Removal of Estrogens from Water

A Major Qualifying Project
submitted to the Faculty of
WORCESTER POLYTECHNIC INSTITUTE
in partial fulfilment of the requirements for the
degree of Bachelor of Science

by
Matthew Kurtz
Brian Momani

With help from:
Zachary DeLoughery
Assumption College

Date:
29 April 2010

Report Submitted to:

Professors Robert W. Thompson and Robert E. Connors
Worcester Polytechnic Institute

Jim Hauri
Assumption College

ABSTRACT

The purpose of this project was to study the effects of co-solvents on the adsorption of estrone into zeolite Y for use in water treatment. Estrogen contamination of the water supply is an important issue because it is an endocrine disruptor. Current wastewater treatment methods are not effective at removing estrone. The concentration of estrone in solution was determined by fluorometry. Several co-solvents were found to increase both the rate and equilibrium concentration of estrone adsorption into zeolite Y.

ACKNOWLEDGEMENTS

We would like to thank the following people for their assistance in this project:

Professor Robert Thompson of WPI's Chemical Engineering Department for advising the project and giving us access to his lab and equipment.

Professor and Department Head Robert Connors of WPI's Chemistry Department for co-advising the project, providing lab access, providing a quartz cuvette, and help with the fluorometer.

Professor James Hauri of Assumption College's Chemistry Department for co-advising the project.

Professor Destin Heilman of WPI's Biochemistry Department for providing a quartz cuvette and advice on equipment.

Professor and Department Head David DiBiasio of WPI's Chemical Engineering Department for providing access to his lab and a shaker table.

Professor John MacDonald of WPI's Chemistry Department for advice on molecular interactions involving non-covalent bonding.

Laila Abu-Lail, a graduate student of WPI's Civil and Environmental Engineering Department, for providing zeolites and activated carbon.

We would also like to thank Perkin-Elmer for helping us trouble shoot the LS55 flourometer.

TABLE OF CONTENTS

TABLE OF FIGURES

TABLE OF TABLES

CHAPTER 1: INTRODUCTION

Endocrine Disruptors

In order to understand why estrogens in the environment are of concern, it is necessary to understand their role as endocrine disruptors. The endocrine system controls behavior and regulates bodily functions. It carries this out using proteins and hormones. An endocrine disruptor is a chemical that disrupts the endocrine system.

An endocrine disruptor can interfere with the endocrine system in several ways. The first method of interference is mimicry. The endocrine disruptor mimics a natural hormone and produces an over-stimulation. This is the method by which estrogens affect the body. Estrone, specifically, is not mimicking a natural bodily hormone because it is a hormone that is naturally produced in the body. The second method of interference is an endocrine disruptor blocking the receptor for a hormone. With the receptor blocked, the hormone cannot express its intended function. The third method for an endocrine disruptor to interfere with the endocrine system is for it to block the way a hormone or receptor is made or regulated. This often results from blocking the hormone's metabolism in the liver. To sum up, an endocrine disruptor has three possible methods of interfering with the endocrine system.[1]

Estrogen

Estrogens are female hormones that are present to a lesser extent in males, which influence the differentiation and function of tissues, the development of secondary sexual characteristics, and growth.[2] The term estrogen covers several compounds with similar structure. The structure of estrone, the estrogen used in this paper, is shown Figure 1. The structures of four other estrogens are shown in Figure 2.

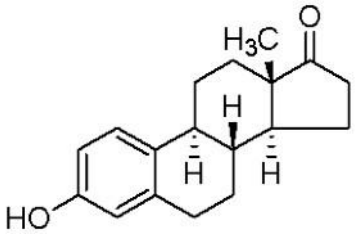


Figure 1: Structure of Estrone.[3]

1 National Institute of Environmental Health Sciences, *Endocrine Disruptors*, U.S. Department of Health and Human Services, June 2006, www.niehs.nih.gov

2 Wakeling, A.E., Bowler, J. *STEROIDAL PURE ANTIOESTROGENS*, Journal of Endocrinology. 1987, 112, R7-R10

3 Sigma-Aldrich, *E9750 Estrone ≥99%*, Retrieved: April 27, 2010, http://www.sigmaaldrich.com/catalog/ProductDetail.do?lang=en&N4=E9750|SIGMA&N5=SEARCH_CONCAT_PNO|BRAND_KEY&F=SPEC>

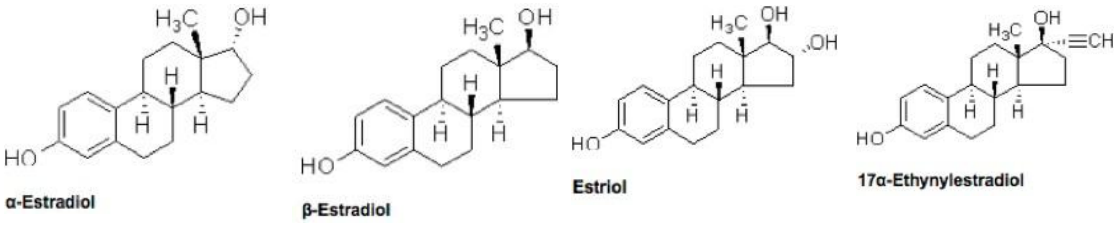


Figure 2: Structure of Several Estrogens.[4]

All estrogens share the same ring system and have a hydroxyl group at the same location on the phenyl ring. The different estrogens are differentiated by the substituents on the pentane ring.

Estrone has a solubility in water of 1.30±0.08 mg/L at a pH of 7 and a temperature of 25°C.[5] This is a very low solubility but estrone has been shown to effect biological systems in concentrations as low as 0.1ng/L.[6] General information on estrone is presented in Table 1.

Table 1: General Information on Estrone.[7]

CAS#	53-16-7
Molecular Weight	270.37 g/mol
Melting Point	255°C

Molecular modeling of estrone was carried out and used to estimate the size of an estrone molecule in its lowest energy conformation.[8] Estrone was found to have dimensions of 6.4×11.4×6.0 Angstroms. A space filling molecular model of estrone is shown in Figure 3. It has a twisted structure leading it to be larger than what it would be if it were planar.

4 Ibid.

5 Shareef, A., Angove, M., Wells, J., Johnson, B., *Aqueous Solubilities of Estrone, 17β-Estradiol, 17α-Ethynylestradiol, and Bisphenol A*. J. Chem. Eng. Data 2006, 51, 879-881.

6 Desbrow, C., Routledge, E.J., Brighty, G.C, Sumpter, J.P., Waldock, M., *Identification of Estrogenic Chemicals in STW Effluent. I. Chemical Fractionation and In Vitro Biological Screening*., Environ. Sci. Technol. 1998, 32, 1549-1558.

7 Sigma-Aldrich, *SAFTEY DATA SHEET*, Retrieved: April 27, 2010, http://www.sigmaaldrich.com/catalog/ProductDetail.do?lang=en&N4=E9750|SIGMA&N5=SEARCH_CONCAT_PNO|BRAND_KEY&F=SPEC>

8 Zhurova, E., Matta, C., Wu, N., Zhurov, V., Pinkerton, A., *Experimental and Theoretical Electron Density Study of Estrone*., J. AM. Chem. Soc. 2006, 128, 8849-8861.

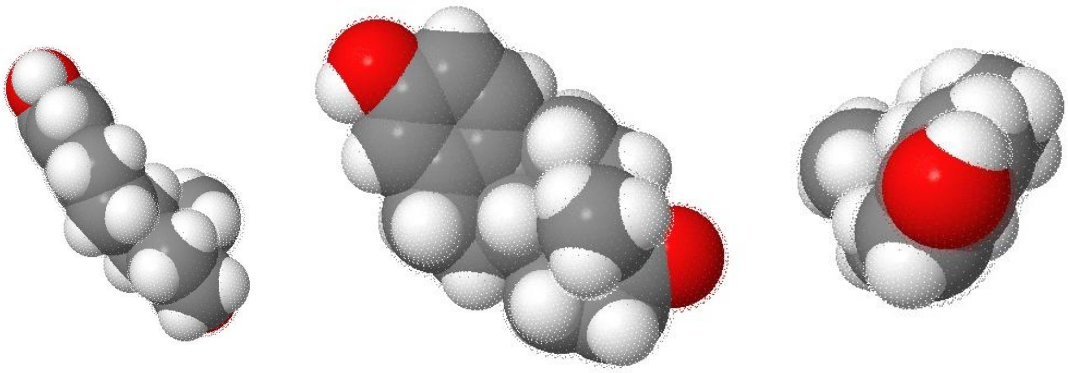


Figure 3: A molecular model showing estrone in its lowest energy conformation.

