/L (17β-estradiol), 50 µg/L (PFOA), and 100 µg/L (BPA); Adsorbent dosage: 1.5 g/L; initial pH: 6.1-6.8; contact time: 48 hr]

The removal of the ECs can be attributed to the amount of BCD loading on silica, as higher loading of BCD showed higher removal of the ECs. A significant difference in EC removal was observed when the BCD loading was increased from 0.15 to 0.23 g/g. Further increase in BCD loading from 0.23 to 0.76 g/g showed only slight increase in the removal of the ECs. So, it appears that BCD loading of 0.23 g/g would be a recommended loading for the effective removal of the ECs studied. The amount of BCD loading on the adsorbent was also examined by TGA analysis. As shown in Figure 3.3, the adsorbent decomposition percentage increases as the BCD loading increases from 0.15 to 0.76 g/g. The TGA results confirmed that the BCD loading on the adsorbents was in the order A14 > A13 > A12 > A11.

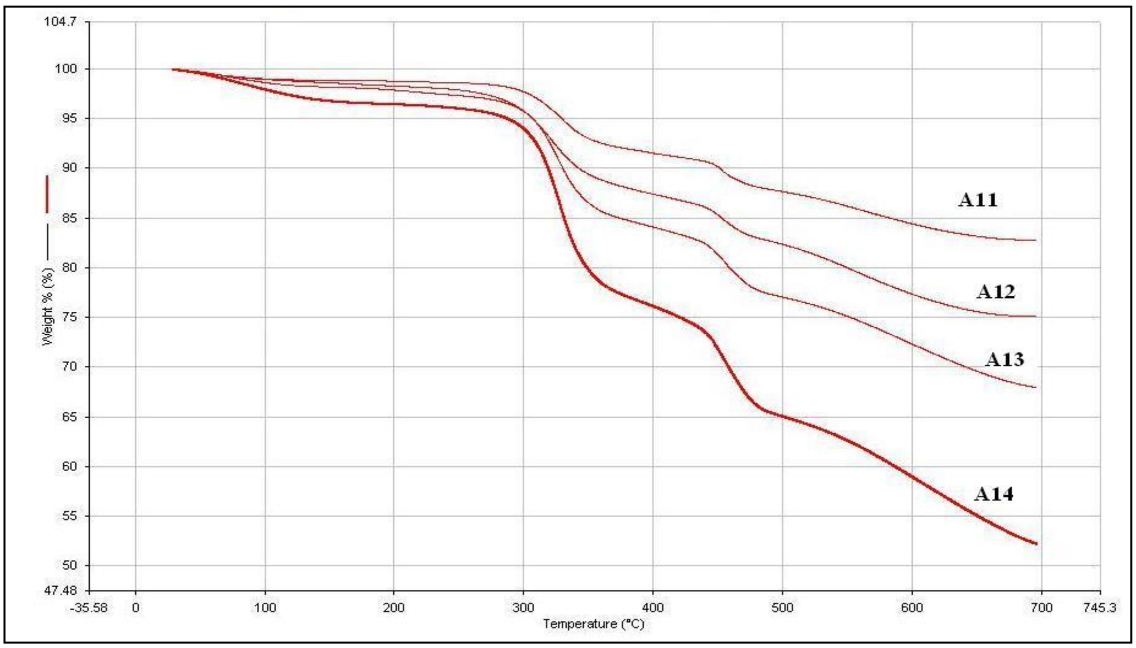
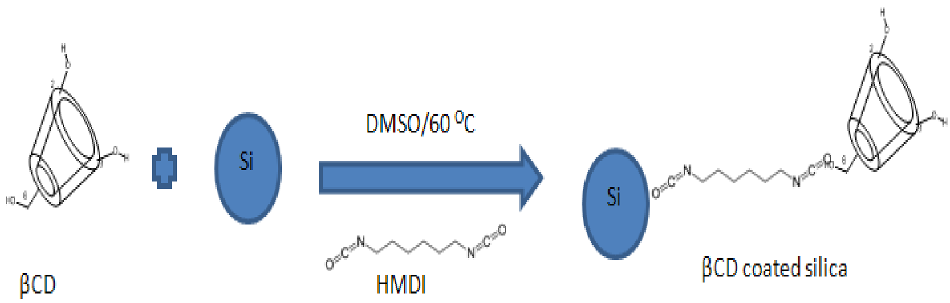
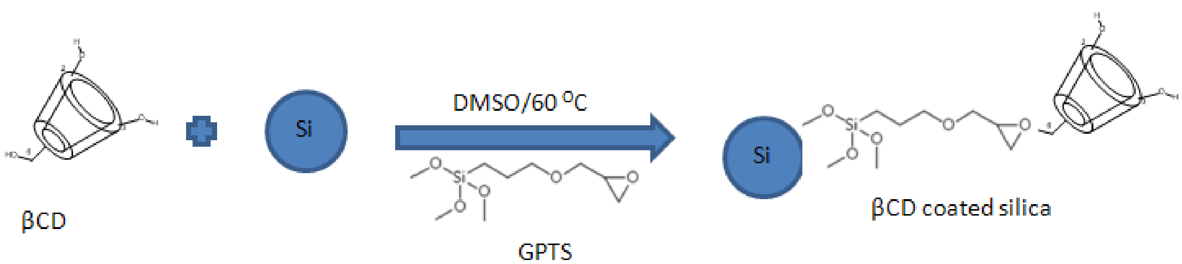


Figure 3.3. TGA analysis of A11 - A14 Adsorbents [purge gas: Air; heating rate: 10 ^{O}C min^{-1}]

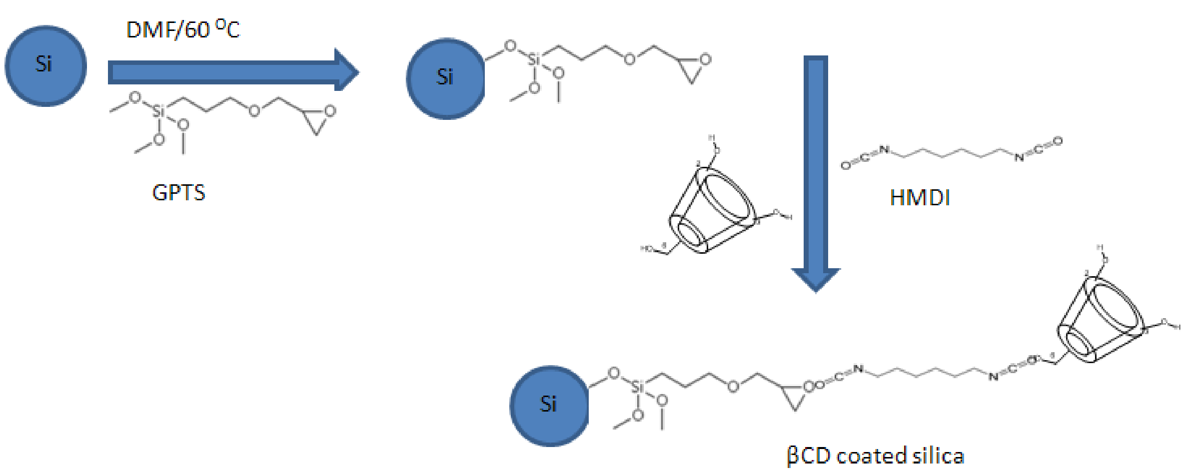
In case of the third adsorbent preparation approach, there are two possible ways of how BCD attaches on the silica particles. Since the silica was silanized, the co-polymers may bind with BCD as shown in scheme-3. On the other hand, if silica surface was not completely silanized, the crosslinking agent may directly bind with silica and BCD, which is similar to scheme 1 mechanism. However, it is difficult to estimate how much unsilanized silica surface was available for the reaction with crosslinking agent. As described earlier, higher BCD loading was noted in C1 to C4 adsorbents than B1-B4 adsorbents. The B-series adsorbents were prepared using silanized silica without any crosslinking agent (scheme-2), whereas C-series adsorbents were prepared using silanized silica with crosslinking agent (scheme-3). Since higher loading of BCD was observed in C-series adsorbents, it appears that the presence of crosslinking agent enhanced the BCD loading. However, adsorbents prepared by using unsilanized silica and crosslinking agent provided highest loading of BCD, as observed for A-series adsorbents (scheme-1). Hence, A-series was most efficient, followed by C-series and B-series adsorbents.



Scheme 1: Coating of BCD onto silica particles with HMDI



Scheme 2: Coating of BCD onto silica particles with GPTS



Scheme 3: Coating of BCD onto silanized silica with HMDI

Since the adsorbent A1 was observed to be the most effective in removing all ECs studied, the adsorbent A1 was synthesized seven times under identical conditions. The obtained adsorbents were tested under identical experimental conditions for the removal of estrogens in multicomponent system (mixture of 10 estrogens at an initial concentration of 100 μg/L each). The removal of estrogens was studied at different adsorbent dosages (0.2 to 1.5 g/L). The adsorbents obtained from seven batches showed consistent (relative standard deviation < 15%; Table 3.3) removal of estrogens. The data showed excellent reproducibility of the preparation method which was also confirmed with multiple ANOVA (p=0.0729). The removal of estrogens increased with higher dosages of the adsorbent (Table 3.3). The equilibrium concentrations ranged from 89.0 to 0.2 μg/L, for adsorbent dosage of 0.8 and 1.5 g/L, respectively, for various hormones.

Table 3.3 Average removal of estrogens (%) with Adsorbent A1 in seven batches with relative standard deviation (%); Initial concentration of estrogens: 100 μg/L; initial pH: 6.7-7.1; contact time: 48 hr; sample volume: 400 ml; temperature: 293 K.

Estrogens	Adsorbent dosage (g/L)			
	0.2	0.6	1	1.5
estriol	34.5±2.8	60.8±15.3	76.8±10.0	90.4±5.9
17α-dihyrdoequilin	42.5±7.4	68.5±13.6	84.9±6.5	92.5±4.3
Equilin	35.6±10.9	74.9±12.4	87.7±5.8	94.0±5.2
Estrone	53.4±11.7	81.6±10.5	90.5±5.7	96.9±1.6
17α-estradiol	43.8±5.1	72.9±10.9	88.3±6.8	94.6±3.3
17β-estradiol	60.9±10.3	85.5±9.0	93.5±4.3	97.7±1.5
17α-ethinyl estradiol	48.3±7.5	69.5±14.0	86.2±7.2	92.4±3.9
Norgestrel	24.5±10.0	40.2±9.7	61.8±13.7	72.5±9.7
Progesterone	46.9±6.0	76.6±10.7	88.6±7.2	94.4±3.4
Medrogestone	36.1±7.0	59.0±13.0	81.8±7.8	90.6±5.1

The data obtained for removal of 17β-estradiol in single component study was compared with that of activated carbon (AC) reported in literature at an equilibrium concentration of 1.6 µg/L. The adsorbent A1 (present study) showed an average adsorption capacity of 38.8 µg/g (standard deviation = 5.6; n = 3) for 17β estradiol (Figure 3.4), where as that of ACs ranged from 193 µg/g to 85.1 mg/g (Saha et al. 2010; Fukuhara et al. 2006) depending upon the type of AC used. Due to the wide range of adsorption capacities reported for ACs, isotherm experiments were conducted with commercially available and widely used F400 carbon under the same experimental conditions.

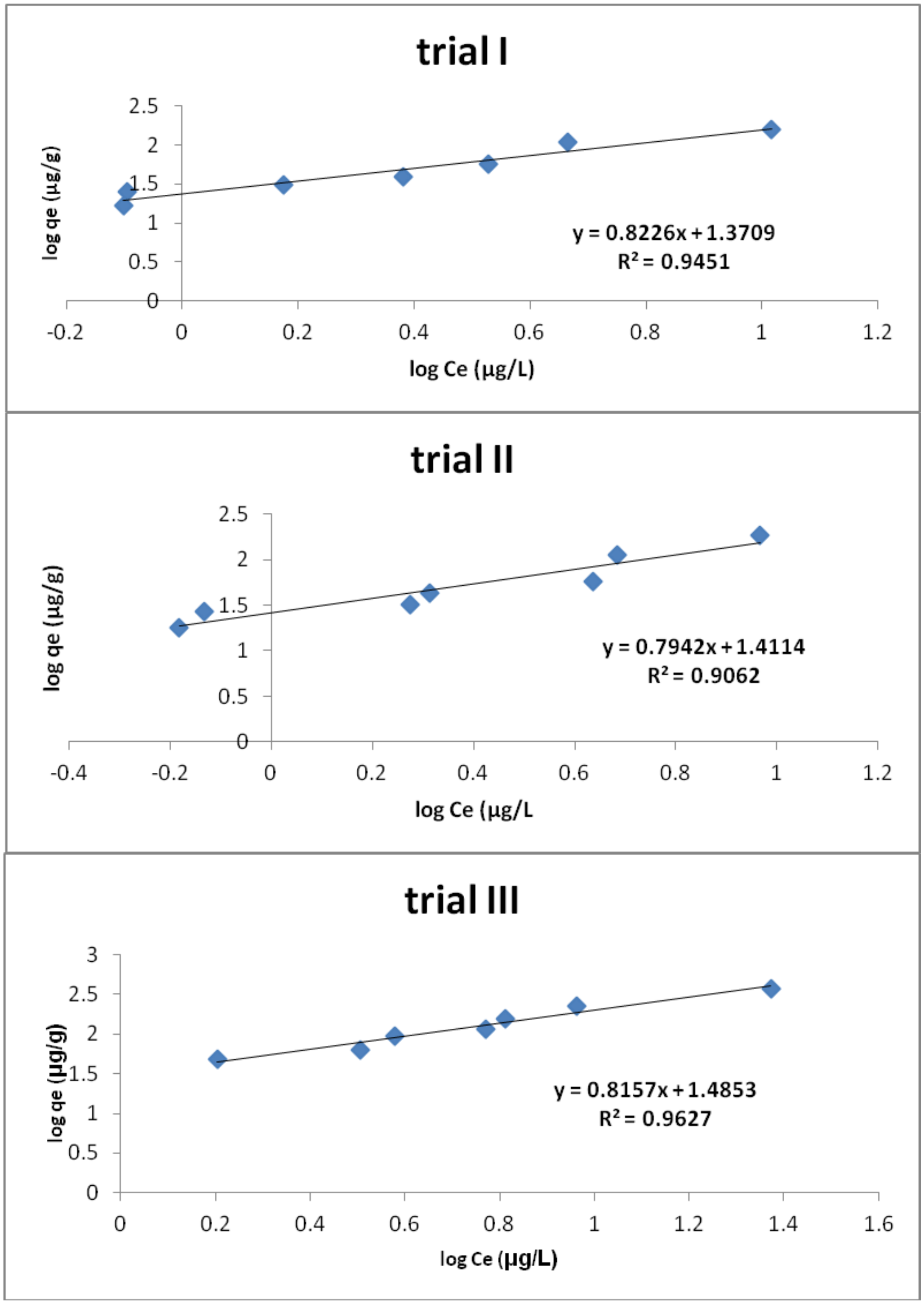


Figure 3.4. Freundlich isotherm for the adsorption of 17β estradiol onto adsorbent A1 showing equilibrium concentration (Ce) of 17β estradiol and adsorption capacity (qe) of adsorbent A1 (i.e, amount of 17β estradiol adsorbed on per g of adsorbent A1).

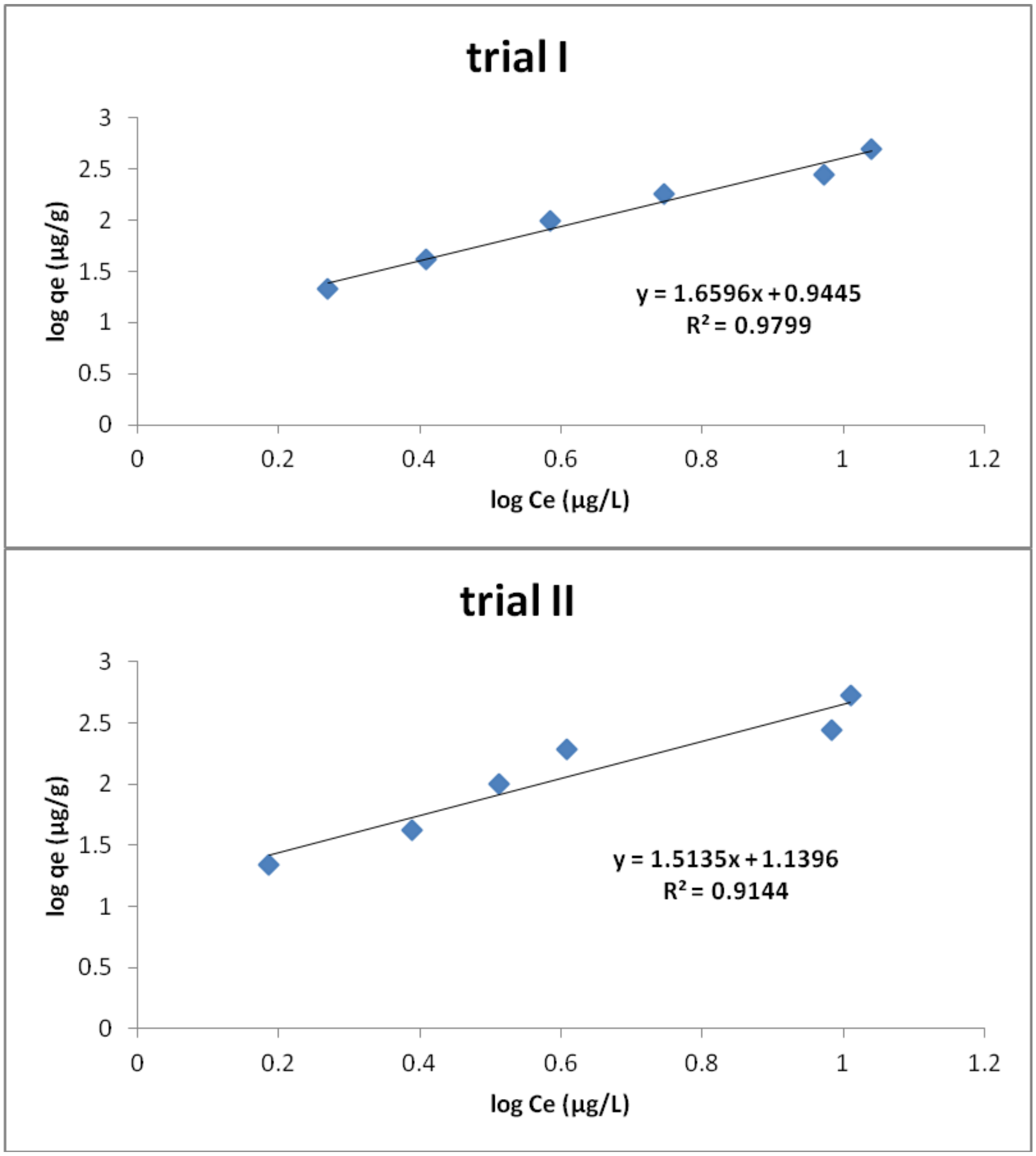


Figure 3.5. Freundlich isotherm for the adsorption of 17β-estradiol onto F400 showing equilibrium concentration (Ce) of 17β estradiol and adsorption capacity (qe) of F400 (i.e, amount of 17β estradiol adsorbed on per g of F400).

The F400 GAC showed adsorption capacity of 23.6 µg/g (standard deviation = 6.3; n = 2) for 17β-estradiol at an equilibrium concentration of 1.6 µg/L (Figure 3.5). This shows that the synthesized adsorbent A1 has higher adsorption capacity for 17β-estradiol than that of commercially available F400 GAC. Furthermore, since the role of silica in removing the ECs is negligible, the adsorption capacity of the BCD becomes much higher if only the amount of loaded BCD is considered for the removal of ECs. The present study showed 32% loading of BCD polymer (discussed later) onto silica. Based on this information, the adsorption capacity of the adsorbent A1 would be 121.2±17.5 μg/g for 17β estradiol considering only the mass of BCD as the adsorbent. The removal efficiency of BCD supported adsorbents could be enhanced by using high surface area substrates. It may be observed from Figures 3.4 and 3.5 that the slope of the Freundlich isotherm was approximately 0.8 and 1.6 for A1 and F400 GAC adsorbents, respectively, thereby indicating that the A1 adsorbent has a more favorable adsorption tendency than F400 GAC.

Though ACs have shown promising results in removing certain ECs from water, they also possess disadvantages such as decrease in adsorption capacity of the target contaminants due to water matrices. A significant reduction in adsorption capacity of estrogens using GAC was observed in the presence of high content of natural organic matter (Rowsell et al. 2009; Zhang and Zhou 2005). Further research would be done to compare the effectiveness of BCD based adsorbents with that of activated carbons for the removal of ECs in wastewater and natural waters.

The FTIR spectra of pure BCD, polymer (BCD-HMDI) and polymer coated silica particles (BCD-HMDI-Si; adsorbent A1) are shown in Figure 3.6. The FTIR spectrum of BCD was consistent with the earlier reports assigned for BCD, and is also evident from the strong C-O-C stretching vibration absorbance band at 1153 cm^{-1} (Pratt et al. 2010; Trotta and Cavalli 2009; Mohamed et al. 2011). The FTIR spectra of the synthesized pure polymer (BCD-HMDI) showed a characteristic polymerized carbamate group at 1546 cm^{-1}, which confirmed the polymerization of BCD with HMDI. The absence of isocyanate group at 2270 cm^{-1} also suggested that the polymerization process was complete. The BCD absorbance band position in the polymer appeared to be very close to the band position in pure BCD, which confirmed that the BCD did not change during the polymerization process. The υ OH stretching vibration of BCD showed a shift towards longer wave number from 3299 cm^{-1} to 3394 cm^{-1}, which could be due to the polymerization process. However, in the polymer coated silica the υ OH stretching band position shifted towards the lower wave number of 3316 cm^{-1}. The υ (C-O-C) band position of BCD showed similar absorbance band in all three samples. The carbamate group at 1546 cm^{-1} also appeared in the silica coated polymer. Based on the FTIR analysis, it was confirmed that the BCD did not change during the polymerization process and the polymers were successfully coated on the silica particles.

The TEM images of BCD and BCD coated silica particles are shown in Figure 3.7. The TEM picture in Figure 3.7a shows the smooth surface structured silica particles. Figure 3.7b shows that the polymer is coated on the edges of the silica particles, and a core-shell like adsorbent was synthesized. Since 40 X 100 mesh size silica particles were used for adsorbent preparation, it was difficult to analyze by TEM. Therefore, the adsorbent was ground for TEM analysis. It should be mentioned that the non-uniform coating of polymers on the silica particles shown in Figure 3.7 could also be due to the grinding process.

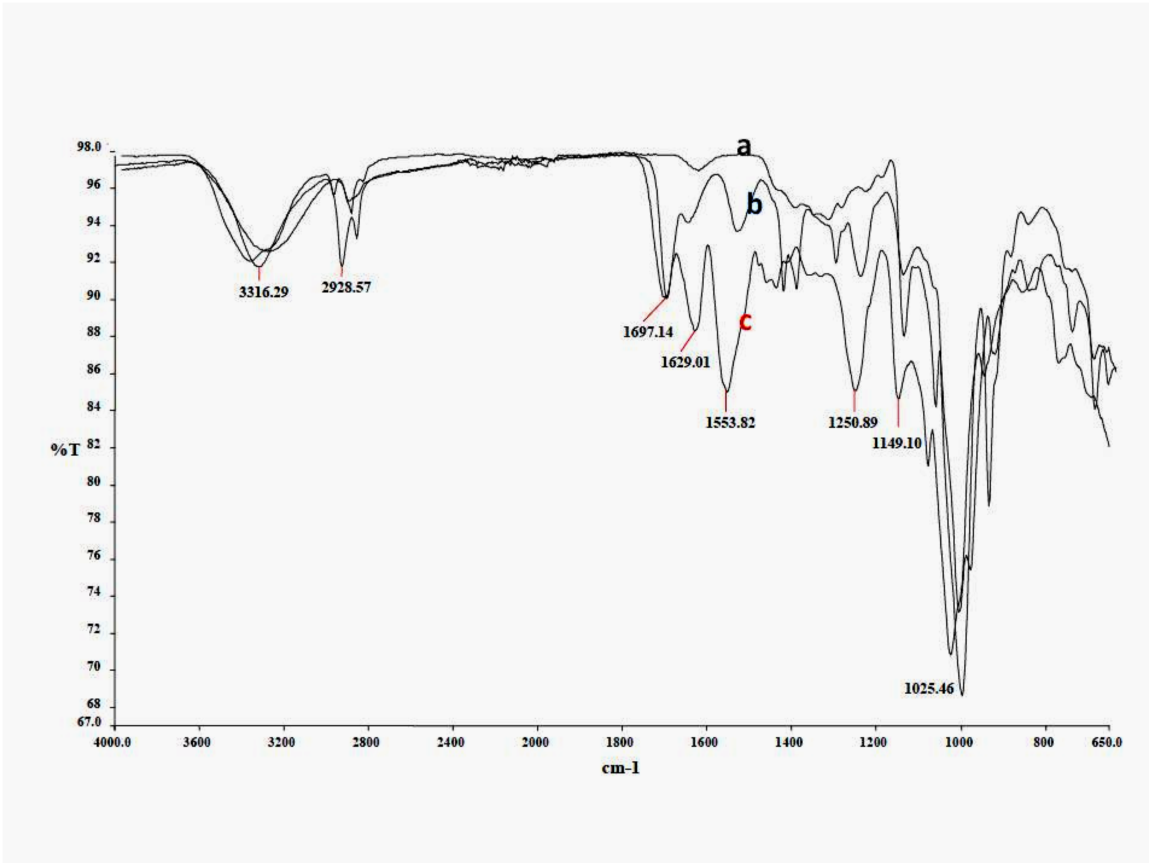


Figure 3.6. FTIR spectra of (a) BCD, (b) BCD-HMDI, and (c) BCD-HMDI-Si

The thermal analysis of BCD, synthesized polymer and BCD coated silica are shown in Figure 3.8. As expected, the silica particles were stable under the experimental conditions studied (1000 ºC). It was observed that the BCD-HMDI-Si based adsorbent was very stable upto 300 ^{o}C (<5% loss). BCD, BCD polymer (without silica), and BCD-HMDI-Si showed significant thermal degradation after 300^{o}C. The BCD is completely decomposed at 600 ºC and decomposition pattern is in good agreement with the results reported by Mohamed et al. (2011). The synthesized polymer (without silica) also showed more than 80% decomposition at 600 ºC. On the other hand, the BCD-HMDI-Si based adsorbent showed only 5% weight loss upto 300 ^{o}C, approximately 30% loss upto 500 ºC and then the weight loss was insignificant from 500 ºC to 1000 ºC. The initial 5% weight loss could be due to the water moisture present in the adsorbent. Based on its decomposition (upto 500 ºC), the polymer loading on the silica was estimated to be approximately 32% w/w. These results show that the polymer coated on silica have excellent thermal stability at temperatures as high as 300 ºC.

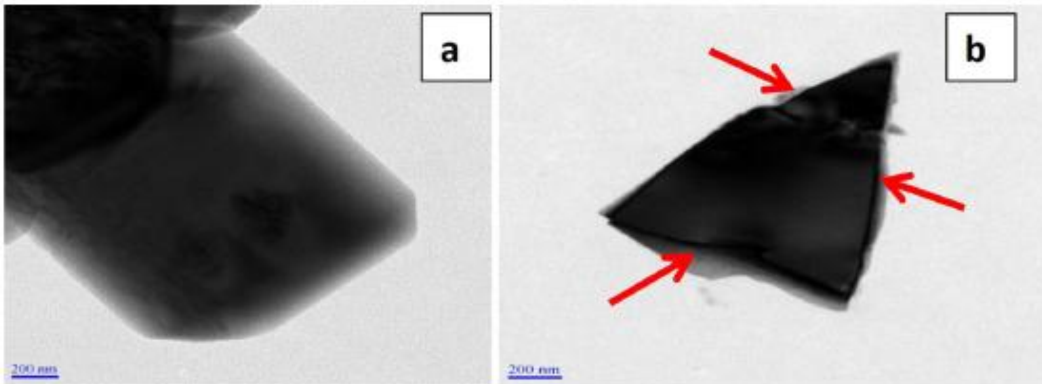


Figure 3.7. TEM images of (a) silica and (b) BCD coated silica

The surface area of the synthesized adsorbent (A1) and silica particles was analyzed. The BET surface area of the silica and the prepared adsorbent was less than 1.0 m^2/g, which is due to large particle size of silica used for its synthesis. It is well known that surface area is an important factor for the adsorption of adsorbates. In this study, the adsorption mechanism was expected to be complex formation between BCD supported on silica and organic pollutants.

