Removal of Estrone from Water with Adsorption and UV Photolysis

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ABSTRACT

This work investigated the combined technology of adsorption on hydrophobic molecular sieves (zeolites) and direct UV (254 nm) photolysis for removing estrone (E1) from water. The target compound estrone belongs to the group of endocrine-disruptor compounds (EDCs) that are raising more and more concern due to increasing evidence of their adverse estrogenic effects on aquatic organisms and humans.

Current wastewater treatment processes remove less than 80% of estrone on average. However, because of its strong biological potency, small amounts are still able to exert adverse estrogenic effects on aquatic systems. Consequently, advanced treatment technologies have been investigated in the hope of reaching higher removal efficiency.

Adsorption of estrogens on hydrophobic zeolites in this work is a potential new alternative. Based on the hydrophobic nature of estrogens including E1, two types of zeolites, dealuminated Y (DAY) and silicalite-1, and a type of granular activated carbon Centaur® activated carbon (GAC) were evaluated for adsorption capacity. The results demonstrated that DAY is the best adsorbent for E1 in that 99% E1 can be removed by DAY. Silicalite-1 was the least effective. Moreover, adsorption of E1 to DAY is much faster. Estrone reached adsorption equilibrium in 4 hours on DAY versus 8 days for GAC. The adsorption data of DAY for E1 were fit to the Freundlich and Langmuir equations and the maximum adsorption capacity is estimated as 74 mg E1/g DAY.

Direct UV photolysis of E1 in solution was also evaluated. Short-wave UV (λ = 254 nm) degraded E1 in solution much more effectively than long-wave UV-light (λ = 365 nm). No significant increase in degradation of E1 in UV photolysis was found with the addition of hydrogen peroxide. The regeneration of E1-contaminated DAY was investigated by a series of adsorption/direct UV (λ = 254 nm) irradiation cycles. No significant deterioration of adsorption capacity of DAY was observed over nine adsorption/regeneration cycles.

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PART I INTRODUCTION AND BACKGROUND

I.1. Endocrine Disrupting Compounds (EDCs)

Endocrine-disrupting compounds (EDCs) are a group of substances that can cause adverse health effects in an intact organism or its offspring or (sub) population by interfering the normal function of hormones and the way hormones control growth, metabolism and body functions. They can interact with endocrine systems in different ways as mimic or blocker [1]. The specific mechanisms by which EDCs disrupt endocrine systems are very complex, and not yet completely understood. Generally, it is accepted that three major classes of endocrine disruption endpoints [52] are:

Estrogenic – compounds that mimic or block natural estrogen

Androgenic – compounds that mimic or natural testosterone

Thyroid – compounds with direct or indirect impacts to the thyroid

There is a wide range of substances in the group, including natural and synthetic hormones, industrial chemicals and pesticides. Out of an identified candidate list of 553 substances, evidence of endocrine disruption was found for 160 compounds as well as 2 natural estrogens estrone and 17β-estradiol and 1 synthetic estrogen 17α-ethinyloestradiol, and potential endocrine disruption was found for 105 compounds [2]. The natural and synthetic estrogens such as estrone (E1), 17β-estradiol (E2), estriol (E3) and 17α-ethinyloestradiol (EE2) display much stronger estrogenic effects than others [3]. This could be due to the common phenol ring of their molecules that is regarded as one of the essential functional groups to interact with the estrogen receptor. Their chemical structures

are shown in Figure 1.

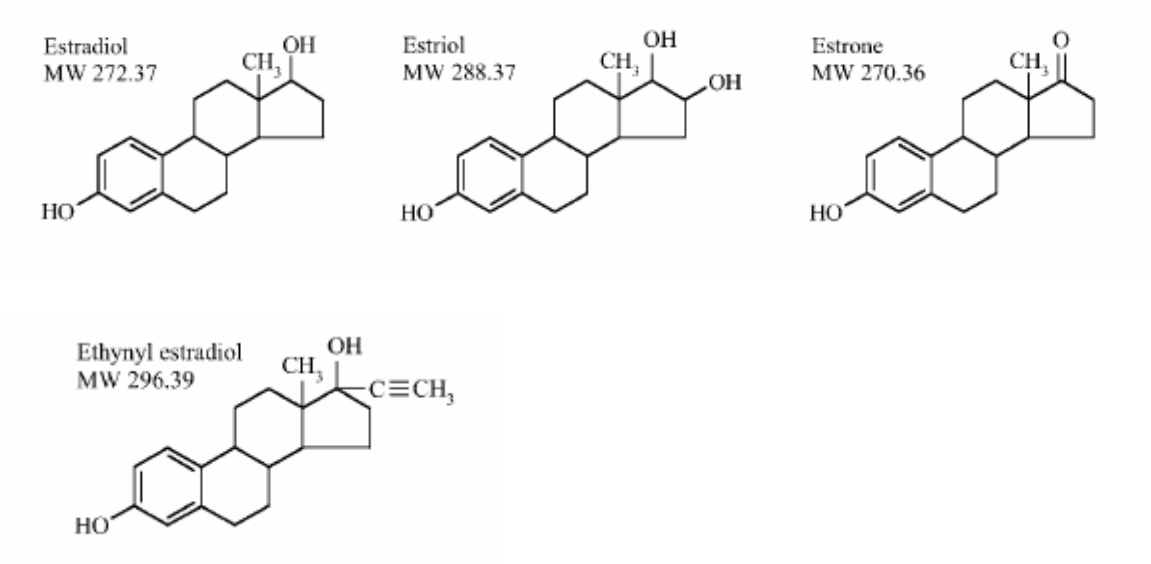

Figure 1: The molecular structure of natural and synthetic estrogens [76]

Although the topic of endocrine disruption is considered an “emerging issue” in the environment, scientists have known about the ability of natural and synthetic compounds to interfere with the hormone systems of animals for over 70 years. The discovery that certain compounds can mimic the endogenous hormones of animals was reported as early as the 1930s [4][5]. Schueler explained that molecular configurations of natural and synthetic compounds influenced the degree of estrogenic and androgenic bioactivity in rodents in 1946 [6]. The ability of estrogenic and androgenic compounds to interfere with the natural metamorphosis of amphibians was reported in 1948 [7].

I.2. Adverse Effects of EDCs in The Environment

In recent years, there is growing concern of EDCs in the environment since more and more evidence has been gathered showing their adverse effects on both aquatic systems and humans, which are proving those early studies presented in part I.1. Many studies demonstrated the impacts of industrial chemicals on aquatic animals. One of the first documented connections between an environmental contaminant and reproductive impacts via a hormone-mediated mechanism is that gulls living areas contaminated with DDT exhibited deformed sex organs and skewed sex ratios [8][9]. Gibbs *et al.* reported in 1991 that marine gastropods exposed to tributyltins, which leach from certain antifouling paints and PVC pipes, experienced severe population declines and reproductive disorders including imposex (development of male sex characteristics in female) [10]. In some amphibian populations, supernumerary limbs and missing limbs have been attributed to certain pesticides and other anthropogenic chemicals [11]. In particular, trace concentrations of the widely used herbicide atrazine have been associated with endocrine disruption in frogs from the Midwestern United States [12]. In the 1990s, reports from the United Kingdom and the United States indicated that fish living below wastewater treatment plants had several reproductive abnormalities [13]-[17].

Natural estrogens from plant sources, known as phytoestrogens, have been linked to reproductive failures in animals since 1930s [5], [18]-[21]. The sheep grazing on certain strains of clover in New Zealand exhibited severe reproductive impairment due to phytoestrogens [22][23]. Likewise, the inability of captive

cheetahs to reproduce at the Cincinnati Zoo was linked to a diet high in phytoestrogens [24].

Moreover, a series of studies employing *in vitro* bioassay-directed chemical fractionation implicated 17β-estradiol (E2) and 17α-ethinyloestradiol (EE2) as the most potent estrogens in complex mixtures [25]-[27]. The disrupting activity of E2 is 1000-10,000 times greater than that of nonylphenol [28]. Just due to their extremely high biological potency, trace amounts as low as ng/l are capable of exerting biological effects on aquatic organisms. Related research involving exposure of fish to E2 and EE2 under laboratory conditions even at 2 ng/l could induce measurable changes in fish reproduction [29]-[32]. Even at 0.1 ng/l, EE2 is biologically active in fish [16][53]. Nimrod and Benson, and Merland found that several fish species have undergone forced sex reversal by exposure to E2 experimentally too [33][34]. Meanwhile, there is growing evidence showing adverse alterations in gonadal tissue in feral fish populations exposed to estrogenic contaminants of wastewater treatment plant (WWTP) [15] [36]-[39]. Some studies observed feminized ducts, reduced sperm production and intersex in the male fish by exposure to domestic sewage treatment work (STW) [40][41]. In aquaculture, phenotypic expression of the female genotype in male fish can be easily induced by exposure of eggs, embryos or fry to steroid estrogens [42].

The unexpected impacts of trace concentrations of EDCs on wildlife raised concerns about the potential effects of these chemicals on humans [43]. However, it is a very controversial topic. Some researchers attributed decreases in human sperm quality to EDCs in the environment [44]-[46]. Likewise, it has been

suggested that sharp increases in breast, testicular and prostate cancers are related to EDCs in the environment [46]-[51]. But other scientists have produced data refuting these arguments. Estrogenic hormones in water are less likely to cause adverse effects in humans than they are in fish due to differences in exposures. Fish may be constantly exposed to EDCs present in the aquatic environment, while humans are exposed mainly through ingestion of limited quantities of water [52].

So far, the majority of research has focused on estrogenic compounds; however, disruption of androgen and thyroid function may be of equal or greater importance biologically.

I.3. Analytical methods of estrogens

Since EE2, E2, E1and E3 are regarded as the most potent estrogenic compounds based on the available research presented in part I.2 and the major contributors to the estrogenic activity observed in sewage effluents [25][41][54] and natural water bodies, the subsequent research of concern focuses on them.

At present, a variety of analytical procedures have been developed to determine estrogens in water and wastewater. However, determination of estrogens is a difficult task, considering the low concentrations at ng/l (ppt) and even sub-ng/l detected in wastewater treatment plants (WWTPs), sewage treatment works (STWs) influents and effluents and rivers [55], and the complexity of the real water/wastewater matrix (Some selected surveys in Europe, USA and Canada are listed in Table 1.). Although direct measurement such as

high-performance liquid chromatography (HPLC) with fluorescence (FL) detection [56] or stripping voltammetry [57] is possible, most methods involve sample preparation / preconcentration / extraction followed by instrumental and/or biological analyses in order to reach as low detection limit as possible close to environmental level concentrations. Off-line solid-phase extraction (SPE) is recently the most popular method of extracting estrogens from water and wastewater, compared with liquid-liquid partition (LLE) and on-line SPE. However, a new technique solid-phase microextraction (SPME) is being applied to extract estrogens and it can perform as well as SPE when it is assisted by derivatization, for example, on-fiber silylation [75]. More importantly, SPME is a solvent-free and fast method. It will, therefore, gain the domination of determination of estrogens in the near future in respect of environmental protection. The widely used analytical instruments are gas chromatography (GC) coupled with mass spectrometry (MS) or tandem MS and HPLC / liquid chromatography (LC) coupled with MS or tandem MS, although a few biological assays have been employed to detect estrogens such as enzyme-linked immunosorbent assay (ELISA) and radioimmunoassay (RIA). A summary of the applied analytical procedures is shown in Table 2. In order to increase accuracy of the analytical data, stable isotopically labeled surrogates and internal standards, for instance, deuterated 17β-estradiol (d_4) [75], estrone (d_4), 17α-ethinyloestradiol (d_4) [69], deuterium labeled [$^2H_{14}$] bisphenol A [74] and hydrocodone(d_6) [77], were added to the initial water sample and were followed through the entire extraction and analytical steps.

It is much more complicated to measure estrogens in wastewater than just water spiked with estrogens because of the considerations of sample collection, preservation and handling. It is recommended to collect samples in amber glass containers commonly pre-cleaned with an organic solvent and reagent water [76]. Sampling periods between 6h [62] and 5days [41] have been used to collect composite, representative samples, whereas discrete wastewater samples have been analyzed in many other instances. Sample preparation is mainly divided into filtration, extraction, purification, enzymatic hydrolysis and derivatization [76]. While to pure water spiked with estrogens of interest, only extraction and derivatization are needed. However, if HPLC/LC – MS (-MS) is used for detection, derivatization can be disregarded. How to store samples to guarantee no significant losses of estrogens before analysis is an issue of importance too. Baronti et al. [59] performed the first stability study to evaluate estrogen degradation during storage of river water samples. The storage period varies from 1 day to longer than 2 months under different pretreatment conditions, for example, using 1% formaldehyde (v/v) as preservative or not. The unpreserved wastewater samples are usually stored from the moment of collection until extraction within one week at 4°C [60][78] or –20°C (freezed) [41][67]. Other researchers, following the same procedures as that of Baronti et al. [59], added some chemicals to water samples for storage up to 24 days, such as 1% formaldehyde (v/v) [79], methanol [25] and sulfuric acid [71] as preservative, and/or stored the samples on the solid supports used for extraction [25][41].