When subjected to UV radiation, estrone absorbs at a frequency of 285nm and emits at a frequency of 325nm. [9]

Zeolites

Zeolites are crystals composed of silicon, oxygen, and aluminum. Their structure is a uniform semi-rigid porous framework that can be used to sequester compounds. The structure is semi-rigid because vibrations prevent it from being completely rigid. Both the intracrystalline volume and the affinity for water are dependent on the ratio of silicon to aluminum in zeolites. As the percentage of aluminum increases, both the intracrystalline volume and affinity for water increase. De-aluminated zeolites are hydrophobic and as such exclude water to some extent.[10]

The zeolites used in this experiment were all zeolite Ys formed into pellets with the use of a clay binder. Zeolite Y has a structure that is termed faujasite. The pores of zeolite Y line up to form channels in the x, y, and z dimensions. A twelve-member oxygen ring defines the pores. The diameter of the pores is 7.4 Å and the diameter of the internal cavities is 12Å.[11] Therefore, when estrone is diffusing into a zeolite crystal it can only fit in end first. It is too large to fit through the pore on its longest side. Once inside the cavity the estrone is free to rotate. It must be kept in mind that molecules are dynamic at room temperature and the molecular movement contributes to the molecule of estrone being able to diffuse into the crystal through a pore that is only slightly bigger than estrone. A simulation of estrone absorbed onto zeolite Y is shown in Figure 4.[12]

9 Meshalkin, Y., Cherkasova, O., Fedorov, V., Samoilova, E., *Laser-Induced Fluorescence of Estrogens*, Optics and Spectroscopy, 2002, 92,1, 32-35.

10 Chen, N., *Hydrophobic Properties of Zeolites*, Journal of Physical Chemistry, 1976,80, 1, 60-65.

11 Rahman, M., Hasnida, N., Wan Nik, W., *Preparation of Zeolite Y Using Local Raw Material Rice Husk as a Silica Source.*, J. Sci. Res., 2009, 1(2), 285-291.

12 Yazaydin, A. O., Unpublished results from Ph.D. dissertation research. Chemical Engineering, Worcester Polytechnic Institute, 2007.

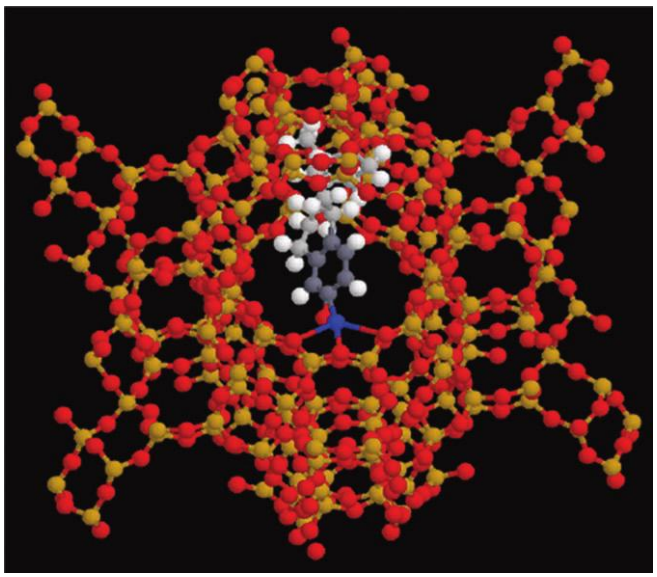


Figure 4: Simulation of Estrone sequestered inside the cavity of zeolite Y.[13]

Activated Carbon

Activated carbon is very commonly used in industry for metal extraction, gas separation, water separation, and is used in the medical field.[14] It can be produced from many carbon-based raw materials including coal, nutshells, and peat. It is produced by oxidation with CO_2 or steam. It can also be prepared by acid or base chemistry. Activated carbon's use as an absorbent is due to its very high surface area of $1500 m^2/g$ or greater. The proposed structure of activated carbon is a series of curved fragments containing pentagonal, hexagonal, and heptagonal carbon rings.[15] The structure is shown in Figure 5.

13 Yazaydin, A. O., Unpublished results from Ph.D. dissertation research. Chemical Engineering, Worcester Polytechnic Institute, 2007.

14 Marsh, H., Reinoso, F., Activated Carbon., Elsevier Science & Technology, 2006.

15 Harris, P., Liu, Z., Suenaga, K., *Imaging the Atomic Structure of Activated Carbon*., J. Phys,: Condens. Matter 20, 2008.

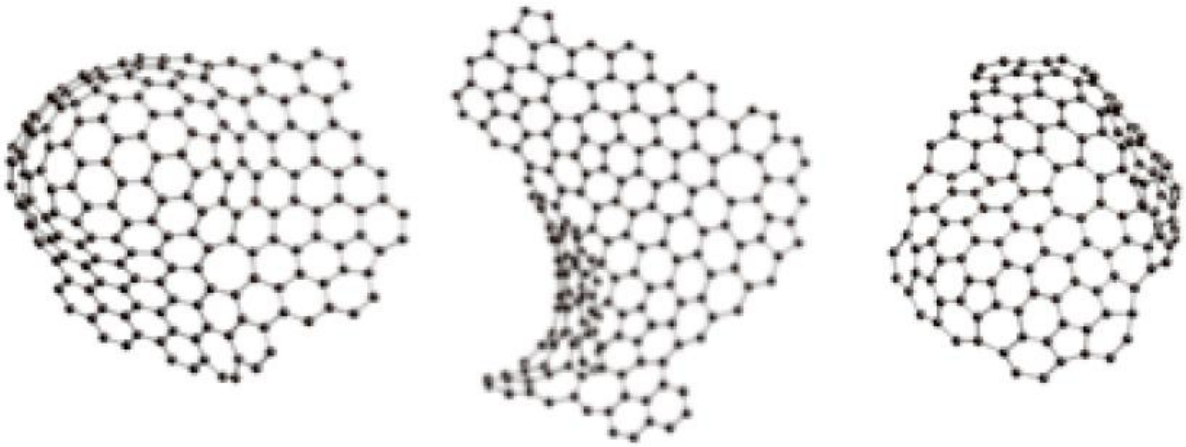


Figure 5: Proposed structure of activated carbon.[16]

Due to the irregular construction of activated carbon, estrone should fit into some of the pores. There is a distribution of pore sizes. The ability of estrone to absorb onto activated carbon would also depend on any chemical modification performed on the activated carbon.

Effects of Estrone

Estrone is naturally excreted by women at 2-12μg/day per person, men at 5μg/day per person and female animals.[17] Estrogens are also used in medicine for hormone therapy and birth control. Current systems of wastewater treatment are not entirely effective at removing estrone as demonstrated by the presence of estrone in the effluent of wastewater treatment plants.[18] Fish exposed to the effluent from wastewater treatment plants clearly show feminization.[19] This can be seen in Figure 6.

16 Ibid.

17 Belfroid, A.C., Van der Hors, A., Vethaak, A.D., Schafer, A.J., Rijs, G.B.J., Wegener, J., Cofino, W.P., *Analysis and Occurrence of Estrogenic Hormones and Their Glucuronides in Surface Water and Wastewater in the Netherlands*., Sci. Total Environ. 1999. 255, 101-108.

18 Baronti, A., Curini, R., D'Ascenzo, G., Gentili, A., Samperi, R., *Monitoring Natural and Synthetic Estrogens at Activated Sludge Sewage Treatment Plants and in a Receiving River Water*. Environ. Sci. Technol. 2000. 34, 5059-5066.

19 Liney, K., Hagger, J., Tyler, C., Depledge, M., Galloway, T., Jobling, S., Health *Effects in Fish of Long-Term Exposure to Effluents from Wastewater Treatment Works*., Environ. Health Perspect. 2006, Apr; 114.

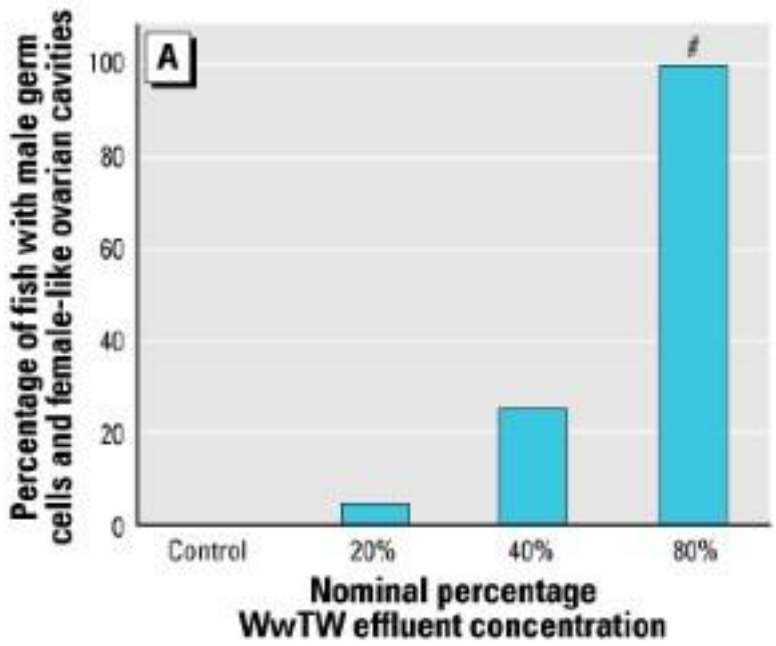


Figure 6: Relation between wastewater treatment works (WwTW) effluent exposure and feminization in fish.[20]

In humans the effects of estrogen exposure include undescended testicles, low sperm count, increased incidence of breast and uterine cancer, altered sex ratios, and neurological effects.[21]

Fluorescence Spectrophotometry

In this paper, fluorescence was utilized to determine the concentration of estrone in a sample. Fluorescence works by irradiating a sample with a certain frequency of light to excite the molecule. The molecule is excited electronically, vibrationally, and rotationally. The vibrational and rotational states relax leaving the molecule in an electronic excited state. When the molecule relaxes from this electronic excited state back to the ground state, a photon of light is given off. This photon is lower energy and thus lower wavelength than the photon that was absorbed. Both the amount of light absorbed and the amount emitted are functions of the concentration of the molecule. In theory, fluorescence could be used to detect a single molecule in solution. However, in practice, scattering in the solvent reduces accuracy.[22]

20 Ibid.

21 Zhang, Y., Zhou, J.L., Ning, B., *Photodegradation of Estrone and 17 β-Estradiol in Water*., Water Research, 2007, 41, 19-26.