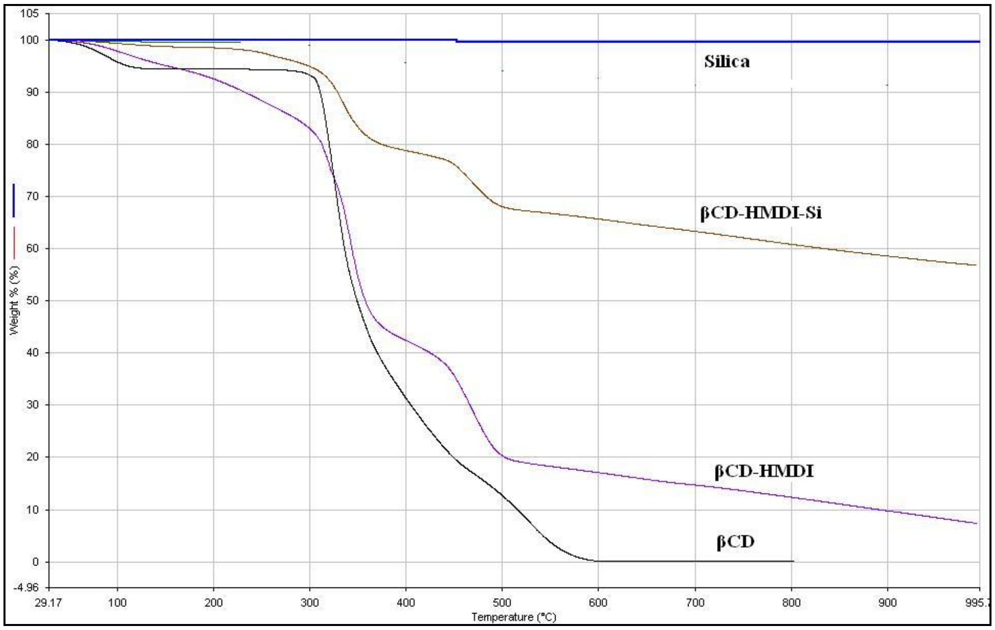
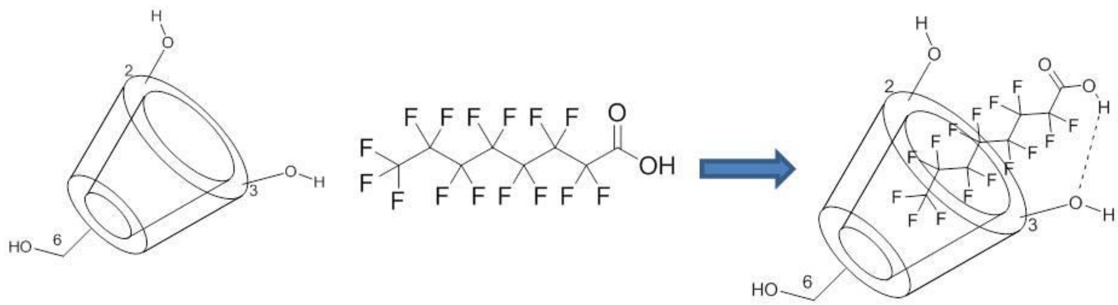


Figure 3.8. Thermographs for BCD and BCD coated silica [purge gas: air; heating rate: 10 ^{O}C min^{-1}]

Considering the structure of ECs used in this study, the mechanism of the adsorption may be explained in a two-step process. First, the hydrophobic nature of the ECs would provide necessary conditions to enter into the cavity of BCD molecules. The second step involves the formation of inter-molecular hydrogen bonding between the ECs (guest molecules) and BCD molecules (host molecules) as shown in Scheme-4. The tendency of 17β-estradiol, PFOA, and BPA to form hydrogen bonding due to the presence of hydroxyl groups provides suitable conditions for the stability of inclusion complex with BCD molecules. However, the removal efficiencies of these compounds may vary because of other factors such as shape, size, and hydrophobicity (Crini 2005; Crini and Morcellet 2002).



(A) (B) (C)

Scheme-4 Inclusion complex formation through host guest interaction (A) BCD, (B) PFOA, and (C) inclusion complex formation

With steroid hormone mixture, a significant variation in removal percent ($p < 0.0001$) was observed from ANOVA test. It was observed that the adsorbents showed high removal efficiency for certain hormone compounds such as estradiol and estrone, and low efficiency towards norgestrel. This significant variation in removal of hormones despite having similar hydrophobicity shows that the structure of the guest molecules, such as presence of functional groups, affects the inclusion complex formation. Although these hormones have similar hydrophobicity (K_{ow}), the difference in removal was probably due to the variation in functional groups available to form hydrogen bonding with the hydroxyl groups present at the rim of the BCD molecules. In general, the adsorption potential towards hormones may be attributed to the tendency of hormones to form intramolecular hydrogen bonding and presence of bulky groups. Both factors can hinder the formation of inter-molecular hydrogen bonding (Patton and Dmochowski 1963). In this study, the low adsorption potential towards certain hormones such as norgestrel and progestrone may be attributed to either deficit of hydroxyl groups for hydrogen bonding or presence of bulky groups adjacent to the hydroxyl groups hindering the formation of hydrogen bonding. Higher binding affinity of BCD towards hydroxylated estrogens has been reported by others (Moon et al. 2008).

3.3.2. Regeneration studies

In this study the inclusion complex formation was proposed as the adsorption mechanism, therefore it was of interest to study the regeneration ability of the synthesized adsorbents. Methanol was used to desorb the contaminants trapped in the cavity of BCD. Methanol was expected to break down the weak bond formed between the host and guest molecules, and the trapped guest molecule would be released and eluted with methanol. The adsorbent was tested for its regenerability by using it for four successive cycles of adsorption and regeneration. The regeneration potential of the adsorbent was tested with PFOA (200 μg/L initial concentration) and steroid hormones (mixture of 10, each at 100 μg/L initial concentration) in batch experiments. For compounds other than 17α estradiol, 17α-dihydroequilin and trimegesterone, the adsorbent showed very good regeneration potential in four successive cycles without significant loss in its adsorption capacity as shown in Figure 3.9. It seems that there is a decrease in adsorption capacity in the fourth cycle for 17α-estradiol, trimegesterone, estrone and 17α-dihydroequilin. The high regeneration potential of BCD-based adsorbents has also been reported in the literature. Wang et al. (2011) synthesized mesoporous carbon by the carbonization of hpBCD/silica composites, and the catalytic activity did not reduce notably after reusing it for six adsorption cycles by regenerating it with ethanol. Good regeneration potential of BCD-based adsorbents has also been observed in other studies (Badruddoza et al. 2011; Mhlanga et al. 2007; Fuhrer et al. 2011).

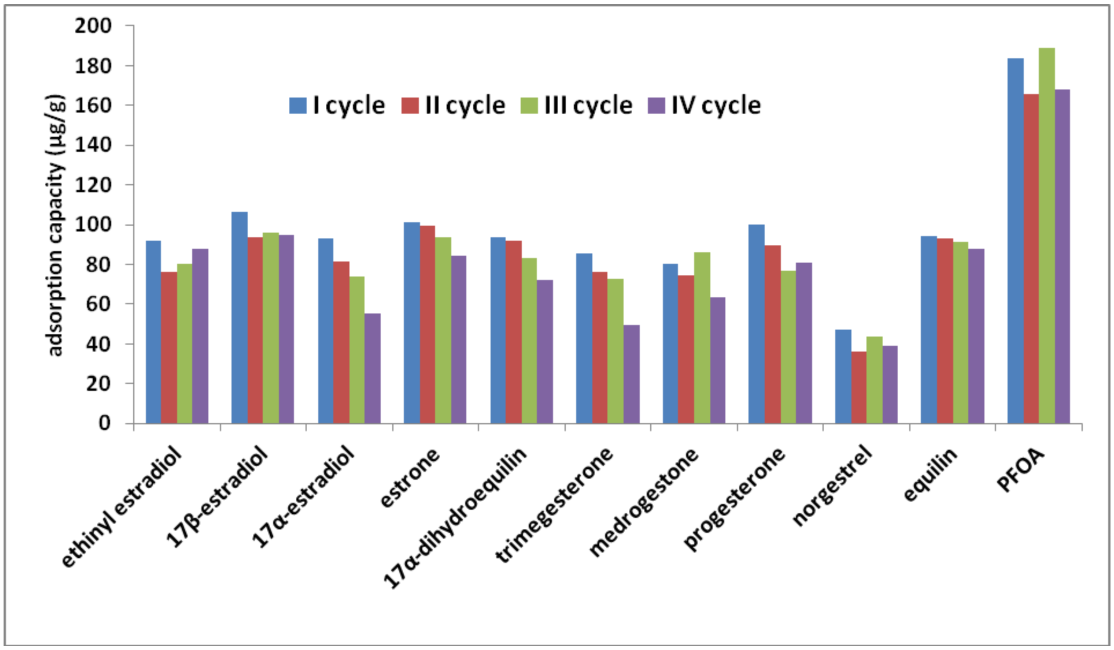


Figure 3.9. Regeneration of the adsorbent A1 with PFOA and steroid hormones over four successive cycles. (Initial conc: PFOA =200 µg/L, Estrogens =100 µg/L each, adsorbent dosages: PFOA= 1.5 g/L, estrogens = 1.0 g/L, temperature: 293 K; pH: 5.5-6.3; contact time: 48 hr)

3.4. CONCLUSIONS

BCD coated silica adsorbents were successfully prepared by using two crosslinking agents, two copolymers, and three solvents. The performance of the adsorbents was evaluated by testing them for the removal of 17β-estradiol, PFOA, and BPA in batch condition. The combination of HMDI as a crosslinking agent and DMSO as a solvent was observed to be the best for the synthesis of the most efficient adsorbent (best adsorbent) in removing the target contaminants. The best adsorbent removed more than 90% of 17β-estradiol, PFOA, and BPA from MQ water. The removal efficiency of the best adsorbent was observed to increase as the BCD loading on silica (BCD/silica) increased, and a loading of 0.23 g/g is recommended. The FTIR, TEM and TGA analysis confirmed coating of BCD onto silica particles. The TGA showed a thermal stability upto 300 ^oC for the best synthesized adsorbent. The best adsorbent was also effective in removing more than 90% of most of hormones from a mixture of 10 steroid hormones at 1.5 g/L adsorbent dosage. The performance of the adsorbent was consistent for seven batches of synthesis for adsorption of 10 hormone compounds. The synthesized best adsorbent showed higher adsorption capacity (38.8 ± 5.6 μg/g) for 17β-estradiol when compared with that of commercially available activated carbon F400 (23.6 ± 6.3 μg/g), as well as a more favorable adsorption process. The best adsorbent was successfully regenerated with methanol over four successive without significant loss in its adsorption capacity for most of the steroid hormones and PFOA. The efficiency of the adsorbent could be improved by coating it on higher surface area substrates. More work is needed to evaluate its performance with other contaminants and with environmental water.

CHAPTER 4
REMOVAL OF EMERGING CONTAMINANTS FROM AQUEOUS PHASE USING Β-CYCLODEXTRIN BASED HYBRID ADSORBENT

4.1. Introduction

Emerging contaminants (ECs) are unregulated chemicals, which have become of environmental concern due to their occurrence in environmental components (Kolpin et al. 2002; Suri and Velicu 2009) and potential toxicity to wildlife and humans at low concentrations (Richardson 2009). ECs which includes pharmaceuticals and personal care products (PPCPs), endocrine disrupting chemicals (EDCs), polybrominated flame retardants (PBDEs), perfluorinated compounds (PFCs), nanomaterials, organisms and nonliving pathogens (Fent et al. 2006).

In previous chapter, the synthesis of various β-Cyclodextrin (BCD) coated silica adsorbents was discussed for the removal of selected ECs such as 17β-estradiol, Perfluorooctanoic acid (PFOA), and bisphenol A (BPA). These compounds were chosen as model contaminants and the experiments were done in MQ water system. In this chapter, the best adsorbent from previous work was selected, resynthesized, and further experiments were conducted on the removal of these compounds under various experimental conditions. Various adsorption technologies have been reported in the literature for the removal of ECs such as activated carbon adsorption (Bautista-toledo et al. 2005; Fukuhara et al. 2006), membrane adsorption (Snyder et al. 2006; McCallum et al. 2008), molecularly imprinted polymers (Fernandez-Alvarez et al. 2009), and activated sludge (Hashimoto et al. 2008). The removal mechanism of BCD differs from these adsorption technologies as it involves formation of inclusion complex (Crini 2005). Inclusion complexes are chemical species consisting of two or more associated molecules in which one of the molecules, the host, can admit a guest component into its cavity, resulting in a stable encapsulation without formation of any covalent bonds (Croft and Bartsch 1983; Saenger 1980; Clarke et al. 1988). The structure of Cyclodextrin (CD) molecules gives rise to the remarkable ability to form inclusion complexes with inorganic (Bender 1978; Szejtli 1982), organic (benzene and phenol derivatives, amino acids, barbiturates, prostaglandins, pesticides, glycolipids, proteins, tryptophan) (Croft and Bartsch 1983; Mu et al. 2001; Liu et al. 2001) and ionic compounds (Bender 1978; Szejtli 1982). The successful removal of the above mentioned model compounds reported earlier shows that the BCD has tendency to from inclusion complexes with these compounds.

This chapter deals with the successful applications of BCD coated silica as adsorbent (synthesis procedure reported earlier) for the removal of steroid hormones, PFCs, and BPA. The adsorbent showed high adsorption capacity towards these ECs and was successfully regenerated with ozone without significant loss in adsorption capacity.

4.2. Experimental

4.2.1. Analysis of Dissolved organic carbon (DOC)

HA was used as a source of DOC to simulate wastewater. First of all, 1g of HA was dissolved in 1 L of 0.1 M NaOH and stirred for 24 hr. The solution was filtered through

0.45 μ membrane filter and the pH was adjusted to 7. The solution was stored at 4 ^{O}C for future experiments. The DOC of the samples were measures by TOC-V_{CSH} instrument (Shimadzu, Kyoto, Japan). Before measuring DOC of the samples, the pH of the sample was adjusted to 2, filtered through 0.45 μ syringe filters and purged with N_2 gas.

4.2.2. Analysis of Cr (VI)

To study the simulatneous removal of ECs and chromium, potassium dichromate ($K_2Cr_2O_7$) was used as a source of hexavalent chromium ion (Cr (VI)) and was quantified by colorimetric analysis. The Cr (VI) solutions (5.25 mL) were taken into test tubes, o-phosphoric acid (0.50 mL, 4.5 M) and 1,5-diphenyl carbazide (0.25 mL, 5 g/L) were added. After incubated at room temperature for 30 min for color development, the absorbance of the samples was measured in a UV-vis spectrophotometer. Peaks with varied intensities were observed in the spectrometer scans at 540 nm wavelength depending on the concentrations of the remaining Cr (VI) in the samples.

4.2.3. Effect of solution pH

The effect of solution pH on the removal of the selected ECs was examined by varying the initial pH of the solutions from pH 4 to 11. In order to adjust the solution pH, 0.1 M HCl and 0.1 M NaOH were used. The solution pH was measured using a pH meter (Oakton pH 11 series). The experiments were done at initial concentration of 25 µg/L, 25 µg/L, and 100 µg/L of E2, PFOA, and BPA, respectively.

4.2.4. Batch kinetic studies

To study the kinetics of adsorption for the removal of selected ECs, 900 ml solution in 1 L amber glass bottles was used for each EC. These experiments were done at triplicates and samples were taken at certain time intervals till the equilibrium was ascertained.

4.2.5. Column adsorption

For column experiments, chromatographic columns of 2.5 cm diameter and 30 and 45 cm long were used. Following equations were used to calculate column design parameters.

$$Bed\ depth\ (d) = EBCT \times V_s \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots..(1)$$

$$Bed\ volume\ (V) = \pi r^2 \times \mathrm{d} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots..(2)$$

$$Mass\ of\ adsorbent\ (m) = bulkdensity\ of\ the\ adsorbent \times V \ldots\ldots\ldots.(3)$$

$$Flow\ rate\ (Q) = \pi r^2 \times \mathrm{V_s} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots.(4)$$

The column was packed with the calculated amount of adsorbent. The air bubbles trapped along the bed depth were removed by tapping the column gently or by backwashing. The column was conditioned for about 15 hrs before starting the experiment. In order to supply a continuous flow of initial samples (known concentration of ECs), a 20-liter glass carboy was used to prepare initial sample solutions. The prepared initial sample solution was continuously fed to the column with the help of a low flow pump (set to the desired flow rate). PTFE tubes were used to for connection with three-way valves in order collect influent and effluent samples. The influent and effluent samples were taken at regular intervals till the breakthrough was observed.

4.2.6. Regeneration studies

In order to regenerate the adsorbent with ozone, first of all, the adsorbent was saturated with the respective adsorbant (17β-estradiol or BPA) separately. To saturate the adsorbent, 900 ml of the respective adsorbant at an initial concentration of 200 μg/L was mixed with 0.9 g of adsorbent and left on the shaker at 160 rpm for 48 hours. After saturation, the adsorbent was transferred into a glass reactor filled with 2 L of DI water and ozone was passed through the reactor at 5% (w/w) and flow rate of approximately 20 L/hr for 2 hr (Wedeco ozone generator). After ozonation, the adsorbent was separated from the solution, washed three times with DI water and used for another batch of adsorption under the same experimental conditions.

4.3. Results and discussion

4.3.1. Batch adsorption in single component system

Initially, isotherm experiments were done with the model contaminants (17β-estradiol, PFOA, and BPA) separetely to compare the removal efficiency of the adsorbent for each EC. These experiments were conducted at initial concentrations of 25 μg/L for 17β-estradiol and PFOA, and 100 μg/L for BPA. The adsorbent dosage was varied from 0.1 to 1.5 g/L. The adsorption experimental results are summarized in Figure 4.1. Control experiments with silica particles showed no significant removal (data not shown) of any of the ECs studied. This indicates that the ECs are not adsorbed on the silica particles as we reported in previous chapter.

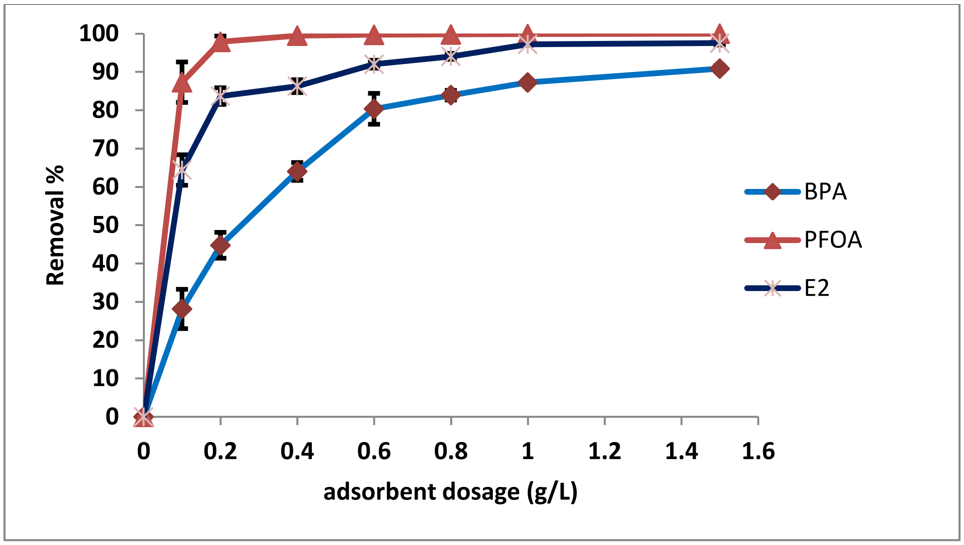


Figure 4.1 Removal of 17β-estradiol, PFOA, and BPA [contact time: 48 hr; temperature: 293 K]

It was observed that the adsorbent showed the strongest affinity with PFOA by removing more than 99% at adsorbent dosage of 0.2 g/L and higher. At the same adsorbent dosage, about 86% of E2 and 64% of BPA removal were observed. When the adsorbent dosage was increased to 1.5 g/L, maximum removal of 97% of E2 and 91% of BPA were observed (Figure 4.1).

The present study showed significant removal of all the selected ECs, which shows the ability of BCD to form inclusion complexes with these contaminants. The formation of such inclusion complexes is also reported in the literature in both solution phase (Yanez et al. 2007) and by using BCD polymers (Moon et al. 2008; Kikuchi et al. 2005; Oishi and Moriuchi 2010b). The adsorption potential of the synthesized adsorbents is dependent on the properties of both contaminants and the adsorbents. The molar ratio of BCD and the crosslinking agent is one of the important factors that determine the adsorption capacity of the adsorbents. Since native BCD is soluble in water, it should be reacted with crosslinking agents to get insoluble form of BCD. This molar ratio is crucial as the low ratios could give water soluble adsorbents whereas high ratios could decrease the adsorption capacity of the adsorbents due to steric hinderance. Therefore, it is necessary to come up with an optimum ratio of BCD and crosslinking agents. In this study, the molar ratio of 1:7 with HMDI as crosslinking agent was found to be the most efficient in the removal of target compounds. This result is in good agreement with the results observed by Yamasaki et al. (2008) where the adsorbents prepared at a molar ratio of 1:8 showed high sorption capacity for phenols.

To analyze the experimental data, two commonly used isotherm models, the Langmuir (Eq 5) and Freundlich (Eq 6) equations were used which can be expressed as follows

$$q_e = \frac{bq_mC_e}{1+bC_e} \quad \text{……………………..} \; (5)$$

$$q_e = KC_e^{\frac{1}{n}} \quad \text{………………………} \; (6)$$

Where, q_e is the equilibrium sorption amount, Ce is the equilibrium concentration), qm is the maximum sorption capacity, b is sorption equilibrium constant, K is a constant representing the sorption capacity, and n represents the sorption intensity. As shown in Figure 4.2., the sorption isotherms of 17β-estradiol and BPA showed good fit to both Langmuir and Freundlich models, whereas, isotherms of PFOA showed a better fit to Freundlich model than Langmuir model.

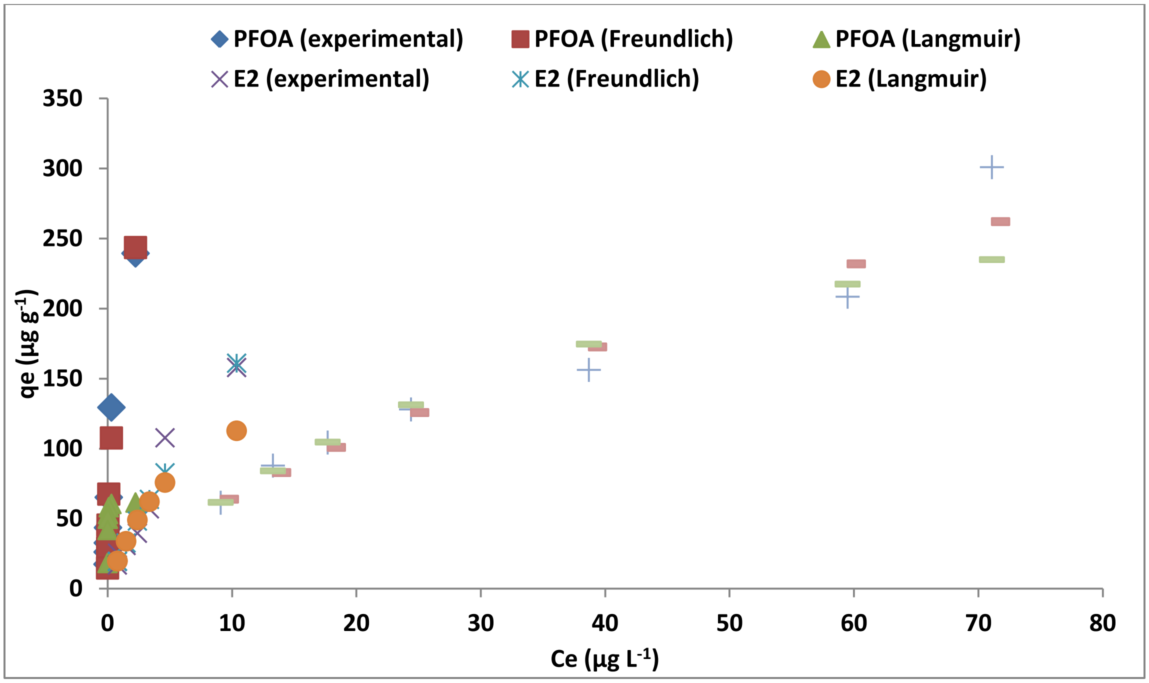


Figure 4.2. Equilibrium results for the removal of 17β-estradiol, PFOA, and BPA [contact time: 48 hr; initial pH: 5.1 - 6.3; temperature: 293 K]

4.3.2. Batch adsorption in mixture of ECs

The performance of the adsorbent was further evaluated in mixture of ECs. For this study, two mixtures were made, one containing 12 different steroid hormones at initial concentration of 100 µg/L. The other mixture containing 10 different perfluorochemicals (PFCs) at initial concentration of 50 µg/L of each EC. In case of PFCs, a variety of compounds were chosen having carbon chain length from six to 14. The adsorbent was successful in removing most of the PFCs (Figure 4.3). The control experiment with silica showed no significant removal at 1.5 g/L (data not shown).

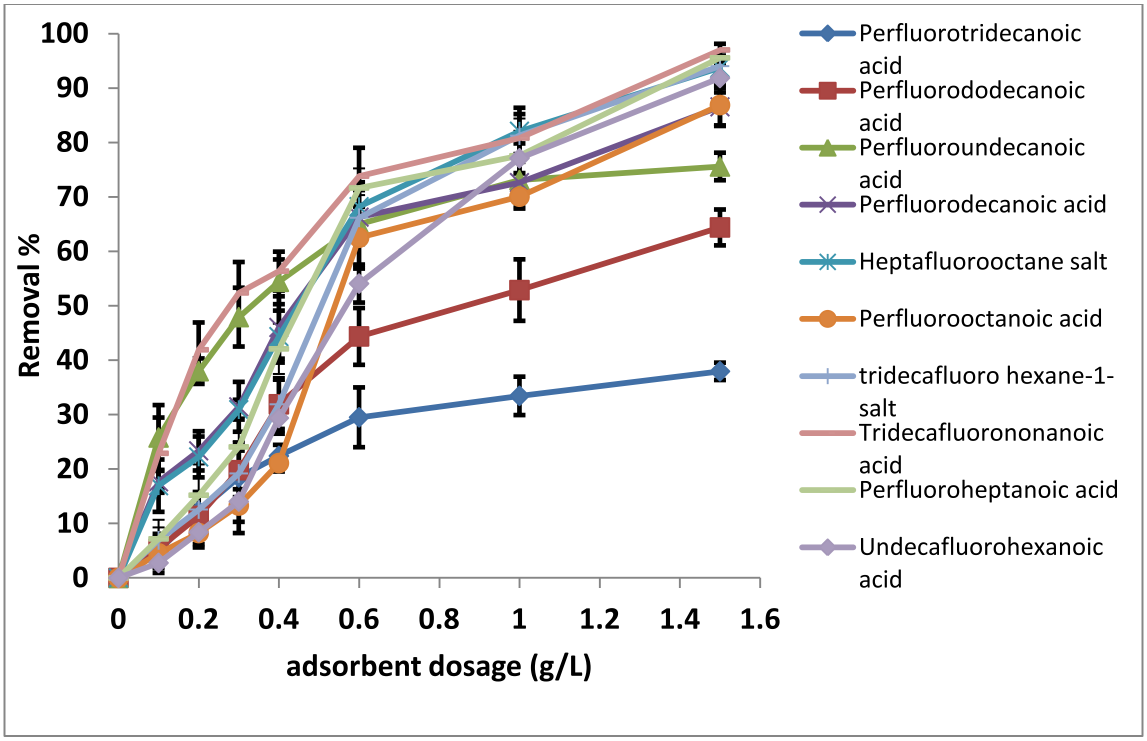


Figure 4.3. Removal of PFCS [initial conc: 50 µg/L; contact time: 48 hr; initial pH: 5.3; temperature: 293 K)

The removal of PFOA from single and multicomponent systems showed a significant change in the adsorption affinity of the adsorbent for PFOA. It was observed that the adsorbent removed more than 97% PFOA at adsorbent dosage of 0.2 g/L in single component system. This trend was not observed in multicomponent system where the removal of PFOA was only 90% at 1.5 g/L of adsorbent dosage. This shows that the adsorbent has higher affinity for other PFCs such as tridecafluorononanoic acid, heptafluorooctane salt, and tridecafluoro hexane-1-salt than PFOA. Certain PFCs such as perfluorotridecanoic acid and perfluorododecanoic acid showed very low removal compared to other PFCs. The reason may be attributed to the structure of these compounds which represent the longest-chained molecules in the mixture. Though the hydrophobicity increases with increase of carbon chain length (Yong 2007), the above mentioned compounds showed the least removal. This shows that the mechanism of removal is dependent on but not limited to hydrophobicity of the contaminants as various other factors play important roles such as size and presence of functional groups. This mechanism in case of CD is different from GAC where longer chained PFCs showed stronger adsorption (Yong 2007; Appleman et al. 2014) than shorter chained.