Table 1: Estrogens concentrations in sewage treatment plant influent and effluent, and river water

Location	E1(ng/l)	E2 (ng/l)	EE2 (ng/l)	E3 (ng/l)	Total(ng/l)	Ref.
INFLUENT						
Paris, France	9.6-17.6	11.1-17.4	4.9-7.1	11.4-15.2	37-57.3	[58]
Italy	52	12	3	80	147	[59]
Roma, Italy	31	9.7	4.8	57	102.5	[60]
Spain	<2.5-115	<5-30.4	<5	<0.25-70.7	<12.75-221.1	[61]
EFFLUENT						
England	1-80	1-50	0-7.0	/	2-137	[65]
German	7	6	3	3	19	[63]
German	<70	<3	<15	/	<88	[66]
Italy	3	1.4	0.6	20.4	25.4	[59]
Roma, Italy	24	4	1.4	11.7	41.1	[60]
Spain	<2.5-8.1	<5-14.5	<5	<0.25-21.5	<12.75-49.1	[61]
California,USA	/	0.2-4.1	0.2-2.4	/	0.4-6.5	[66]
Canada	3	6	9	/	18	[64]
Canada	48	64	42	/	154	[66]
Sweden	5.8	1.1	4.5	/	11.4	[67]
RIVER						
France	1.1-3.0	1.4-3.2	1.1-2.9	1.0-2.5	4.6-11.6	[58]
Netherlands	<0.1-3.4	<0.3-5.5	<0.1-4.3	/	<0.5-13.2	[62]
England	0.2-10	<LOD[a]-7.1	<LOD[c]	<LOD[b]-3.1	<0.75-20.25	[65]
Italy	1.5	0.11	0.04	0.33	1.98	[59]
California,USA	/	0.05-0.8	<0.05-0.07	/	<0.1-0.87	[64]

Note: LOD – Limit of Detection; a – 0.2ng/l; b – 0.3ng/l; c – 0.05ng/l

Table 2: Analytical methods for the determination of estrogens in water/wastewater

Analyte	Sample preparation	Detection	LOD[a] (ng/l)	RSD[b] ()	Ref.
E2	SPE (C_{18} column)	RIA	2	6.7-8.9	[68]
E2, EE, E1	SPE (C_{18} column), HPLC fraction, LLE	GC-MS	0.2	/	[25]
E2, EE, E1	SPE (SDB-XC disk), Hydrolysis, SPE(C_{18} or NH_2 column) HPLC fraction	GC-MS-MS	0.1-2.4	8-14	[62]
EE	SPE (SDB-XC disk), HPLC fraction	HPLC-FL	4	3-7	[26]
E2, EE	SPE (SDB-XC disk), HPLC fraction	RIA	0.107(E2) 0.053(EE)	/	[26]
E2, E1	SPE (C_{18} or NH_2 column), Silica gel,Derivatization	GC-MS-MS	1	0-13	[66]
E2,EE,E1,E3	SPE (Carbograph-4)	HPLC-MS-MS	0.08-0.6	4.8-7.4	[59]
E2, EE, E1	SPE (SDB -XC disk), SPE (C_{18} or NH_2 column), HPLC fraction	GC-MS-MS	0.1-1.8	8-14	[60]
E2,EE,E1,E3	SPE (Carbograph-4)	HPLC-MS-MS	0.2-0.5	<10	[60]
E2, EE, E1	SPE (C_{18} disk)	GC-MS-MS	1	2.2-5.9	[69]
E2,EE,E1,E3	SPE(Envi-Carb column)	HPLC-MS-MS	0.5-1	7-11	[70]
E2,EE,E1,E3	SPE (C_{18} column)	HPLC-DAD[c]-MS	2-500	14-25	[71]
E2,EE,E1,E3	On-line SPE (PLRP-s)	HPLC-DAD-MS	10-200	1-3	[72]
E2, EE	SPE (C_{18} disk), Hydrolysis, HPLC fraction	ELISA	0.1	11-26	[64]
E1, E2, EE	SPE (C_{18} cartridge)	LC-MS-MS	3.7, 4.1, 4.4	<15	[73]
E2, EE	No	HPLC-FL	313, 284	/	[56]
E1, E2, E3	No	Voltammetry	270	/	[57]
EE, BPA	SPME	GC-MS	1000, 40	8	[74]
E1, E2, EE	SPME, On-fiber derivatization	GC-MS-MS	1, 0.7, 3	<7.5	[75]

Note: a :LOD – Limit of Detection; b :RSD – Relative Standard Deviation;
c :DAD – Diode array detector

I.4. Estrogens removal from wastewater

Natural hormones are excreted mainly in the urine of both female and male mammals as biologically inactive forms, following their conjugation to water-soluble glucuronide and/or sulphate ester groups [80]. For example, E1, E2 and E3 are excreted by woman in amounts ranging from 10 to100 µg/day and up to 30 mg/day by pregnant woman [60]. Another synthetic estrogen EE2 is present in many contraceptives and other drugs prepared with this and other analogous compounds for treatment of cancers or hormonal disorders.

The conventional sewage treatment plants (STPs) can remove estrogens at a broad range of rates and the extent of removal differs among estrogens, depending on the treatment methods. Typically, sewage treatment plants transform organic compounds to biomass and remove it aerobically by biological oxidation in activated sludge, trickling filters, or biorotors. Among these biological treatments, the most commonly used method, activated sludge, was found the most effective to remove estrogens. The highest removal performances (>97% removal) were obtained by a combination of activated sludge and another treatment process such as nitrogen removal or trickling filter [84]. However, different studies have agreed on average removal rates for steroid estrogens by STPs from around 85% for E2 and EE2 and only 70% for E1. Between individual STPs large differences were observed from 19% to 98% for E1, 62% to 98% for E2 and 76% to above 90% for EE2 [81]. The table 3 lists the relevant field data.

I.5. Recent research on estrogens removal

Since conventional biological treatment plants cannot completely eliminate estrogens in wastewater effluents are still one of the major sources of estrogens which adversely affect animal reproduction and human health due to their potent estrogenicity. Moreover, several studies suggested that deconjugation (release free estrogens from conjugated forms in excretion of body) could occur through microbial processes in the sewage treatment plants and in river so as to increase estrogens amounts in the environment [55]. In addition, some researchers presumed that the removal mechanisms of estrogens during wastewater treatment could be sorption on sludge and biodegradation, considering the hydrophobic nature of estrogens with low volatility [55]. If so, part of removed estrogens could accumulate in the wastewater treatment plants sludge and suspended solids, and may cause a potential contamination of soil and ground water [55] when that sludge is landfilled. There is a need to develop practical advanced technologies and/or optimize the operational conditions of present STPs in order to minimize the threat of estrogens to the environment. In recent years, more and more studies have investigated the removal effectiveness of a variety of advanced technologies. Some of these technologies were researched for removing EDCs from drinking water treatment facilities as well [52]. Table 4 quantifies estrogens removal by advanced treatment processes. Reverse osmosis (RO) can reach greater than 90% removal of steroid hormones [64] and nanofiltration (NF) can remove some estrogens [77]. But microfiltration didn't remove two estrogens [64] and ultrafiltration cannot remove estrogens too [77]. In

addition, granular activated carbon (GAC) could be able to remove EDCs [52]

Table 3: Estrogens removal evaluation from activated sludge plants

Country	E2% removal	E1% removal	EE2% removal	Reference
Brazil (n=18)	99.9	83	78	[66]
Canada (n=6)	99	71	NA	[81]
European av (n=8)	88 (SD 13)	74 (SD 27)	NA	[81]
Germany (n=1)	98	98	90	[81]
Italy (n=30)	87 (SD 6)	62 (SD 33)	85 (SD 14)	[81]
Italy (n=18)	85	61	NA	[81]
Japan (n=27)	67	NA	NA	[81]
Roman (n=30)	87 (SD 9)	61 (SD 38)	85 (SD 14)	[83]

Table 4: Removal of estrogens by advanced treatment processes

Treatment	Estrogen	Ci	Removal %	Contact Time	Added dose	Ref.
Ozonation	E1	15ng/L[c]	>80	18min	5mg O_3/L	[82]
Ozonation	E1, E2	9.7-28ng/L[d] 3.0-21ng/L[d]	95	10min	5mg O_3/L	[89]
Chlorination	E2	50μg/L[e]	100	10min	1.46mg $NaClO_4$/l	[90]
Chlorination	E2	27.2μg/L[e]	100a	36h	1.5mg Cl_2/L	[91]
Chlorination	EE2	54.4mg/L[e]	100	5min	71mg Cl_2/L	[92]
TiO_2	E2	13.6-816μg/L[e]	98	3.5h	/	[86]
TiO_2+UV	E2	272μg/L[e]	99 100b	30min 3h	1.0g TiO_2/L	[87]
TiO_2+UV	E1,E2,EE2	10μg/L[e]	100	60	/	[88]
PAC	E2, EE2	27.2μg/L[e] 29.6μg/L[e]	49.4 - >99 80.6 - >99	4h	5mg PAC/L 15mg PAC/L	[56]
MnO2	EE2	15μg/L[e]	81.7	1.12h	/	[85]
UV	E1, E2	10mg/L[e]	>90(E1),60(E2)	1h	1500μW/cm^{-2}	[93]
UV	EE2	1.6-20mg/L[e]	90	80min	1500μW/cm^{-2}	[94]
UV-vis/H_2O_2/Fe	E2	10mg/L[e]	61.7	180min	1.7×10^5 lx	[95]
UV/ H_2O_2	E2, EE2	/[e]	>95	/	1000mJ/cm^{-2}	[96]

[a] Completed removal of estrogenic activity. [b] Decomposed completely into CO_2.
[c] Municipal STP effluent. [d] Wastewater from secondary treatment. [e] Synthetic water.

I.6. Background & Objectives of this research

(1) Selection of EDCs

There are hundreds of compounds in the group of EDCs and these compounds are various effects on the environment and humans. Four estrogens (E1, E2, E3, EE2) are present in the environment, and may be of concern.

Some researchers concluded that estrone (E1) is the toughest one to deal with [81][55]. Although it may have only half the potency of E2, it is frequently found at

concentrations in the effluent greater than double that of E2 and is also very consistently found in effluents. D'Ascenzo *et al*. even reported that the amount of E1 discharged from STPs into the receiving water was more than ten times greater than E2 [98]. This could be due to conversion/oxidation of E2 to E1 during treatment processes [66][97], poor removal effectiveness of the plants compared to other estrogens, and probable deconjugation by bacteria which releases free E1 from conjugated forms entering STPs. For example, E1 was the only estrogen detected in 15 German rivers and streams investigated under the condition that the detection limit was as low as 0.5 ng/l [66]. As EE2 concentrations in the environment are often very low, or perhaps in some cases undetectable, it would not be as important as E1, although it is an extremely potent estrogen based on both *in vitro* and *in vivo* studies [16][53][99]. However, EE2 may have the greatest single impact on the estrogenicity of the effluents, but the present analytical techniques must achieve lower detection limits to quantify.

As a result, E1 was selected as the target compound in this research to evaluate an alternative treatment technology for removing these types of compounds. Estron's main physical and chemical properties are presented in Table 5. And the picture of estrone molecule is shown in Figure 2.

Table 5: The physical & chemical properties of estrone

Molecular formula	Molecular Weight[a]	Solubility (20°C)	Melting point[a]	Specific gravity of solid[a]	Molecular dimensions[b]	$LogK_{ow}$[c]	pK_a[c]
$C_{18}H_{22}O_2$	270.4 g/mol	13 mg/l	255°C	1.23	10.8 Å (length); 3.8 Å (width)	3.13	10.3

[a] values from Estrone MSDS of Sciencelab.com,Inc.
http://www.sciencelab.com/Xmsds-Estrone-9923934

[b] dimensions of estrone molecule from [106]

[c] values from [77]

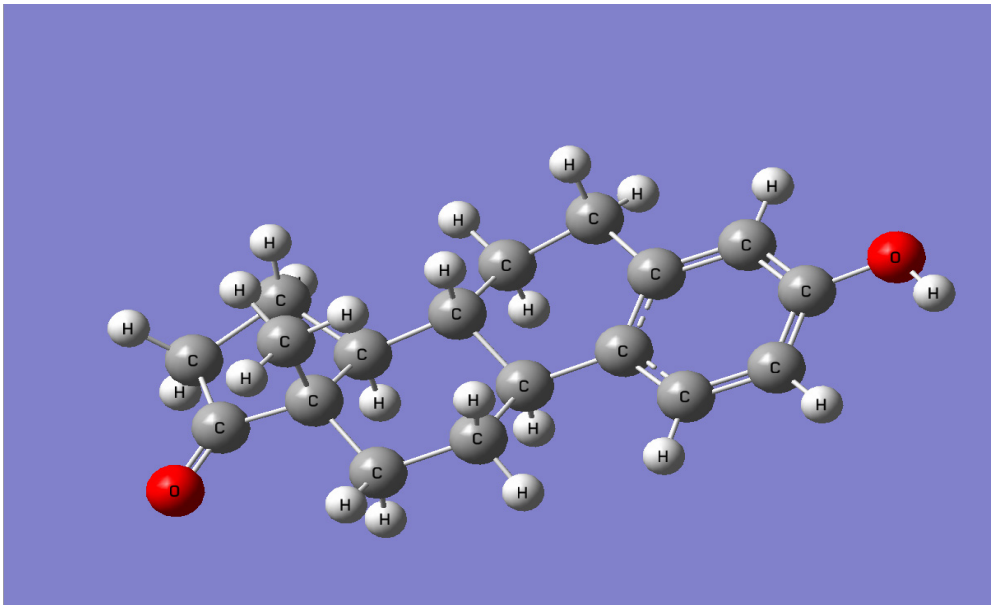

Figure 2: Picture of estrone molecule

(2) Analytical method

Commonly used analytical methods for the determination of estrogens in water/wastewater employ GC/HPLC-MS (-MS). However, a new analytical procedure employing GC-FID coupled with SPME was developed for detecting E1 in this research.