22 Harris, D., Quantitative Chemical Analysis (Seventh Edition), 390-399, W.H Freeman and Company, 2007.

Previous Research

This paper is primarily an extension of work done by Huajing Wen of the Environmental Engineering Department of Worcester Polytechnic Institute. Both zeolite Y and activated carbon were studied. The zeolite was not bound by a clay binder and thus had to be centrifuged out of the water / estrone solution. It was found that zeolite Y removed 99% of estrone from solution and came to equilibrium in five hours while activated carbon removed 69% of the estrone and came to equilibrium in eight days.[23]

Co-Solvents

In order to improve the adsorption of estrone onto zeolite, a series of co-solvents were used. The co-solvents were selected in terms of size, polarity, and ability to hydrogen bond. Size was important because the molecules had to easily fit into the zeolite pores. Polarity was a concern because the solvent had to be partially soluble in water, yet better able to solvate the relatively non-polar estone molecule. The requirement that the co-solvent be somewhat soluble in water was because some of the co-solvent must leave the cavity of a zeolite crystal in order for an estrone molecule to enter. If the co-solvent were completely non-polar then it would form its own phase and not leave the crystal. Ability to hydrogen bond was important because the estrone molecule has two substituents available for hydrogen bonding. The hydroxyl group located on the phenyl ring and the keto group of the pentane ring in estrone can hydrogen bond. The co-solvents selected were ethanol, ethyl acetate, and diethyl ether. The structure of these co-solvents is shown in Figure 7 and their properties are shown in Table 2.

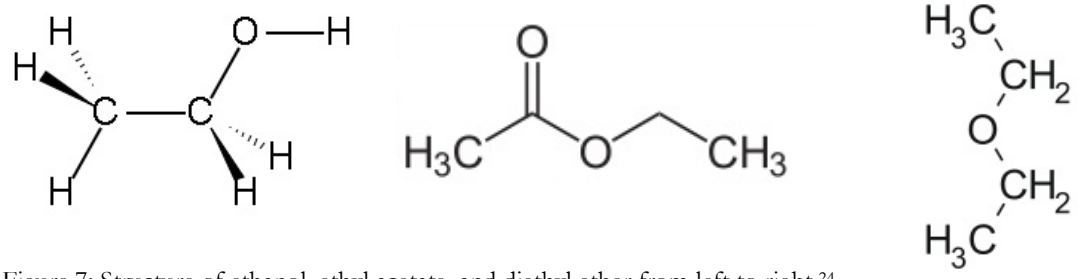


Figure 7: Structure of ethanol, ethyl acetate, and diethyl ether from left to right.[24]

Table 2: Properties of co-solvents[25]

Co-Solvent	MW	Dielectric Constant
Ethanol	46.07	24.3
Ethyl Acetate	88.11	6.02
Diethyl Ether	74.12	4.3

23 Wen, H., Bergendahl, J., Thompson, R., *Removal of Estrone from Water by Adsorption on Zeolites with Regeneration by Direct UV Photolysis.* Environ. Eng. Sci., 2009, 26, 2, 319-326.

24 Sigma-Aldrich

25 Wade, L.G., Organic Chemistry (sixth edition), Pearson Prentice Hall, 2006.

As can be seen, all co-solvents used are small molecules and all three have the ability to hydrogen bond due to the oxygen atoms in their structure. Dielectric constants are related to polarity. The dielectric constant of water is 80 at room temperature, so all of the solvents used are less polar than water.[26]

26 Clipper Controls, *Dielectic Constants of Materials*, Retrived April 27, 2010, http://clippercontrols.com/info/dielectric_constants.html#W

CHAPTER 2: METHODOLOGY

The following materials presented in Table 3 were used throughout the laboratory work.

Table 3: Materials List

Material	Use	Specification	Supplier
Estrone	solute	Powder, 99% min. Assay	Sigma-Aldrich
Hexane	solvent	99.9% Assay	Pharmco-AAPER
Diethyl Ether	Co-solvent	99.8% Assay	Fisher Scientific
Ethyl Acetate	Co-solvent	99.9% Assay	Pharmco-AAPER
Ethanol	Co-solvent	200 Proof	Pharmco-AAPER
Zeolite Y1	Adsorber	Pellets	Engelhard
Zeolite Y2	Adsorber	Pellets	Englehard
HISIV 1000	Adsorber	Pellets	UOP
Activated Carbon	Adsorber	Granulated, Coconut Shells	Res-Kem Corp.
Filter Paper	Solution Filtration	70 mm diameter	Whatman
Büchner Funnel	Solution Filtration	55mm	
Medium Rubber Filter Adapter	Solution Filtration		
Separatory Funnel	Separate Hexane from DI water		
Photometer Cell	Measure Samples	Quartz	VWR North America
LS55 Fluorometer	Measure Samples	Using WINLAB control software	Perkin-Elmer
Controlled Environment Incubator Shaker	Shake samples	0-500 rpm shaking 0-100˚C heating	New Brinswick Scientific Co.
Magnetic Stirrer Plate	Stir Solution	Isotemp 0,60-1200rpm stirring 0,20-500˚C heating	First Scientific
Furnace	Adsorber Reactivation	Lab Heat 0-1100˚C heating	Blue M
Drying Furnace	Filter Drying		Thermo Scientific

Additionally, a magnetic Teflon stir bar was used with the magnetic stirrer plate. A 1ml automatic pipette was used along with 625µL pipette tips. Additionally, 6” pasture pipettes and a 1 ml pipette bulb was used. Glassware included 250 ml flasks, 1L side arm flasks, 1 Dram vials, 50ml vials, and a 1 L glass bottle. Aluminum foil was used to cover all the samples, ensuring no UV degradation of the estrone occurred. Parafilm was also placed around the caps of all samples in order to maintain an airtight seal.

Solution Preparation

The estrone solution was prepared by mixing 0.03 ±0.002g estrone powder with 1 L of DI water. This solution was then stirred for 24 hours at 600rpm. A vacuum filtration setup was then used to remove any estrone crystals not dissolved in solution. No filters fit the Büchner Funnel in the setup used, so a filter was cut to size. The cut filter was massed before filtration occurred. After filtration, the filter was dried at 80˚C for 24 hours and then massed.

Zeolite Preparation

The zeolites were acquired from Laila Abu-Lail in Worcester Polytechnic Institute's Water Treatment Laboratory. All the information available on these zeolites is displayed in Table 4.

Table 4: Zeolite Specifications

Name	**Size In**	**Si/Al**	**Zeolite %**	**Surface area m^2/g**	**Micropore Area m^2/g**	**Distributor**
Zeolite Y1	0.15		9	158.6	73.4	Engelhard
Zeolite Y2	0.15		14	158.3	58.7	Englehard
HISIV 1000	0.0625	35-40	80	379.9	247.1	UOP

The zeolites were reactivated by placing them in a furnace at 240˚C for four hours. After being allowed to cool, the zeolites were placed into a 50 ml vials for storage. The liquid co-solvent-treated zeolites were prepared by dropping 1±0.02g of the zeolite into 20ml of the co-solvent and left for one week. The vapor co-solvent-treated zeolites were prepared by pouring 80 ml of solvent into a small desiccator. Then, 1±0.02g of each zeolite was put into a 1 dram vial. The vials were then placed, caps off, into a 100 ml beaker which was placed into desiccator and left for a week.

Activated Carbon Preparation

The activated carbon was acquired from Laila Abu-Lail in Worcester Polytechnic Institute's Water Treatment Laboratory. All the information available on activated carbon used is displayed in Table 5.

Table 5: Activated Carbon Specifications

Name	**Type**	**Ash Content**	**Particle Size**	**Company**
RES-KARB CS-1240	Coconut Shell	3%	12x40	Res-Kem Corp.

Similar to the zeolites, the activated carbon was reactivated by placing it in a furnace at 240˚C for four hours. After being allowed to cool, the activated carbon was then placed into a 50 ml vial for storage. The liquid co-solvent-treatment activated carbon was prepared by dropping 1.654 ±0.002g of the activated carbon into 20ml of ethanol and left for a week. The vapor co-solvent-treated activated carbon was prepared by pouring 80 ml of ethanol into a small desiccator. Then, 1.217±0.002g of the activated carbon was put into a 1 dram vial. The vial was

then placed, cap off, into a 100 ml beaker which was placed into desiccator and left for one week. Only one co-solvent was used due to a communication error between the Assumption College site and the Worcester Polytechnic Insitute site.