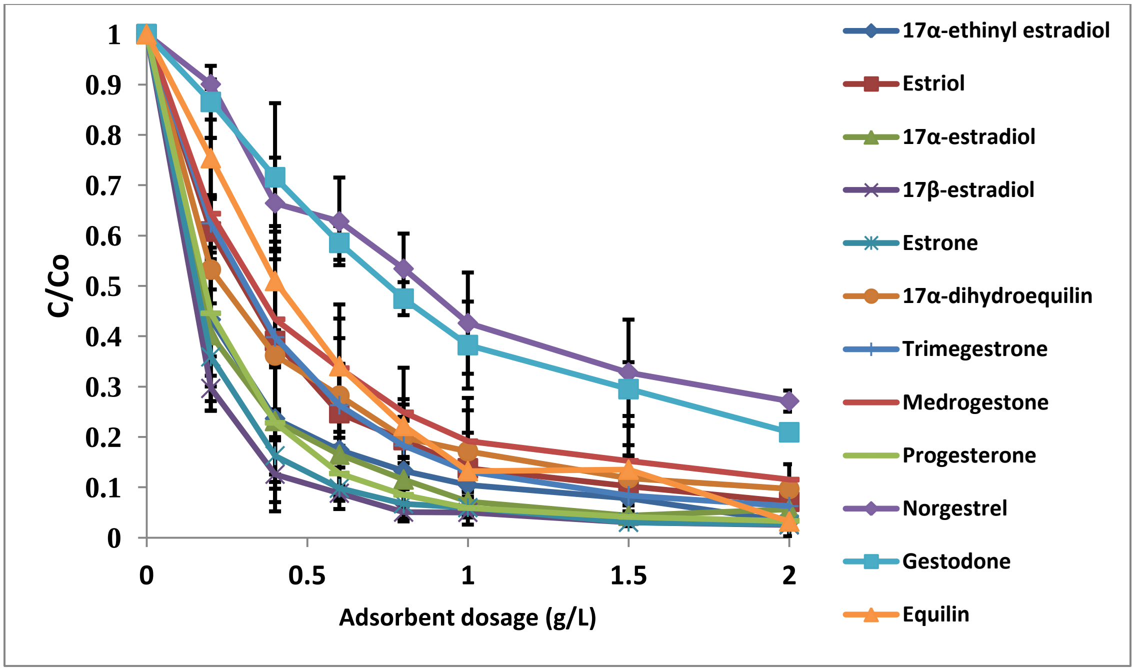


Figure 4.4. Removal of estrogens with BCD/silica [initial conc = 100 µg/L, contact time: 48 hr]

The experimental results in removing estrogens from both single component and multicomponent showed good removal of estrogens. The removal of 17β-estradiol was not affected by the introduction of other estrogens in the mixture. This may be due to high adsorption affinity of the adsorbent for 17β-estradiol. The lower adsorption of estrogens such as norgestrel and gestodone shows the lower affinity of the adsorbent for these compounds.

The molecular structures of contaminants play a crucial role in forming host-guest inclusion complex with BCD molecules. Though all the estrogens studied have similar hydrophobicity and structural patterns in terms of size (Appendix A), the developed adsorbents were quite selective for the removal of certain estrogens. This mechanism can be clearly understood by studying the removal of enantiomers: 17α-estradiol and 17β-estradiol where the adsorbent showed high affinity for 17β-estradiol than 17α-estradiol. This shows that the removal mechanism is also dependent on the orientation of the functional groups present in the contaminants. This selective property of BCD is used in developing chromatographic columns for the separation of enantiomers (Kim et al. 2003; Park et al. 2001).

The adsorbent showed high removal efficiency for certain estrogen compounds such as 17α-estradiol, 17β-estradiol, and estrone where as low efficiency towards norgestrel, medrogestone, and gestodone. Considering the structure of these estrogens and their removal, the mechanism of the removal may be explained in a two-step process. First, the hydrophobic nature of the estrogens provides necessary conditions to enter into the cavity of BCD molecules. The second step is the formation of inter- molecular hydrogen bonding between the estrogens and BCD molecules. This mechanism can be well understood when the estrogens having similar hydrophobicity (Kow) showed different removal due to the variation in functional groups available to form hydrogen bonding with the hydroxyl groups present at the rim of BCD molecules. In general, the adsorption potential towards estrogens may be attributed to two factors: the tendency of estrogens to form intramolecular hydrogen bonding and presence of bulky groups, both factors hinder the formation of inter-molecular hydrogen bonding (Patton and Dmochowski 1963). In this study, the low adsorption potential towards certain estrogens may be attributed to either deficit of hydroxyl groups for hydrogen bonding or presence of bulky groups adjacent to the hydroxyl groups hindering the formation of hydrogen bonding. The higher binding affinity of β-CD towards hydroxylated estrogens was also observed by Moon et al. (2008).

4.3.3. Adsorption kinetics studies

For kinetic studies, samples were taken to determine the liquid phase concentration at different time intervals till the equilibrium was ascertained. These experiments were done separately in triplicates for BPA, PFOA, and 17β-estradiol in MQ water at initial concentration of 100 μg/L for BPA and 25 μg/L for PFOA and 17β-estradiol. The results are shown in Figure 4.5.

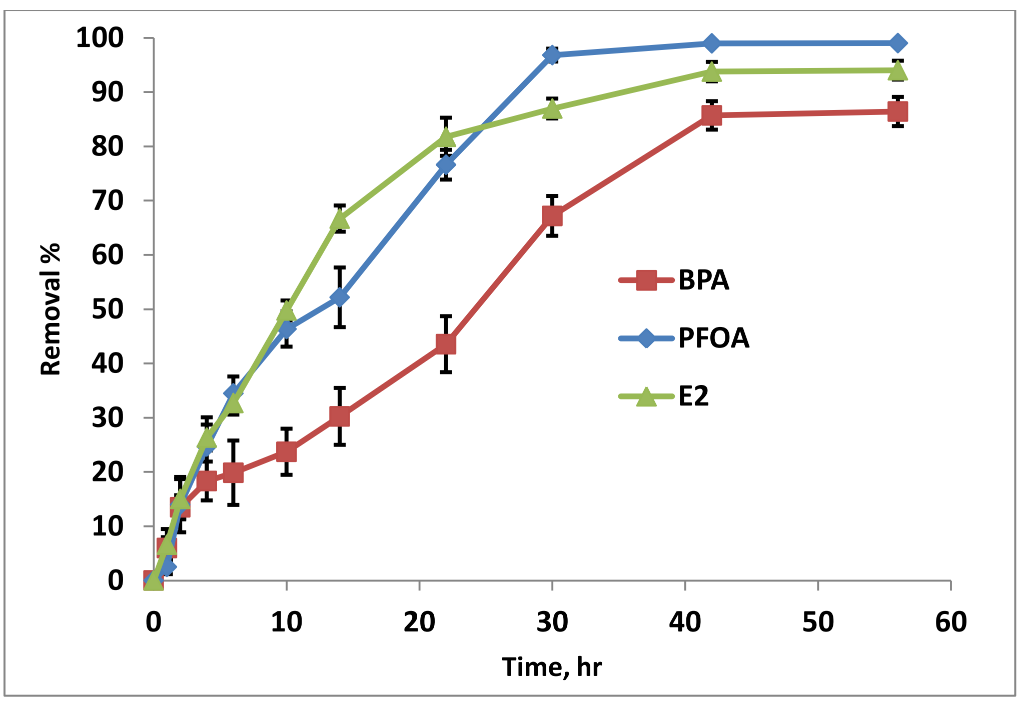


Figure 4.5. Adsorption kinetics of 17β-estradiol, PFOA and BPA

The data obtained from the adsorption kinetics was fitted with pseudo first order model to calculate the rate constant for each EC studied. The results are shown in Figure 4.6.

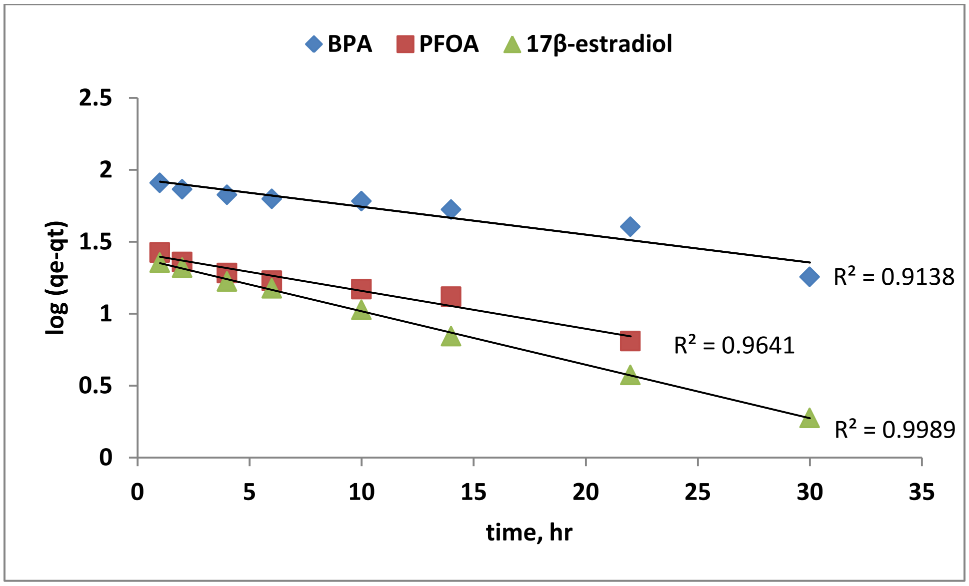


Figure 4.6. Pseudo first order kinetic for 17β-estradiol, PFOA and BPA

It was observed that the adsorption kinetics of 17β-estradiol was the fastest with a rate constant of 0.0372 hr^{-1}(R^2 = 0.9989) followed by PFOA with a rate constant of 0.0309 hr^{-1} (R^2 = 0.9641). The lowest rate constant of 0.0194 hr^{-1} (R^2 = 0.9138) was observed in case of BPA.

Table 4.1. Rate constants for the removal of 17β-estradiol, PFOA, and BPA

EC	**Rate constant, hr^{-1}**	**R^2**
17β-estradiol	0.0372	0.9989
PFOA	0.0309	0.9641
BPA	0.0194	0.9138

4.3.4. Effect of solution pH

To study the effects of solution pH on the removal of ECs, batch experiments were done at three different pH (4, 7, and 11) in triplicates. Two separate experiments were done with a mixture of 8 steroid hormones, and BPA at initial concentration of 100 µg/L each. The results are shown in Figure 4.7.

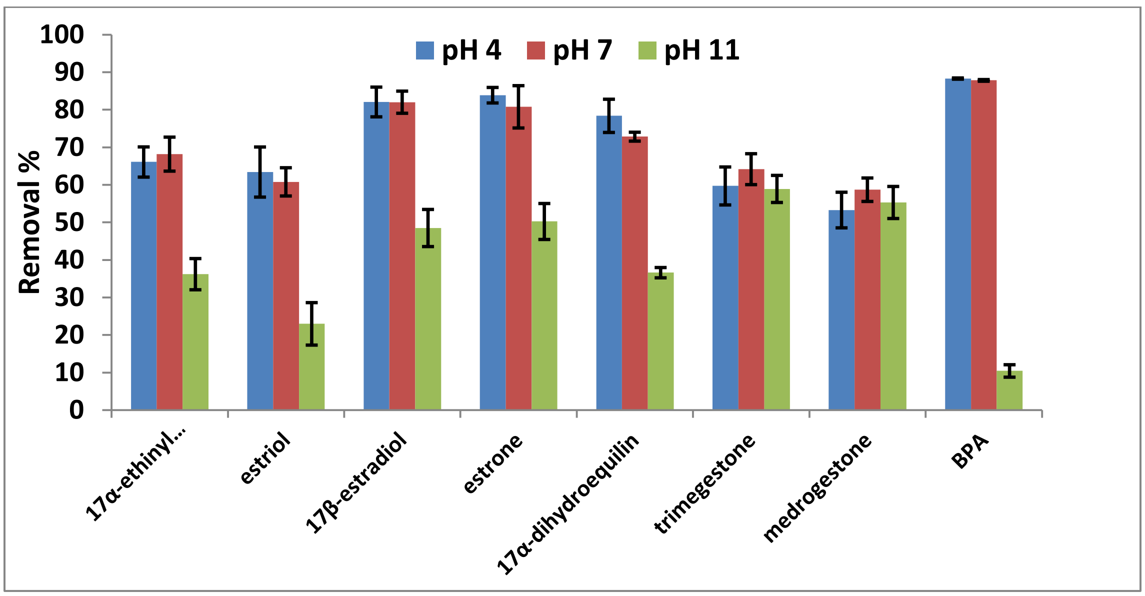


Figure 4.7. Effect of pH on the removal of estrogens [initial conc: 100µg/L; adsorbent dosage: 0.8 g/L; contact time: 48 hr; temperature: 293 K]

The results show that the adsorption capacity of the adsorbent is dependent on the pH condition of the water by influencing the structure of the contaminants or the structure of BCD itself. Most of the estrogens have pKa values around 10.5. A significant decrease in removal of estrogens such as 17α-dihydroequilin, 17α-estradiol, 17β-estradiol, and estrone was observed at pH 11.0. The reason may be due to the dissociation of these molecules as these molecules have pKa values in between 10.3 to 11.0. So, at pH 11.0, the deprotonation of these molecules may reduce hydrogen bonding with BCD molecules resulting in lower adsorption of the estrogens. However, certain estrogens such as medrogestone, norgestrel, and progesterone were not affected significantly by the change in pH. The reason can be attributed to the structures of these compounds which do not possess any dissociating hydrogen molecules. In other words, these compounds do not have any pKa values. The zeta potential measuresments of the adsorbent showed that the pHzpc of BCD/Silica is about 2.9 (Figure 4.8). Therfore, at all pH range that was used in the study, the adsorbent was negatively charged, indicating that the variation in removals at different pH is due to changes in the property of the adsorbates, but not the adsorbent.

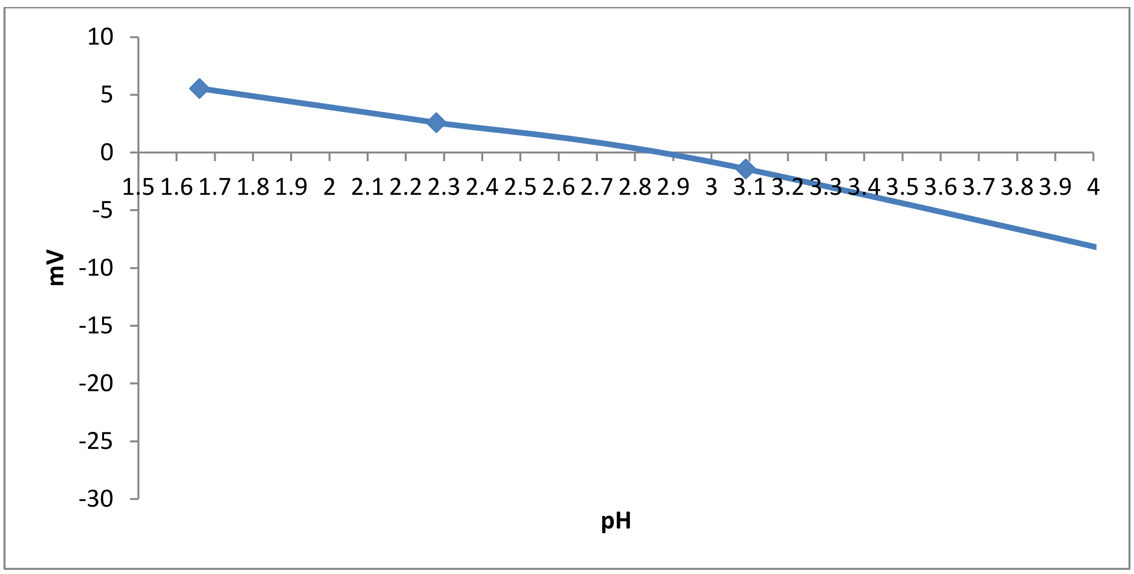


Figure 4.8. Zeta potential measurements for BCD/silica

The decrease in adsorption capacity of GAC towards 17β-estradiol at higher pH was also reported by Zhang and Zhou (2005). However, under the same conditions, the adsorption capacity of estrone was found to increase dramatically (Zhang and Zhou 2005). This shows that the mechanism of adsorption of estrogens onto GAC is primarily governed by hydrophobic interactions unlike hydrogen bonding which was observed in case of BCD-based adsorbents (Moon et al. 2008). About 91% removal of BPA was observed at neutral pH (pH 7.0). The removal was not affected at acidic pH (pH 4.0). However, when the pH was raised to 11.0 (pka of BPA is around 10.5), about 50% reduction in the removal of was observed. A significant reduction in removal capacity of the adsorbent around pka value of the contaminants was also observed in case of estrogens. This shows that the inclusion stability of the BCD molecules with contaminants decreases when the contaminants are negatively charged.

4.3.5. Effect of humic acid (HA) in ECs removal

HA represents one of the major components of natural organic matter (NOM) that is present in natural water. In real world scenario, such compounds are present in mg/L level where as the ECs are commonly found in ng/L to low μg/L range. Therefore, it is important to understand how the removal process of the ECs gets affected in presence of relatively high concentration of NOM. In this study, HA was chosen as a source of NOM and PFOA and PFOS are selected as model contaminants in a mixture containing 50 μg/L each. The concentration of HA was measured as dissolved organic carbon (DOC). First, batch experiments were done with the adsorbent in MQ water and the removal efficiencies of the adsorbent were determined for PFOA and PFOS (mixture containing 50 μg/L each). These results were compared with another set of batch experiments done in presence of HA at two different concentrations (4 and 12 mg/L of DOC). All other experimental conditions were kept constant. These experiments were done in duplicates. The results are summarized in Figure 4.9.

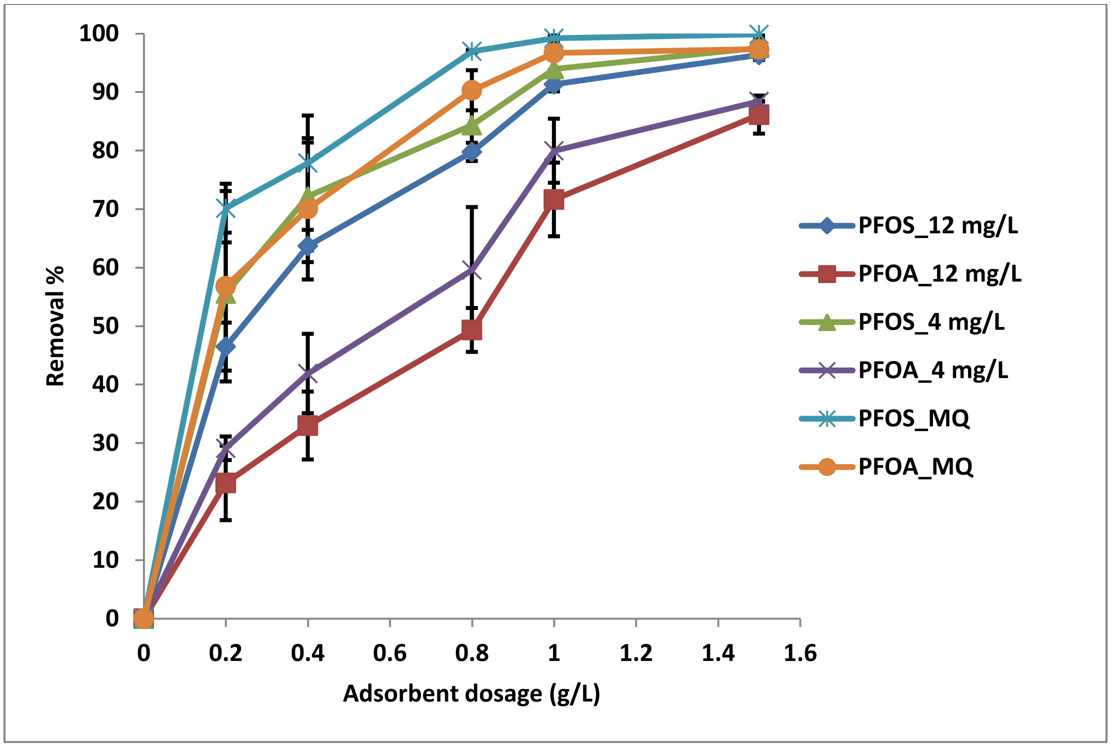


Figure 4.9. Effect of HA in removal of PFOA and PFOS

It was observed that the removal efficiencies of the adsorbent for PFOA and PFOS were decreased in presence of HA than MQ water. However, the removal of PFOS was less affected compared to PFOA, which showed significant reduction in removal when HA was introduced in the water matrix. At 0.8 g/L, about 97 % (SD = 0.2, n = 2) removal of PFOS was observed in MQ water which decreased to about 84 % (SD = 4.9, n = 2) and 80% (SD = 1.6, n = 2) in 4 mg and 12 mg/L of DOC, respectively. Therefore, it was noted that there was a little effect in the performance of the adsorbent in case of PFOS removal in the presence of HA in water. Moreover, the removal efficiency was not significantly affected when the concentration of HA was increased from 4 mg/L to 12 mg/L of DOC. On the contrary, the performance of the adsorbent was significantly affected in the removal of PFOA. At 0.8 g/L of adsorbent dosage, about 90 % (SD = 3.4, n = 2) removal of PFOA was observed in MQ water which decreased to about 60 % (SD

= 10.8, n = 2) and 49% (SD = 3.7, n = 2) in 4 mg and 12 mg/L of DOC, respectively. The variation in the removal of PFOA and PFOS in presence of HA could be attributed to the higher affinity of the adsorbent towards PFOS than PFOA. If we look at the structures of PFOA and PFOS, both molecules have the same number of carbon chain length with two different functional groups. PFOA has a carboxylic acid functional group where as PFOS has a sulfonic acid functional group. Therefore, the higher affinity of the adsorbent for PFOS could be due to the stronger interaction of the cyclodextrin molecules with the sulfonic acid functional group of PFOS. The more efficient removal of PFOS than PFOA was also observed with GAC F300 (Appleman et al. 2013), PAC (Yu et al. 2012), mulitwalled carbon (Li et al. 2011), and GAC F300 in full scale treatment system (Appleman et al. 2014).

The DOC of each sample after adsorption was analyzed and no removal of DOC was observed. This confirms that the decrease in the removal efficiency of the adsorbent for PFOA and PFOS in presence of HA is due to steric effect and not due to the competition effect. The presence of DOC in water is likely to reduce the removal efficiency of any adsorbent for a given contaminant due to two reasons: competition with the target contaminant for adsorption sites and steric hindrance (obstructing the target contaminant from reaching the adsorption sites due to the bulky nature of the non-target compounds present in the water matrix). However, the selective nature of the adsorbent in removing PFOS much more efficiently than PFOA is still not fully understood.

4.3.6. Removal of ECs from wastewater at environmentally relevant concentrations

All previous experiments were done at μg/L (ppb) leval initial concentration of the ECs studied. In real workd scenario, these ECs would be found in mostly ng/L (ppt) level. Therefore, in order to represent the real environmental concentration of ECs, further experiments were done in wastewater by spiking the environmentally relevant concentration i.e, 500 ng/L of each EC studied. For wastewater, grab samples of secondary effluent were taken from a municipal wastewater treatment plant and experiments were done by filtering the samples with 0.4 μ membrane filter and then spiked with 500 ng/L of selected ECs. The wastewater samples were characterized prior to performing experiments and the details are provided in Table 4.2.

Table 4.2. Characterization of wastewater

Parameter	**Unit**	**Value**
pH		6.9
Conductivity	μs/cm	780
Total dissolved solids	mg/L	561
Salinity	mg/L	394
Alkalinity	mg/L as CaCO3	125
Dissolved organic carbon	mg/L	6.4
Chemical oxygen demand	mg/L	12

To compare the removal efficiencies of the adsorbents for ECs, batch experiments were also perfomed in MQ water at 500 ng/L initial concentration under same experimental conditions. The results are summarized in Figure 4.10.

The adsorbent removed more than 99% of both PFOS (SD = 0.06, n = 2) and PFOA (SD = 0.2, n = 2) from MQ water at adsorbent dosage of 1.5 g/L where as in case of wastewater, 91 % of PFOS (SD = 2.6, n = 3) and 82 % of PFOA (SD = 2.5, n = 3) from wastewater at 2.0 g/L adsorbent dosage.

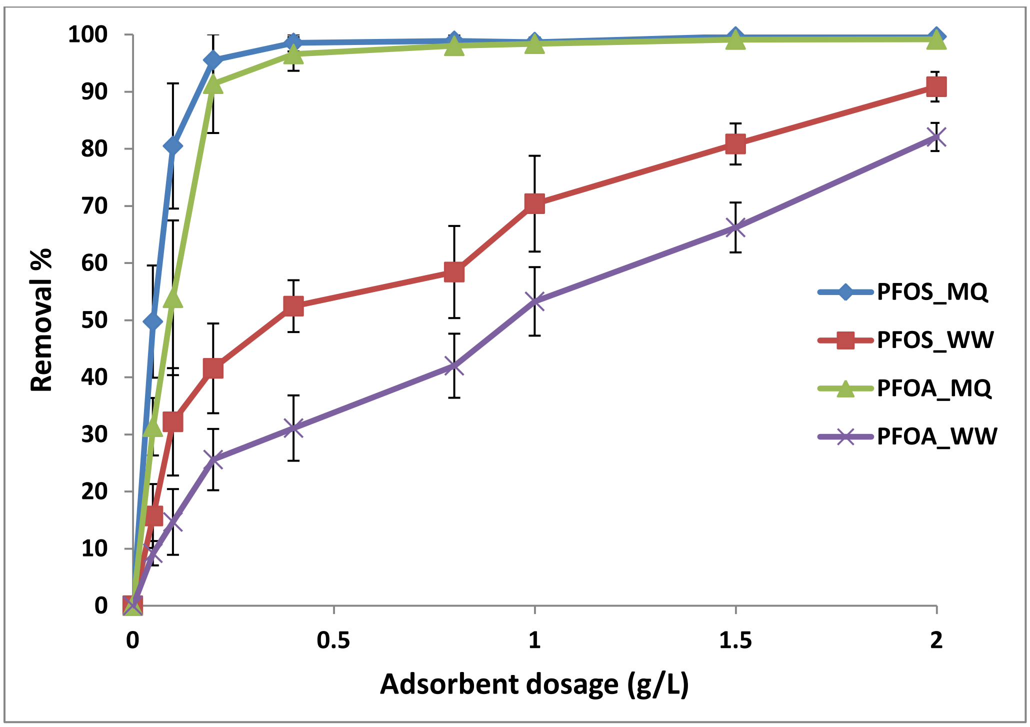


Figure 4.10. Removal of PFOA and PFOS in MQ water and municipal wastewater secondary effluent

As observed earlier in case of HA, the removal of PFOA was supressed due to the matrix effect in case of wastewater as well and the removal of PFOS was less affected than PFOA. However, in both cases, the remmoval efficiency of the adosrbent was reduced more than that was observed in case of HA. The DOC of the wastewater was about 6 mg/L. So, if the results are compared with the previous results with HA, the further reduction in the removal efficiency of the adsorbent for PFOS and PFOA in wastewater could be due to the presence of other contamiants present in the wastewater matrix that could be removed by the adsorbent.