(3) Advanced treatment technology

The main purpose of this research was to investigate adsorption of E1 on hydrophobic zeolites, and to evaluate regeneration of zeolites by UV photolysis and UV/H_2O_2 advanced oxidation.

The zeolites may remove estrone from water due to their hydrophobic nature. Some studies showed that adsorption capacity of powered activated carbon increased with increasing octanol-water partitioning coefficient K_{OW} of EDCs [56]. The logK_{OW} values of estrogens (Table 6) indicate that these compounds should be appreciably adsorbed on hydrophobic adsorbents. Moreover, the hydrophobicity of E1 is in the middle, so it could be the best representative of the group of compounds to examine this treatment. In general, activated carbon adsorption is considered technically and economically feasible when contaminants' logK_{OW} values are greater than 2, so estrogens may be amenable to removal by PAC or GAC [52].

However, the main disadvantage of adsorption is that the contaminants may be ?, but may remain toxic to the environment. As a result, we need to use another treatment such as oxidation or UV to destroy the contaminants, transferring them into less toxic byproducts, and re-establish the adsorptive capacity of zeolites for the target compound. On the other hand, if we only use oxidation or UV to treat wastewater/water directly, that will need much more oxidants or UV light due to a continuous contact with a huge volume of fluid which will certainly increase costs of treatment plant.

Consequently, the best alternative is a combination of the two processes. In the combined process, E1 is first adsorbed from a large volume of wastewater/water and pre-concentrated on hydrophobic zeolite. The contaminated zeolite is then treated with UV or UV/H_2O_2 for the destruction of adsorbed E1 and regeneration of the zeolite.

Table 6: logK_{OW} of estrogens (Reference [77])

Estrogen	E1	E2	E3	EE2
logK_{OW}	3.13	4.01	2.45	3.67

(4) Hypothesis

Hydrophobic molecular sieves (zeolites) can remove estrone from water.

(5) Summary of my research objectives

1. Develop an appropriate analytical method according to the available instruments

2. Investigate the removal efficiency of E1 by adsorption on hydrophobic zeolites and granular activated carbon

3. Evaluate the regeneration of zeolites by UV photolysis and UV/H_2O_2 advanced oxidation

PART II MATERIALS AND METHODS

II. 1 List of materials

Table 7: List of chemicals and instruments

Chemical	Use	Grade	Company
Methanol	Solvent	HPLC grade, UV cutoff 205nm	Fisher scientific
Ethyl acetate	Solvent	HPLC grade	Fisher scientific
Estrone	Contaminant	Minimum 99%	Sigma-Aldrich
17β-estradiol (d_4)	Internal standard	2,4,16,16-D_4 isotope, 95-97%	Cambridge Isotope Laboratories.
MSTFA	Derivatization	Derivatization grade	Sigma-Aldrich
Dealuminated Y (DAY)	Adsorbent	/	Zeolyst
Silicalite-1	Adsorbent	/	Union Carbide
Centaur® activated carbon	Adsorbent	Granular activated carbon	Calgon Corporation
$CaCl_2$	Drier		Sigma-Aldrich
H_2O_2	Oxidant	30%, certified A.C.S	Fisher scientific
Water	Solvent	E- pure	Barnstead Ropure ST/E-pure system
air	Igniting gas (GC)	. Air ultra zero<0.1ppm thc	AGA
N_2	Carrier gas (GC)	99.999% N_2	ABCO welding supply
H_2	Igniting gas (GC)	Ultra high purity	Airgas east

Instrument	Use	Type	Company
GC/FID	Detection	Series 6890	Agilent Technologoes
GC Column	Detection	Equity^{TM}-5 Capillary column	Supelco
SPME	Extraction	85μm polyacrylate coating	Supelco
UV light	Regeneration	Model 11SC-1 Mercury Pen-Ray lamp (254nm, 6650μW/cm^2)	UVP, Inc.
Power supply	UV power	Model SCT-1A (325V, 20mA)	UVP, Inc.
Quartz tube& tube	Regeneration	ACE–7506-10; #25	ACE Glass Inc.
Oven	Derivatization Heat	/	Shon's scientific refrigeration Service Inc.
Long-wave UV	Degradation	36-380 long-wave lamp 365nm, 1000μW/cm^2	Spectronics Corp.
Centrifuge	Separation	5804	Eppendorf
Weigher	Weighing	10mg - 101g	Mettler Toledo
Shaker	Mixing		Lab-line instruments, Inc.
Magnetic stirrer	Stirring	/	/
pH meter	Measure pH	AB15	Fisher scientific
Glass fiber filter	Sample prep.	47mm, 0.7μm Nominal	Pall Gelman Laboratory
Membrane filter	$Ba(OH)_2$ Prep.	47mm, 0.45 μm	Pall Gelman Laboratory

In addition: Dessicator, magnetic stir bars,
5ml, 1000μl and 200μl pipettes and tips,
Glassware: 1.5ml and 45ml vials, 125,250,495 and 1050ml brown bottles, 25ml burette, 250ml and 1000ml flasks, 25ml and 50ml glass pipettes.

II. 2 Adsorption experiments

(1) Standards, adsorbents and water samples preparation

Stock solution of 1g/l estrone was prepared by dissolving 100 mg estrone (minimum 99%; sigma-aldrich) in 100 ml methanol (HPLC grade; fisher scientific), then stored at 4°C in refrigerator. To determine calibration curves for quantification of estrone, it was diluted with water (from Barnstead Ropure ST/E-pure system) to

a series of standard solutions ranging from 1 μg/l to 1000 μg/l when needed. Solution of 17β-estradiol (d_4) ($E2d_4$) at 100 mg/l was prepared by dissolving 5 mg deuterated $E2d_4$ (2,4,16,16-D4, Cambridge Isotope Laboratories) in 50 ml methanol and used as internal standard throughout the analytical procedure.

All adsorbents DAY, silicalite-1 and GAC, were dried in oven at 120°C for 12-14 h, then stored in a dessicator containing supersaturated solution of $CaCl_2$ in water prepared by adding 80 g $CaCl_2$ in 500ml water that produced moisture equilibrium in a saturated humidity atmosphere [102].

Spiked water samples were made by dissolving an amount of E1 in the range 10 mg to 95 mg (minimum 99%, Sigma-Aldrich) to 1000 ml water, magnetically stirring for 4-8 h, then filtering through glass fiber filters (47 mm, 0.7 μm pore size, Pall Gelman Laboratory). The final dissolved concentration of E1 solution ranged from 900 ppb to 2500 ppb. The solutions were stored at 4°C until use.

(2) Analytical procedure

The method of sample preconcentration /extraction developed in my experiments was adapted from that used by J. Carpinteiro *et al.* [75], P. Braun *et al.* [74], A. Erdem-Senatalar *et al.* [100] and J. Bergendahl *et al*. [107]. A manual SPME holder and fiber with coating polyacrylate (PA, 85 μm film thickness, Supelco) were selected for extracting estrone. At the beginning of the use of a new fiber, it was conditioned by baking in the back injection port of the GC (Agilent Technologies, Series 6890) at 300°C for at least 2 h (referring to Guidelines attached to the product package). Two blank GC injections were carried out at the

GC analysis conditions reported below, following water rinses of 30min each, before analyses daily. For each fiber, only one calibration curve was created as the basis of quantification of E1 concentration, because of the assistance of the internal standard $E2d_4$. It was determined by plotting at least three standard concentrations of E1, 1 ppb, 50 ppb and 1000 ppb versus their corresponding E1 peak areas, including a zero point. Generally, the life of a fiber was found to be about 50 uses.

40 ml samples with 0.4 ml $E2d_4$ standards were contained in tightly capped 45 ml vials. The fiber was immersed in the solution to be analyzed at room temperature (20°C±2°C) for 1 hour with magnetic stirring at 400 r.p.m. After finishing the micro-extraction step, the fiber was exposed to the headspace of a 1.5 ml vial containing 50 µl of *N*-methyl-*N*-(trimethylsilyl) trifluoroacetamide (MSTFA) (Derivatization grade, Sigma-Aldrich) that converts E1 to its silyl derivative [75]. The derivative is much easier to be detected by GC/FID than E1 itself. On-fiber derivatization/silylation was carried out at 60°C for 15 min in oven, before each GC injection. Each 40.4 ml sample was tested only once to avoid variation due to removal of E1 from the solution. While the addition of NaCl to the sample was expected to improve the micro-extraction efficiency [74][75], no significant difference was observed between the sample with NaCl and that without it in preliminary tests. Moreover, considering that frequently fiber breakage happened easily with NaCl addition [100], most extractions were conducted without NaCl addition. Since the effect of sample pH was not statistically significant on micro-extraction [75], no pH adjustment was performed in these

experiments.

The GC was equipped with a flame ionization detector (FID), and an Equity^{TM}-5 Capillary column 12 m in length, 200 µm in nominal diameter and 0.33 µm film thickness. The inlet and detector temperatures were set at 280°C and 280°C, respectively. Nitrogen gas was used as carrier gas at a constant flow of 0.8 ml/min. Hydrogen gas and air were used to keep the detector flame at a flow of 40 ml/min and 180 ml/min, respectively. The flow rate of make up nitrogen gas is 19.2 ml/min. The GC oven was programmed as follows: 1min at 80°C, ramp at 15°C /min to 260°C held for 20 min. SPME fiber was desorbed for 5min in the splitless mode at 280°C and was additionally heated for 5min at the same temperature to avoid contamination problems during the analysis of samples containing different concentrations of E1 [75], therefore the total desorption time of the fiber is 10 min between consecutive injections.

The overview of the analytical procedure is presented in Figure 3.

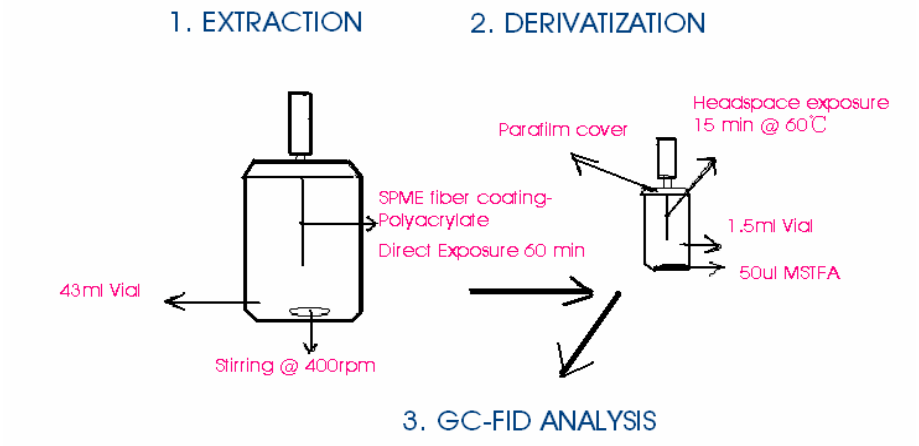

Figure 3: The analytical procedure

(3) Quantification of E1

Past studies indicated that the efficiency of the SPME method could be affected by the water matrix and the age of the fiber [75][100], so proper quantification was important. Because the isotopic dilution (ID) technique showed the advantages of less time and labor and improved precision and accuracy of the results [75], I employed the method and used $E2d_4$ as internal standard. 0.4 ml of $E2d_4$ solution at 100 mg/l was added in each single sample. The calibration curve was made by plotting the peak areas of E1 against the concentrations of standards. The concentration of E1 could be calculated using the following simplified equation:

Y(Conc.) = K * A(E1) * F

Where:

F: performance factor of the fiber at day basis

F = A($E2d_4$) @ 50ppb in calibration curve /A($E2d_4$) @ 50ppb every working day

K: Slope of the linear calibration curve

A (E1): Peak area of E1

A ($E2d_4$): Peak area of $E2d_4$

Conc.: Concentration of E1

(4) Evaluation of removal efficiency of E1 on silicalite-1, DAY and Centaur® activated carbon

The adsorption experiments for comparing the removal efficiencies of E1 on

silicalite-1, DAY and Centaur® activated carbon were carried out in 45 ml vials placed on an orbital shaker table at room temperature for 24 h, for the adsorption equilibrium. A contact time of 24 h was found to be sufficient for MTBE adsorption on similar materials [101]. The working conditions of the three adsorbents are exactly the same: the common lot of initial water sample spiked with E1, 41 ml water, 41 mg adsorbent, 24 h contact time and shaking at 120 r.p.m.