Sample Measuring

After the fluorometer was allowed to warm up for 30 minutes, as per Perkin Elmer's instructions, a sample of 3.5 ml DI water was pipetted into the quartz cuvette and placed into the fluorometer. The fluorometer was then run with the settings seen in Table 6. If the sample returned a negative excitation spectra, the excitation slit was changed to 3.0, the emission slit was changed to 15.0, and the sample was remeasured. This would normally fix the problem, and the slit size would be returned to normal. If the fluorometer did not return a measurement from the initial scan, the computer, WINLAB, and /or the fluorometer would be restarted in order to regain connection with the fluorometer. Once an accurate spectra was measured, the quartz cuvette was removed. The DI water was pipetted out carefully, to ensure that as little water as possible was left in the cuvette. Kim wipes were not used to remove any excess water since they could scratch the surface of the cuvette.

Table 6: Fluorometer Settings

Start Scan (nm)	275	**Excitation (nm)**	285	**Excitation Slit**	2.5	**Scan speed (nm/sec)**	100
End Scan (nm)	295	**Emission (nm)**	325	**Emission Slit**	20	**Number of Accumulated Scans**	5

Once the fluorometer was set up, a 3.5 ml sample was pipetted into a clean cuvette, and run using the settings in Table 6. The amplitude of the excitation spectra was recorded at 285nm. After the sample was run, the sample was put back into its 1 dram vial. After this, the cuvette would be rinsed out twice with DI water. On the second rinsing, the water was removed using a pipette to ensure that as much of the water was removed as possible. The samples were measured in reverse order to minimize the effect of contamination between samples.

Calibration Curve Preperation

The calibration curve samples were prepared by mixing DI water with the base esterone solution. Table 7 shows the concentrations and amounts of estrone solution and DI water used in the calibration curve. Each sample was 3.5 ml and placed into a 1 dram vial. Care was taken to place the calibration solutions into the storage box as quickly as possible to reduce UV degradation of the estrone.

Table 7: Concentrations of samples in calibration curve.

Name	Fraction Estrone	Estrone solution ml	DI water ml
C.1	1	3.5	0
C.2	0.75	2.625	0.875
C.3	0.5	1.75	1.75
C.4	0.25	0.875	2.625
C.5	0.2	0.7	2.8
C.6	0.166667	0.583333	2.916667
C.7	0.142857	0.5	3
C.8	0.125	0.4375	3.0625
C.9	0.0625	0.21875	3.28125
C.10	0.03125	0.109375	3.390625

These samples were then run through the fluorometer, and the amplitude of their excitation at 285nm was recorded. All of the samples were run on three different days. These values were then plotted as a function of concentration. A single trend line was fit to the data. The equation of the trend line was used to calculate the concentration of estrone from a sample's excitation amplitude.

Zeolite Sample Preperation

One gram of a zeolite sample was placed into a 250ml flask with 50 ml of solution. Parafilm was placed on top of the flask. The flask was then placed onto the shaker tray set at 150rpm at 25˚C. After one hour, the flask was removed. Then, 3.5 ml of sample was removed and placed into a dram vial. The parafilm was then re-attached and the flask placed back onto shaker tray. This was repeated for the next five hours. This was done for three sets of the plain zeolites, and one time for each zeolite per co-solvent and method of co-solvent adsorbtion. This means there were a total of 27 runs and 162 samples. This means that 42% of the solution was removed during the run. This should not affect the equilibrium between the solution and zeoltes since the concentration of the solution was not altered. The driving force may have been effected by reducing the amount of estrone, but an excess of zeolites was maintained during the entire experiment.Therefore, only the rate at which the solution comes to equilibrium was affected. Since the purpose of these experiments was to develop a method to remove estrone from water, irregardless of time, the objective can still be fulfilled. Theoretically, if the rate of adsorbtion was also going to be accurately measured, a maxmim of 10% of the solution could have been removed over time. This means that 200ml of solution would be needed for each of the 27 runs. Six liters of solution would have been needed to complete all 27 runs. Resources were not avalible to create estrone solution in such large quanties.

Activated Carbon Sample Preperation

One gram of an activated carbon sample was placed into a 250ml flask with 50 ml of solution. Parafilm was placed on top of the flask. The flask was then placed onto the shaker tray set at 150rpm at 25˚C. After one day, the flask was removed. Then, 3.5 ml of sample was removed and placed into a dram vial. The parafilm was then re-attached and the flask placed back onto shaker tray. This was repeated for the next eight days. This was done for one co-solvent using either the vapor and liquid method, and one standard. This means there was a total of 3 runs and 24 samples.

Hexane Solvent

In an attempt to achieve better fluorometer readings, hexane was researched as a secondary solvent for the estrone in the solution. Since hexane is extremely non-polar, it was belived that the non-polar estrone would dissolve into the hexane phase. To test this, 10 ml of the stock estrone solution was mixed with 10 ml of hexane in a 50 ml flask. Parafilm was placed over the top of the flask. The flask was then placed onto the shaker tray set at 400 rpm at 25˚C. After 72 hours, the flask was removed. After the hexane and water phases separated, a seperatory funnel was used to remove the hexane phase from the water phase. 3.5 ml of the hexane phase was then run through the fluorometer. The same fluorometer settings were used as in previous runs, yet an emission spectra at 285nm was also taken. It was found that the hexane phase made it more difficult to get a fluorescence reading of estrone and was not used in the experiment.

CHAPTER 4: RESULTS AND DISCUSSION

Calibration Curve

In order to correlate fluorescence intensity to concentration of estrone a calibration curve using known concentrations of estrone was constructed and is presented in Figure 8.

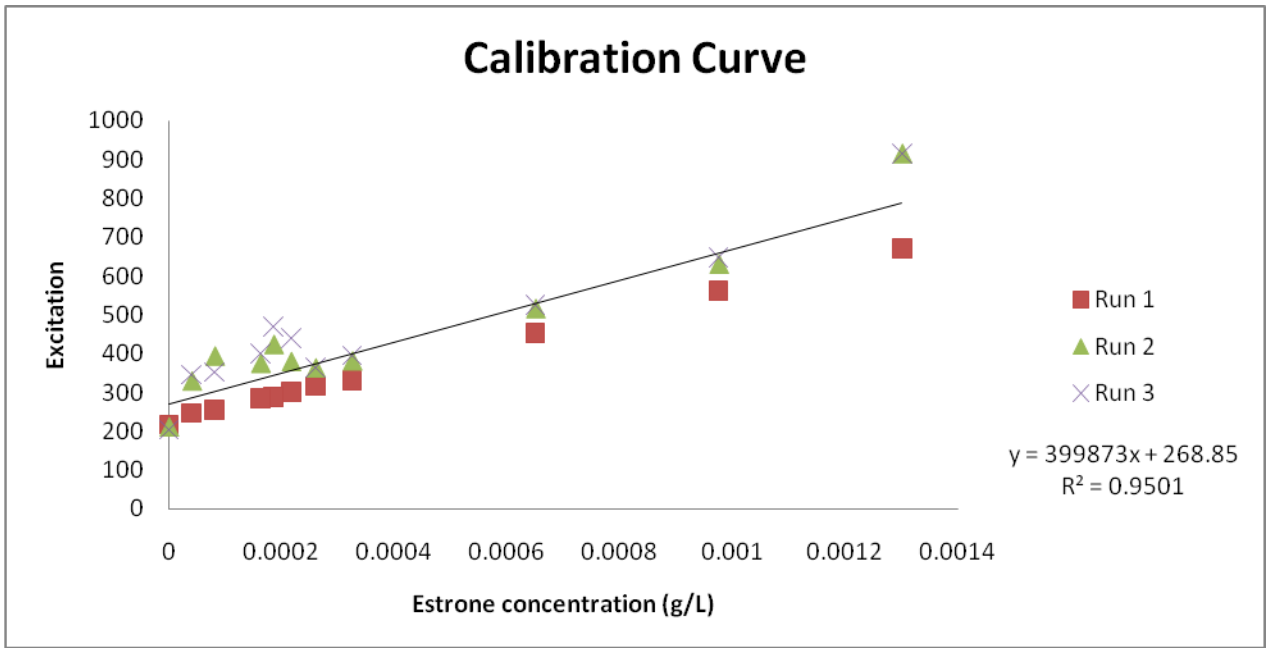


Figure 8: Estrone fluorescence calibration curve.

The relationship between excitation intensity and concentration of estrone was linear. This was as expected for fluorescence. The relatively high degree of scatter, for a piece of equipment that is normally very precise, about the linear fit was due to a number of reasons. First, the excitation spectrum of estrone in water was partially obscured by Rayleigh scattering. Second, the emission spectrum of estrone in water was partially obscured by Raman Scattering. Both types of scattering are inherent properties of water and coincidentally lined up with the fluorescence spectrum for estrone. This was determined by a built in pre-scan function in the fluorometer. Third, the fluorometer varied from day to day. The same sample run on two different days yielded different results. This was unexpected in a fluorometer. Since the samples were scanned over weeks, it would have been difficult to make a new calibration curve every day. Fourth, the fluorometer failed a built in calibration test on one occasion, indicating that an equipment problem may have been affecting the machine.

Zeolite Y1 with Co-Solvent Adsorbed from the Vapor Phase

Zeolite Y1 was only 9% zeolite by mass. It was expected that it would have the poorest performance of the three zeolites used. The results of the zeolite Y1 runs with the co-solvent adsorbed from the vapor phase for one week are presented in Figure 9.