Therefore, unlike the effect of HA, the reduction in the removal efficiency of the adsorbent in wastewater matrix could be explained as a cumulatve effect of steric hindrance as well as compeition for adsorption sites with non-target contaminants. Similar results were also observed in case of 17β-estradiol and BPA as shown in Figure 4.11. At 2.0 g/L adsorbent dosage, more than 99 % removal (SD = 0.1, n = 2) of 17β-estradiol in MQ water. In case of BPA, as observed in earlier studies, BPA showed the least removal both in MQ water and wastewater matrices. The low adsorption capacity for BPA was also observed in previous studies.

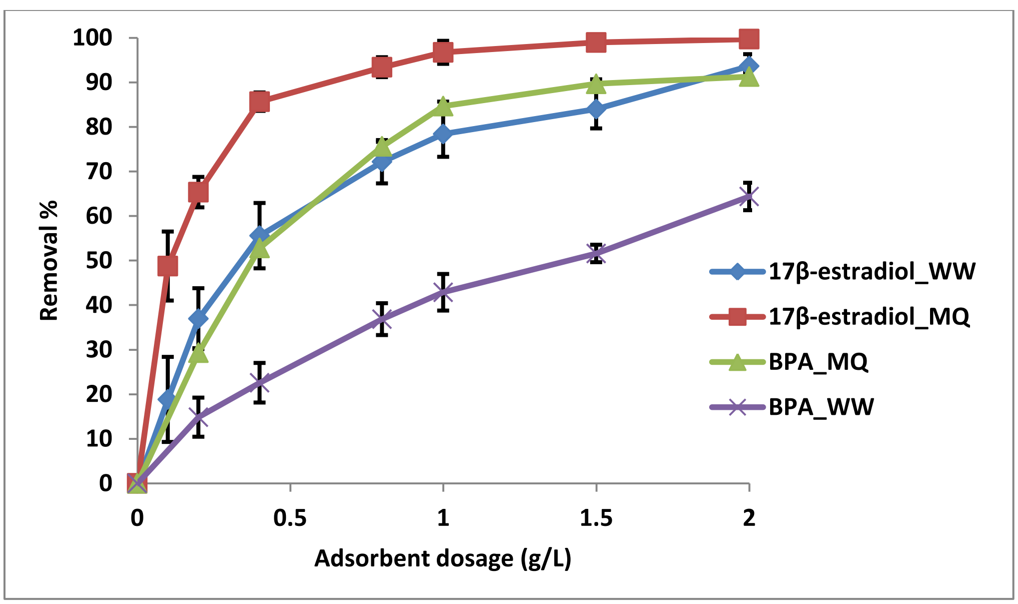


Figure 4.11. Removal of 17β-estradiol and BPA in MQ water and wastewater secondary effluent

In order to study the efficiency of the adsorbent for the simultaneous removal of organic and inorganic contaminants, isotherm experiments were done for the removal of PFOA and PFOS in presence of Cr (VI). At 0.8 g/L of adsorbent dosage, about 97 % of PFOS and 93% of PFOA were removed in presence of Cr (VI). At the same adsorbent dosage, about 14% removal of Cr (VI) was also observed. However, the adsorbent was able to remove upto 40 % of Cr (VI) when the adsorbent dosage was increased to 5.0 g/L (Figure 4.12).

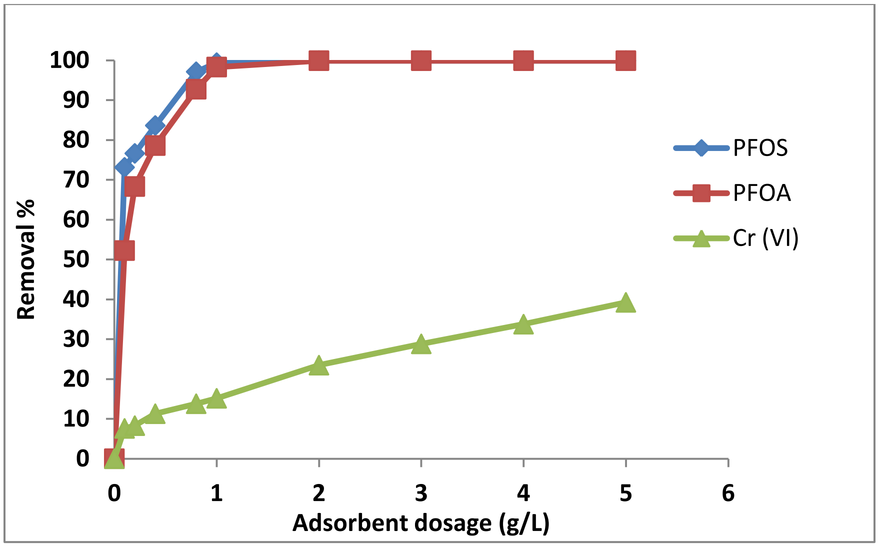


Figure 4.12. Removal of PFOA and PFOS with BCD/silica in presence of Cr (VI)

CDs are known to have unique property to remove both organic and inorganic contaminants. The hydrophobic cavity of CDs serves as sites for the removal of organic contaminants whereas the hydroxyl groups present at the rim of the cavity of CDs serve as additional sites for the complexation with inorganic compounds (mostly metals). Complexation of CDs with various metals have been well documented in the literature such as cobalt, cadmium, lead, arsenic. Some studies have also shown that CD based adsorbents have potential for simultaneous removal of organic and inorganic contaminants from water.

4.3.7. Column experiments

In column experiements with both 17β-estradiol, no breakthrough was observed till 4500 bed volumes (BVs) (Figure 4.13). In order to study the breakthrough pattern, 90 % removal of the initial concentration of 17β-estradiol was set as the breakthrough point (i.e. breakthrough concentratrion = 2.5 μg/L). Same benchmark was also established for the removal of PFOA and PFOS. In case of PFOA and PFOS, no breakthrough was observed till 6300 BVs (Figure 4.14). These results showed favorable conditions for the removal of all ECs studied in continuous flow systems.

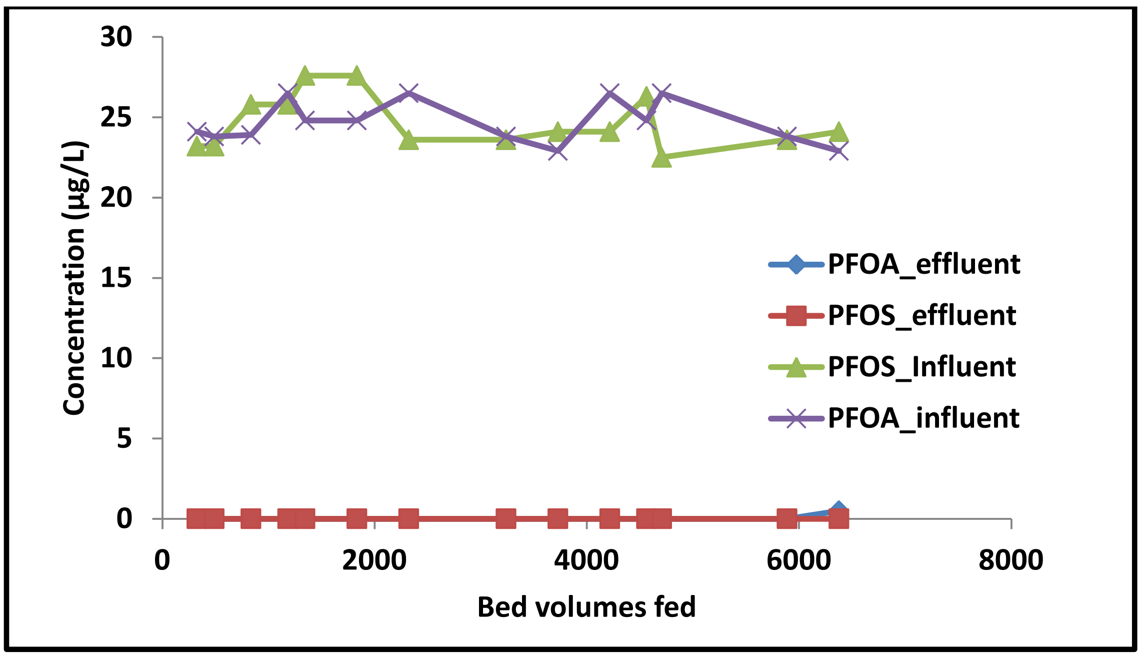


Figure 4.13. Breakthrough curves for the removal of PFOA and PFOS [EBCT = 3 min; flow = 10 ml/min; bed volume = 30 ml; wt of adsorbent = 20 g]

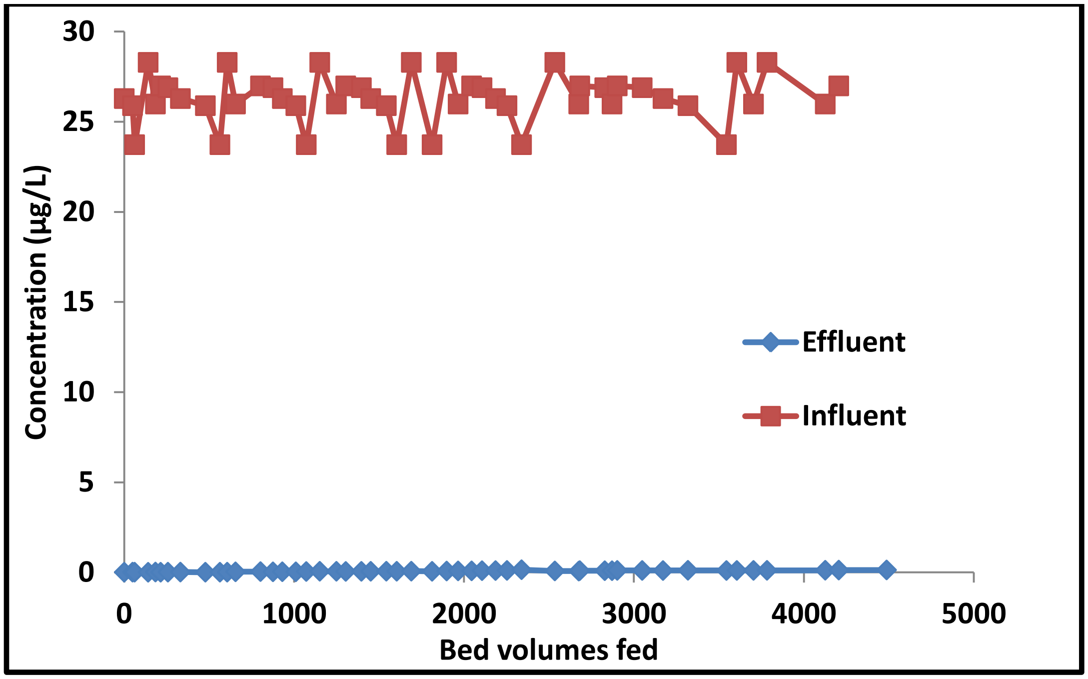


Figure 4.14. Breakthrough curves for the removal of 17β-estradiol [EBCT = 10 min; flow = 15 ml/min; bed volume = 147 ml; wt of adsorbent = 100 g]

4.3.8. Regeneration of adsorbent

The approach of using ozone for the regeneration of adsorbent was observed to be very effective over seven successive cycles in case of 17β-estradiol and BPA. The results showed successful regeneration of the adsorbent by destroying the contaminant (trapped in the cavity of BCD) with ozone over seven successive cycles. It was also observed that the adsorbent showed a slight decrease in its adsorption capacity in first cycle but later on it continued to remove the target contaminant with almost the same efficiency (Figure 4.15).

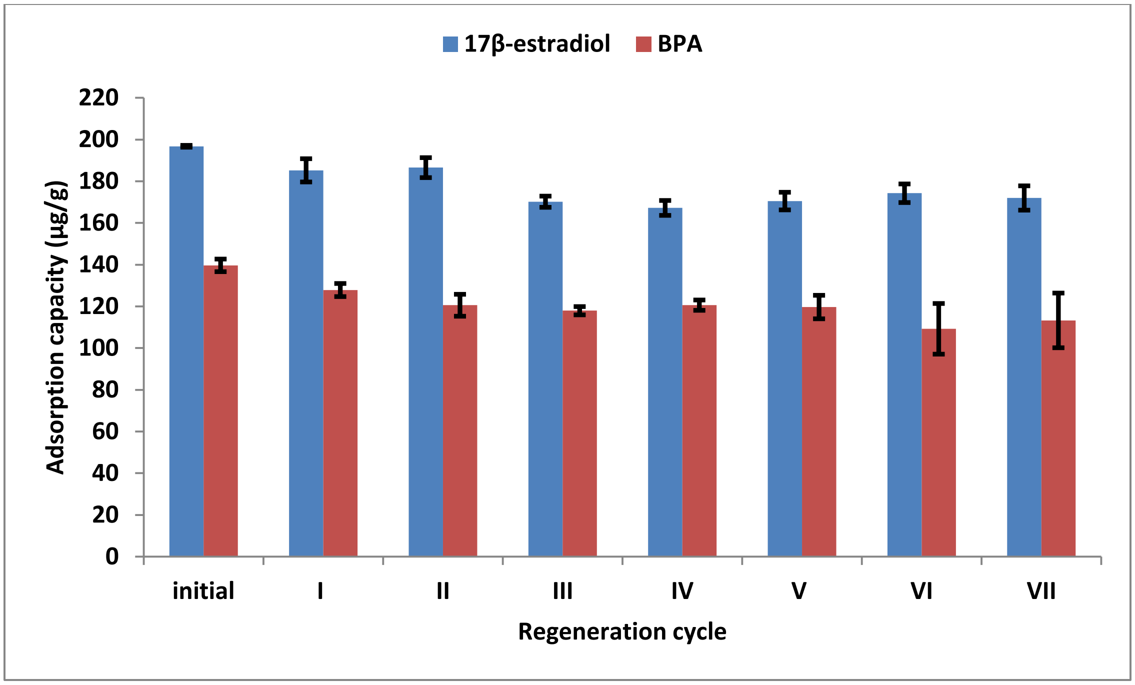


Figure 4.15. Regeneration of BCD/silica with Ozonation for the removal of 17β-estradiol and BPA in triplicates [intial conc: 200 µg/L; adsorbent dosage: 1.0 g/L; intial pH: 6.2 - 7.1; Ozonation at 5 wt% and 10 L/hr for 2 hr].

The regeneration results also showed that the adsorbent was stable under ozonation over seven successive cycles (total of 14 hr exposure time to ozonation). The ozonation time for regeneration was not optimized in this study. Therefore, further optimization of the ozone dosage and exposure time could provide more understanding of the regeneration process which could be helpful in determining the life of the adsorbent under ozonation. Though this regeneration technique worked well for 17β-estradiol and BPA, it should be noted that this technique would be applicable to only those contaminants that can be degraded with ozone. The same technique was unable to regenerate the adsorbent when PFOA was used as a model contaminant. The adsorbent was unable to remove PFOA (<5 % removal) after it was regenerated with ozone. The inability of ozone to degrade PFOA was also reported in the literature (Lin et al. 2012).

In order to regenerate the adsorbent saturated with PFOA, another approach was used to desorb PFOA with 0.2 M NaOH. In this case, the adsorbent was first saturated in two successive adsorption cycles and then the saturated adsorbent was washed with 20 ml of 0.2 M NaOH (for 0.1 g adsorbent). The solution was allowed to shake for 16 hr and the adsorbent was retained for another batch of adsorption cycle. This experimental procedure was followed upto four successive regeneration cycles and the results are shown in Figure 4.16. The adsorption capacity shown in the Figure 4.16 is the cumulative from two adsorption cycles in each cycle.

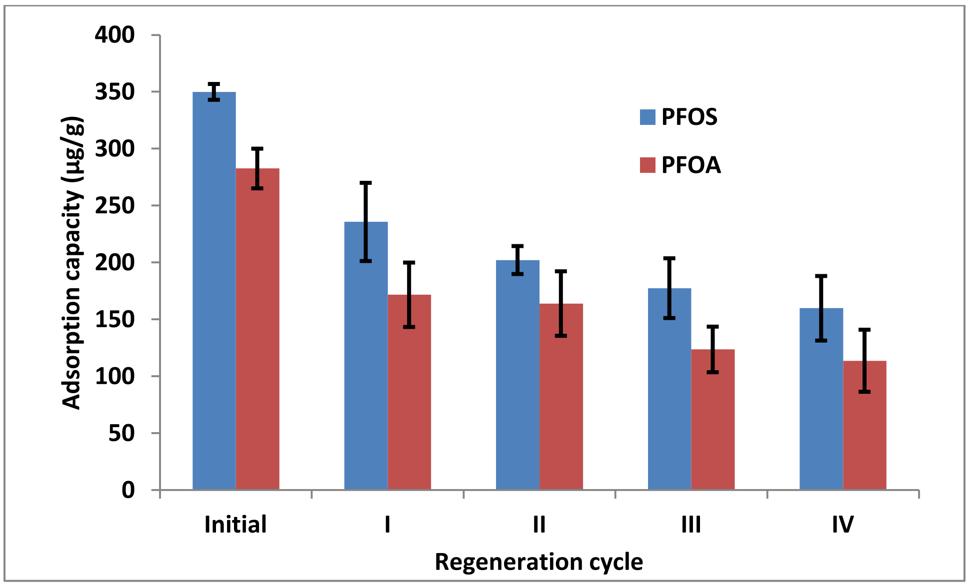


Figure 4.16. Regeneration of BCD/silica with 0.2 M NaOH for PFOA and PFOS

It was observed that the adsorption capacity of the adsorbent was significantly reduced for both PFOA and PFOS after first regeneration with 0.2 M NaOH. Based on the results, it was assumed that the regenerating solution was not able to desorb the total amount of PFOA and PFOS adsorbed onto the adsorbent. To validate this hypothesis, the desorbed sample was analyzed to quantify the concentration of PFOA and PFOS. The data from both adsorption cycle and desorption cycle was used to calculate the recovery of each contaminant in the regeneration process with 0.2 M NaOH. The average recoveries for PFOA and PFOS were 70 % (SD = 13.2, n = 2) and 35 % (SD = 6.6, n = 2), respectively.

4.4. CONCLUSIONS

The best adsorbent selected from previous studies was used to evaluate the performance of the adsorbent in removing the selected ECs. The adsorbent was found to be effective in removing 17β-estradiol, PFOA, and BPA in single component and estrogens and PFCs in multicomponent systems from MQ water. Results from batch experiments showed more than 95% removal of 17β-estradiol in single component system and more than 90% removal of most of the estrogens from multicomponent system (mixture of 12 estrogens). Similarly, more than 99% removal of PFOA was observed in single component system and more than 90% in multicomponent system. The adsorbent was able to remove upto 90% of BPA in MQ water. The effect of pH showed that the removal capacity of the adsorbent decreases when the adsorbates are negatively charge. So, the mechanism of removal may be attributed to the formation of inclusion complexes of BCD molecules with the contaminants which is influenced by various factors such as size, shape, presence of functional group, and hydrogen bonding. In presence of HA, the removal of PFOA was significantly reduced where as a slightly affected in case of PFOS. However, the effect of HA was not observed to be increased in the removal of both PFOA and PFOS when the concentration of DOC was increased from 4 to 12 mg/L. The isotherm experiements done with municipal wastewater showed a significant decrease in removal efficiency of the adsorbent for all ECs studied, demanding high adsorbent dosage to meet the same removal as in MQ water system. The adsorbent showed very good regeneration ponential and successfully regnerated with ozone over seven succesive cycles for the removal of 17β-estradiol and BPA. The adsorbent was regenerated with 0.2M NaOH in case of PFOA over four successive cycles.

CHAPTER 5

SYNTHESIS OF CYCLODEXTRIN-BASED ADSORBENTS BY PHYSICAL IMPREGNATION OF 2-HYDROXY-PROPYL BETA CYCLODEXTRIN FOR THE REMOVAL OF SELECTED EMERGING CONTAMINANTS OF CONCERN

5.1. Introduction

Chemically bonded cyclodextrins or its derivatives onto various supports have been widely reported in the literature. However, chemical bonding may not be applicable in all cases, especially when the material to be coated does not possess any functional groups. In such cases, either the support has to be functionalized (if applicable) prior to coating using suitable techniques or the support could be physically impregnated without any chemical binding between the polymer and the support. Physcial impregnation could be used when the support is not very stable either thermally and/or chemically to withstand the experimental conditions required for the coating processes. Moreover, this type of technique could be used for coating a large surface at room temperature by applying on the surface of the support such as spraying.

In this chapter, a simple method was developed to phycially impregnate 2-hydroxy propyl beta cyclodextrin (hpBCD) polymer onto various supports such as zeolite, iron oxides, and filter paper by solvent evaporation method. The objective of the study was to to examine the compatibility of the developed techniques for a wide varieties of supports and use the developed products as adsorbents to remove emerging contaminants (ECs) of concern from water and wastewater. This approach could be used as a new filtration system or with existing filtration system where the support can not be modified chemically.

5.2. Materials and Methods

5.2.1. Materials

2-hydroxy propyl beta cyclodextrin (hpBCD), dimethylformamide (DMF), hexamethylene diisocyanate (HMDI), Iron oxides (< 5 μm and < 50 nm), filter paper and humic acid (HA) were purchased from Sigma-Aldrich. Zeolite Y (CBV 100) was purchased from Zeolyst International. All the ECs studied (PFOA, PFOS, and BPA) were purchased from Sigma-Aldrich.

5.2.2. Methods

5.2.2.1. Preparation of adsorbents

5.2.2.1.1. Synthesis of water insoluble hpBCD polymer

For the synthesis of water insoluble hpBCD polymer, 2.92 g of hpBCD was dissolved in 50 ml DMF. The solution was transferred to an oil bath set at 60 ^{o}C and stirred for 20 min. To the solution, 4.6 ml of HMDI was added dropwise under continuous stirring and the solution was left stirring for 16 hr. In order to check the formation of polymer, a few drops of the solution was taken and added to a beaker containing water. A white precipitate was observed which confirmed the completion of polymerization reaction between hpBCD and the crosslinking agent HMDI. The solution was allowed to cool down to room temperature.

5.2.2.1.2. Synthesis of hpBCD impregnated Fe_3O_4 particles

After the polymerization reaction was complete, 3.0 g of Fe_3O_4 micro particles (< 5 μm) was added in the solution and mixed on a shaker at 160 rpm for 48 hr. The final adsorbent was separated from the solution with a bar magnet and washed with MQ water, methanol and acetone, respectively. The adsorbent was dried at 60 ^oC under vacuum overnight. Finally, the adsorbent was ground gently and stored in a glass container for future experiments. Another batch of adsorbent was also preapared by using the same experimental procedure where nano sized Fe_3O_4 particles (< 50 nm) were used.

5.2.2.1.3. Synthesis of hpBCD impregnated Zeolite

For the synthesis of hpBCD polymer impregnated zeolite, the same experimental procedure was followed as in the synthesis of Fe_3O_4 particles. The support was replaced with zeolite in this case.

5.2.2.1.4. Synthesis of hpBCD impregnated filter paper

A different approach was used in impregnation of hpBCD polymer onto filter paper as the previous approach of mixing the polymer solution with the substrate was not appropriate in case of filter paper. Here, after the synthesis of hpBCD polymer, the polymer solution was sprayed on the surface of filter paper and the amount of polymer loading on the filter paper was varied in different batches.

Batch I: The solution was sprayed over the filter paper making a thin layer with the help of a glass pipette and a dropper. The solution was not added twice on the same spot or not allowed to overlap to ensure a very thin layer of coating with 100% coverage on the filter paper. The impregnated filter paper was left for drying at room temperature. Impregnation was done only on one side of the filter paper.

Batch II: The solution was sprayed all over the filter paper and was kept adding till the filter paper was completely soaked with the solution. Here, the solution was added twice on the same spot to ensure the increment in loading, but once the filter paper was completely soaked, it was left for drying at room temperature. Impregnation was done only on one side of the filter paper.

Batch III: The same procedure as mentioned in Batch II was followed. In addition to that, after one hour of drying period, another layer of solution was added following the same procedure as before to increase the loading of polymer. Impregnation was done only on one side of the filter paper.

Batch IV: Here, another set of impregnated filter paper was prepared by following the same procedure as described in Batch III. Furthermore, the loading of polymer was increased by spraying the solution on both sides of the filter paper.

All the impregnated filter papers were left for drying at room temperature for 48 hr. The dried impregnated filter papers were washed five times with DI water and then two times with methanol. Finally, they were dried at 60^{o}C under vacuum for 4 hr. Thus obtained filter papers were allowed to cool down to room temperature and weighed. The polymer loading was calculated for each set based on the difference in weights of the filter papers before and after impregnation.

5.2.2.2. Characterization of the adsorbents

Perkin Elmer Spectrum 100FT-IR Spectrometer was used to analyze the samples for FTIR. The samples were scanned from 600 to 4000 cm-1 at resolution 4 and number of scan was 16. Perkin Elmer Pyris 6 TGA was used for the thermal analysis of the samples. The temperature range was 30 to 800 ^{o}C with heating rate of 10 ^{o}C per minute under air atmosphere. Micromeritics ASAP 2020 was used to analyze the surface area and porosity of the samples. N2 gas was used for adsorption and desorption in order to calculate the surface area and porosity of the samples. The degassing temperature was set to 120 ^{o}C and the degassing time was 600 min for each sample.

5.2.2.2.1. Scanning electron microscopy (SEM)

SEM (FEI Quanta 450FEG SEM) equipped with the latest Energy Dispersive Spectrometer (Oxford Aztec Energy Advanced EDS System) was used to take images of the samples.

5.2.2.2.2. Zeta potential

The pHzpc and zeta potentials of the oxides were measured using a Zetasizer Nano ZS

(Malvern Instruments).

5.3. Results and Discussions

5.3.1. hpBCD impregnated Fe_3O_4 magnetic adsorbent

5.3.1.1. Removal of ECs in MQ water

As a preliminary experiment, the synthesized hpBCD polymer impregnated Fe_3O_4 (micro) was tested for the removal of PFOA and BPA in MQ water at initial concentrations of 50 μg/L and 100 μg/L, respectively. These experiments were conducted separately at 1.0 g/L adsorbent dosage and the contact time was 48 hr. The equilibrium time was obtained by monitoring the concentration of EC in the solution over time. Control experiments were also done with Fe_3O_4 only for each contaminant at 1.0 g/L adsorbent dosage. The results are shown in Figure 5.1.