Liquid-solid separation was performed by centrifugation for 10 min at 2000 r.p.m. (Eppendorf 5804 centrifuge, Eppendorf, Germany) and the supernatants were removed by 5 ml pipette for 8 times.

The removal efficiency can be evaluated by the ratio removed E1 over initial E1. The equation is:

$$\text{removal of E1}(\%) = \frac{C_{\text{initial}} - C_{\text{equilibrium}}}{C_{\text{initial}}} \text{x}100$$

(5) Kinetics of adsorption

Kinetics experiments were carried out in 45 ml vials placed on the shaker table at room temperature for a series of contact times with constant adsorbent/liquid ratio, treating one spiked water sample in all tests. For DAY, 14.5 mg DAY was added in 42 ml water, and the contact times ranged from 2 to 20 h. While for granular activated carbon, 19 mg carbon was added in 42 ml water, and the contact times ranged from 1 to 8 d. All other conditions were the same as those above.

(6) DAY adsorption isotherm

The adsorption isotherm was developed by applying varied adsorbent/liquid ratios 10~315 mg DAY/l to adsorb E1 from spiked water samples containing different initial concentrations. That was realized by placing different amounts of DAY in the range of 10-40 mg into different water samples with volumes ranged from 125 ml to 1045 ml. 4 ~ 5 h was selected as the contact time for determining the adsorption isotherm of E1 on DAY because 4 h was observed to be sufficient for equilibrium for E1 on DAY. To improve the effect of mixing, magnetic agitation was employed in place of shaking. When the adsorption process ended, transferred 40 ml solution to 45 ml vial and followed the analytical procedure to measure the equilibrium concentration of the solution. The relationship used to compute the amount of E1 adsorbed, q, is:

$$q = \frac{V_{water} \cdot \left(C_{L,initial} - C_{L,equilibrium}\right)}{m_{DAY}}$$

Where:

q — the amount of adsorbate (E1) per unit of adsorbent (DAY), μg E1/g DAY

V_{water} — the volume of sample water, l

$C_{L,\ initial}$ — initial concentration of E1 in water, μg / l

$C_{L,\ equilibrium}$ — equilibrium concentration of E1 in water, μg E1 / l

m_{DAY} — the amount of adsorbent (DAY) added into the sample water, g

II.3 Regeneration experiments

The water sample preparation and analytical procedure were the same as for the adsorption experiments. The experimental light sources for irradiation were an UV-light (Mercury pen-ray lamp, Model 11SC-1, 254 nm, 6650 μW/cm^2, UVP Corp.) and a long-wave UV-light (36-380 long wave UV lamp, 365 nm, 1000 μW/cm^2, Spectronics Corp.). Irradiation under UV was performed in the quartz tube (ACE-7506-10, ACE glass incorporated) approximately 13 cm long and 1.2 cm diameter with 5mm thickness of tube wall and the solution was filled in the outer tube (#25, ACE glass incorporated) approximately 11 cm long and 2.5 cm diameter with 2 mm thickness of tube wall.

(1) Direct UV irradiation of E1 solution

40 ml initial water sample was divided into 8 runs of irradiation with the constant contact time under direct UV-light or UV-light coupled with different concentrations of H_2O_2 solution. That results in 5 ml per run because the tube can only hold 8 ml maximum. The contact times were 10 s, 20 s, 30 s, 1 min, 3 min, 6 min and 30 min.

(2) Adsorption and UV regeneration

The experiment involving both adsorption of E1 on DAY and regeneration of adsorbed DAY by direct UV irradiation (λ = 254 nm) is called one cycle. 39 mg DAY was used as adsorbent and the volume of spiked water for all cycles was fixed at 125 ml. After the liquid-solid separation step (125 ml was allocated into three 45 ml vials.), the separated DAY was resuspended in 15 ml water. The direct

UV photolysis was performed in quartz tube for three times with 6 min and 30 min irradiation time (based on the result of kinetics). At last, the resuspended solution was separated again by centrifuge and stored in the dessicator for the next cycle.

PART III RESULTS AND DISCUSSION

III.1 Comparison of adsorbability

Two types of zeolites dealuminated Y (DAY) and silicalite-1, and a type of granular activated carbon Centaur® activated carbon were studied. All experiments were conducted under the same operational conditions. The results of the screening experiment are shown in Table 8 which includes some key properties of adsorbents too. (These properties are obtained from references [102] and [101].)

Table 8: Properties and Removal efficiency of GAC, DAY and Silicalite-1 for E1 (Experimental Conditions: Initial conc. of the common sample is 1131 ppb. 41 mg absorbent was added to each 41 ml water sample. All samples were agitated for 24 hours. More data are presented in Appendix D.)

Adsorbent	**hi**	**V_t (cm^3/g)**	**Framework density (number of T atoms/ $Å^3$)**	**d_L(Å)**	**SiO_2/Al_2O_3**	**Removal%**
Centaur® activated carbon	0.97	0.51	/	7.8	/	69.34
DAY	0.99	0.38	13.3	7.4	80	>99.66
Silicalite-1	0.98	0.21	18.4	5.6,5.5	>1000	38.71

Framework density – from [101]

hi — hydrophobicity applying Giaya and Thompson *et al.* [102] definition

V_t — total pore volume determined by N2 adsorption

d_L —average largest dimensions of the pores

DAY shows the highest capacity for E1 from water compared to Centaur® activated carbon (GAC), and silicalite-1. Among the five physical properties listed

in Table 8, the parameter, the largest dimension of the pores d_L indicates its influence on the adsorptive capacity of the three adsorbents studied. E1 molecules have a width of about 3.8 Å and length of about 10.8 Å [106]. This indicates that silicalite-1 should be able to allow E1 to pass through its 5.6 Å windows. So, it is unknown why estrone does not favorably sorb to silicalite-1. The reason may be that estrone usually aligns itself so that it passes through a larger window such as DAY's. Of course, some other physical and/or chemical properties could interfere adsorption process. As Erdem-Senatalar and Bergendahl *et al.* [101] concluded that low concentration range sorption correlated very well with the SiO_2/Al_2O_3 ratios and framework densities among zeolites, the quite differences of the two parameters between DAY and silicalite-1 could be the causes for their different affinities for E1. In spite of the very close value of hydrophobicity of the three adsorbents, the adsorption capacity did not correlate. So hydrophobicity does not seem to affect the adsorbent's sorption ability, which agrees with the conclusion derived in Giaya and Thompson *et al.* [102].

Furthermore, since the values of $LogK_{ow}$ of E2 and EE2 are larger than E1 (See Table 5), they are supposed to be adsorbed more easily on DAY than E1 based on the presumption that adsorption capacity increased with increasing octanol-water partitioning coefficient K_{OW} of EDCs [56].

III. 2 Kinetics of adsorption

Because of the extremely low sorption performance of silicalite-1, the kinetics study was completely using only DAY and GAC. The results for DAY are shown on

Figure 4, and for GAC on Figure 5, respectively. The time needed to reach adsorption equilibrium for DAY was approximately 4 h. A contact time of 4-5 h was selected throughout all subsequent adsorption and regeneration experiments as equilibrium was achieved within this time.

For Centaur® activated carbon, it needed more than 8 days to reach equilibrium. In this case, Centaur® activated carbon was not good at removing estrone from water due to its low removal efficiency and long contact time. However, that does not mean all activated carbon cannot remove estrogens effectively and Centaur® activated carbon cannot work well to remove other compounds. In fact, some studies have found a variety of activated carbons [56] [103] were able to remove estrogens from wastewater/water. So, there must be some properties of activated carbon besides hydrophobicity and pore size to affect adsorption efficiency.

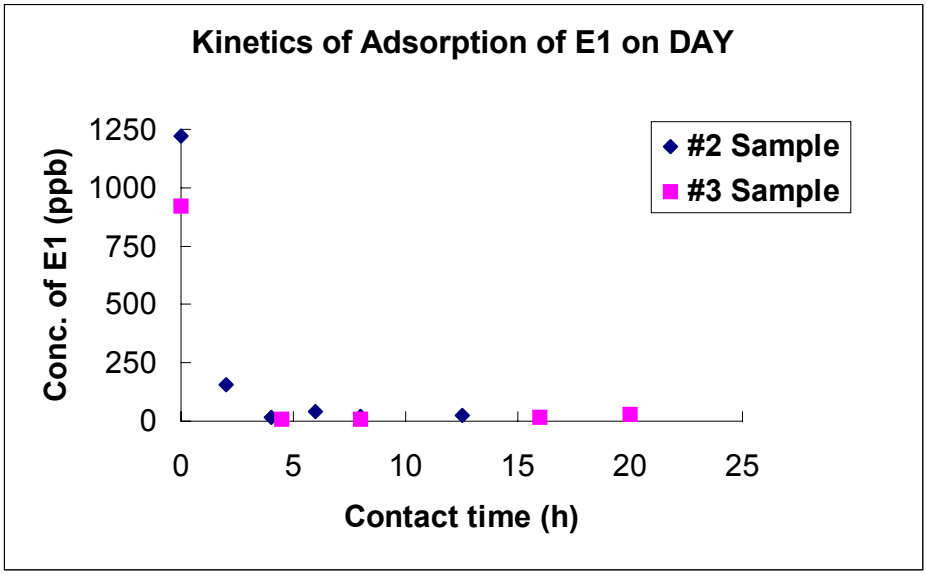

Figure 4: Kinetics of Adsorption of E1 on DAY

Experimental conditions: Two sets were performed. One set used the third sample #2 with Ci 1223 ppb, and 15.2 mg DAY was added into 42 ml sample each, being shaked for 2, 4, 6, 8 and 12.5 hours. The other one used the fourth sample #3 with Ci 919 ppb, and 14.9 mg DAY was added into 42 ml sample each, being shaked for 4.5, 8, 16 and 20 hours. More details are presented in Appendix E.

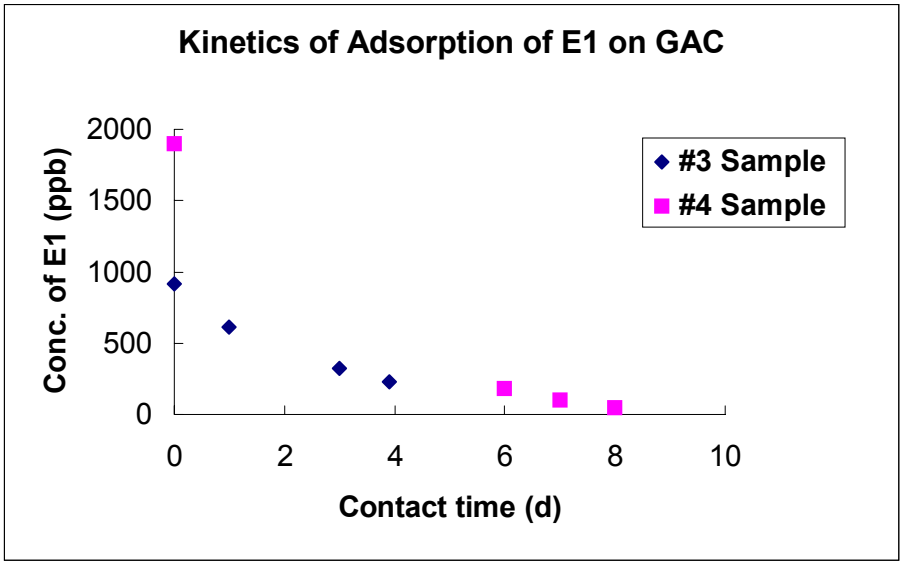

Figure 5: Kinetics of Adsorption of E1 on GAC

Experimental conditions: Two sets were performed. One set used the third sample #3 with Ci 919 ppb, and 18.7 mg GAC was added into 42 ml sample each, being shaked for 1, 3 and 3.9 days. The other one used the fourth sample #4 with Ci 1896 ppb, and 18.5 mg GAC was added into 42 ml sample each, being shaked for 6, 7 and 8 days. More details are presented in Appendix E.

III. 3 Adsorption isotherm

According to the previous experimental results, only DAY was worth investigating further. In order to evaluate the adsorption and understand the working capability of an adsorbent, appropriate adsorption isotherm models were determined. The constant-temperature equilibrium relationship between the quantity of adsorbate per unit of adsorbent and its equilibrium solution concentration is called adsorption isotherm.

The adsorption isotherm of E1 in pure water on DAY was developed with

bench tests at room temperature. See Figure 6. The adsorption data were fit into two most common models: the Freundlich equation and Langmuir equation, and the corresponding parameters were estimated through [104]. The linear Freundlich isotherm and Langmuir isotherm derived from the original adsorption isotherms (Figure 6) are presented on Figure 7 and Figure 8, respectively.