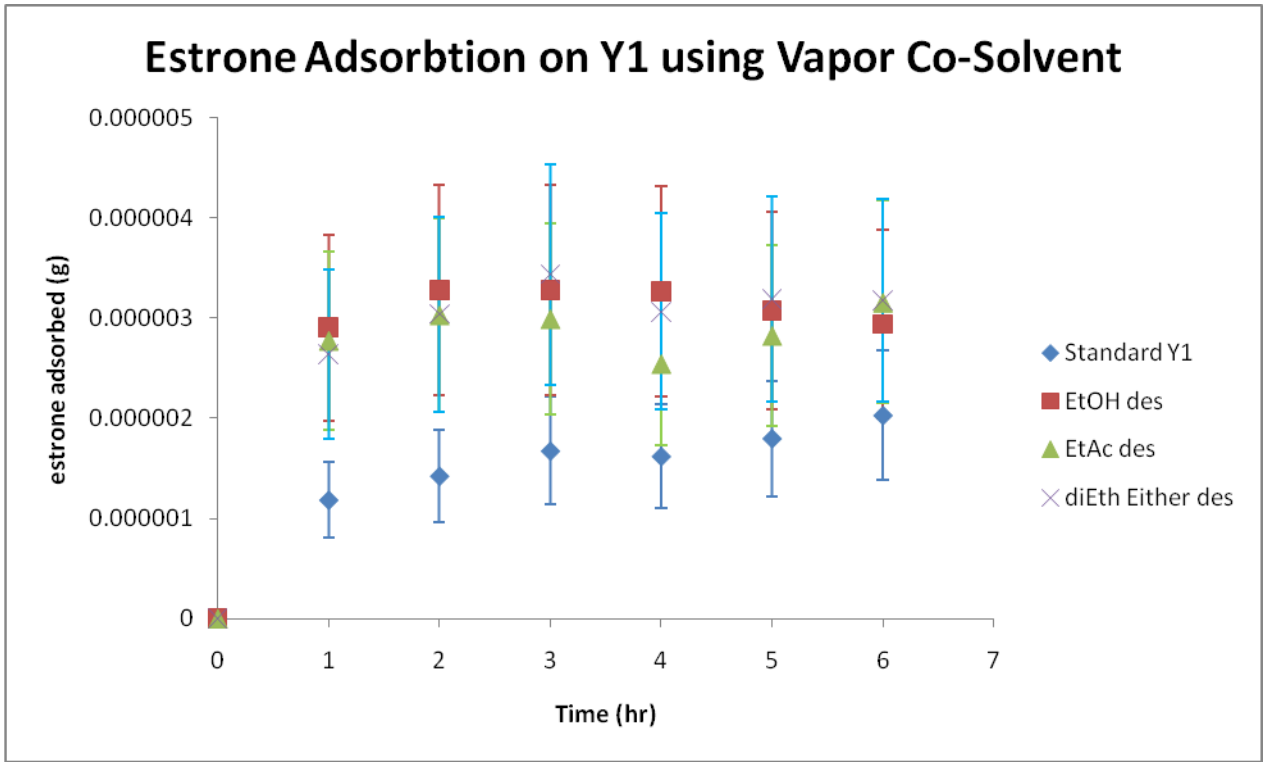


Figure 9: Sorption of Estrone into Y1 with and without Co-Solvents adsorbed from the vapor phase. (des) means that the zeolite with co-solvent was prepared in a desiccator.

As expected, zeolite Y1's performance was poor. Without co-solvent it removed about 41% of the estrone and came to equilibrium slowly. It appeared to still be sorbing estrone at the end of six hours in disagreement with Haujing's zeolite Y equilibration time of five hours. It is probable that the large amount of binder slows down the sorption since the estrone must diffuse through the binder to reach the zeolites. The addition of co-solvent dramatically improved zeolite Y1's performance. All three co-solvents caused the sorption to reach equilibrium in approximately three hours, which was several hours faster than Y1 without co-solvent and two hours faster than Wen's zeolite Y without any binder. The zeolites with ethanol and diethyl ether removed about 71% of the estrone and the zeolite with ethyl acetate removed about 69%. The large error bars in the results are caused by the same reasons listed under the section on the calibration curve, only now they are compounded by the inaccuracies of that curve.

Zeolite Y2 with Co-Solvent Adsorbed from the Vapor Phase.

Zeolite Y2 was 14% zeolite by mass. It was thus expected that it would have better performance than Y1, but worse than HSIV 1000. The results of the zeolite Y2 runs with the co-solvent adsorbed from the vapor phase are presented in Figure 10.

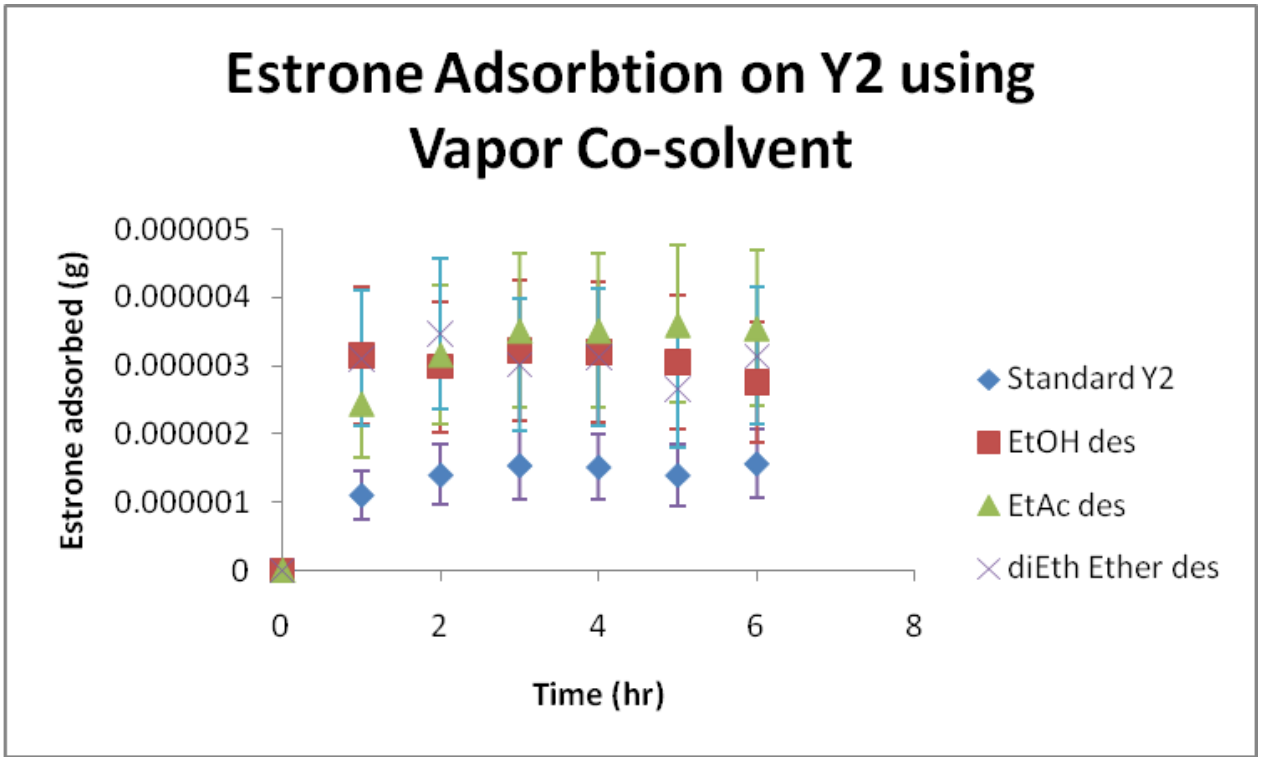


Figure 10: Sorption of Estrone into Y2 with and without Co-Solvents adsorbed from the vapor phase. (des) means that the zeolite with co-solvent was prepared in a desiccator.

Unexpectedly, Y2 without a co-solvent performed worse than Y1 without a co-solvent removing only 36% of the estrone. However it came to equilibrium in only three hours, which was much faster than Y1 time of over 6 hours and Wen's equilibration time of five hours. When co-solvents were added there was once again significant improvement. Sorption of estrone using ethanol and diethyl ether as co-solvents came to equilibrium in about one hour, but removed the same amount of estrone as in Y1 at 71%. When using ethyl acetate, estrone came to equilibrium slower at 3 hours, but it removed 79% of the estrone. The prediction that Y2 would outperform Y1 was only true for the cases with co-solvent.

Zeolite HSIV 1000 with Co-Solvent Adsorbed from the Vapor Phase

Zeolite HSIV 1000 was 80% zeolite by mass. It was thus expected that it would have the best performance. The results of the HSIV 1000 runs with the co-solvent adsorbed from the vapor phase are presented in Figure 11 and Figure 12.