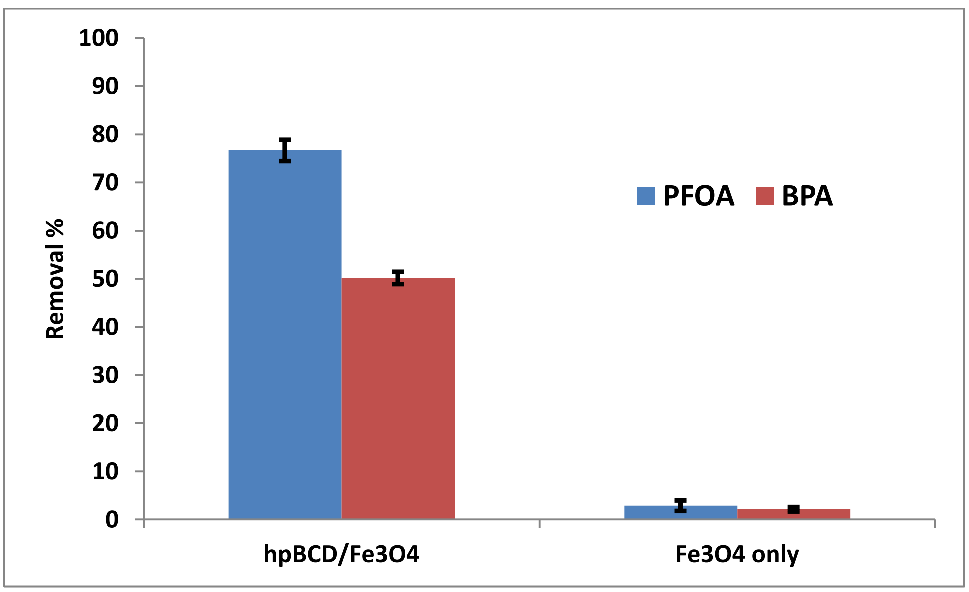


Figure 5.1. Screening results for the removal of PFOA and BPA with hpBCD/Fe_3O_4

It was observed that the synthesized magnetic adsorbent (hpBCD coated Fe_3O_4) removed an average of 76 % of PFOA (SD= 2.9; n = 2) and 50 % of BPA (SD= 2.2; n = 2) initially present in the solution. Control experiments with Fe_3O_4 only did not show any significant removal (< 5%) of any of the contaminants studied. Therfore, it was confirmed that the removal of both PFOA and BPA was due to the presence of hpBCD polymer that was impregnated onto the magnetic particles. This result also confirmed the successful impregnation of the polymer onto the support. However, the removal efficiency of the adsorbent was less than that was observed in previous studies with other adsorbents (BCD coated silica). It was assumed that the polymer loading onto the support was not enough to remove the contaminants efficiently. Therefore, another batch of adsorbent was synthesized following the same procedure other than the reaction time for impregnation. This time, after the synthesis of hpBCD polymer, the mixing time of the polymer with the Fe_3O_4 particles was increased from 48 hr to 96 hr. In order to compare the effect of mixing time for polymer impregnation in the removal of the ECs studied, two sets of isotherm experiments were conducted using the old adsorbent (with 48 hr impregnation time) and new adsorbent (with 96 hr impregnation time) under same experimental conditions as mentioned before. The results are summarized in Figure 5.2.

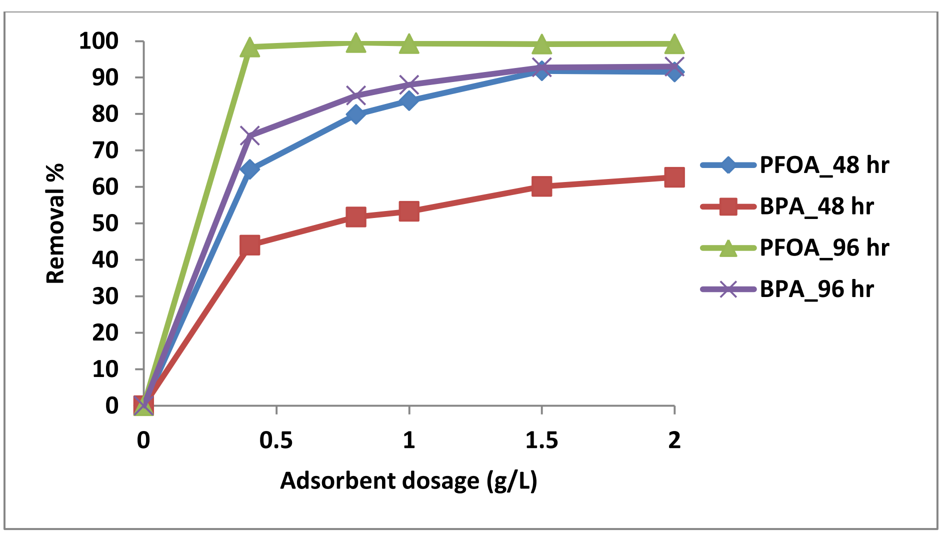


Figure 5.2. Isotherm experiments with hpBCD/Fe_3O_4 for the removal of PFOA and BPA

It was observed that the new adsorbent was more efficient in removing both PFOA and BPA than the old adsorbent. At 0.4 g/L adsorbent dosage, with the new adsorbent, the removal of BPA was increased from 44% to 74% and an increase from 65% to 98% was observed in case of PFOA. The new method of synthesis was used to prepare new batches of adsorbents for furthur experiments.

The adsorbent was also tested for the removal of PFOA at an initial concentration of 50 μg/L in MQ water. The results are shown in Figure 5.3. The adsorbent was very effective in removing more than 99% of PFOA at very low adsorbent dosage. The data obtained from isotherm experiment was fitted to Freundilch model and the result is shown in Figure 5.3. From Freundlich isotherm, the Freundlich constants were calacuated (K = 282 μg/g; n = 1.42).

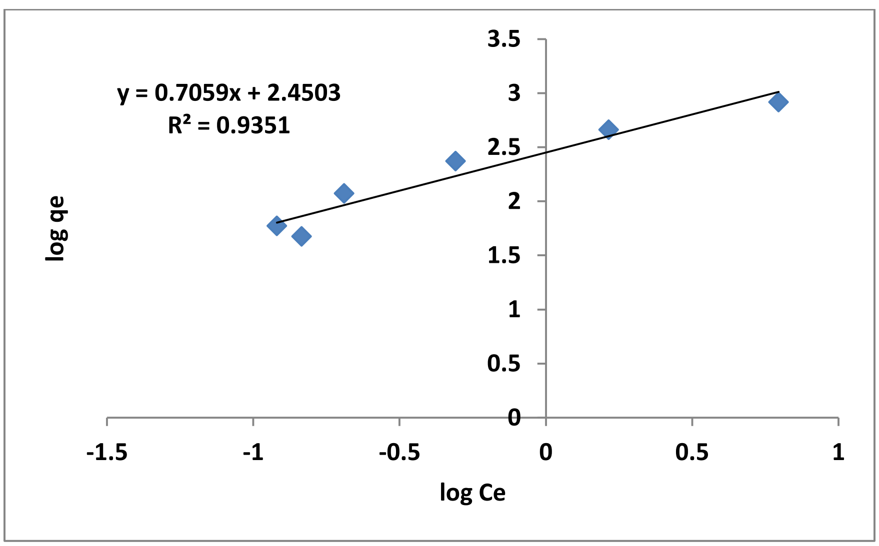


Figure 5.3. Freundlich isotherm for the removal of PFOA

Control experiments done with Fe_3O_4 only did not show any significant removal (< 5%) in case of both PFOA and BPA.

5.3.1.2. Effect of HA in ECs removal

In order to study the effect of HA in the removal of ECs, PFOA and PFOS were taken as model contaminants in mixture and two different concentrations of 4 mg/L and 12 mg/L of DOC were prepared. Only adsorbent synthesized using nano Fe_3O_4 was used for all experiments. All experiments were conducted at initial concentration of 50 µg/L of both PFOA and PFOS. The results are shown in Figure 5.4.

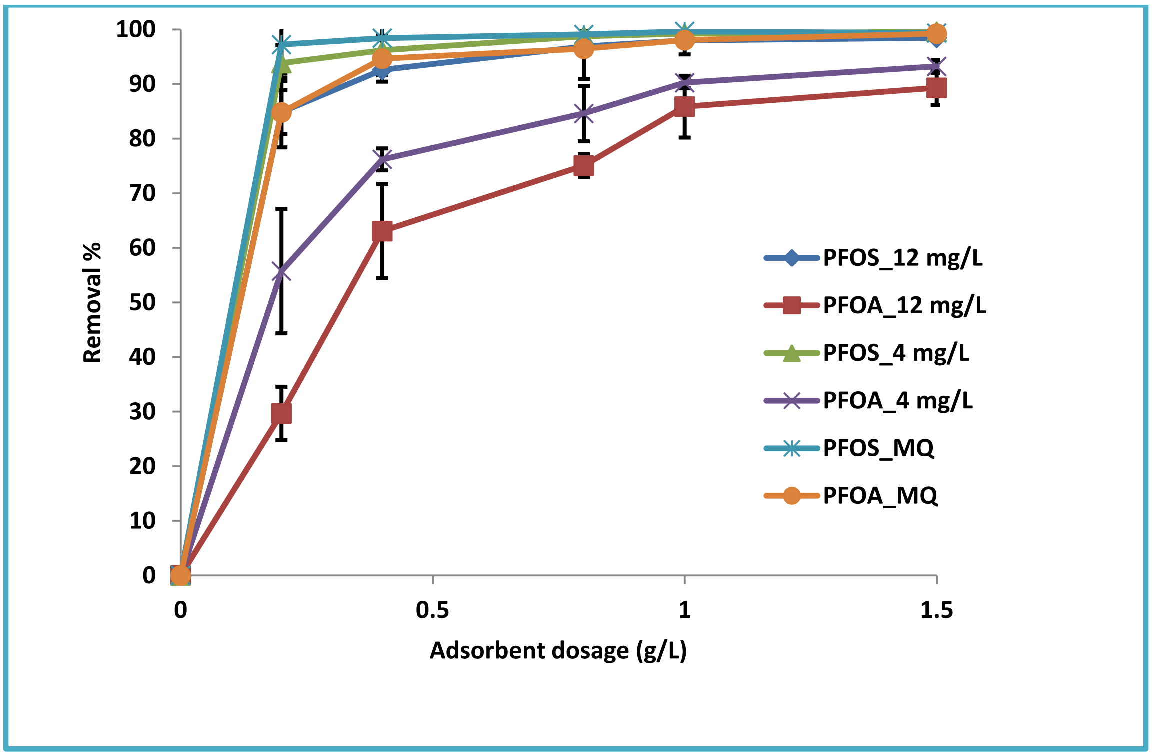


Figure 5.4. Effect of HA in the removal of PFOA and PFOS with hpBCD/Fe3O4 nano adsorbent

It was observed that the presence of HA influenced PFOA removal significantly than PFOS. At 0.8 g/L of adsorbent doage, an averge removal of 99 % of PFOS (SD = 1.2, n = 2) and 96 % of PFOA (SD = 3.5, n = 2) were observed in MQ water. In case of PFOS, the removal percent was maintained at 99 % (SD = 0.2, n = 2) and 97 % (SD = 0.4, n = 2) in presence of 4 mg/L and 12 mg/L of DOC, respectively. Therfore, the prsence of HA at both cocenntrations (4 and 12 mg/L of DOC) did not have a significant influence on the removal of PFOS when compared with the removal in MQ water. However, removal of PFOA was significantly affected by the presence of HA. At the same adsorbent dosage of 0.8 g/L, an average removal of 85 % (SD = 5.1, n = 2) and 75 % (SD = 2.1, n = 2) were obsereved in case of PFOA in presence of 4 mg/L and 12 mg/L of DOC, respectively. The mechanism is not well understood. However, it is believed that the higher affinity of PFOS to get adsorbed onto the adsorbent makes it less successptible to the possible effects of HA in reducing the adsorption capacity.

5.3.1.3. Removal of ECs from wastewater at environmentally relevant concentrations

In order to represent real world scenario, the adsorbent was tested for the removal of PFOA and PFOS in wastewater. Secondary effluent of a municipal wastewater treatment plant was collected and spiked with 500 ng/L of PFOA and PFOS. The characteristics of wastewater are given in Table 5.1.

Table 5.1 Characteristics of Wastewater

Parameter	Unit	Value
pH		6.9 -7.3
Conductivity	µs/cm	735 - 880
Alkalinity	mg/L as $CaCO_3$	120 - 150
DOC	mg/L	6.4 - 7.6
Chloride	mg/L	312 - 362
Nitrate	mg/L	12 - 63
Nitrite	mg/L	0 – 22
Sulfate	mg/L	40 – 45
Phosphate	mg/L	16 - 18

Isotherm experiments were conducted under the same experimental conditions as before. To study the effect of matrix on the removal of target ECs, the adsorbents were also tested for the removal of PFOA and PFOS at 500 ng/L in MQ water. At 0.4 g/L adsorbent dosage, an average removal of 99 % of PFOS (SD = 0.1, n = 2) and 96 % of PFOA (SD = 0.9, n = 2) were observed in MQ water (Figure 5.5). In wasewater matrix at the same adsorbent dosage, the removal efficiency was decreased to 83 % for PFOS (SD = 8.7, n = 3) and 36 % (SD = 10.2, n = 3) for PFOA. As observed earlier in case of HA, the removal of PFOA was affected more than PFOS due to the wastewater matrix effect.

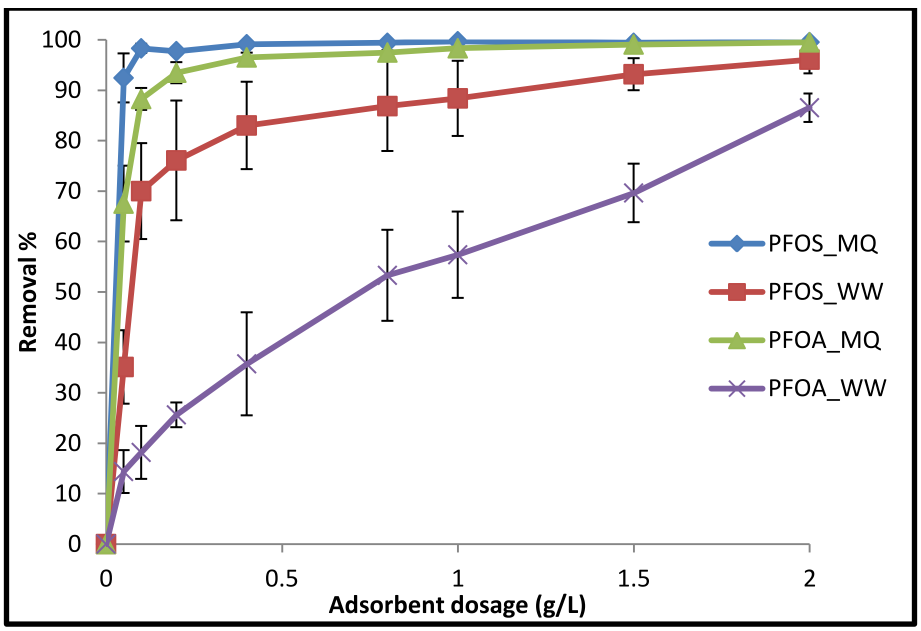


Figure 5.5. Removal of PFOA and PFOS in MQ water and wastewater secondary effluent

5.3.1.4. Removal of PFOA and PFOS in presence of hexavalent chromium

In presence of Cr (VI), at 0.1 g/L adsorbent dosage, about 95 % removal of PFOS and 41 % removal of PFOA were observed in MQ water (Figure 5.6). It was observed that the removal of PFOA in presence of Cr (VI) was suppressed significantly. This trend can be well understood if we compare the removal of PFOA and PFOS in MQ water in the absence of Cr (VI) (discussed earlier). The removal of PFOS was unaffected by the introduction of Cr (VI) in the solution unlike the removal of PFOA. At the same time, about 66 % removal of Cr (VI) was also observed at 1.5 g/L adsorbent dosage (Figure 5.6). However, when control experiments were done with Fe_3O_4 particles only, about 49 % removal of Cr (VI) was observed at 1.0 g/L (no removal of PFOA or PFOS was observed). This result indicats that the Fe_3O_4 particles alone are capable of removing Cr (VI) from water. Therefore, the removal of Cr (VI) from the water in presence of the adsorbent is the sum of the signifcant removal due to Fe_3O_4 particles and a very minimum contribution from the hpBCD polymer present in the adsorbent. The ability of BCD based polymer to remove Cr (VI) was also studied by several scholars.

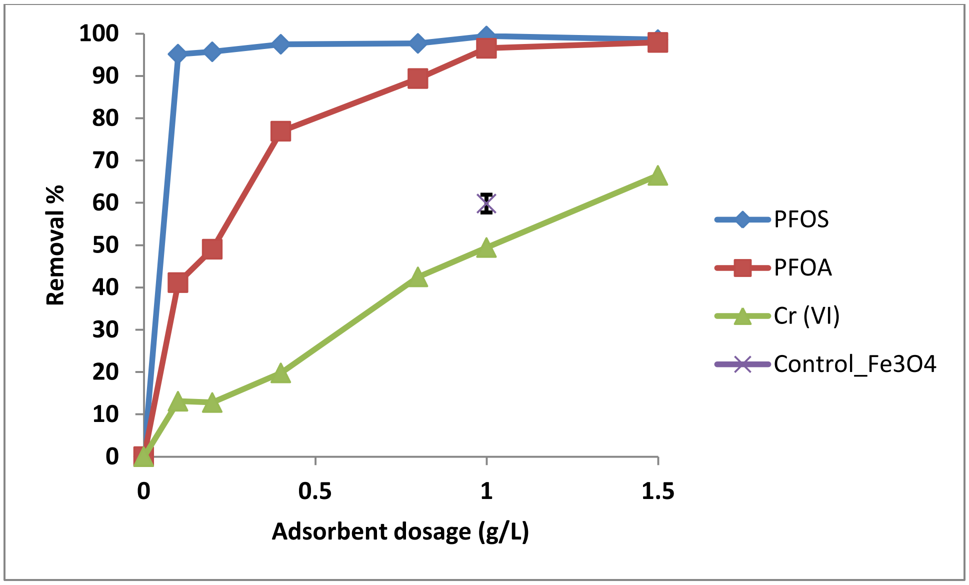


Figure 5.6. Removal of PFOA and PFOS in presence of Cr (VI)

In case of hpBCD impregnated Fe_3O_4 adsorbent, the removal of Cr (VI) seemed to be associated with the suppression of removal of PFOA without influencing the removal of PFOS. In previous studies with BCD/Silica adsorbent, no such trend was observed, as the adsorbent was able to remove a small fraction of Cr (VI) present in water. Therfore, in case of Fe_3O_4, eventhough the adsorption sites for Cr (VI) are different than PFOA, the removal of PFOA was signficantly affected due to the presence of Cr (VI) in the water matrix. These results are in agreement with the results obtained in presence of HA where presence of HA supressed the removal of PFOA without being removed. Therfore, it is futher evident that PFOS has higher affinity to get adsorbed onto the adsorbent than PFOA.

5.3.1.5. Characterization of adsorbent

5.3.1.5.1. FTIR

The adsorbent was subjected to FTIR analsysis and the results were compared with the unmodified substrates along with all other reagents used in the chemical reaction. The FTIR spectra are shown in Figure 5.7. The band at 3346 cm-1 correspond to –OH groups which is present on hpBCD spectrum and adisappears on hpBCD + HMDI + Fe_3O_4 spectrum after crosslinking with HMDI. The absence of the characteristic peak for –NCO (isocyanate group) at 2270 cm-1 confirms the compeltion of polymerization process.

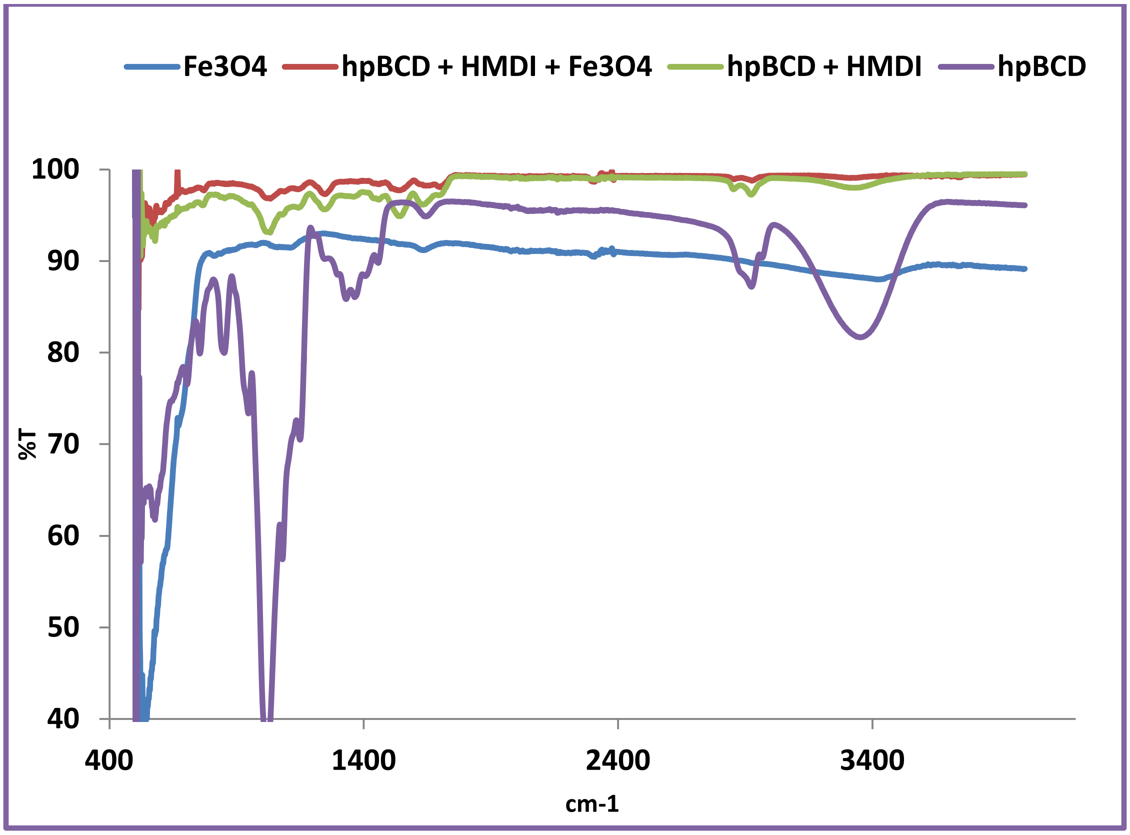


Figure 5.7. FTIR spectra of Fe_3O_4, hpBCD polymer and hpBCD/Fe_3O_4

5.3.1.5.2. SEM

The images obtained from SEM are shown in Figure 5.8. Figure a corresponds to unmodified Fe_3O_4 particles with particle size <50 nm. After modification or impregnation of hpBCD polymer onto Fe_3O_4, the particles seemed to be embedded in the polymer matrix (Figure b1). The hpBCD/Fe_3O_4 showed agglomeration of particles within the hpBCD polymer matrix with a wide range of particle size. The Figure b2 showed a smaller particle size than that was observed in figure b1. Therefore, it was observed that after impregnation of hpBCD polymer onto Fe_3O_4 particles, the nano Fe_3O_4 particles were agglomerated in the hpBCD polymer matrix and a wide range of particle size distribution was observed ranging from about 300 nm to >2 μm. The lack of uniformity in particle size of the adsorbent could be due to the physical impregnation approach used in the synthesis process.

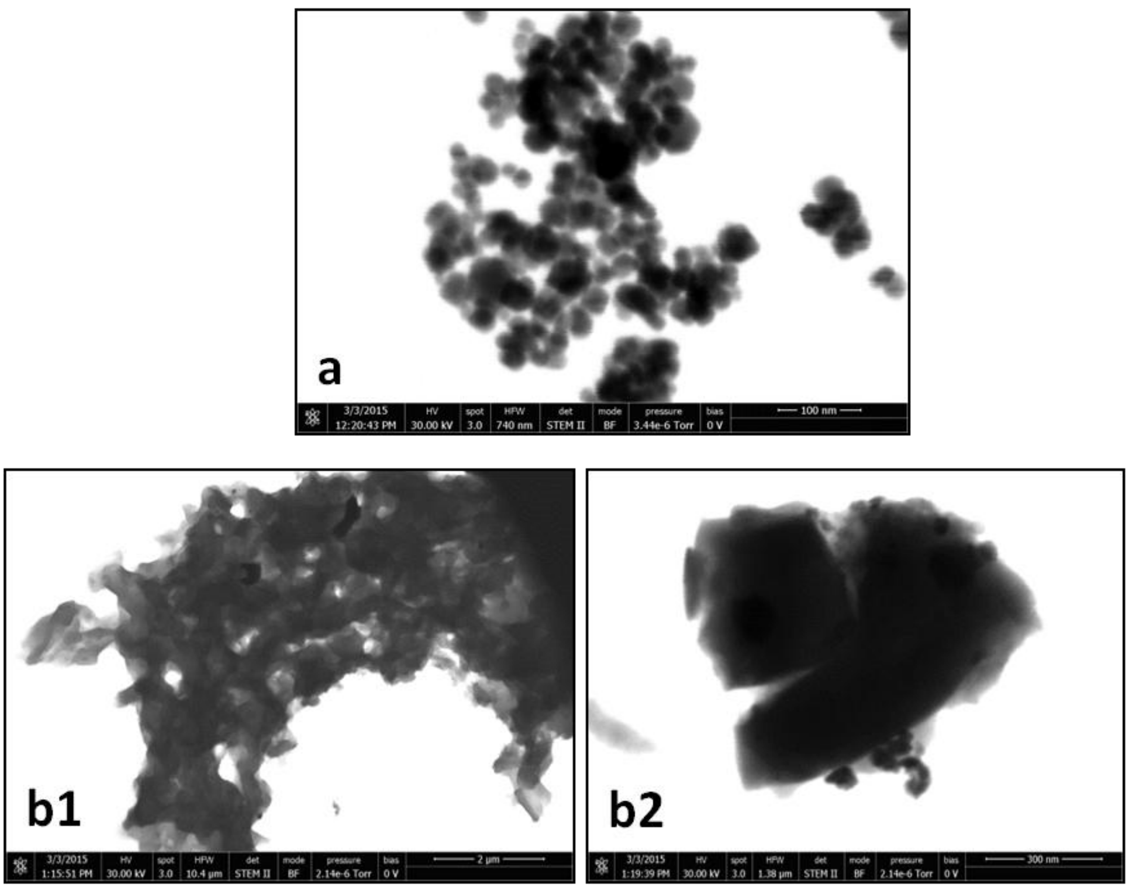


Figure 5.8. SEM images of a) unmodified Fe_3O_4 and b) hpBCD/Fe_3O_4

5.3.1.5.3. BET

The surface area and the pore size of the adsorbent were determined and compared with that of virgin iron oxide particles. The results are summarized in Table 5.2.

Table 5.2 Surface area and porosity of Fe_3O_4 and hpBCD/Fe_3O_4

Adsorbent	BET surface area (m^2/g)	Pore size (nm)
Fe_3O_4 nano	41.1	26.1
hpBCD/Fe_3O_4	9.6	30.0

The unmodified or virgin Fe_3O_4 particles showed a surface area of about 41 m2/g with pore size of 26 nm. After impregnation of hpBCD polymer, the adsorbent (hpBCD/Fe_3O_4) showed a surface area of 9.6 m2/g with pore size of 30 nm. The decrease in surface area after impregnation may be due to the agglomeration of particles in the polymer matrix. The decrease in surface area of the substrate after modification (coating or impregnation) has been well studied by several scholars. It was also observed that the higher loading of polymer on the substrate can reduce the surface area of the finished product further. Such effects become more pronounced when the particles are coated physically rather than chemically.

5.3.1.5.4. Zeta potential

From zeta potential measurements, the point of zero charge (pH_{ZPC}) of the adsorbent was calculated to be about 4.7 (Figure 5.9). This value indicates that the adsorbent will be negatively charged at pH > 4.7. Since all experiments were done around neutral pH which would be above 4.7, the adsorbent will be negatively charged.