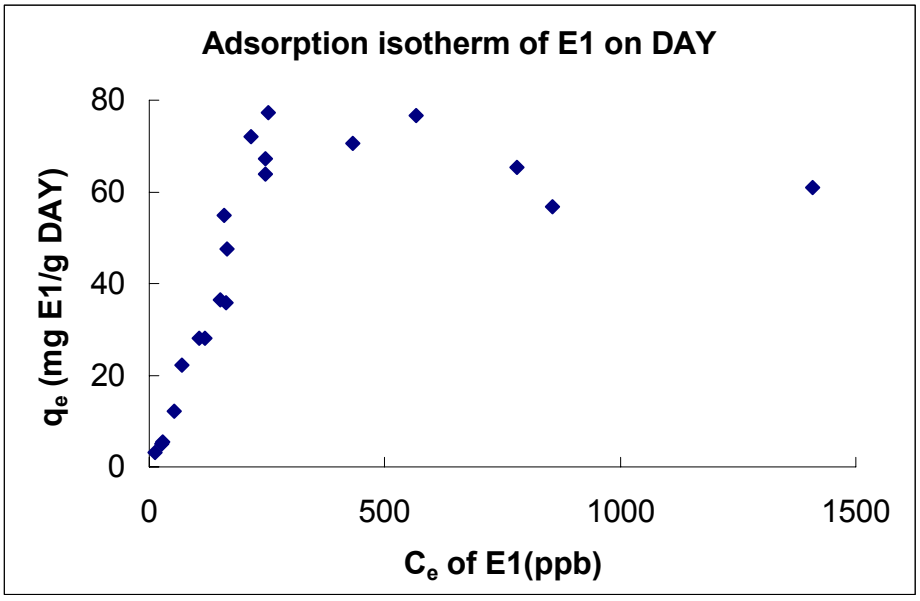

Figure 6: Adsorption isotherm of E1 on DAY at 20°C

Experimental conditions: Totally 13 different samples were employed for delineating the adsorption isotherm. A range of the amount of DAY 10-40 mg were added into different size of sample ranged from 125ml to 1045ml. 4 ~ 5 h was selected as the contact time. More details are presented in Appendix F.

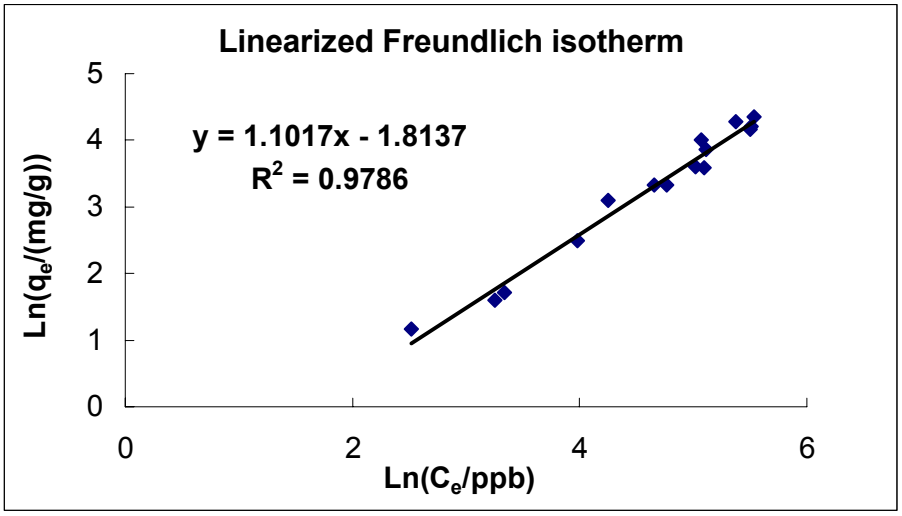

Figure 7: Linearized Freundlich isotherm of E1 on DAY at 20°C

The Freundlich equation as an empirical equation has the form:

$q = K C_{L,e}^{1/n}$

But, in order to get a linear form, the formula needs to be converted to:

$\ln(q) = \ln(K) + (1/n) \ln(C_{L,e})$

Where:

q — the amount of adsorbate (E1) per unit of adsorbent (DAY), µg E1/g DAY

$C_{L,e}$ — equilibrium concentration of E1 in water, µg / l

K, 1/n — constants for a given system

In this case, $\ln(q) = 1.1017 \ln(C_{L,e}) - 1.8137$

Where: 1/n = 1.10; ln(K) = -1.8137, so $K = 0.163(mg / g)(l / \mu g)^{1.10}$

Generally, the parameter K is related primarily to the capacity of the adsorbent for the adsorbate, and 1/n is a function of the strength of adsorption. Other work provided some larger values of K and smaller values of 1/n for the adsorption of E1 on a variety of activated carbons [96], See Table 9. This illustrated that E1 has

a higher affinity for those activated carbons than DAY in this work. However, activated carbon is frequently fouled with natural organic matter, which can promote bacterial growth on the carbon particles. But zeolites could exclude some large substances like NOM (natural organic material).

Specific surface area S seems like the most influential factor for K, while the constant1/n does not change much with the three physical properties listed in Table 9. But the diameter of pore is not correlated with K [96].

Table 9:Comparison of Freundlich constants of activated carbons and DAY for E1

Adsorbent	V_t (cm^3/g)	S (m^2/g)	d (Å)	K	1/n	R	Ref.
A-1	**0.46**	**1038**	**17.7**	**25.6**	**0.33**	0.963	[96]
A-2	**0.839**	**1831**	**18.3**	**73.5**	**0.40**	0.996	[96]
A-3	0.677	1514	17.9	35.9	0.41	0.991	[96]
B-3	1.149	1467	31.3	47.2	0.51	0.998	[96]
C-3	2.44	1187	24.4	36.7	0.35	0.960	[96]
DAY	**0.38**	**/**	**7.4**	**0.163**	**1.10**	**0.989**	

The constants were determined at the following dimensions: C (ppb), q (mg/g).

S : Specific area;

V_t — total pore volume determined by N2 adsorption

D: mean pore diameter

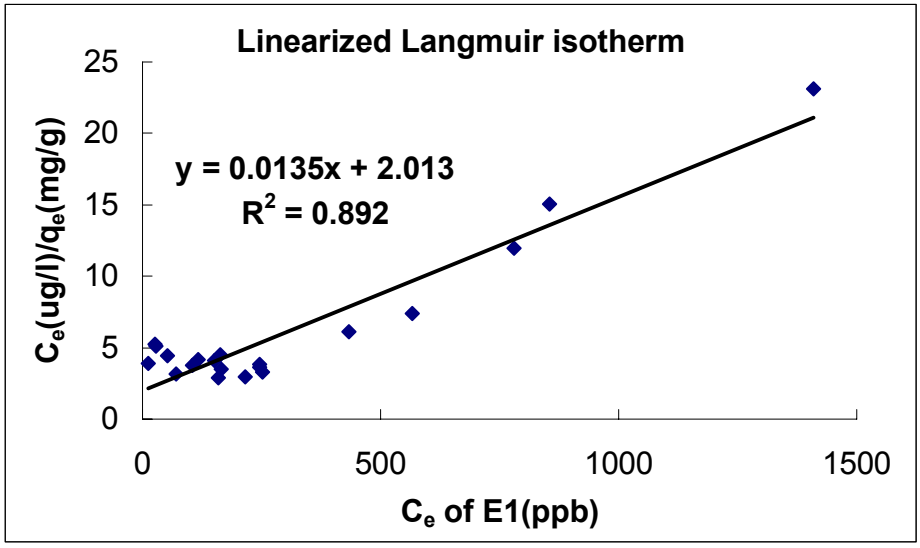

Figure 8: Linearized Langmuir isotherm of E1 on DAY at 20°C

However, at saturation, q is a constant, independent of further increases in C_e, and the Freundlich equation no longer applies. While the Langmuir equation is able to include all points on the curve. The Langmuir equation is expressed as:

$$q_e = \frac{q_{max} \cdot b \cdot C_e}{1 + bC_e}$$

But, in order to get a linear form of the equation, the formula needs to be converted to:

$C_e / q_e = (1 / b\ q_{max}) + C_e\ (1 / q_{max})$

Where:

b — a constant for a given system

q_{max} — the maximum value of q that can be achieved as C_e increases, a constant for a given system

In this case, $C_e / q_e = 0.0135\ C_e + 2.013$

Where q_{max}=74 mg / g, b = 6.7×10^{-3} l / µg

The correlation coefficient R^2 is low, possibly indicating that the assumption of monomolecular adsorption layer might not accurately describe the true adsorption process in this case. Despite this, the maximum adsorptive capacity of DAY for E1 is estimated to be about 74 mg/g which is close to the data observed with the adsorption isotherm.

III. 4 Direct UV (254nm) photolysis of E1 solution

The data in Figure 9 demonstrates that E1 was degraded very quickly with UV irradiation within 1 min, but after 6min, the concentration of E1 did not decrease any further. So, 6min was regarded the contact time for E1 to reach photolysis equilibrium. Given that the intensity of the UV lamp is 6650 µW/cm^2 (at 1/2" distance from lamp center to sensor surface), the UV fluence, F, needed to photolyze E1 can be correlated with the degree to which degradation of E1 could occur. This relationship is shown on Figure 10 where F is equal to the intensity 6650 µW/cm^2 multiplied by contact time.

For direct photolysis, photons need to be absorbed and the adsorbed radiation must be capable of degrading the compound. Rosenfeldt and Linden observed that radiation emitted from LP lamp (254 nm) had a low probability of being absorbed by the EDCs in water, especially compared to the absorption of radiation between 220 and 230 nm or between 270 and 290 nm [96]. This observation brings a promising presumption that other types of UV lamps with

220-230 nm or 270-290 nm could work better than what the lamp did in the experiment. They could need less fluence and/or reach greater removal efficiency.

Meanwhile, Ohko et al. concluded that the phenol moiety of the E2 molecule may be the starting point of the photocatalytic oxidation [87] and presumed that the estrogenic activities of the intermediate products without a phenol ring were negligible. Liu and Liu showed that the photolysis of estrogens caused the breakage and oxidation of benzene rings to produce compounds containing carbonyl groups [95]. As a result, since the most important estrogenic source, the phenol ring of estrogen molecule was destroyed by UV photolysis, the byproducts of the process could not be estrogenic in the environment.

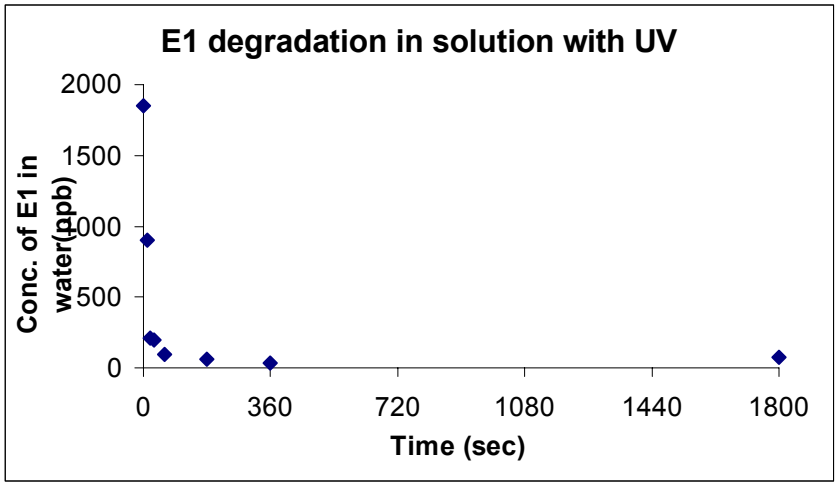

Figure 9: E1 degradation in solution with UV (Conc. VS. Time)

Experimental conditions: The #18 sample was used. The total volume of each test was 40ml and 5ml was for a single UV irradiation. A series of time interval were evaluated. More details are presented in Appendix G.

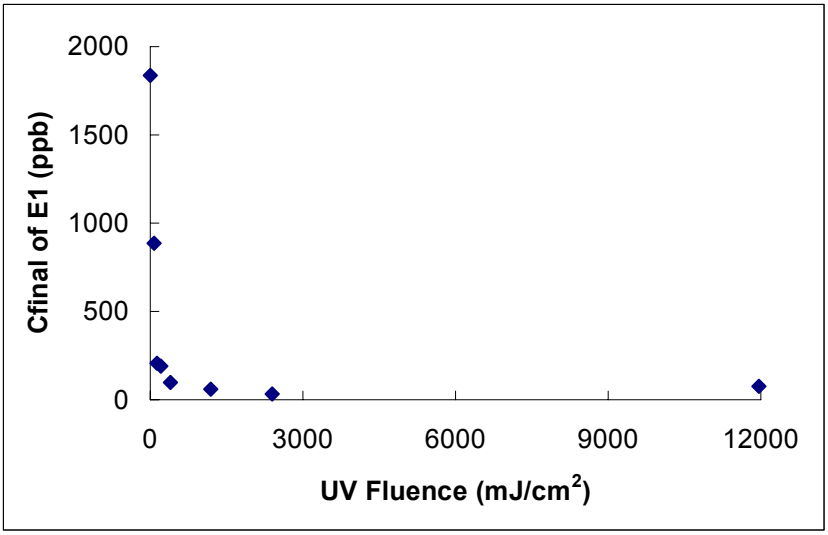

Figure 10: E1 degradation in solution under UV (as a function of fluence)

III. 5 Evaluation of UV/H_2O_2 and direct long-wave UV (365nm)

(1) UV / H_2O_2 Advanced oxidation

Some studies indicated that the removal efficiency of estrogens by UV radiation could be raised by the addition of H_2O_2 [96] [95]. When H_2O_2 is added, the dominant mechanism of estrogen destruction becomes hydroxyl radical mediated advanced oxidation, and the highly reactive OH radical species produced in the process are expected to quickly react with estrogens [96]. However, the results from this work did not agree with this hypothesis. In these experiments, H_2O_2 dose were determined according to both theoretical calculation and other work [96] [95]. The results (See Table 10) obviously demonstrated that the addition of H_2O_2 could not improve the removal of E1 at all, but even decrease it somehow.