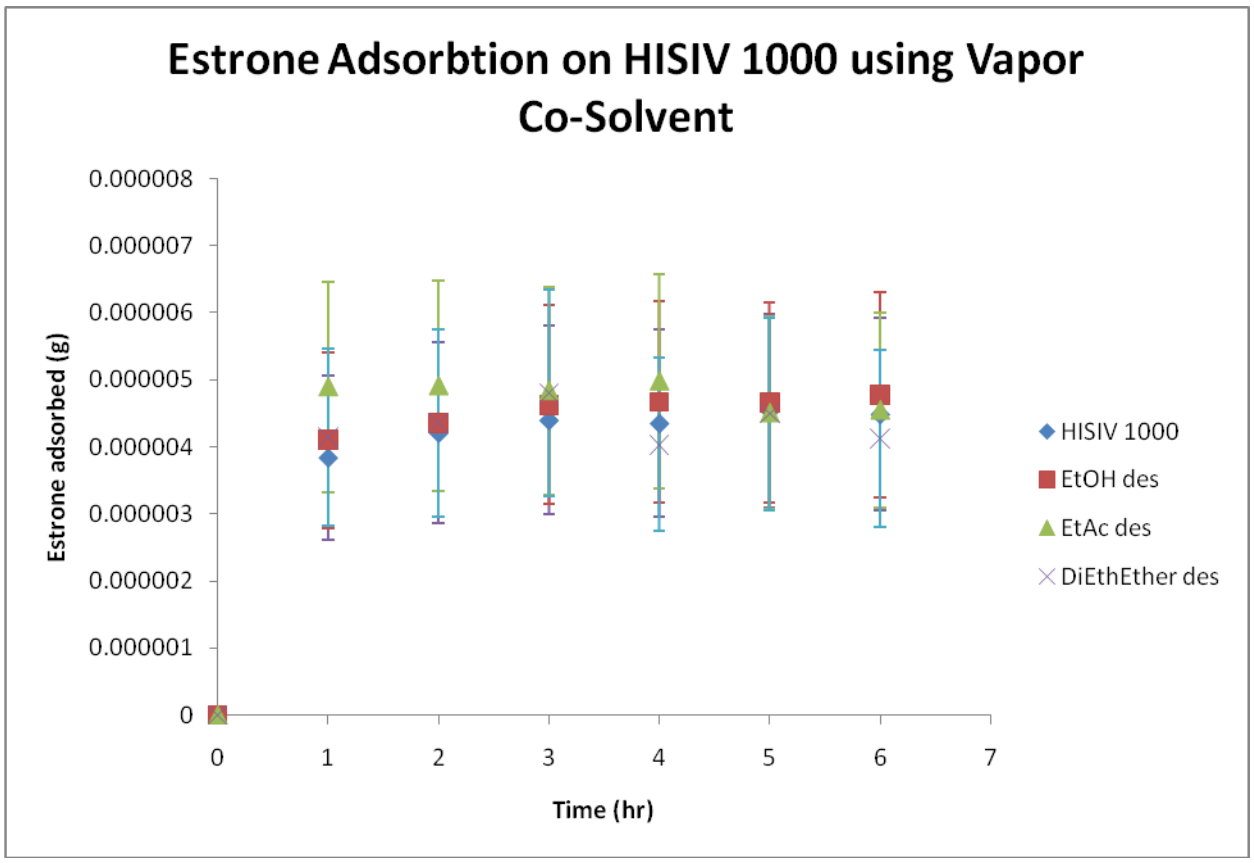


Figure 11: Sorption of Estrone into HSIV 1000 with and without Co-Solvents adsorbed from the vapor phase. (des) means that the zeolite with co-solvent was prepared in a desiccator.

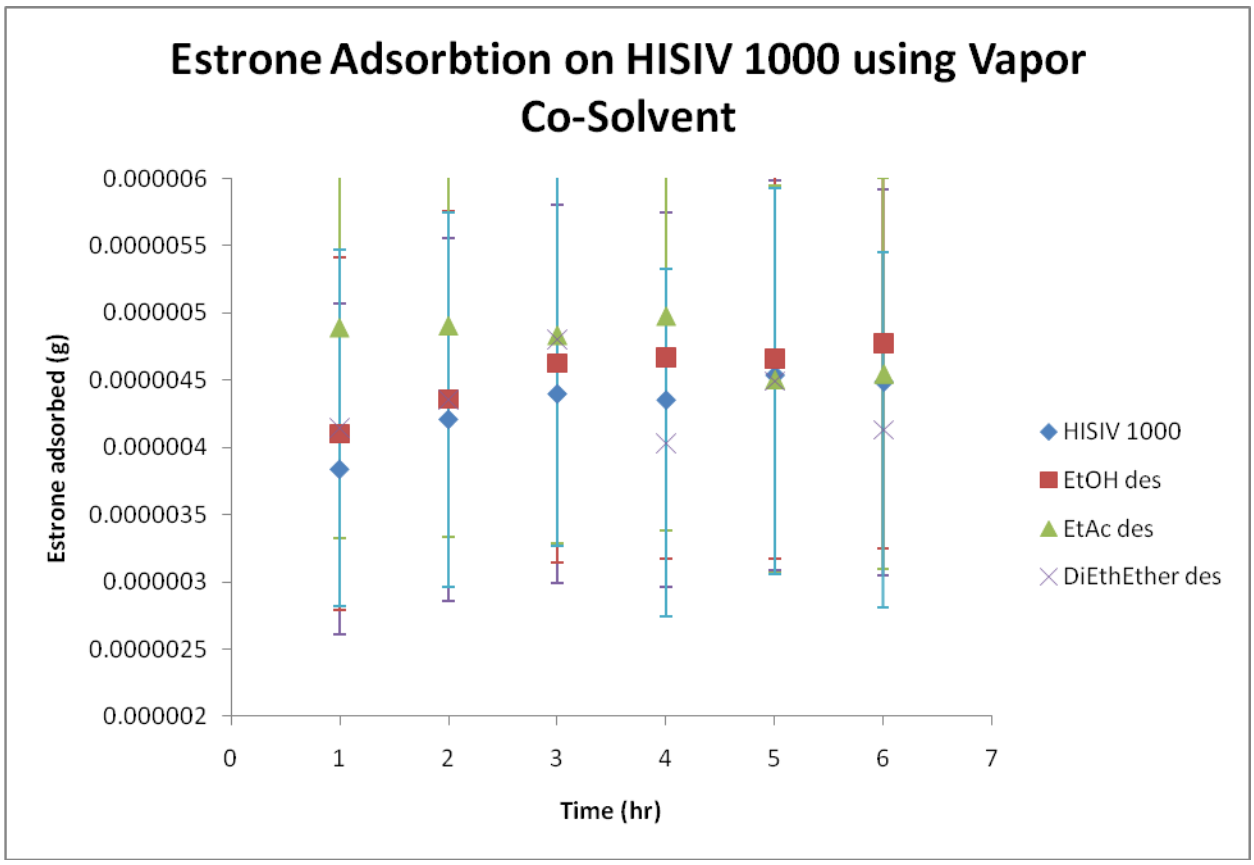


Figure 12: Close up of sorption of Estrone into HSIV 1000 with and without Co-Solvents adsorbed from the vapor phase. (des) means that the zeolite with co-solvent was prepared in a desiccator.

As expected, HSIV 1000 had the best performance. All runs removed all of the estrone in agreement with Haujing's findings that zeolite Y was capable of removing 99% of estrone from water. HSIV 1000 without a co-solvent removed all estrone in about four hours. With ethanol or diethyl ether co-solvents it only took three hours to remove all estrone from the water. With ethyl acetate as co-solvent, estrone was sequestered in one hour.

Zeolite Y1 with Co-Solvent Adsorbed from the Liquid Phase

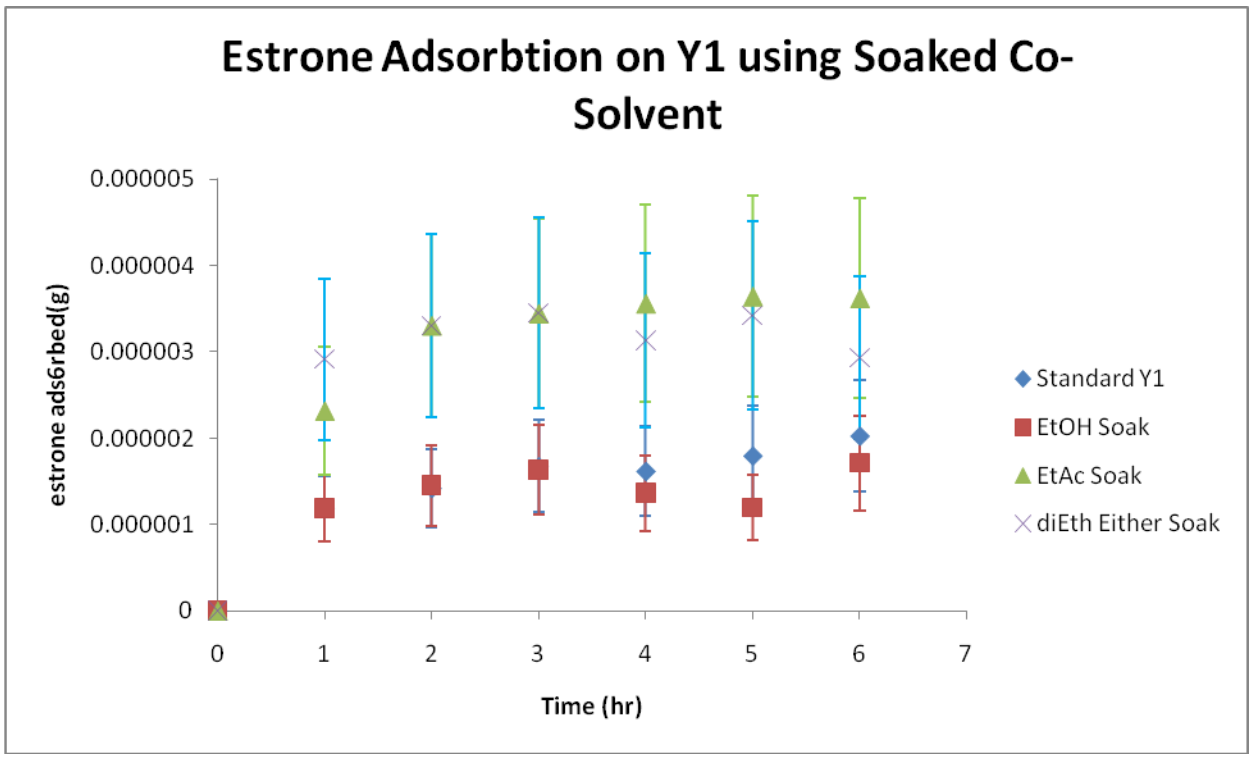


Figure 13: Sorption of Estrone into Y1 with and without Co-Solvents adsorbed from the liquid phase.(soak) means that the zeolite with co-solvent was prepared by soaking.