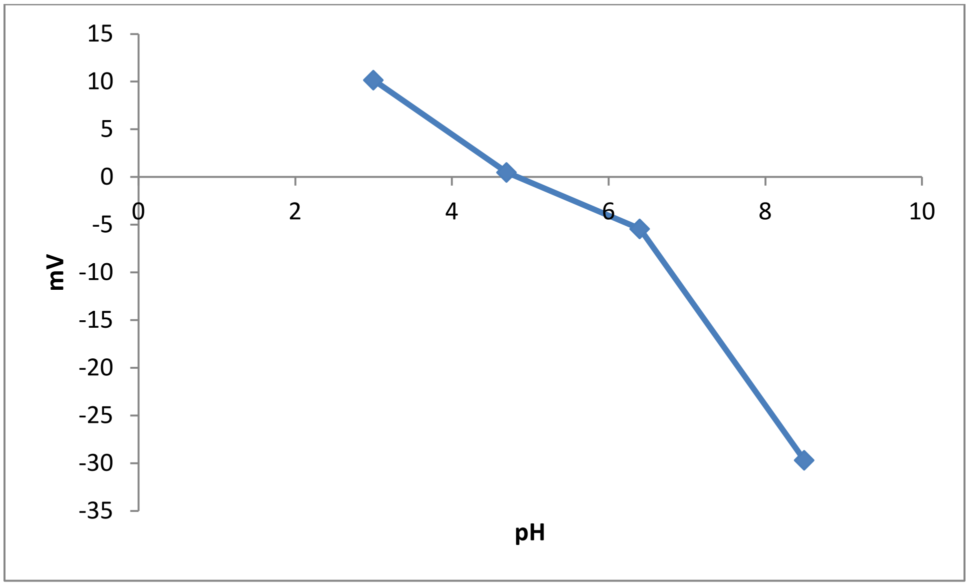


Figure 5.9. Zeta potential measurements for hpBCD/Fe_3O_4

5.3.2. hpBCD impregnated Zeolite (hpBCD/Zeolite)

5.3.2.1. Removal of ECs in MQ water

In order to test the efficiency of the synthesized hpBCD impregnated zeolite, the adsorbent was tested for the removal of PFOA and BPA in MQ water at initial concentrations of 50 μg/L and 100 μg/L, respectively. Separate isotherm experiments were done by varying the adsorbent dosage from 0.05 to 1.0 g/L. The results are shown in Figure 5.10.

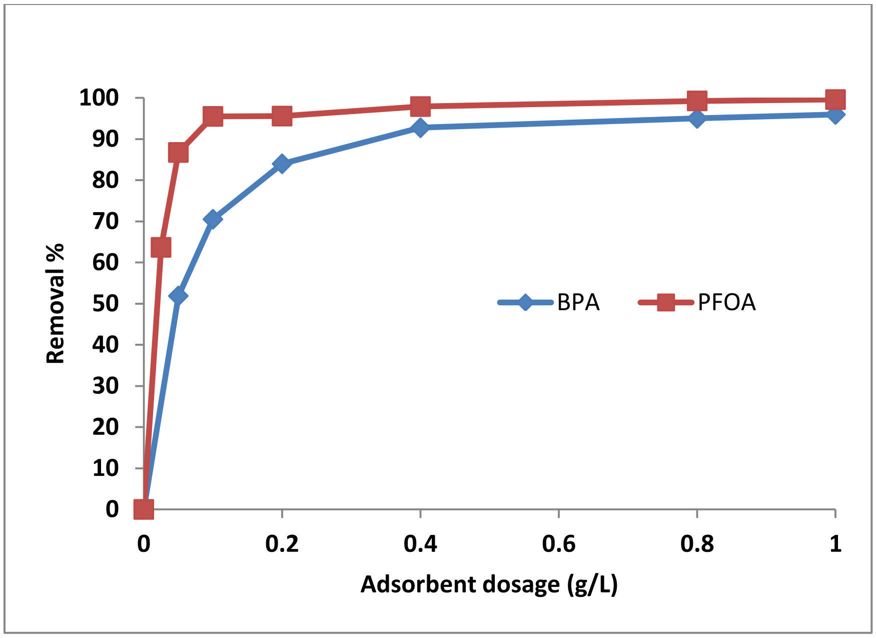


Figure 5.10. Removal of PFOA and BPA with hpBCD/Zeolite

The adsorbent was effective in removing more than 99% of PFOA and 95% of BPA from the solution. The adsorbent showed higher affinity in removing PFOA than BPA by removing 95% of PFOA at 0.1 g/L adsorbent dosage whereas only 70% removal was observed in case of BPA at the same adsorbent dosage. The data from each isotherm were fitted to Freunlich isotherm model and the results are shown in Figure 5.11. and the Freundlich constants are provided in Table 5.3.

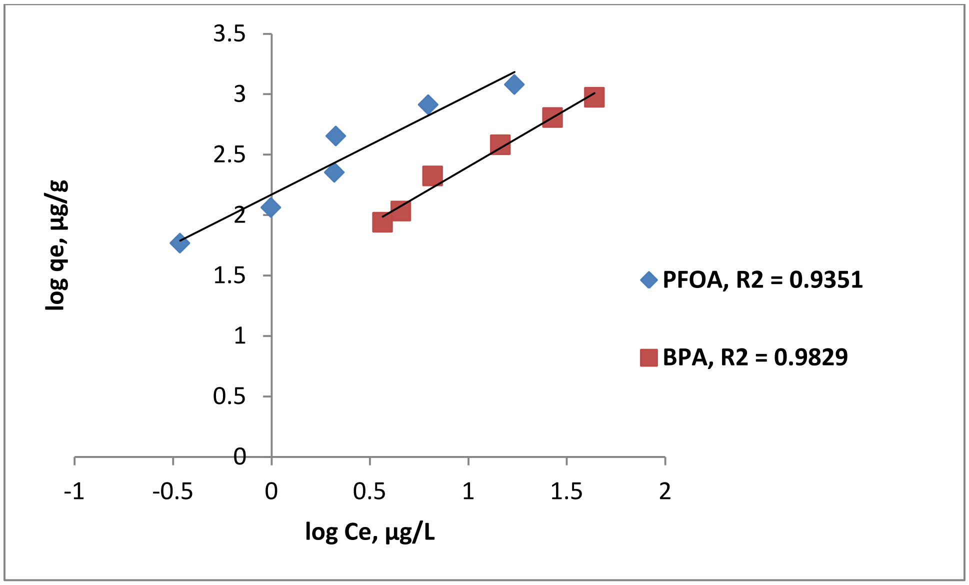


Figure 5.11. Fredundlich isotherm model for the removal of PFOA and BPA

The Freundlich constant 'K' was observed to be higher for PFOA than BPA which shows higher adsorption capacity of the adsorbent for PFOA than BPA.

Table 5.3 Freundlich constants for PFOA and BPA

EC	Freundlich Constants	
	K	n
PFOA	154.6	1.3
BPA	28.2	1.0

The adsorbent was further tested with a mixture of ECs containing PFOA and PFOS at initial concentration of 50 µg/L each in MQ water. The adsorbent was very efficient in removing more than 90% of both PFOA and PFOS at 0.2 g/L adsorbent dosage. However, the adsorbent showed higher affinity for PFOS than PFOA and such results were observed in earlier experiments with other BCD based adsorbents. The data were fitted to Freundlich model and the results are shown in Figure 5.12.

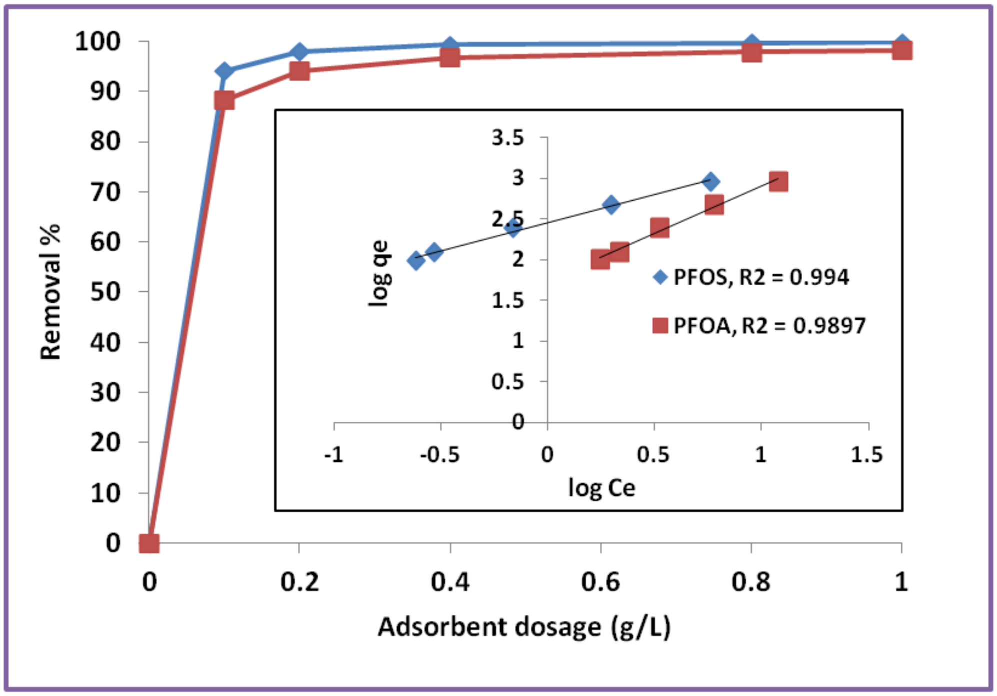


Figure 5.12. Removal of PFOA and PFOS with hpBCD/Zeolite

5.3.2.2. Effect of HA in ECs removal

In order to study the effect of HA in the removal of ECs, PFOA and PFOS were taken as model contaminants in mixture and two different concentrations of 4 mg/L and 12 mg/L of DOC were prepared. All experiments were conducted at initial concentration of 50 μg/L of both PFOA and PFOS. The results are shown in Figure 5.13.

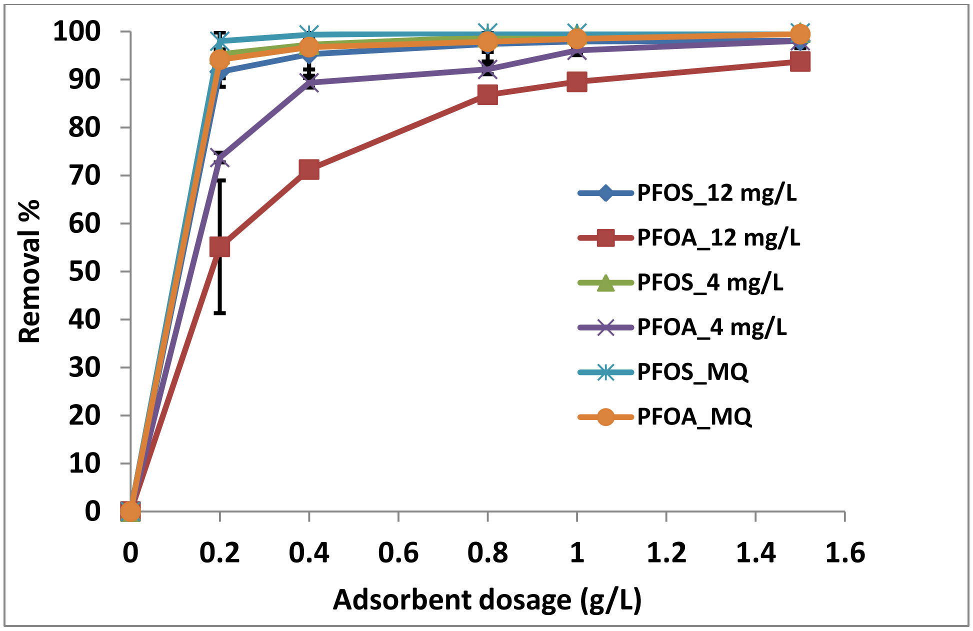


Figure 5.13. Effect of HA in the removal of PFOA and PFOS

To better understand the effect of HA on removal of PFOA and PFOS, the removal efficiency of the adsorbent was compared at 0.4 g/L adsorbent dosage for both PFOA and PFOS. In MQ water, the adsorbent removed an average of 99 % of PFOS (SD = 2.2, n = 2) and 97 % of PFOA (SD = 6.0, n = 2) from the solution. When HA was introduced into the system, at the same adsorbent dosage, the adsorbent removed an average of 97 % of PFOS (SD = 2.3, n = 2) and 89 % of PFOA (SD = 0.5, n = 2) at 4 mg/L of DOC, and an average of 95 % of PFOS (SD = 3.2, n = 2) and 71 % of PFOA (SD = 1.7, n = 2) at 12 mg/L DOC. Once again, significant supression of PFOA removal in presence of HA was observed with very little effect on the removal of PFOS. Similar results were also observed in case of other BCD based adsorbent discussed earlier.

5.3.2.3. Removal of ECs from wastewater at environmentally relevant concentrations

In order to represent real world scenario, the adsorbent was tested for the removal of PFOA and PFOS in wastewater. Secondary effluent of a municipal wastewater treatment plant was collected and spiked with 500 ng/L of PFOA and PFOS (Figure 5.14).

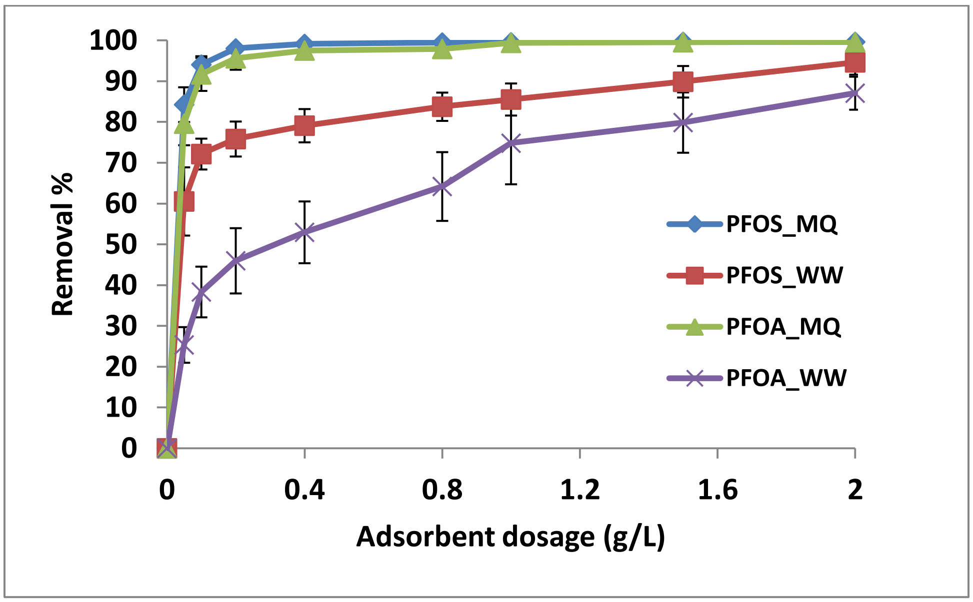


Figure 5.14. Removal of PFOA and PFOS in MQ water and wastewater secondary effluent

In MQ water, at 0.2 g/L adsorbent dosage, an average of 98 % removal of PFOS (SD = 0.7, n = 2) and 96 % removal of PFOA were observed. In wastewater matrix at the same adsorbent dosage, the removal efficiency was reduced to an average of 76 % for PFOS (SD = 4.3, n = 3) and 46 % for PFOA (SD = 8.0, n = 3). Unlike in case of HA, both PFOS and PFOA removals were affected due to the wastewater matrix. The initial concentration of DOC was about 6.0 mg/L in wastewater which is within the range of DOC studied in presence of HA (the composition of DOC may vary in real wastewater and simulated wastewater with HA). A significant decrease in removal efficiency of

PFOS in wastewater matrix indicates that the competition with non-target contaminants present in wastewater for the adsorption sites. These results and the possible mechanisms for removal were discussed in details in previous chapter.

In order to compare the performance of BCD based adsorbents with commercially available adsorbents, commonly used GAC F400 was selected and isotherm experiments were done for the removal of PFOA and PFOS in MQ water and wastewater under same experimental conditions.

The results are summarized in Figure 5.15.

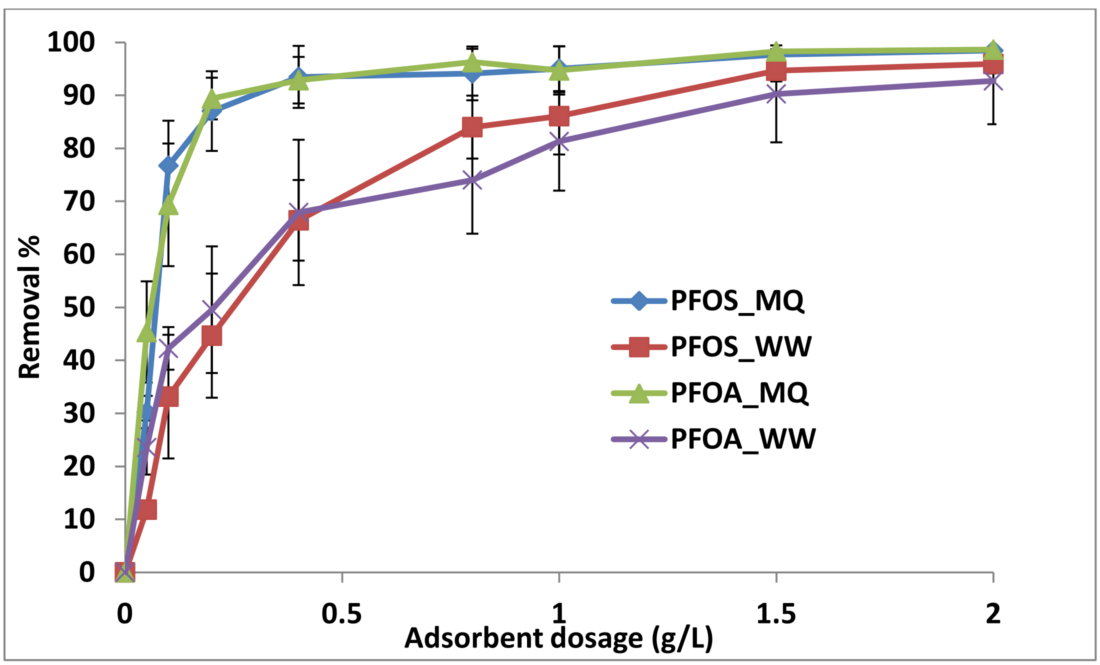


Figure 5.15. Removal of PFOA and PFOS in MQ water and wastewater secondary effluent with F400

At 0.4 g/L adsorbent dosage, an average of 93 % removal of both PFOS (SD = 5.8, n = 2) and PFOA (SD = 4.4, n = 2) was observed in MQ water. At the same adsorbent dosage, the removal efficincies were decreased to an average of 66 % for PFOS (SD = 7.6, n = 2) and 68 % for PFOA (SD = 13.7, n = 2).

5.3.2.4. Removal of PFOA and PFOS in presence of hexavalent chromium (Cr (VI))

The removal of PFOA and PFOS in presence of Cr (VI) was studied to investigate the potential ability of the adsorbent to simultaneously remove inorganic and organic contaminants from water. The results are summarized in Figure 5.16. At 0.1 g/L adsorbent dosage, the adsorbent removed about 98 % of PFOS and 77 % of PFOA. A maximum of about 13 % removal was observed for Cr (VI) at 0.8 g/L. The removal of Cr (VI) was in close agreement with BCD/Silica adsorbent (discussed in previous chapter). However, hpBCD/Fe_3O_4 adsorbent showed an increased removal of Cr (VI) due to the support (Fe_3O_4 particles) as discussed earlier. If we study the removal efficiency of all these adsorbents for PFOA and PFOS in presence and absence of Cr (VI), it is evident that with the significant removal of Cr (VI) (in case of hpBCD/Fe_3O_4), the removal of PFOA was greatly reduced. This trend was also observed in case of other adsorbents (BCD/Silica and hpBCD/Zeolite) to a lesser extent with low removal of Cr (VI). Therefore, presence of Cr (VI) in water matrix was observed to suppress the removal of PFOA and the effect was further enhanced when the adsorbent tend to remove Cr (VI) from the solution. In all cases, however, the removal of PFOS remains unaffected.

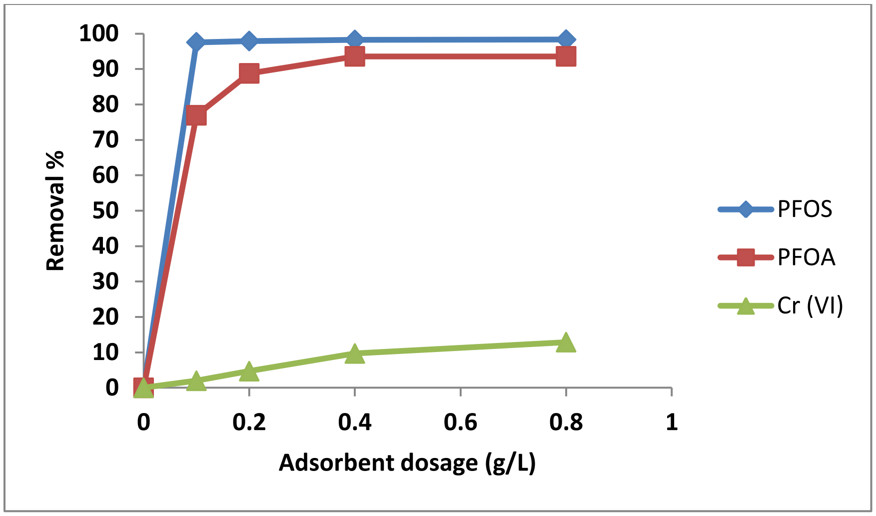


Figure 5.16. Removal of PFOA and PFOS in presence of Cr (VI)

5.3.2.5. Characterization of adsorbent

5.3.2.5.1. FTIR

The adsorbent was subjected to FTIR analsysis and the results were compared with the unmodified substrates along with all other reagents used in the chemical reaction. The FTIR spectra are shown in Figure 5.17. The band at 3346 cm^{-1} correspond to –OH groups which is present on hpBCD spectrum and adisappears on hpBCD + HMDI + Fe_3O_4 spectrum after crosslinking with HMDI. The absence of the characteristic peak for –NCO (isocyanate group) at 2270 cm^{-1} confirms the compeltion of polymerization process.

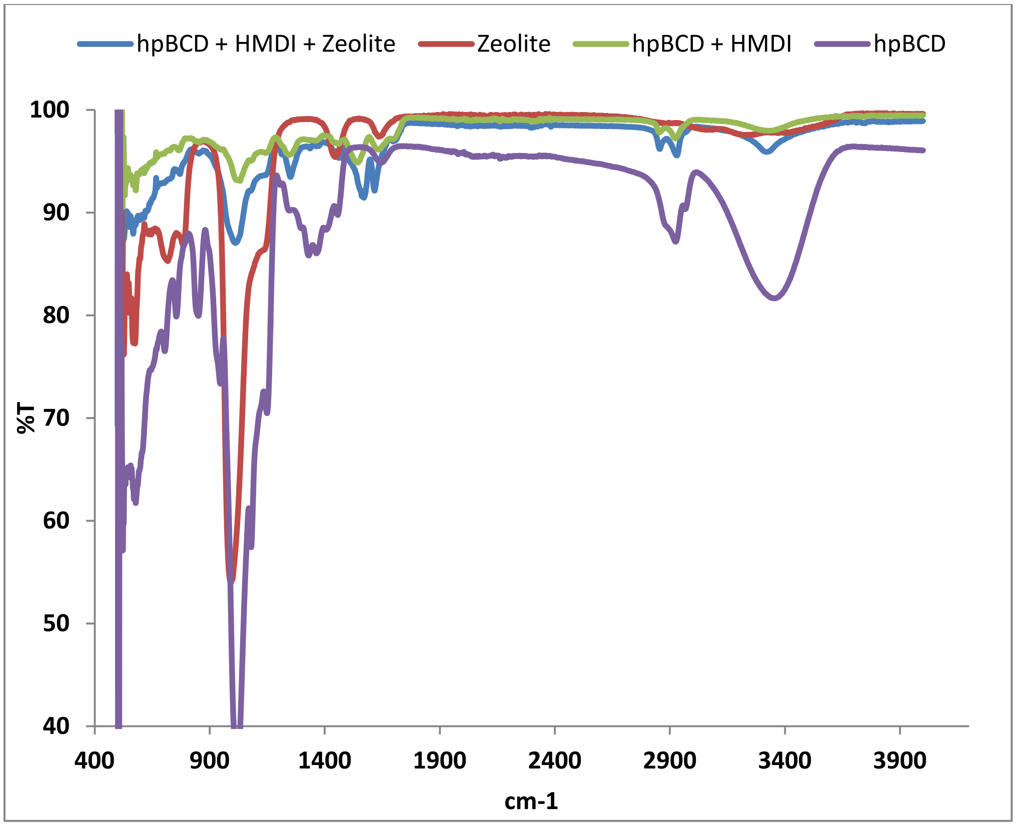


Figure 5.17. FTIR spectra of zeolite, hpBCD polymer and hpBCD/zeolite

5.3.2.5.2. SEM

The SEM images of the unmodified zeolite and modified zeolite by polymer impregnation are shown in Figure . The images a1 and a2 correspond to the unmodified zeolite where as b1 and b2 correspond to the adsorbent (hpBCD/Zeolite) (Figure 5.18). It was observed that the zeolite particles that were used as a support had particle size about 1 μm (images a1 and a2). After impregnation with hpBCD polymer, larger blocks of polymer with different sizes were observed (image b1). When these polymer blocks were studied closely, zeolite particles were observed embedded in the polymer matrix (image b2). Agglomeration of particles in the polymer matrix was also observed in case of hpBCD/Fe_3O_4 adsorbent. Therefore, it could be due to the physical approach that was used to impregnate hpBCD polymer onto the support.

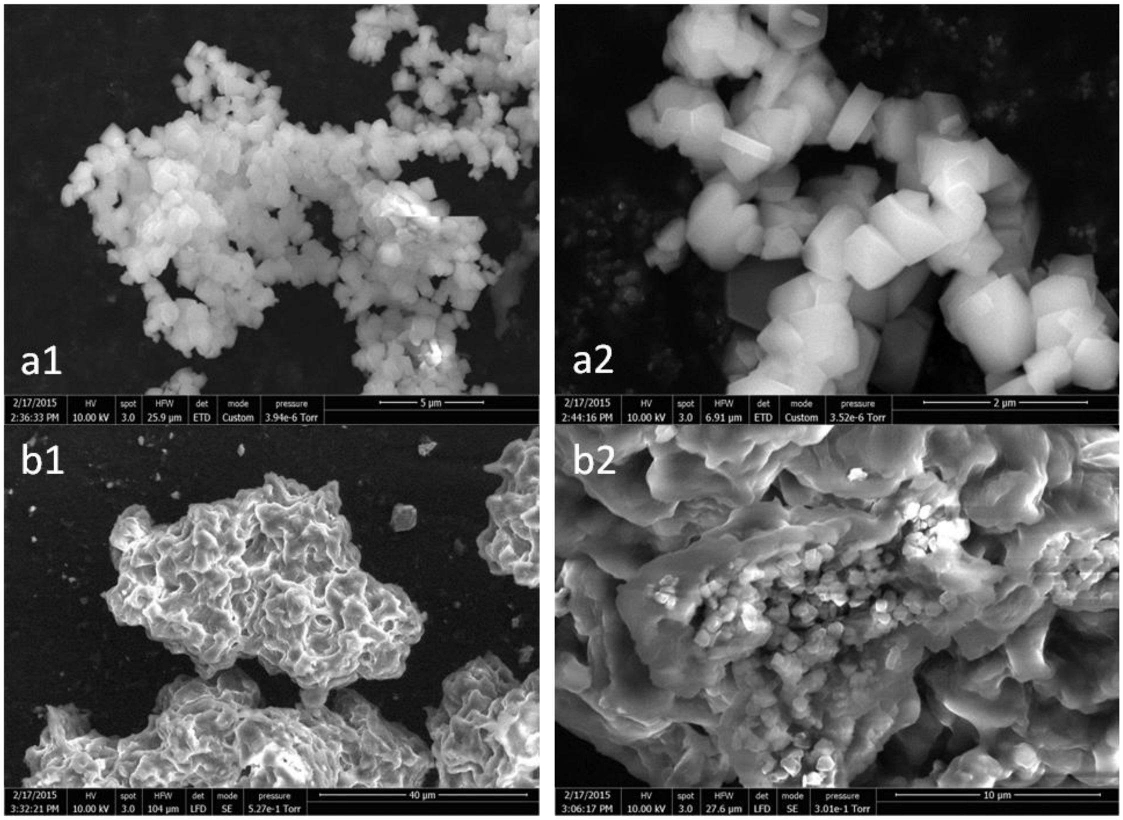


Figure 5.18. SEM images of unmodified zeolite (a) and modified zeolite (b)

5.3.2.5.3. BET surface area

The unmodified zeolite showed a high surface area of about 602 m^2/g. After modification, the adsorbent (hpBCD/Zeolite) showed a huge reduction in surface area with about 58 m^2/g. The pore size of the adsorbent was about 2.6 nm which was slightly more than the unmodified zeolite with 2.2 nm (Table 5.4).