Table 10: Comparison of UV and UV/H_2O_2 degradation in water

(Experimental conditions: #18 Sample, $C_{initial}$ = 1836.65 ppb; 15, 26 and 55 µl 30% H_2O_2 solution was added to 50ml sample to get the doses used in the experiments, respectively.)

Dose of H_2O_2	**10s Final Conc. of E1(ppb)**	**60s Final Conc. of E1(ppb)**
0	900.439	98.19
9 mg/l H_2O_2	1143.308	82.219
15.6 mg/l H_2O_2	873.356	438.908
33 mg/l H_2O_2	1131.987	/

(2) Long-wave UV-light photolysis

The test is aimed to evaluate the possibility of direct photolysis of E1 with long-wave UV light (λ = 365nm, intensity = 1000µW/cm^2). The data were:

When the UV fluence = 360 mJ/cm^2 (Time = 6 min, $C_{initial}$ = 916.82 ppb, C_{final} = 824.61ppb), the removal was 10.06%.

While for 254 nm UV, when the UV fluence = 200 mJ/cm^2 (Time = 30 s, $C_{initial}$ = 1848.08 ppb, C_{final} = 192 ppb), the removal was= 89.5%.

Long-wave UV with wavelength 365 nm in my experiment did not reach as high removal efficiency as UV with wavelength 254 nm, even though it exerted more fluence. This result is consistent with others. Liu and Liu found that long-wave light (λ ≥ 365 nm) was less effective than short-wave UV-light (λ = 254 nm) on photolysis of E1 and E2 in aqueous solution [95]. Rosenfeldt and Linden indicated that EDCs could not absorb UV radiation at 365 nm, because they found all EDCs studied only absorbed UV radiation in the range of 200-300 nm [96]. As a result, it could be very hard for visible light to photolyze estrone. Of course, it

needs more tests of longer contact time to prove the point.

III. 6 Adsorption / UV regeneration

The efficiency of 254 nm light for the photolysis of E1 on DAY was investigated by combining the adsorption step with a subsequent UV irradiation step. Two different radiation times, 6 min and 30 min, were applied. The relationship of C_e (ppb) and q_e (mg/g) during adsorption/UV regeneration cycles is compared to the original adsorption isotherm determined in previous experiments (See Figure 11). Under 30 min UV radiation, a pronounced decrease in q_e was observed since the eighth cycle (See Table 11). The fluctuation observed in the sixth cycle could be resulted from experimental error. But, under the condition of 6 min radiation, no significant decrease in q_e was found over the nine cycles. Such may tell us that the longer the radiation time, the greater the degree to which the adsorptive capacity of DAY could be decreased. To some extent, it is understood that UV could destroy some physical and/or chemical properties of adsorbent, especially its surface. It was observed that the color of DAY was turned to yellow from its natural white after the use of UV.

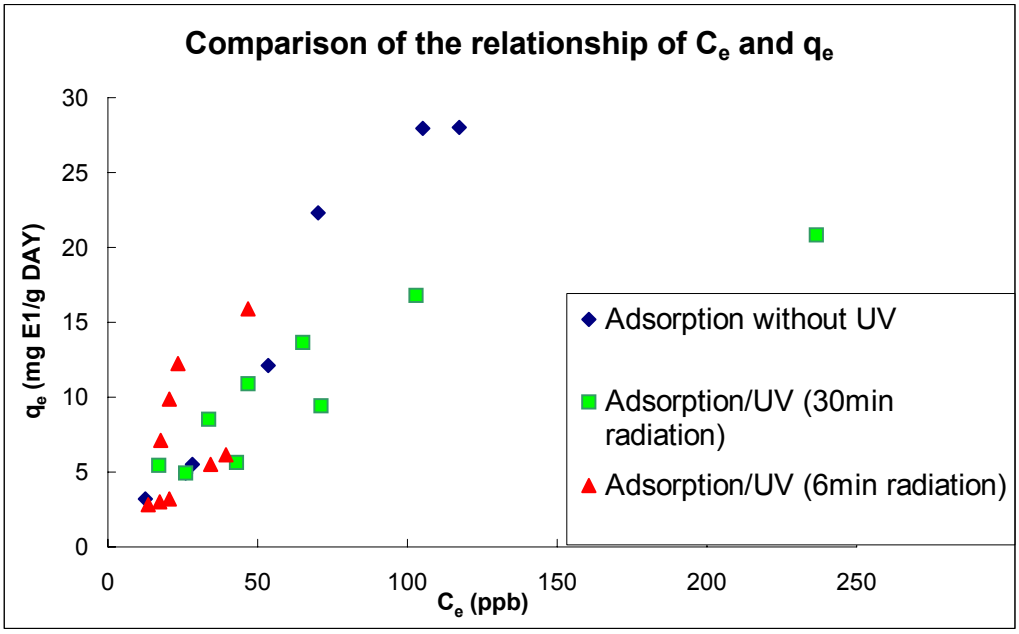

Figure 11: Comparison of the relationship of C_e and q_e with UV and without UV (The points of "adsorption without UV" in Figure 11 are selected from the data used in Figure 6. More details are presented in Appendix H.)

Table 11: Adsorption/Direct UV(254 nm, 6650uW/cm^2) regeneration

	6 min UV Radiation			**30 min UV Radiation**		
Cycle	**C_e(ppb)**	**q_e(mg/g)**	**Ci(ppb)**	**C_e(ppb)**	**q_e(mg/g)**	**Ci(ppb)**
0	13.60	2.794	908	25.92	4.945	1581
1	17.16	3.033	908	17.12	5.435	1581
2	20.59	3.187	908	42.85	5.609	1581
3	34.20	5.550	1358	33.66	8.315	2036
4	39.33	6.148	1358	71.17	8.917	2036
5	17.55	7.128	1358	46.82	9.867	2036
6	/	/	1358	157.43	10.184	2036
7	20.48	9.889	1358	65.22	10.493	1837
8	23.50	12.261	1358	103.04	11.223	1837
9	46.69	15.908	1358	236.63	11.320	1837

The sample volume was fixed at 125 ml and the contact time was 4 h for adsorption experiments.

The average loss of DAY in each cycle is estimated to be about 0.0033 g, according to the difference between the amount of the DAY added to the first cycle and the final left DAY (heated at 120°C for 14 h) after the ninth cycle.

$W_{difference} = (W_{i, DAY} – W_{f, DAY}) / 9 \text{ Cycles} = (0.0393g – 0.0092g) /9 = 0.0033g/cycle$

No pH adjustment was performed throughout the experiments. The pH of the DAY resuspension ready to be photolyzed was in the range 8.5-9 (after contaminated DAY was resuspended in E-pure water.).

PART IV CONCLUSIONS

A simple and solvent-free GC/FID analytical method with SPME followed by on fiber derivatization for determination of E1 in water was developed. An internal standard $E2d_4$ was successfully utilized for the quantification of E1, avoiding problems with fiber performance variation. The detection limit of the procedure was 1 ppb.

DAY, Silicalite-1 and Centaur® activated carbon (CAC) were evaluated for the removal of estrone. DAY has higher adsorption capacity for estrone than silicalite-1 and CAC. More than 99% of estrone can be removed by DAY. Adsorption of E1 to DAY is much faster than to CAC. DAY requires 4 h to reach equilibrium, while CAC takes more than 8 days. The maximum adsorption capacity of estrone on DAY is about 74 mg/g.

Direct short-wave UV (254 nm) was able to degrade E1 in solution more effectively than long-wave UV (365 nm). H_2O_2 was not found to be helpful in improving short-wave UV photolysis in solution. More than 98% E1 could be destroyed when the UV fluence was greater than about 2230 mJ/cm^2. The results from adsorption/UV regeneration experiments indicated that strong UV produced by long radiation time decreased the adsorption capacity of DAY for E1. But no significant deterioration of adsorption capacity of DAY was observed over nine cycles when 6 min radiation was employed.

PART V FUTURE WORK

This work found significant information on the potential application estrone adsorption on zeolites, and regeneration of contaminated zeolites by UV. More research is needed to understand how estrone is adsorbed to adsorbents, especially zeolites, the adsorption process, the influence on degradation of E1 by UV wavelength, the relationship of the destructive degree of adsorption capacity of zeolite and UV light fluence, and the reasonable life (cycles) of DAY with UV regeneration.

To determine which physical and chemical properties of adsorbents are the most important to adsorption of E1, a variety of adsorbents, especially zeolites such as zeolite beta and Mordenite with variables SiO_2/Al_2O_3 ratios, framework densities and dimensions of pores are between DAY and silicalite-1 should be investigated. Theoretical simulation and analysis may help our understanding. An alternative model for describing the function of C_e and q_e based on multilayer adsorption may help us to understand the mechanism of adsorption.

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APPENDIX A - CALIBRATION CURVES OF FIBERS

Fiber No.	Standard Conc. of E1 (ppb)	Peak area of E1 from GC	Peak area of $E2d_4$ from GC
#1	*1*	*0.53*	*130.69*
	1	*0.64*	*123.99*
	5	3.09	115.62
	10	2.2	91.56
	10	2.56	112.52
	50	*14.98*	*138.42*
	50	*15.82*	*152.48*
	50	*11.71*	*111.42*
	100	26.21	134.8
	500	113.33	117.89

K = 4.3403; R2 = 0.9956; Peak area of E2d4 A(E2d4) = 134.11

Fiber No.	Standard Conc. of E1 (ppb)	Peak area of E1 from GC	Peak area of $E2d_4$ from GC
#2			
	50	6.045	176.792
	500	50.398	130.793

K = 9.8976; R^2 = 0.999; Peak area of $E2d_4$ A($E2d_4$) = 176.792

Fiber No.	Standard Conc. of E1 (ppb)	Peak area of E1 from GC	Peak area of $E2d_4$ from GC
#3(I)			
	1	1.5822	130.165
	50	8.41295	160.8452
	1000	139.7452	181.2049

K = 7.1507; R^2 = 0.9997; Peak area of $E2d_4$ A($E2d_4$) = 160.845

#3(II)			
	50	3.25903	54.49745
	2500	168.4723	56.61952

K = 14.839; R^2 = 1; Peak area of $E2d_4$ A($E2d_4$) = 54.497

Fiber No.	Standard Conc. of E1 (ppb)	Peak area of E1 from GC	Peak area of $E2d_4$ from GC
#4			
	1	2.14091	206.0603
	50	8.34249	172.6069
	100	15.41254	162.6252
	1000	154.1286	176.4164

K = 6.4855; R^2 = 0.9997; Peak area of $E2d_4$ A($E2d_4$) = 172.60689

Fiber No.	Standard Conc. of E1 (ppb)	Peak area of E1 from GC	Peak area of $E2d_4$ from GC
#5			
	1	0.814408	/
	50	8.09326	91.37642
	1000	46.50261	44.03088

K = 21.048; R^2 = 0.976; Peak area of $E2d_4$ A($E2d_4$) = 91.37642

Fiber No.	Standard Conc. of E1 (ppb)	Peak area of E1 from GC	Peak area of $E2d_4$ from GC
#6(I)			
	50	10.63507	214.0056
	1000	91.91218	110.86

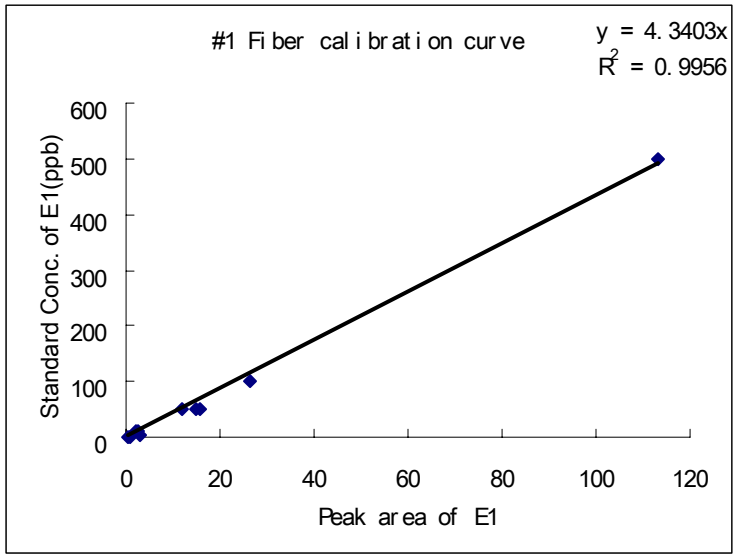
K = 10.798; R^2 = 0.9906; Peak area of $E2d_4$ A($E2d_4$) = 214.00563