When the zeolite was soaked in the co-solvent for one week it reached equilibrium in four hours for all three cases. For zeolite Y1 with diethyl ether or ethyl acetate as co-solvents, about 80% of the estrone in the water was sequestered at equilibrium. The results for ethanol are surprising in that it performed slightly worse than zeolite Y with no co-solvent. A possible explanation for this is that ethanol is the most polar of the three co-solvents and would dissolve out into water the fastest. When soaked, excess ethanol would saturate the clay binder, rapidly leaving when exposed to water. This would create a solvent system in the water that estrone would be more soluble than in pure water.

Zeolite Y2 with Co-Solvent Adsorbed from the Liquid Phase

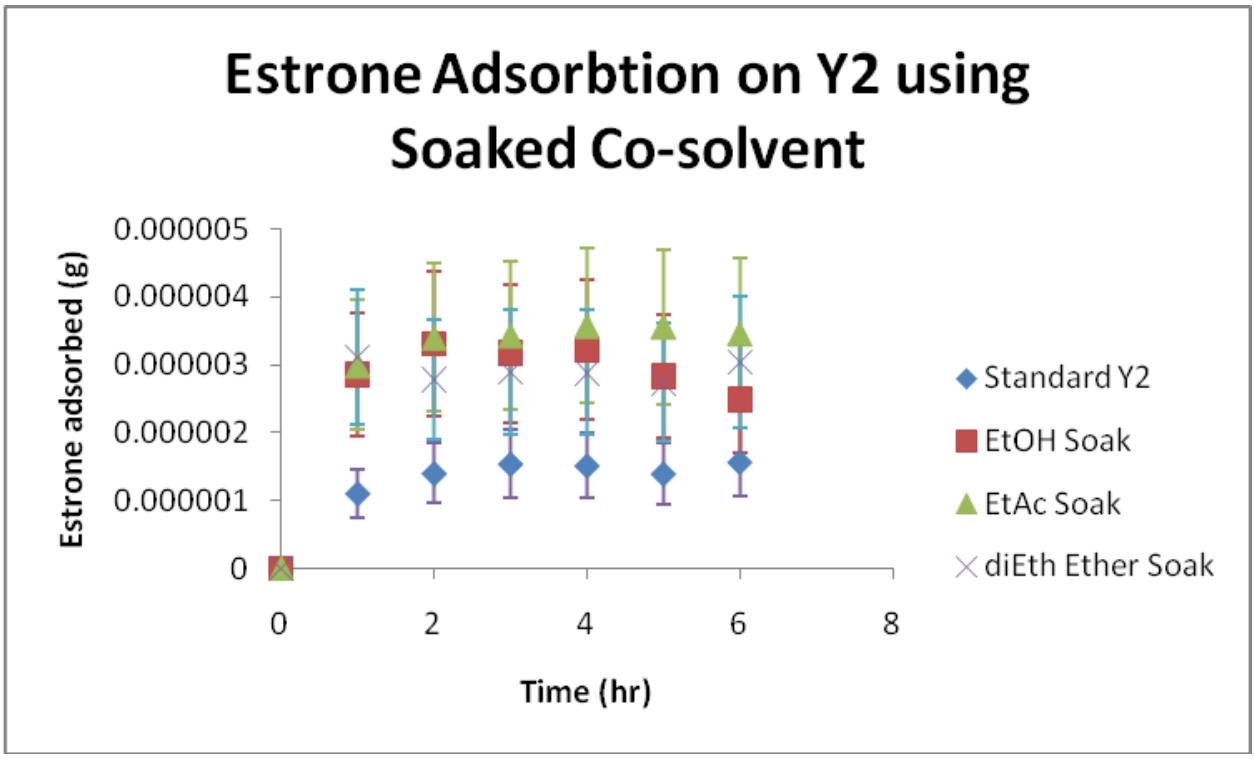


Figure 14: Sorption of Estrone into Y2 with and without Co-Solvents adsorbed from the liquid phase. (soak) means that the zeolite with co-solvent was prepared by soaking.

Zeolite Y2 with ethyl acetate or diethyl ether reached equilibrium in about 4 hours (Figure 14). Ethyl Acetate removed 80% of the estrone while diethyl ether removed 68%. Once again zeolite with ethanol as a co-solvent behaved unexpectedly. It started to release estrone back into solution at about four hours. One possible explanation is related to the explanation for the anomaly with zeolite Y1 when soaked in ethanol. Y2 had less binder than Y1 but it still has a significant amount. It is possible that as the ethanol diffuses out into the water, it brings solvated estrone molecules with it. It is the same reasoning for ethanol with Y1 but slower in this case because of the higher percentage of zeolites. However, the only way to determine if this speculative reasoning is correct is to carry out experiments using zeolite Ys with many different amounts of binder.

Zeolite HSIV 1000 with Co-Solvent Adsorbed from the Liquid Phase

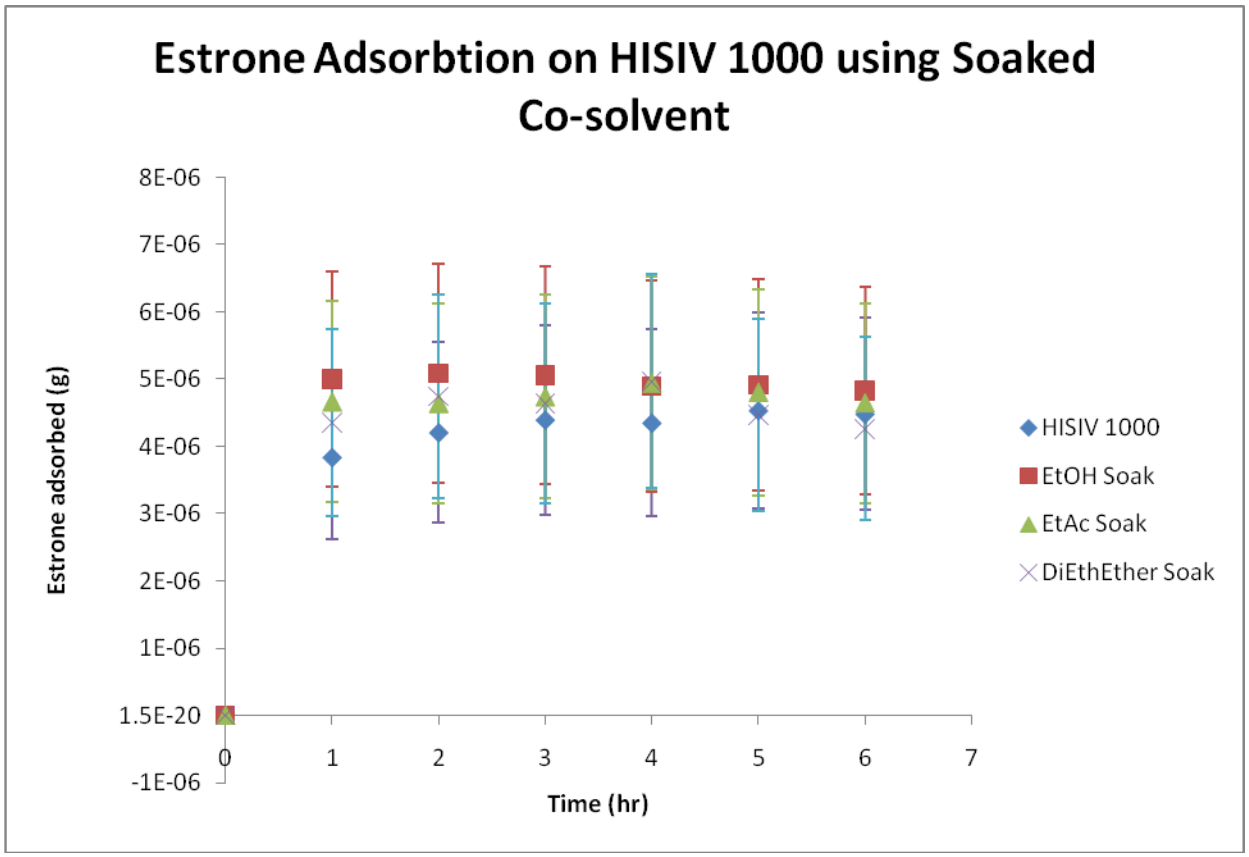


Figure 15: Sorption of Estrone into HSIV 1000 with and without Co-Solvents adsorbed from the liquid phase. (soak) means that the zeolite with co-solvent was prepared by soaking.