Table 5.4 Surface area and porosity of zeolite and hpBCD/zeolite

Adsorbent	BET surface area (m^2/g)	Pore size (nm)
Zeolite	602	2.2
hpBCD/Zeolite	58.2	2.6

The decrease in surface area after impregnation may be due to the agglomeration of particles in the polymer matrix. The decrease in surface area of the substrate after modification (coating or impregnation) has been well studied by several scholars. It was also observed that the higher loading of polymer on the substrate can reduce the surface area of the finished product further. Such effects become more pronounced when the particles are coated physically rather than chemically.

5.3.2.5.4. Zeta potential

From zeta potential measurements, the point of zero charge (pH_{ZPC}) of the adsorbent was calculated to be about 0.9 (Figure 5.19). This value indicates that the adsorbent will be negatively charged at pH > 0.9. Since all experiments were done around neutral pH which would be above 0.9, the adsorbent will be negatively charged.

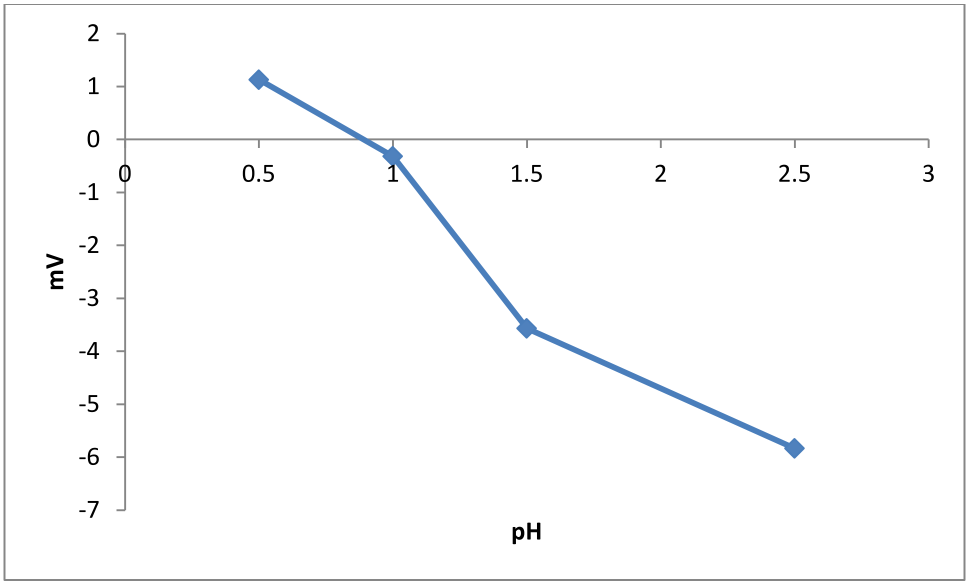


Figure 5.19. Zeta potential measurements for hpBCD/zeolite

5.3.3. hpBCD impregnated Filter paper

5.3.3.1. Testing and optimization of hpBCD loading onto filter paper

As described earlier, four different hpBCD impregnated filter papers were developed by varying the loading of hpBCD polymer and tested for the removal of PFOA and BPA at 5.0 g/L. To test the efficiency of the impregnated filter papers with different loadings for the removal of organic chemicals, PFOA and BPA were taken as model contaminants. One point adsorption experiment was done with 5 g/L adsorbent dosage and the initial concentration of PFOA and BPA were 50 µg/L and 100 µg/L, respectively. The performance of the modified filter paper was compared with that of virgin filter paper in removing the selected ECs as well as their filtration capacity. The results are summarized in Figure 5.20 and Table 5.5. In order to test the filtration efficiency of the impregnated filter papers, a filtration unit was set up with the impregnated filter paper. The impregnated filter paper was fed with working solution of the selected organic chemicals at certain initial concentration continuously at a certain flow rate. The removal efficiency of the impregnated filter paper for the respective contaminants was calculated based on the difference in concentration before and after filtration.

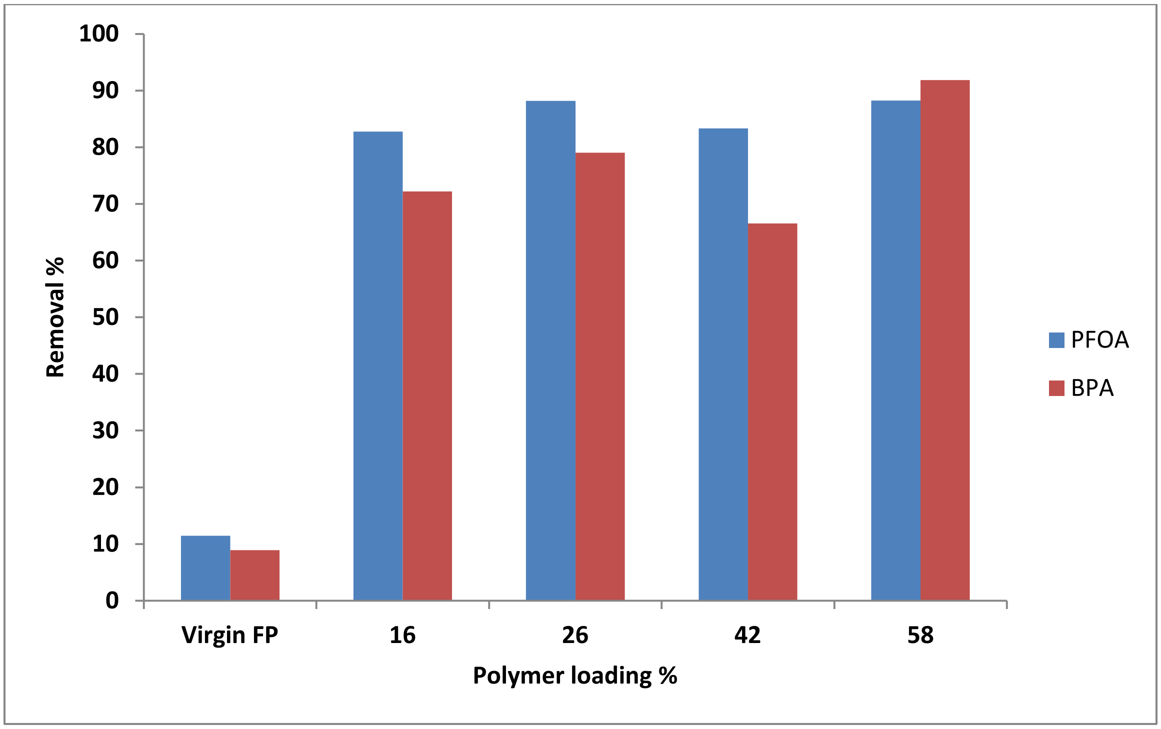


Figure 5.20. Testing and optimization of hpBCD loading for the removal of PFOA and BPA

Table 5.5 Polymer loadings and filtration rates of hpBCD impregnated FPs

	Polymer loading (%)	Filtration rate (ml/min)
Batch I	16	500
Batch II	26	1.5
Batch III	42	0.72
Batch IV	58	0.3
Virgin filter paper	0	600

It was observed that the impregnated filter papers with different loadings were successful in removing the target contaminants from water. It was also observed that the virgin filter papers (without modification/impregnation) showed very low removal of the contaminants. Furthermore, it was observed that the virgin filter papers started disintegrating as the adsorption process continued. On the contrary, no such disintegration of the material was observed in case of impregnated filter papers. This confirmed the stability of the impregnated filter papers for the adsorption processes. Based on the results mentioned above, the polymer loading of 16% showed the optimum loading in terms of good filtration rate and good removal of the selected organic chemicals. Therefore, the same procedure was followed as explained in Batch I to synthesize more impregnated filter papers for further experiments.

5.3.3.2. Removal of ECs in batch and continuous filtration

Another batch of adsorbent was synthesized and used for isotherm experiment. Based on the previous removal data for PFOA and BPA, the adsorbent dosage was varied from 1 to 5 g/L. All other experimental conditions were kept constant. Control experiment with virgin filter paper was done at the same adsorbent dosage. The results are shown in Figure 5.21.

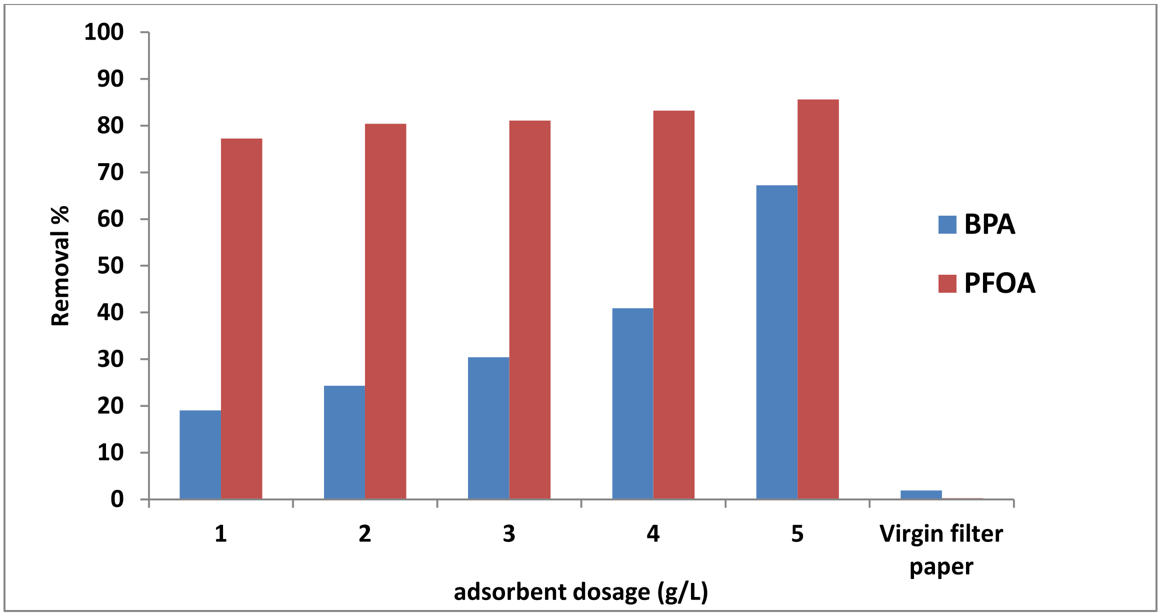


Figure 5.21. Removal of PFOA and BPA with virgin FP and hpBCD impregnated FP

In order to understand the efficiency of the impregnated filter papers towards filtration rate as well as the removal of the selected organic chemicals, filtration experiments were done. The results are shown in Figure 5.22.

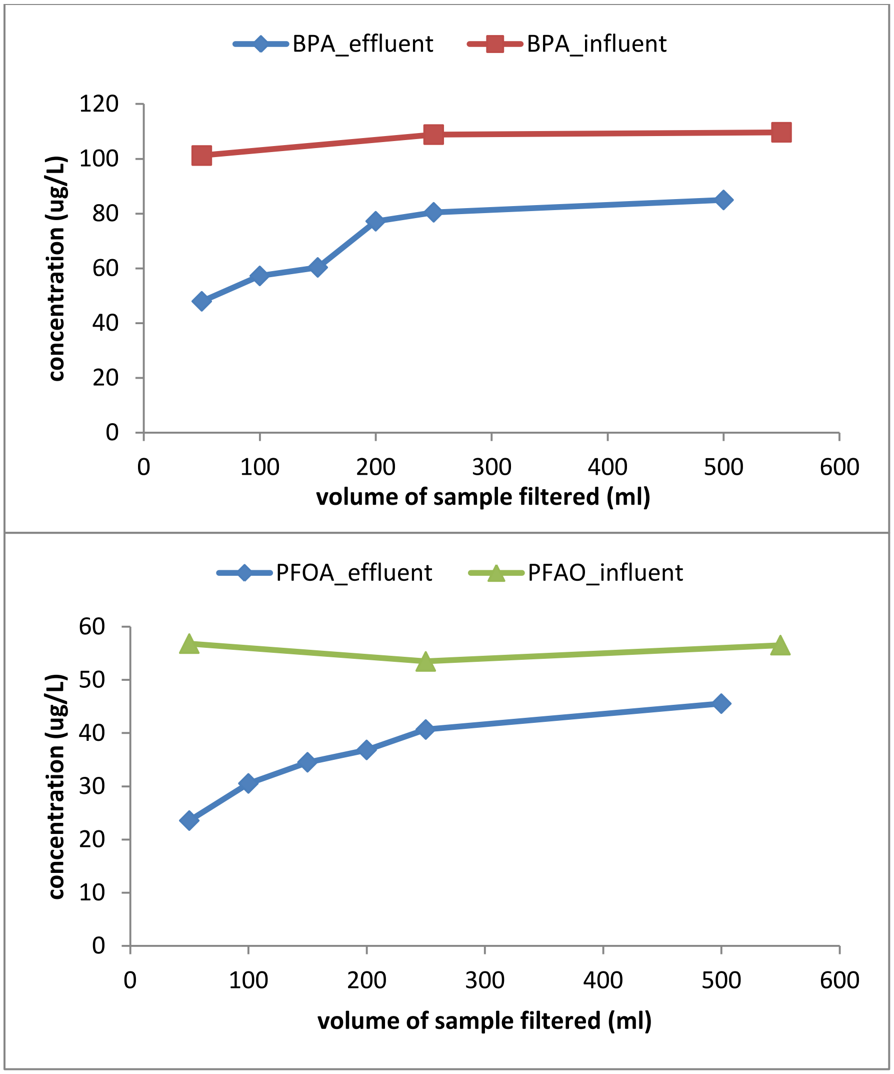


Figure 5.22. Removal of BPA and PFOA with modified filter paper through filtration (flow rate: ~10 ml/min; wt of adsorbent: 0.21 g) (initial conc: 50 ug/L (PFOA) and 100 ug/L (BPA). The concentrations in the figure represent average concentrations measured for every 50 ml of sample)

The impregnated filter paper showed good removal of both BPA and PFOA along with good filtration capacity. Further experiments were done to improve the efficiency of the impregnated filter papers by increasing the filtration depth. In this case, four filter papers were used in series to provide some filtration depth and the experiment was done under vacuum. The results are shown in Figure 5.23.

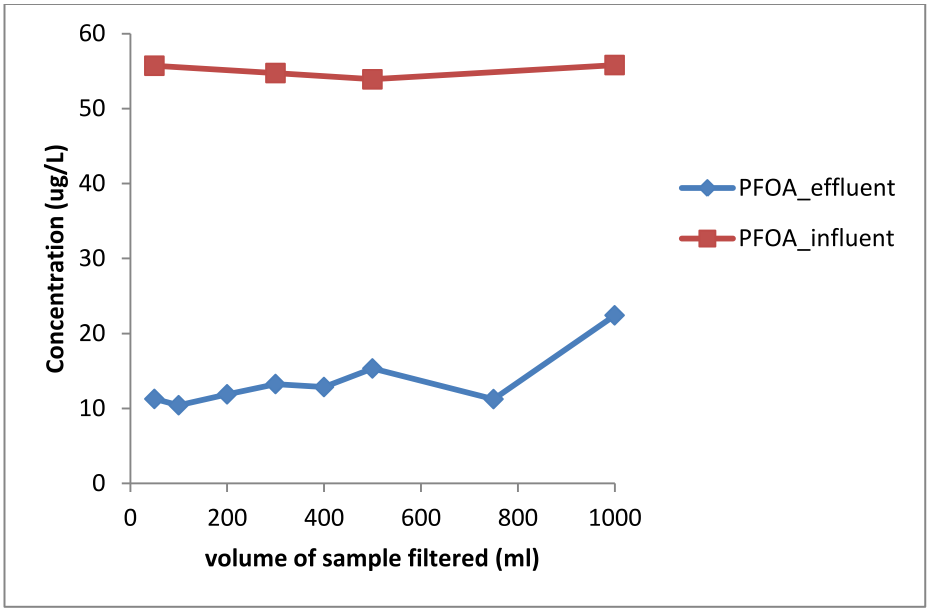


Figure 5.23. Removal of PFOA (intial conc: 50 ug/L; flow rate ~ 5 ml/min under vacuum); wt of impregnated filter paper: 0.66 g The concentrations in the figure represent average concentrations measured for every 50 ml of sample)

After filtering 1 liter of working solution of PFOA, the experiment was continued by passing 500 ml of working solution of BPA (Figure 5.24).

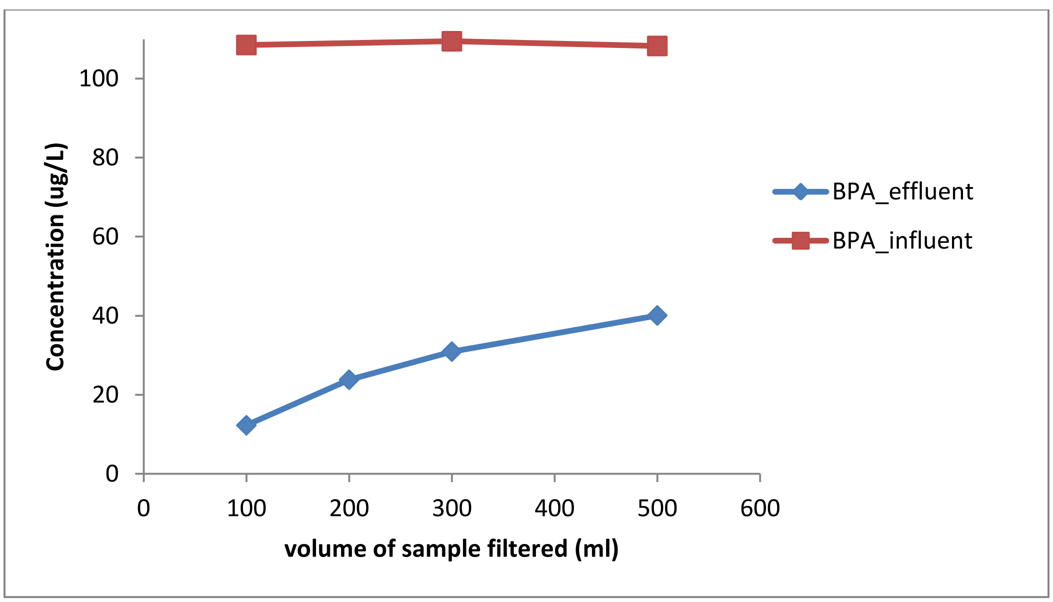


Figure 5.24. Removal of BPA (intial conc: 100 ug/L; flow rate ~ 5 ml/min under vacuum). The results here are the continuation of the experiment with PFOA solution. The concentrations in the figure represent average concentrations measured for every 50 ml of sample)

It was observed that by increasing the depth of filtration, the removal efficiency of the impregnated filter papers increased markedly in removing both PFOA and BPA. The impregnated filter paper showed average removal of 72% for both PFOA and BPA.

5.3.3.3. Stability of hpBCD impregnated FP

In order to study the stability of hpBCD impregnated FP, two pieces of virgin and modified FPs were taken. Each FP was cut into four pieces and finally, the 8 pieces of virgin and modified FPs were suspended in 200 ml of MQ water in two different erlenmeyer flasks. No suspended particles were observed in the beginning after adding the respective FP into water and shaking for about 5 min. Each flask was placed on a magnetic stir plate with continuous stirring for 24 hr. With stirring, the virgin FP started to disintegrate and showed complete disintegration after 24 hr as shown in Figure 5.25. On the other hand, the impregnated FP was stable which confirmed the stability of the polymer impregnation onto the FP. Both samples were transferred to a shaker at 140 rpm and monitored periodically. After 62 days, few suspended particles were observed in case of impregnated FP as shown in Figure 5.25.

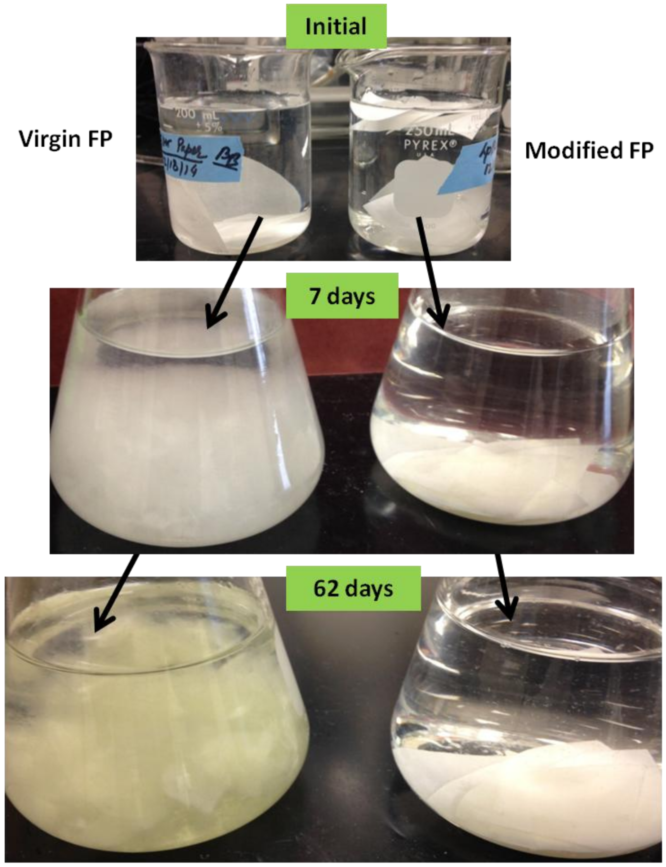


Figure 5.25. Stability of hpBCD impregnated FP

5.4. Conclusion

Various adsorbents were synthesized by physically impregnating hpBCD polymer onto Fe_3O_4 particles (magnetic adsorbent), zeolite, and FP. The hpBCD impregnated filter papers were synthesized by solvent evaporation method and different adsorbents were synthesized by varying the polymer loadings. The polymer loading was optimized based on the performance of the modified filter paper in terms of its filtration capacity as well as adsorption capacity to remove PFOA and BPA. The impregnated FP showed better stability than the virgin FP. The magnetic adsorbent was prepared by mixing hpBCD polymer with iron oxide (Fe_3O_4) particles. It was observed that by increasing the mixing time of the support (Fe_3O_4) with the polymer from 48 to 96 hr, the adsorption capacity of the adsorbent could be significantly enhanced. The same approach was also used to synthesize hpBCD polymer coated zeolite adsorbent and both adsorbents (hpBCD/zeolite and hpBCD/Fe_3O_4) were effective in removing PFOA and PFOS from MQ water, simulated water, and wastewater. The hpBCD/Fe_3O_4 was also effecive in simulatneous removal of Cr (VI) and PFOA and PFOS from water. The impregnation of hpBCD polymer onto the supports was confirmed by FTIR and SEM analyses.

CHAPTER 6
OVERALL CONCLUSIONS AND RECOMMENDATIONS

6.1. Conclusions

This study provided detailed investigations on the application of CD based adsorbents that could be used to remove ECs from water and wastewater. The study was focused on application of BCD and hpBCD (to represent CD) and 12 steroid hormones, 11 PFCS, and BPA were selected as model contaminants to represent the diverse group of ECs. Furthermore, to investigate the effect of crosslinking agent in order to obtain water insoluble BCD polymers as well as to coat them onto various supports, HMDI and EPI were evaluated. For conducting experiments, three water matrices were considered: MQ water (clean water), simulated wastewater (in presence of HA), and real municipal wastewater secondary effluent to evaluate the performance of the developed adsorbents in removing the selected ECs. For comparative studies on the performance of the developed adsorbent and commercially available adsorbent, GAC F400 was used for selected experiments. Based on the data obtained from the studies and analysis of the obtained data, the overall conclusions of the dissertation are summarized below:

1. The native water soluble BCDs were successfully crosslinked with HMDI and EPI to obtain water insoluble BCD polymers. The degree of substitution between BCD and the crosslinking agent determines the water soluble property of the final products. For example, the molar ratio 1:7 of BCD and HMDI was required to obtain water insoluble polymer. This ratio was maintained for all experiments done with BCD.

However, in case of hpBCD, 1:7 ratio with HMDI gave water soluble polymer. Therefore, the ratio was increased to 1:14 in order to get water insoluble polymer.

2. 14 different adsorbents were synthesized by coating BCD onto silica by using various combinations of two crosslinking agents (HMDI and EPI) and two copolymers (GPTS and APTES). DMF, DMSO, and NaOH (30% w/w) were used as solvents for BCD. The best adsorbent, synthesized using DMSO as solvent and HMDI as crosslinking agent, was selected based on its performance in removing selected ECs (17β-estradiol, PFOA, and BPA). The best adsorbent was further optimized and a ratio of 0.23 (w/w) between BCD and silica was observed to be the optimum loadings to remove the selected ECs. This method of synthesis was used for further experiments.

3. The adsorbent (BCD/silica) was effective in removing 12 steroid hormones, 11 PFCs, and BPA in MQ water. The reproducibility of the method of synthesis was determined by using adsorbents synthesized in seven different batches and excellent reproducibility was observed in removing mixture of estrogens from water.

4. The adsorbent (BCD/silica) showed good regeneration potential with methanol and ozone over four and seven successive cycles, respectively.

5. Adsorbents synthesized by physically impregnating hpBCD polymer onto Fe_3O_4, zeolite, and filter paper also showed effective removal of ECs studied. hpBCD/Fe_3O_4 and hpBCD/Fe_3O_4 successfully removed PFOA and PFOS in MQ water, simulated wastewater and real wastewater.

6.2. Recommendations

The present study was able to answer some basic research questions regarding the application of BCD based adsorbents to remove selected ECs from water and wastewater, and their regeneration potential using selected techniques. However, there are a few research areas that could not be addressed in the present study, but are very important to ensure the technical and economic viability of the technology. These recommendations may be broadly divided into two categories a) for better scientific understanding of the subject matter and b) challenges associated with the commercialization of the technology (present study).

1. **Inclusion complex**: In order to better understand the interaction between CD molecules and ECs, it is recommended to perform thermodynamic studies on inclusion complex formation in solution phase as well as solid phase (with adsorbent). Interactions of different ECs having different size, hydrophobicity, and functional groups with different CDs (αCD, BCD, and γCD) in solution phase could provide quick understanding on possible inclusion formation (determines possible removal) and stability of inclusion complex.

2. **Removal of highly water soluble ECs**: One of the limitations of the adsorbent (present study) was its inability to remove highly water soluble ECs such as 1,4-dioxane. Therefore, it would be useful to study different CDs and derivatives of CDs (with different functional groups) for the removal of such contaminants. An alternative approach would be to use hybrid adsorbents i.e. CDs with substrates that are capable of removing highly water soluble ECs.

3. **Stability and leachability**: It is critical to know the long term stability of the adsorbent when it is subjected to ozonation repeatedly. During regeneration process, ozone may react with the polymer component of the adsorbent and breakdown or oxidize the polymer matrix. This will reduce the efficiency of the adsorbent to remove contaminants. Moreover, during the adsorption cycle, some of the degraded adsorbent polymer may leach into the treated water.