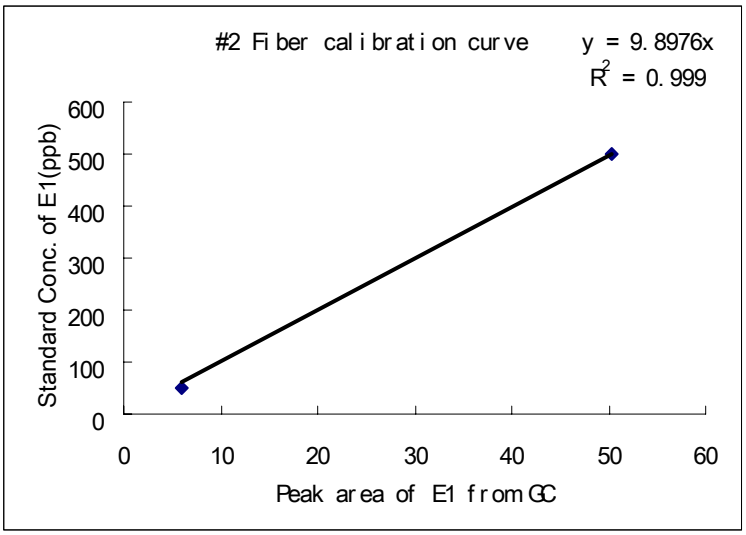
#6(II)			
	1	2.56737	77.07541
	50	9.44432	90.54073
	1000	60.79781	71.30591

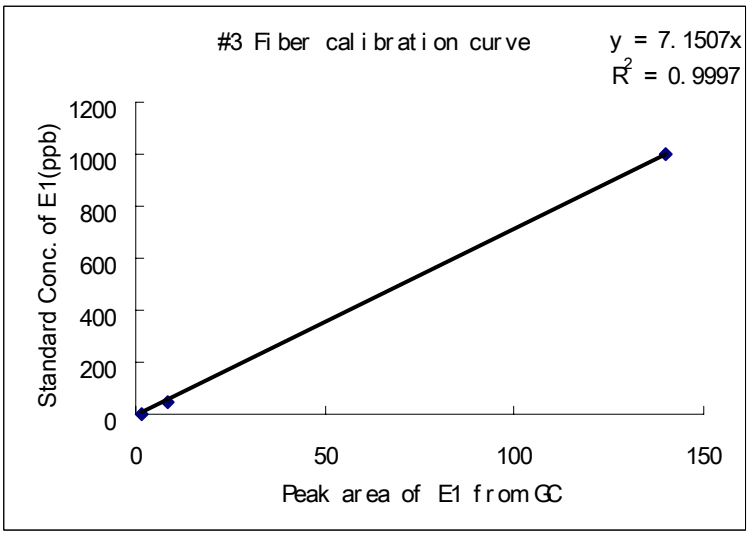
K = 16.158; R^2 = 0.9803; Peak area of $E2d_4$ A($E2d_4$) = 90.54073

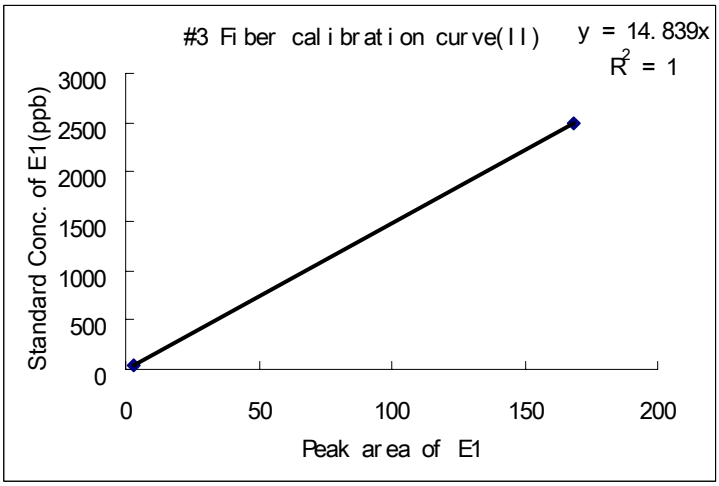
Fiber No.	Standard Conc. of E1 (ppb)	Peak area of E1 from GC	Peak area of $E2d_4$ from GC
#7			
	1	3.39708	218.0989
	50	7.05802	166.4404
	1000	173.5833	207.8981

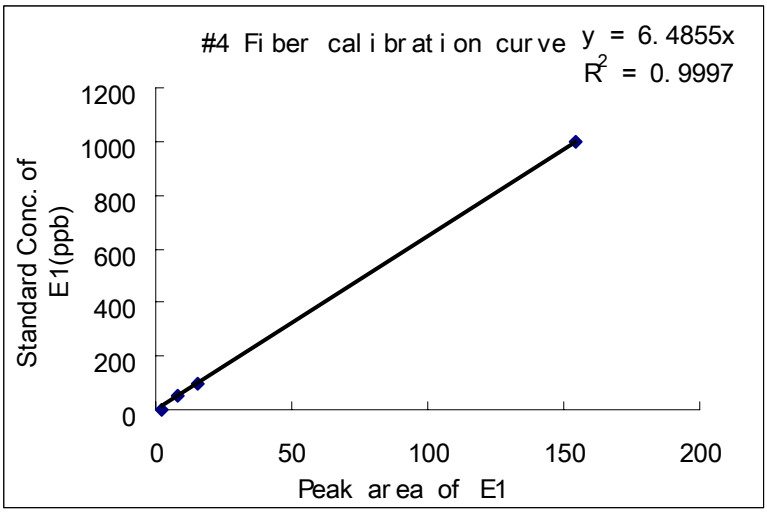
K = 5.761; R^2 = 0.9993; Peak area of $E2d_4$ A($E2d_4$) = 166.44043

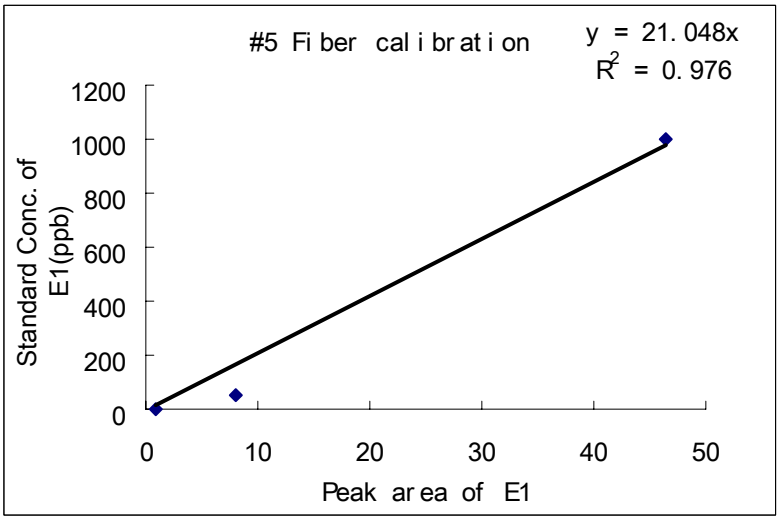


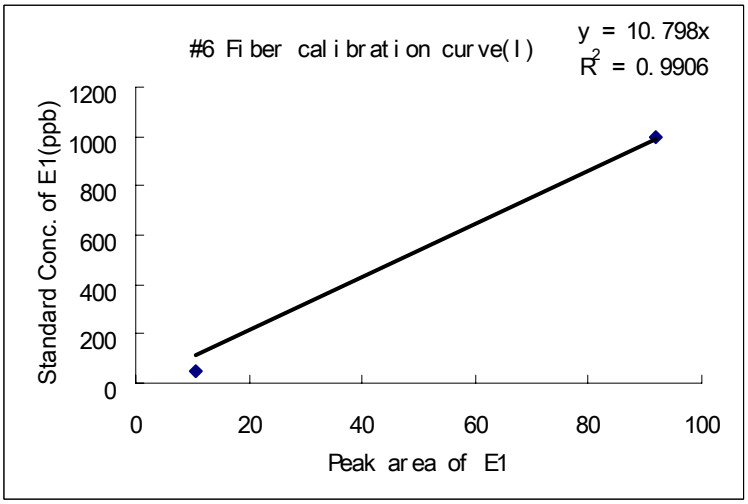

#2 Fiber calibration curve
y = 9.8976x
R2 = 0.999
Standard Conc. of E1(ppb)
600
500
400
300
200
100
0
0
10
20
30
40
50
60
Peak area of E1 from GC

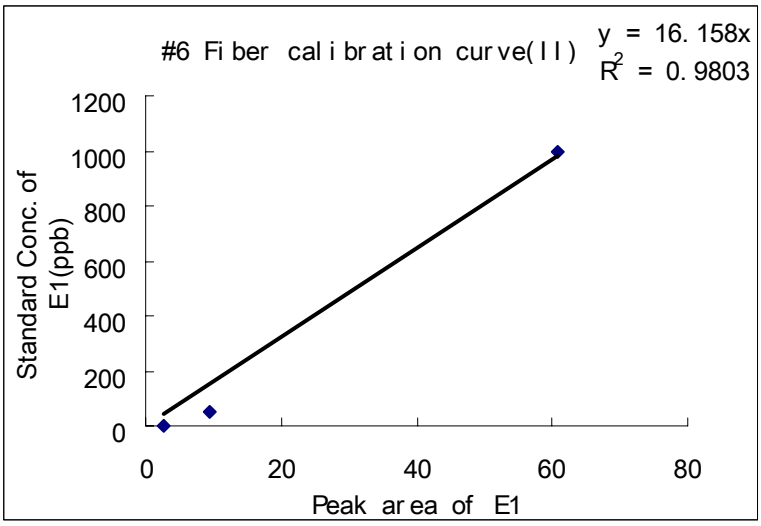

#3 Fiber calibration curve
y = 7.1507x
R2 = 0.9997
Standard Conc. of E1(ppb)
1200
1000
800
600
400
200
0
0
50
100
150
Peak area of E1 from GC

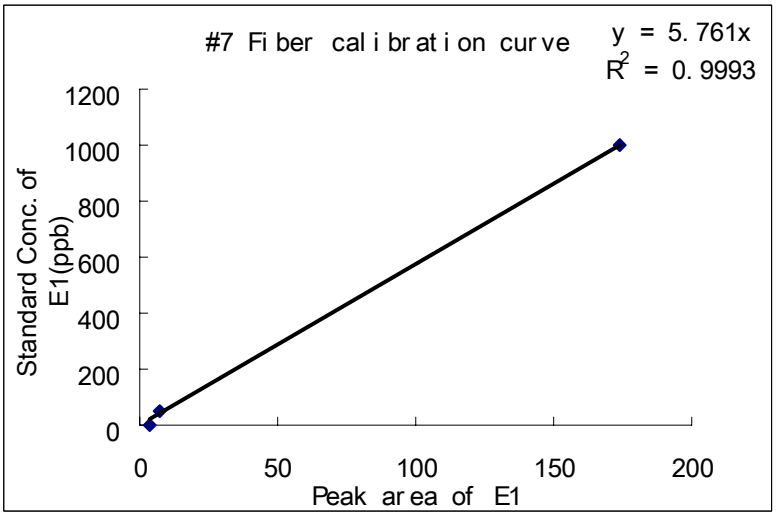

#3 Fiber calibration curve(II)
y = 14.839x
R2 = 1
Standard Conc. of E1(ppb)
3000
2500
2000
1500
1000
500
0
0
50
100
150
200
Peak area of E1


#4 Fiber calibration curve
y = 6.4855x
R2 = 0.9997
Standard Conc. of E1(ppb)
1200
1000
800
600
400
200
0
0
50
100
150
200
Peak area of E1

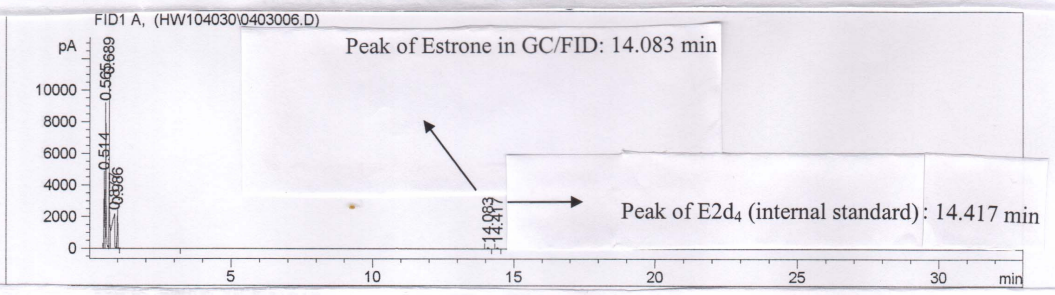

#5 Fiber calibration
y = 21.048x
R2 = 0.976
Standard Conc. of E1(ppb)
1200
1000
800
600
400
200
0
0
10
20
30
40
50
Peak area of E1


#6 Fiber calibration curve(I)
y = 10.798x
R2 = 0.9906
Standard Conc. of E1(ppb)
1200
1000
800
600
400
200
0
0
20
40
60
80
100
Peak area of E1


#6 Fiber calibration curve(II)
y = 16.158x
R2 = 0.9803
Standard Conc. of E1(ppb)
1200
1000
800
600
400
200
0
0
20
40
60
80
Peak area of E1


#7 Fiber calibration curve
y = 5.761x
R2 = 0.9993
Standard Conc. of E1(ppb)
1200
1000
800
600
400
200
0
0
50
100
150
200
Peak area of E1

Appendix B Peaks with retention time of Estrone and E2d$_4$ in GC/FID Signal



Area Percent Report

Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000

Signal 1: FID1 A,

Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	0.514	PV S	0.0225	7835.20703	4689.23047	15.63161
2	0.565	VV S	0.0198	1.07956e4	9081.56250	21.53765
3	0.689	VV S	0.0129	1.03406e4	1.22018e4	20.62992
4	0.877	VB S	0.1272	1.63503e4	2142.15259	32.61972
5	0.986	BB X	0.0292	4233.84229	2446.34644	8.44672
6	14.083	VV	0.0468	284.53821	92.71456	0.56767
7	14.417	VV	0.0515	284.05865	81.87234	0.56671
Totals :				5.01241e4	3.07356e4	

APPENDIX C – SAMPLES INFORMATION

Sample Number(#)		Amount of estrone added (mg)			Volume of water (ml)		Mixing time (h)		Final dissloved C (ppb)		
1	(13/10/05)	10			1000		3		1131		
2	(03/11/05)	/			/		/		1223		
3	(09/11/05)	11.8			1400		2		919		
4	(20/01/06)	48			725		5.5		1896		
5	(08/02/06)	/			/		/		1013		
6	(13/02/06)	40			1400		5		1167		
7	(19/02/06)	31.2			900		6		2163		
8	(20/02/06)	25.7			930		7.5		1800		
9	(22/02/06)	30.4			850		8		1788		
10	(23/02/06)	27.6			830		7.5		2533		
11	(24/02/06)	37			1100		7.5		1796		
12	(28/02/06)	46			1050		7.5		2113		
13	(02/03/06)	64.7			1050		7		1581		
14	(05/03/06)	54.5			1100		6		2003		
15	(06/03/06)	89.2			1100		6		1773		
16	(07/03/06)	66.2			1100		6		1551		
17	(09/03/06)	61.4			1100		6		2036		
18	(16/03/06)	76			1050		7		1837		
19	(07/04/06)	95			1050		6		908		
20	(19/04/06)	77.8			1050		8		1358		

APPENDIX D - DATA OF COMPARISON OF ADSORBABILITY

Sample#1 (fiber #1)	A(E1)	A(E2d4@50ppb)	C of the sample	Removal fraction(%)
Ci(#1)(13/10)	29.32	15.09	1130.954	
Acti. Carbon(13/10)	8.99	15.09	346.7693	69.33834
DAY(13/10)	0.1	15.09	3.857278	99.65894
Silicalite(13/10)	17.97	15.09	693.1528	38.71078

APPENDIX E – DATA OF KINETICS OF ADSORPTION

Sample#2 (fiber #2)	A(E1)	A(E2d4@50ppb)	C_e(ppb)	Time (h)
Ci (#2) = 1223 ppb			**1223**	**0**
DAY IC_{4hr}(03/11)	1.755	176.792	17.37029	4
DAY IIC_{8h}(03/11)	1.952	176.792	19.32012	8
DAY $IIIC_{2h}$(04/11)	1.085	12.286	154.5296	2
DAY IVC_{6h}(07/11)	3.675	152.111	42.27555	6
DAY $VC_{12.5h}$(08/11)	2.071	137.237	26.40593	12.5
The amount of DAY: 15.2mg;		*Volume of sample: 42ml*		

Sample#3 (fiber #2)	A(E1)	A(E2d4@50ppb)	C_e(ppb)	Time (h)
Ci (#3) = 919 ppb			**919**	**0**
DAY IC_{16hr}(10/11)	0.974	117.4	14.51722	16
DAY IIC_{20h}(10/11)	1.901	117.4	28.33391	20
DAY $IIIC_{4.5h}$(11/11)	0.468	109.42	7.484136	4.5
DAY IVC_{8h}(11/11)	0.398	109.42	6.364714	8
The amount of DAY: 14.9mg;		*Volume of sample: 42ml*		

Sample#3 (fiber #2)	A(E1)	A(E2d4@50ppb)	C_e(ppb)	Time (d)
Ci (#3) = 919 ppb			**919**	**0**
GAC IC_{1d}(10/11)	41.157	117.4	613.4344	1
GAC IIC_{3d}(21/11)	6.185	33.266	325.3356	3
GAC $IIIC_{3.9d}$(25/11)	4.379	33.661	227.6357	3.9
The amount of DAY: 18.7mg;		*Volume of sample: 42ml*		

Sample#4 (fiber #3)	A(E1)	A(E2d4@50ppb)	C_e(ppb)	Time (d)
Ci (#4) = 1896 ppb			**1896**	**0**
GAC IC_{6d}(24/01)	11.383(I)	72.729	#VALUE!	6
GAC IIC_{8d}(30/01)	3.001(II)	54.497	#VALUE!	8
GAC $IIIC_{7d}$(30/01)	6.719(II)	54.497	#VALUE!	7
The amount of DAY: 18.5mg;		*Volume of sample: 42ml*		

APPENDIX F - DATA OF ADSORPTION ISOTHERM

Water Sample C	A(E1)	A(E2d_4@50ppb))	$W_{sorbent}$ (g)	V(l)	C_e(ppb)	q_e (mg/g)	Ce/qe	1/Ce	ln(qe)	ln(Ce)
DAY (#5 sample)(#4 fiber)	1.42771	164.80788	0.039	0.125	9.697585556	2920.61479				
DAY (#5 sample)(#4 fiber)	2.21048	164.80788	0.0393	0.125	15.01447697	2881.408788				
DAY (#5 sample)(#4 fiber)	1.58519	196.17493	0.039	0.125	9.045642276	2922.704352				
DAY (#5 sample)(#4 fiber)	2.74913	196.17493	0.0394	0.125	15.68748639	2871.960386				
DAY (#5 sample)(#4 fiber)	Average value		0.039175	0.125	12.3612978	3.192816535	3.871596649	0.080897655	1.160903454	2.5145704
DAY (#6 sample)(#4 fiber)	2.19086	87.34941	0.0258	0.125	28.07735814	5.517982761	5.088337414	0.035615886	1.708012352	3.3349635
DAY (#6 sample)(#4 fiber)	3.5893	75.21595	0.0115	0.125	53.41969512	12.10401418	4.413386692	0.018719688	2.493537148	3.9781795
DAY (#6 sample)(#4 fiber)	3.16781	50.52752	0.0123	0.25	70.1831302	22.29280223	3.148241727	0.014248438	3.104263856	4.251108
DAY (#7 sample)(#4 fiber)	2.79819	18.89816	0.0105	0.25	165.752188	47.54740029	3.486041023	0.006033103	3.861727114	5.1104938
DAY (#8 sample)(#5 fiber)	6.79206	124.32988	0.03	0.495	105.0681229	27.96272947	3.757434445	0.009517635	3.330872533	4.6546089
DAY (#8 sample)(#5 fiber)	7.58222	124.32988	0.015	0.25	117.2913111	28.04146148	4.182781672	0.008525781	3.333684182	4.7646607
DAY (#9 sample)(#5 fiber)	10.64867	135.66345	0.0112	0.25	150.965422	36.54097272	4.131401295	0.006624033	3.598434171	5.0170508
DAY (#9 sample)(#5 fiber)	8.71131	102.9011	0.0224	0.495	162.8202531	35.9135924	4.533666566	0.006141742	3.581115842	5.0926469
DAY (#10 sample)(#5 fiber)	8.52892	102.9011	0.0108	0.25	159.4112611	54.9538134	2.90082255	0.006273083	4.006493076	5.0714874
DAY (#11 sample)(#5 fiber)	10.7257	83.93163	0.012	0.495	245.7791071	63.96558683	3.84236461	0.004068694	4.158345233	5.5044332
DAY (#14 sample)(#6 fiber,I)	2.40046	214.00563	0.0393	0.125	25.92016708	4.945358883	5.24131164	0.038579998	1.598449537	3.2550213
DAY(#18 sample)(#6 fiber,I)	13.28243	142.41646	0.0125	0.495	215.5191529	72.10703995	2.988878104	0.004639959	4.278151681	5.3730498
DAY (#11 sample)(#5 fiber)	11.0267	83.93163	0.0099	0.495	252.6765134	77.18917433	3.273470868	0.003957629	4.346259218	5.5321101
DAY (#14 sample)(#5 fiber)	3.69453	28.87562	0.0098	0.494	246.0780369	67.27790855	3.657635058	0.004063752	4.208831929	5.5056487
DAY (#15 sample)(#5 fiber)	12.00658	16.38905	0.0102	1.046	1408.998442	60.88043627	23.14369818	0.000709724		
DAY (#16 sample)(#6 fiber, I)	57.17071	169.33963	0.0159	1.045	780.1596794	65.24745503	11.95693654	0.001281789		
DAY(#17 sample)(#6 fiber, I)	44.20431	119.46826	0.0128	1.045	855.0285166	56.78831935	15.05641523	0.001169552		
DAY (#12 sample)(#5 fiber)	6.79749	30.21379	0.0118	0.495	432.7014446	70.48131143	6.139236569	0.002311062		
DAY (#12 sample)(#5 fiber)	8.89031	30.21379	0.01	0.495	565.9221242	76.57352385	7.390571776	0.001767028		

APPENDIX G – DATA OF UV(254 nm) PHOTOLYSIS IN SOLUTION

Direct UV(254nm, 6550uW/cm2) Photolysis of E1 in solution (#18 Sample)

UV Contact time (s)	UV Fluence (mJ/cm^2)	C_{final} of E1(ppb)	Removal %
1800	11970	75.137	95.909019
360	2394	33.362	98.183541
180	1197	57.84	96.850788
60	399	96.63	94.738791
30	199.5	192.313	89.529143
20	133	204.36	88.87322
10	66.5	886.12	51.753464
0	0	1836.65	0

Sample volume: 40ml, divided into 8 runs. 5ml for a single UV irradiation.

APPENDIX H – DATA OF ADSORPTION/UV REGENERATION

Adsorption/Direct UV(254nm,4500uW/cm2) regeneration (30min radiation)(#6 Fiber, I)

Sample	Cycle	Ce(ppb)	Ci(ppb)	Removal(%)	DAY(g)	V(l)	qe (mg/g)
DAY(#13)	0	25.92	1580.741	98.3603	0.0393	0.125	4.945358
DAY(#13)	1	17.117	1580.741	98.9172	0.036	0.125	5.429249
DAY(#13)	2	42.852	1580.741	97.2891	0.0327	0.12	5.643628
DAY(#17)	3	33.655	2036.404	95.987	0.0294	0.125	8.515088
DAY(#17)	4	71.168	2036.404	94.1891	0.0261	0.125	9.412048
DAY(#17)	5	46.824	2036.404	95.3558	0.0228	0.125	10.90778
DAY(#17)	6	157.434	2036.404	90.0546	0.0195	0.125	12.04468
DAY(#18)	7	65.223	1836.65	94.134	0.0162	0.125	13.66842
DAY(#18)	8	103.04	1836.65	92.1244	0.0129	0.125	16.79855
DAY(#18)	9	236.634	1836.65	85.0252	0.0096	0.125	20.83354

Adsorption/Direct UV(254nm,4500uW/cm2) regeneration (6min radiation)(#7 Fiber)

Sample	Cycle	Ce(ppb)	Ci(ppb)	Removal(%)	DAY(g)	qe (mg/g)	V(l)
DAY(#20)	0	13.6033	907.76	98.5014	0.04	2.7942397	0.125
DAY(#20)	1	17.1626	907.76	98.1093	0.0367	3.0333699	0.125
DAY(#20)	2	20.5907	907.76	97.7317	0.0334	3.1874346	0.12
DAY(#21)	3	34.2008	1357.52	95.1411	0.0301	5.4955116	0.125
DAY(#21)	4	39.3273	1357.52	94.7725	0.0268	6.1482868	0.125
DAY(#21)	5	17.5538	1357.52	96.338	0.0235	7.1274798	0.125
DAY(#21)	7	20.4852	1357.52	96.1272	0.0169	9.8893107	0.125
DAY(#21)	8	23.4955	1357.52	95.9108	0.0136	12.261255	0.125
DAY(#21)	9	46.6917	1357.52	94.2431	0.0103	15.90811	0.125
DAY(#21)	6	<1	1357.52		0.0202	#VALUE!	0.125

Comparison (selected from the adsorption data of Adsorption Isotherm)

Water Sample C	A(E1)	A(E2d$_4$@50ppb))	$W_{sorbent}$(g)	V(l)	C_e(ppb)	q_e (mg/g)
DAY (#5 sample)(#4 fiber)	Average		0.03918	0.125	12.361298	3.192817
DAY (#14 sample)(#6 fiber,I)	2.40046	214.0056	0.0393	0.125	25.920167	4.945359
DAY (#6 sample)(#4 fiber)	2.19086	87.34941	0.0258	0.125	28.077358	5.517983
DAY (#6 sample)(#4 fiber)	3.5893	75.21595	0.0115	0.125	53.419695	12.10401
DAY (#6 sample)(#4 fiber)	3.16781	50.52752	0.0123	0.25	70.18313	22.2928
DAY (#8 sample)(#5 fiber)	6.79206	124.3299	0.03	0.495	105.06812	27.96273
DAY (#8 sample)(#5 fiber)	7.58222	124.3299	0.015	0.25	117.29131	28.04146