4. **Biodegradability of the adsorbent**: Since the developed adsorbent contains a polymerized form of BCD, a glucose-based molecule, any biodegradable potential of the adsorbent may limit its life in water treatment. The contaminated water may contain microorganisms which can feed on the adsorbent material if the material is biodegradable. This can cause a serious issue by depleting the coated layer of polymer onto sand which would eventually affect the performance of the adsorbent in removing contaminants from water. Therefore, biodegradability studies should be done with appropriate methods.

5. **Effect of ozone resistant contaminants during regeneration**: In present study, the limitation of ozone as regeneration technique was it inability to destroy ozone resistant ECs such as PFOA. Therefore, further studies should be conducted to regenerate CD adsorbent for ozone resistant ECs. Since the ability of CDs to form complexes with metal ions and organic contaminants are well studies, it would be interesting to study the potential of CDs for in-situ generation of hydroxyl radicals (eg, Fenton's process) for the breakdown of trapped ECs (e.g. PFOA).

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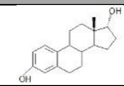
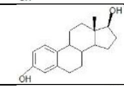
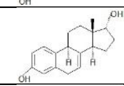
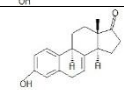
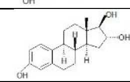
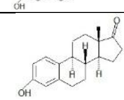
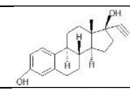
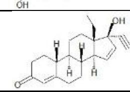
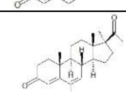
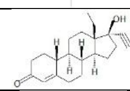
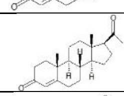
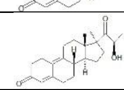
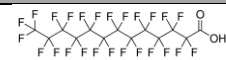
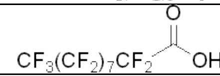
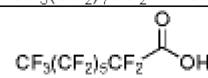
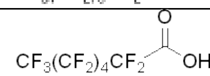
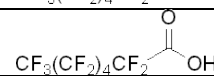
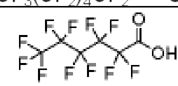
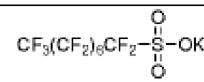
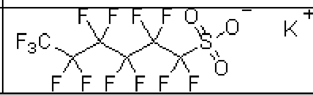
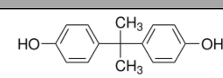
APPENDIX A
STRUCTURE AND PROPERTIES OF ECs STUDIED

Table A1. Structure and properties of ECs studied

Name	CAS number	Formula	Structure	Molecular Weight	Solubility mg/L	Log K_{ow}	pK_a
Estrogens							
17α-estradiol	57-91-0	$C_{18}H_{24}O_2$		272.38	5.4–13.3[5]	4.01[5]	10.46 ± 0.03[3]
17β-estradiol	50-28-2	$C_{18}H_{24}O_2$		272.38	5.4–13.3[5]	4.01[5]	10.71[2]
17α-Dihydroequilin	651-55-8	$C_{18}H_{22}O_2$		270.37	0.88[6]	4.34[6]	10.29 ± 0.02[3]
Equilin	474-86-2	$C_{18}H_{20}O_2$		268.36	8.78[6]	4.22[6]	10.26 ± 0.04[3]
Estriol	50-27-1	$C_{18}H_{24}O_3$		288.38	0.82[6]	2.77[6]	10.46[2]
Estrone	53-16-7	$C_{18}H_{22}O_2$		270.37	0.8–12.4[5]	3.13[5]	10.77[1]
17α-Ethinyl estradiol	77538-56-8	$C_{20}H_{24}O_2$		296.38	4.8–19.1[5]	3.67[5]	10.40 ± 0.01[3]
Gestodene	60282-87-3	$C_{21}H_{26}O_2$		310.43	0.86[6]	4.43[6]	N/A
Medrogestone	977-79-7	$C_{23}H_{32}O_2$		340.50	0.86[6]	5.03[6]	N/A
Norgestrel	6533-00-2	$C_{21}H_{28}O_2$		312.45	0.86[6]	4.27[6]	N/A
Progesterone	57-83-0	$C_{21}H_{30}O_2$		314.45	9.17[6]	4.18[6]	N/A
Trimegestone	74513-62-5	$C_{22}H_{30}O_3$		342.47	9.76[6]	4.25[6]	N/A

Perfluorinated compounds							
Perfluorotridecanoic acid	72629-94-8	$F_3C(CF_2)_{11}COOH$		664.11	N/A	N/A	<0[6]
Tricosafluorododecanoic acid	307-55-1	$F_3C(CF_2)_{10}COOH$		614.10	N/A	N/A	<0[6]
Perfluoroundecanoic acid	2058-94-8	$F_3C(CF_2)_9COOH$		564.09	N/A	N/A	<0[6]
Perfluorodecanoic acid	335-76-2	$F_3C(CF_2)_8COOH$		514.08	N/A	N/A	<0[6]
Perfluorooctanoic acid	335-67-1	$F_3C(CF_2)_6COOH$		414.07	N/A	N/A	<0[6]
Tridecafluorononanoic acid	27854-30-4	$F_3C\ (CF_2)_5(CH)_2$ COOH		392.11	N/A	N/A	<0[6]
Perfluoroheptanoic acid	375-85-9	$F_3C(CF_2)_5COOH$		364.06	N/A	N/A	<0[6]
Undecafluorohexanoic acid	307-24-4	$F_3C(CF_2)_4COOH$		314.05	N/A	N/A	<0[6]
Heptadecafluorooctanesulfonic acid potassium salt	2795-39-3	$F_3C(CF_2)_7SO_3K$		538.22	N/A	N/A	<0[6]
Tridecafluorohexane-1-sulfonic acid potassium salt	3871-99-6	$F_3C(CF_2)_5SO_3K$		438.20	N/A	N/A	<0[6]
Bisphenol A	80-05-7	$C_{15}H_{16}O_2$		228.29	1.2[7]	3.2[7]	9.6[4]

[1]Lewis et al., 1979 [2]Eger el al., 1972 [3]Hurwitz et al., 1977 [4]Zhang, et al., 2006 [5]Song, et al., 2009 (Estrogen removal from treated municipal effluent in small-scale constructed wetland with different depth) [6]Data estimated by SPARC online [7]Yoon, et al., 2003

APPENDIX B
QUALITY ASSURANCE AND QUALITY CONTROL (QA/QC) FOR ANALYSIS OF ECs

B1. Analysis of Estrogens (QA/QC)

Table B1. Recoveries and method detection limits (MDLs) using SPE/UPLC/MS/MS method

Analyte	Recovery(%) ± RSD (%), n = 5 (spiked concentration = 5 µg/L)	MDL, ng/L
	Bond Elute C-18 cartridge	
Estriol	94.1 ± 3.4	141.2
17α-dihyrdoequilin	91.1 ± 2.8	68.3
Equilin	81.5 ± 5.3	73.4
Estrone	89.3 ± 3.2	53.6
17α-estradiol	97.6 ± 4.1	146.4
17β-estradiol	98.4 ± 2.9	147.6
17α-ethinyl estradiol	92.1 ± 3.8	69.1
Norgestrel	80.5 ± 4.6	120.8
Progesterone	85.2 ± 2.2	63.9
Medrogestone	89.9 ± 2.8	80.9
Trimegesterone	92.6 ± 3.1	83.3

B2. Analysis of PFOA and PFOS (QA/QC)

Analytical method

1. Sample preparation

SPE Cartridge: Oasis WAX, 3 cc, 60 mg
Cartridge conditioning : 2 ml Methanol/ 2 ml DI water
Wash 1: 1 ml 2% Formic acid
Elute 1: 3 ml Methanol
Elute 2: 2 ml 1% Ammonia in Methanol

2. Instrumental conditions

Instrument: UPLC/MS/MS (Waters)
Column : ACQUITY UPLC BEH C_{18}, 2.1 X 50 mm, 1.7 µm
Flow rate: 0.3 ml/min
Mobile phase: A: Water B: Acetonitrile

3. Recovery

Matrix	Mean recovery (%)[n=5]		RSD (%) [n=5]	
	PFOS	PFOA	PFOS	PFOA
Wastewater	101.1	105.4	6.1	4.0
MQ water	97.2	102.3	2.4	4.1

Instrument detection limit : 0.05 µg/L for PFOA and PFOS
Method detection limit : 2.5 ng/L for PFOA and PFOS

APPENDIX C
RAW EXPERIMENTAL DATA

Table C1. Removal of PFOA, BPA and 17β-estradiol with adsorbents of different BCD loading in triplicates (Figure 3.2)

Adsorbent	BCD/silica	Removal %								
		PFOA			BPA			E2		
A11	0.15	81.8	87.5	86.4	66.8	63.8	65.1	76.4	73.8	76.0
A12	0.23	93.0	94.1	96.6	88.6	84.3	85.2	90.8	88.2	91.1
A13	0.5	97.0	95.8	93.4	87.8	88.7	85.4	92.5	92.0	91.8
A14	0.76	98.1	98.9	97.6	91.8	91.0	93.7	95.3	93.3	96.7

Table C2. Removal of estrogens (%) with Adsorbent A1 in seven batches (Figure 3.3)

Estrogens	Batch of synthesis of adsorbent								
	I	II	III	IV	V	VI	VII	Avg	Std dev
0.2 g/L adsorbent dosage									
estriol	37.5	29.1	36.0	36.7	33.6	34.4	34.1	**34.5**	**2.8**
17α-dihyrdoequilin	44.7	28.1	48.1	47.3	36.8	46.4	46.0	**42.5**	**7.4**
equilin	33.2	22.5	41.1	45.1	44.7	43.7	19.2	**35.6**	**10.9**
estrone	63.0	36.8	71.7	53.3	45.3	46.8	56.6	**53.4**	**11.7**
17α-estradiol	41.4	41.3	47.4	47.0	34.4	46.1	49.1	**43.8**	**5.1**
17- estradiol	63.0	54.5	76.6	58.6	50.3	51.1	72.2	**60.9**	**10.3**
17α-ethinyl estradiol	46.7	44.1	63.9	45.9	40.2	50.1	47.3	**48.3**	**7.5**
norgetrel	10.9	30.4	37.0	19.3	24.9	34.3	14.4	**24.5**	**10.0**
progestrone	48.4	47.3	53.8	44.2	35.0	50.0	49.4	**46.9**	**6.0**
medrogestone	38.9	39.3	41.1	33.7	29.7	45.2	25.0	**36.1**	**7.0**
0.6 g/L adsorbent dosage									
estriol	59.9	49.3	90.2	50.4	62.0	45.2	68.3	**60.8**	**15.3**
17α-dihyrdoequilin	62.4	48.9	93.9	69.7	71.7	69.6	63.7	**68.5**	**13.6**
equilin	83.8	62.5	90.0	73.1	71.1	57.4	86.8	**74.9**	**12.4**
estrone	88.4	70.6	97.9	76.7	81.8	68.4	87.3	**81.6**	**10.5**
17α-estradiol	70.0	64.9	95.0	67.8	72.5	62.7	77.4	**72.9**	**10.9**
17- estradiol	89.9	79.3	98.7	82.4	84.7	71.6	92.3	**85.5**	**9.0**
17α-ethinyl estradiol	49.3	60.4	92.8	66.6	69.0	67.7	80.9	**69.5**	**14.0**
norgetrel	45.4	38.7	54.4	25.4	46.0	40.4	31.0	**40.2**	**9.7**
progestrone	81.3	68.2	95.5	66.4	72.4	68.7	84.0	**76.6**	**10.7**
medrogestone	42.0	51.7	81.7	58.4	52.1	69.5	57.4	**59.0**	**13.0**

Estrogens	Batch of synthesis of adsorbent								
	I	II	III	IV	V	VI	VII	Avg	Std dev
1.0 g/L adsorbent dosage									
estriol	79.9	70.6	96.0	67.8	73.4	68.5	81.3	**76.8**	**10.0**
17α-dihyrdoequilin	88.3	82.7	97.1	81.1	81.7	86.0	77.0	**84.9**	**6.5**
equilin	91.7	81.6	97.8	81.2	88.5	85.9	87.6	**87.7**	**5.8**
estrone	96.6	83.8	98.7	88.0	90.1	84.5	91.6	**90.5**	**5.7**
17α-estradiol	97.3	84.3	97.3	82.9	83.9	81.9	90.7	**88.3**	**6.8**
17- estradiol	98.1	89.5	99.3	91.6	92.8	87.9	95.7	**93.5**	**4.3**
17α-ethinyl estradiol	94.6	75.7	94.3	85.2	79.5	83.7	90.1	**86.2**	**7.2**
norgetrel	74.8	69.0	78.8	43.5	50.6	65.8	50.3	**61.8**	**13.7**
progestrone	96.5	83.1	98.3	80.3	83.7	85.4	92.8	**88.6**	**7.2**
medrogestone	83.1	78.8	91.5	88.3	69.8	86.4	74.7	**81.8**	**7.8**
1.5 g/L adsorbent dosage									
estriol	95.6	88.4	97.4	81.1	94.4	90.5	85.4	**90.4**	**5.9**
17α-dihyrdoequilin	94.0	91.5	98.1	89.9	96.4	92.2	85.2	**92.5**	**4.3**
equilin	96.2	95.1	98.0	95.1	98.0	92.6	83.1	**94.0**	**5.2**
estrone	97.8	96.3	99.2	94.7	98.2	95.7	96.5	**96.9**	**1.6**
17α-estradiol	98.1	93.0	98.9	90.8	96.7	90.7	94.2	**94.6**	**3.3**
17- estradiol	99.3	97.7	99.2	96.6	98.9	95.6	96.7	**97.7**	**1.5**
17α-ethinyl estradiol	96.3	88.8	98.9	89.0	93.2	90.3	90.3	**92.4**	**3.9**
norgetrel	78.7	71.4	86.6	60.5	73.9	76.6	59.8	**72.5**	**9.7**
progestrone	98.0	92.6	99.0	89.4	94.5	91.7	95.3	**94.4**	**3.4**
medrogestone	94.5	89.1	94.4	92.7	91.1	92.2	79.8	**90.6**	**5.1**

Table C3. Removal (%) of E2, PFOA, and BPA in triplicates (Figure 4.1)

Adsorbent dosage (g/L)	BPA		PFOA		E2	
	avg	std dev	avg	std dev	avg	std dev
0.1	28.1	5.1	87.3	5.3	64.4	4.0
0.2	44.8	3.4	97.8	1.5	83.7	2.2
0.4	64.0	2.3	99.5	0.2	86.3	1.7
0.6	80.4	4.0	99.7	0.2	92.0	1.0
0.8	83.9	1.3	99.8	0.1	94.1	0.8
1	87.2	0.5	99.9	0.1	97.2	0.2
1.5	90.9	0.8	100.0	0.0	97.5	0.5

Table C4. Removal (%) of PFCS in triplicates with average and standard deviation (SD) BCD/silica adsorbent (Figure 4.3)

Adsorbent dosage	Perfluoro-tridecanoic acid		Perfluoro-dodecanoic acid		Perfluoro-undecanoic acid		Perfluoro-decanoic acid		Heptafluo-rooctane salt	
	avg	SD	avg	SD	avg	SD	avg	SD	avg	SD
0.1	4.95	3.1	5.40	2.2	25.80	6.0	17.65	2.0	16.94	4.8
0.2	12.27	3.2	11.39	1.8	37.98	2.3	23.35	3.6	22.22	3.8
0.3	18.47	4.9	19.78	4.9	47.91	5.4	31.44	4.6	30.91	1.8
0.4	22.41	2.0	31.89	4.8	54.40	4.1	46.01	5.7	44.33	4.8
0.6	29.50	5.5	44.36	5.2	64.97	1.7	66.28	5.0	68.21	4.5
1	33.45	3.5	52.88	5.7	73.10	1.2	72.63	4.8	82.07	4.3
1.5	37.95	1.6	64.39	3.3	75.59	2.5	86.55	3.5	93.73	1.3
Adsorbent dosage	**Perfluoro-octanoic acid**		**tridecafluoro hexane-1-salt**		**Tridecafluo-rononanoic acid**		**Perfluoro-heptanoic acid**		**Undecafluoro-hexanoic acid**	
	avg	**SD**	**avg**	**SD**	**avg**	**SD**	**avg**	**SD**	**avg**	**SD**
0.1	4.50	2.4	6.90	3.8	22.89	6.6	7.17	2.1	2.76	1.8
0.2	8.24	2.1	12.56	3.5	41.92	5.0	15.20	5.6	8.39	2.8
0.3	13.30	3.0	19.19	5.9	52.36	5.7	24.07	5.4	14.03	5.8
0.4	21.09	1.5	31.90	4.3	56.37	3.6	42.08	4.6	29.38	2.9
0.6	62.51	5.7	66.17	4.2	73.82	5.2	71.64	3.6	54.08	3.5
1	70.04	2.0	81.26	3.1	80.83	4.4	77.55	4.6	77.10	2.7
1.5	86.87	3.7	94.03	2.2	97.00	1.1	95.55	1.0	91.85	2.7

Table C5. Removal (%) of estrogens in triplicates with average and standard deviation (SD) BCD/silica adsorbent (Figure 4.4)

Adsorbent dosage	17α-ethinyl estradiol		Estriol		17α-estradiol		17β-estradiol		Estrone		17α-dihydroequilin	
	avg	SD	avg	SD	avg	SD	avg	SD	avg	SD	avg	SD
0.2	56.7	13.3	39.2	7.2	59.7	15.1	70.4	2.5	64.1	10.6	46.8	1.2
0.4	76.4	13.9	60.9	19.7	76.8	10.6	87.4	7.4	83.7	9.2	63.8	14.1
0.6	82.6	2.4	75.3	9.8	83.5	8.6	91.2	1.5	90.2	4.1	71.8	11.4
0.8	86.7	1.5	80.6	8.1	88.4	0.8	94.9	1.8	93.3	2.9	80.1	4.1
1.0	89.5	0.8	86.2	7.1	92.8	3.0	95.0	1.0	94.0	3.4	82.8	8.1
1.5	92.2	2.6	89.8	6.1	95.7	2.1	97.0	0.4	96.9	0.7	88.2	4.2
2.0	96.9	2.9	92.9	2.8	94.4	1.3	97.5	0.9	97.3	0.9	90.3	1.3
Adsorbent dosage	**Trimegestrone**		**Medrogestone**		**Progesterone**		**Norgestrel**		**Gestodone**		**Equilin**	
	avg	SD	avg	SD	avg	SD	avg	SD	avg	SD	avg	SD
0.2	37.6	4.8	35.6	15.1	55.4	8.6	9.9	1.0	13.5	7.2	24.6	7.6
0.4	60.2	15.5	56.6	18.5	77.2	11.7	33.6	9.0	28.4	14.7	49.0	9.8
0.6	73.7	8.1	66.3	12.6	87.3	4.6	37.2	8.7	41.5	3.4	65.9	9.4
0.8	81.7	4.9	75.1	8.9	91.5	2.2	46.6	7.0	52.5	3.3	77.8	4.2
1.0	86.9	4.9	80.8	8.6	94.1	1.9	57.4	10.1	61.8	8.6	86.8	1.1
1.5	91.6	3.2	84.7	6.9	95.9	0.8	67.2	10.5	70.5	5.3	86.5	4.8
2.0	93.7	0.2	88.5	3.1	96.7	0.3	72.9	2.1	79.1	1.2	96.8	4.2

Table C6. Average removal of PFOA and PFOS with standard deviation (n = 2) in the presence of Humic Acid (HA) with BCD/silica adsorbent (Figure 4.9)

Adsorbent dosage (g/L)	DOC = 12 mg/L				DOC = 4 mg/L				DOC = 0 mg/L (MQ water)			
	PFOS		PFOA		PFOS		PFOA		PFOS		PFOA	
	avg	stdev	avg	stdev	avg	stdev	avg	stdev	avg	stdev	avg	stdev
0.2	55.6	8.7	29.1	2.0	46.5	4.1	23.2	6.4	70.2	4.2	56.8	16.3
0.4	72.2	9.2	41.9	6.8	63.7	2.8	33.0	5.8	77.9	8.1	70.1	12.1
0.8	84.4	4.9	59.6	10.8	79.8	1.6	49.3	3.7	97.0	0.2	90.3	3.4
1	94.0	2.5	80.0	5.5	91.3	1.2	71.7	6.3	99.2	0.7	96.7	2.9
1.5	97.6	1.6	88.4	0.1	96.3	0.8	86.2	3.3	99.9	0.2	97.3	1.2

Table C7. Average removal of PFOA and PFOS with standard deviation (n = 3) in MQ and wastewater with BCD/silica adsorbent (Figure 4.10)

Adsorbent dosage (g/L)	MQ water				Wastewater (WW)			
	PFOS		PFOA		PFOS		PFOA	
	avg	stdev	avg	stdev	avg	stdev	avg	stdev
0.05	49.7	9.8	31.3	5.0	15.7	5.6	9.2	2.1
0.1	80.5	11.0	53.9	13.5	32.2	9.4	14.7	5.8
0.2	95.6	4.9	91.4	8.6	41.6	7.9	25.6	5.4
0.4	98.5	1.5	96.6	2.9	52.5	4.5	31.1	5.7
0.8	98.9	1.0	98.0	0.8	58.4	8.1	42.0	5.6
1.0	98.7	0.8	98.4	0.5	70.4	8.4	53.3	6.0
1.5	99.7	0.1	99.1	0.2	80.9	3.6	66.2	4.4
2.0	99.7	0.2	99.2	0.1	90.9	2.6	82.1	2.5

Table C8. Removal of 17β-estradiol and BPA in MQ water and wastewater secondary effluent with BCD/silica adsorbent (Figure 4.11)

Adsorbent dosage (g/L)	MQ water				Wastewater (WW)			
	BPA		17β-estradiol		BPA		17β-estradiol	
	avg	stdev	avg	stdev	avg	stdev	avg	stdev
0.1			48.8	7.7			18.8	9.5
0.2	29.3	4.3	65.4	3.4	14.8	4.4	37.0	6.8
0.4	52.8	4.3	85.7	2.1	22.6	4.4	55.6	7.3
0.8	75.6	2.3	93.4	2.2	36.8	3.6	72.2	4.9
1.0	84.7	2.8	96.7	2.6	42.9	4.1	78.4	5.1
1.5	89.7	1.3	98.9	0.6	51.6	2.0	84.0	4.3
2.0	91.3	0.6	99.7	0.1	64.4	3.1	93.6	2.7

Table C9. **Average removal of PFOA and PFOS with standard deviation (n = 2) in the presence of Humic Acid (HA) with hpBCD/Fe_3O_4 adsorbent (Figure 5.4)**

Adsorbent dosage (g/L)	DOC = 12 mg/L				DOC = 4 mg/L				DOC = 0 mg/L (MQ water)			
	PFOS		PFOA		PFOS		PFOA		PFOS		PFOA	
	avg	stdev	avg	stdev	avg	stdev	avg	stdev	avg	stdev	avg	stdev
0.2	84.9	4.0	29.7	4.9	93.8	3.3	55.7	11.4	97.2	5.2	84.8	6.4
0.4	92.6	1.0	63.1	8.6	96.1	2.6	76.2	2.0	98.4	2.9	94.6	4.2
0.8	96.9	0.0	75.1	2.1	98.8	0.2	84.6	5.1	99.1	1.2	96.4	5.5
1	98.0	0.8	85.9	5.7	99.2	0.0	90.2	1.0	99.7	0.3	98.0	2.6
1.5	98.5	0.5	89.3	3.2	99.6	0.1	93.2	1.2	99.3	0.1	99.2	1.1

Table C10. Average removal of PFOA and PFOS with standard deviation (n = 3) in MQ and wastewater with hpBCD/Fe_3O_4 adsorbent (Figure 5.5)

Adsorbent dosage (g/L)	MQ water				Wastewater (WW)			
	PFOS		PFOA		PFOS		PFOA	
	avg	stdev	avg	stdev	avg	stdev	avg	stdev
0.05	92.4	4.9	67.5	7.5	35.1	7.3	14.4	4.3
0.1	98.3	0.9	88.3	2.2	70.0	9.5	18.2	5.2
0.2	97.7	0.7	93.5	2.1	76.1	11.9	25.6	2.5
0.4	99.1	0.1	96.5	0.9	83.0	8.7	35.7	10.2
0.8	99.4	0.2	97.5	0.4	86.8	8.9	53.3	9.0
1.0	99.7	0.1	98.3	1.0	88.4	7.5	57.4	8.6
1.5	99.4	0.4	99.1	0.5	93.2	3.2	69.6	5.8
2.0	99.5	0.1	99.5	0.0	96.1	2.7	86.5	2.8

Table C11. Average removal of PFOA and PFOS with standard deviation (n = 2) in the presence of Humic Acid (HA) with hpBCD/zeolite adsorbent (Figure 5.13)

Adsorbent dosage (g/L)	DOC = 12 mg/L				DOC = 4 mg/L				DOC = 0 mg/L (MQ water)			
	PFOS		PFOA		PFOS		PFOA		PFOS		PFOA	
	avg	stdev	avg	stdev	avg	stdev	avg	stdev	avg	stdev	avg	stdev
0.2	91.6	1.4	55.1	13.8	95.3	4.1	73.7	2.5	98.0	3.9	94.1	5.7
0.4	**95.3**	**3.2**	**71.2**	**1.7**	**97.2**	**2.3**	**89.3**	**0.5**	**99.3**	**2.2**	**96.7**	**6.0**
0.8	97.4	1.7	86.8	0.6	98.8	0.6	92.1	1.3	99.7	0.5	97.9	4.1
1	97.9	1.1	89.5	0.2	99.4	0.2	96.1	2.2	99.7	0.1	98.5	2.7
1.5	98.1	1.6	93.8	0.9	99.8	0.2	98.1	0.5	99.7	0.3	99.4	1.4

Table C12. Average removal of PFOA and PFOS with standard deviation (n = 3) in MQ and wastewater with hpBCD/zeolite adsorbent (Figure 5.14)

Adsorbent dosage (g/L)	MQ water				Wastewater (WW)			
	PFOS		PFOA		PFOS		PFOA	
	avg	stdev	avg	stdev	avg	stdev	avg	stdev
0.05	84.3	4.3	79.6	5.3	60.6	8.4	25.4	4.4
0.1	94.1	2.1	91.7	4.1	72.2	3.8	38.3	6.2
0.2	98.0	0.7	95.6	2.8	75.9	4.3	46.0	8.0
0.4	99.2	0.8	97.6	1.7	79.1	4.1	53.0	7.6
0.8	99.5	0.5	97.9	1.6	83.8	3.5	64.2	8.4
1.0	99.5	0.0	99.4	0.2	85.5	3.9	74.8	10.1
1.5	99.7	0.1	99.6	0.3	89.9	3.9	79.9	7.4
2.0	99.7	0.1	99.6	0.1	94.7	3.0	87.1	4.0

Table C13. Average removal of PFOA and PFOS with standard deviation (n = 2) in MQ and wastewater with F400 adsorbent (Figure 5.15)

Adsorbent dosage (g/L)	MQ water				Wastewater (WW)			
	PFOS		PFOA		PFOS		PFOA	
	avg	stdev	avg	stdev	avg	stdev	avg	stdev
0.05	30.2	3.1	45.3	9.6	11.8	1.5	23.5	5.1
0.1	76.7	8.5	69.3	11.6	33.2	11.7	42.2	4.0
0.2	87.0	7.5	89.4	3.9	44.7	11.7	49.6	12.0
0.4	93.5	5.8	92.9	4.4	66.4	7.6	67.9	13.7
0.8	94.1	5.1	96.3	2.5	84.0	5.9	74.0	10.1
1.0	95.0	4.2	94.7	4.6	86.1	7.2	81.3	9.3
1.5	97.7	0.6	98.3	0.4	94.6	2.0	90.3	9.1
2.0	98.4	0.2	98.6	0.6	95.9	1.8	92.7	8.2