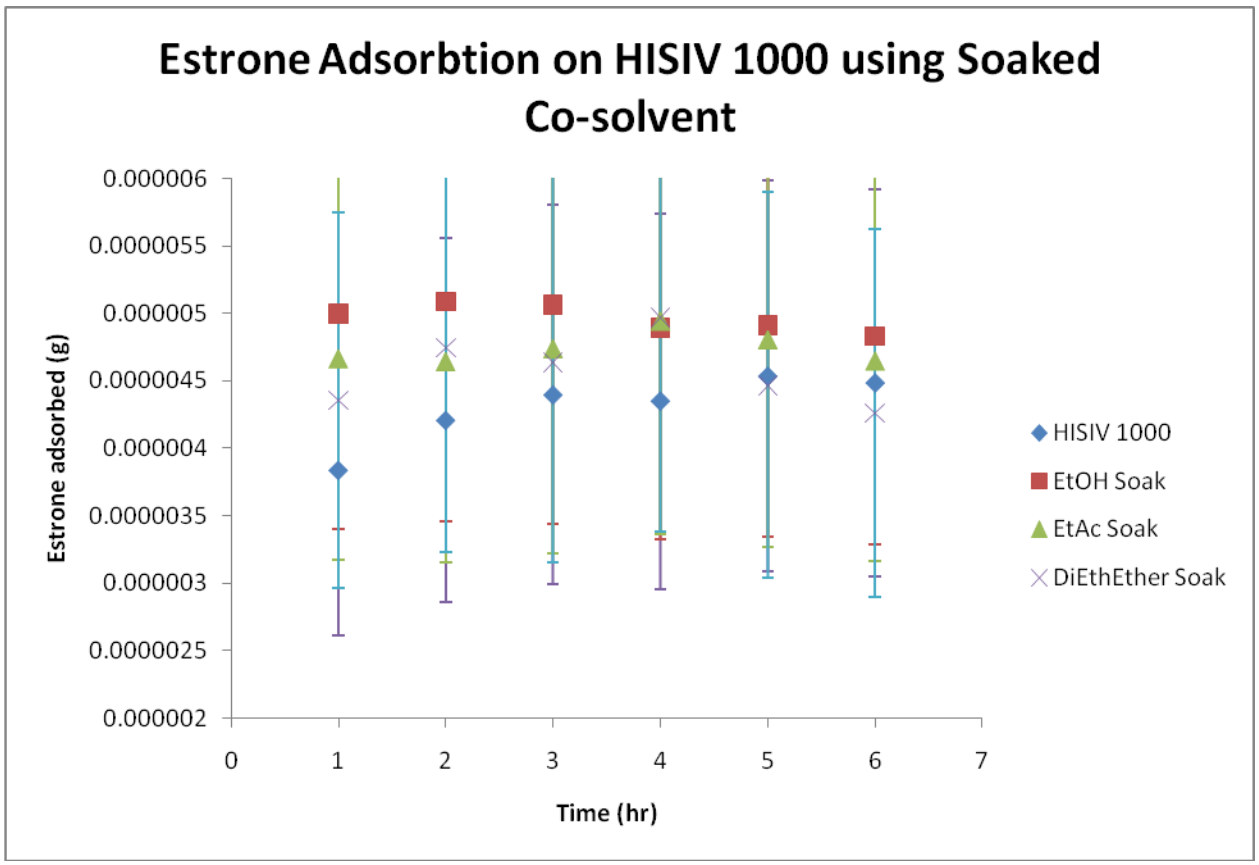


Figure 16: Close up of sorption of Estrone into HSIV 1000 with and without Co-Solvents adsorbed from the liquid phase. (soak) means that the zeolite with co-solvent was prepared by soaking.

Once again, all estrone was removed from the sample in each case (Figure 15 and Figure 16). HSIV 1000 with ethyl acetate or diethyl ether co-solvents removed all estrone within three hours. Ethanol as a co-solvent has the best performance with full removal of estrone from solution in one hour. HISIV 1000 had much less binder than Y1 or Y2 and as such similar abnormalities in the sorption of estrone were not observed.

Ethanol performance varied between runs more than the other two co-solvents because it was the most polar and as such the most soluable in the water phase.

Liquid contact was different from vapor contact because liquid contact allows much more co-solvent into the pellet. Both methods allowed co-solvent to adsorb onto the zeolites but soaking also saturates the clay binder. The co-solvent desorbed from the zeolites equally in both vapor and liquid loading, but there was much more co-solvent to leave the binder when the pellet was soaked.

The fact that the best co-solvent varied between zeolites and method of co-solvent contact implies that the sorption of estrone was more size dependent than dependent on the chemical environment.

Activated Carbon

As seen in Figure 17, Activated Carbon had very low excitation intensity. This was caused by fine particles of carbon suspended in the liquid. The proper filter for removing them could not be obtained and allowing the particles to settle was not sufficient. Therefore the standard graph of estrone sorbed vs. time could not be made.

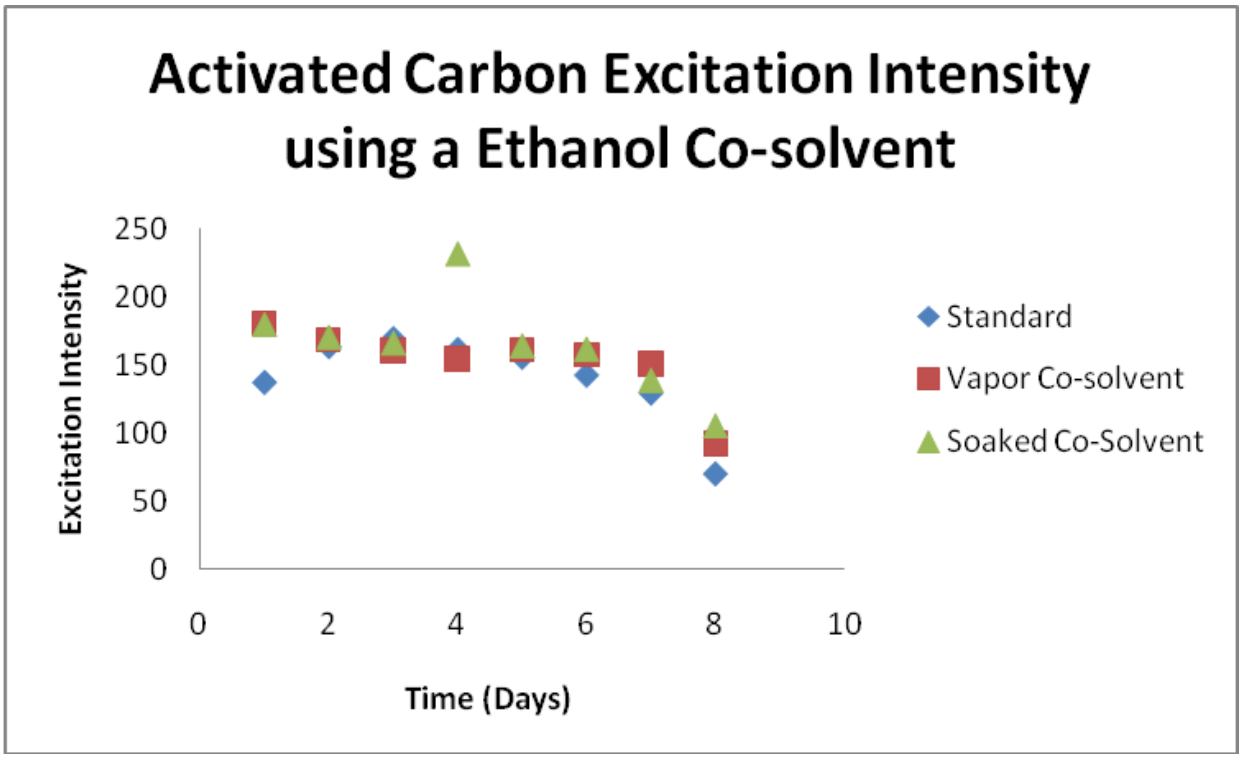


Figure 17: Activated Carbon Excitation Intensity

Excitation intensity was proportional to estrone concentration. It decreaeased over the eight days of the run, but did not come to equilibrium in eight days as reported by Wen. The ethanol co-solvent did not influence the adsorption onto activated carbon to a significant degree. Therefore, activated carbon can not be treated as analogous to zeolites. Activated carbon adsorbs estrone far slower than zeolites, and therefore should not be used to adsorb estrone.

Occupation of Zeolite Cavities

Using the cavity diameter of zeolite Y, the density of zeolite Y, and the percentage of zeolite in the pellets, the number of cavities in a gram of the three zeolites was found. The packing factor , the maximum percentage of cavities filled with estrone, was also found using the moles of estrone in solution. Results are presented in Table 8.

Table 8: Number of zeolite cavities per gram and packing factors for estrone in zeolite.

Sample	**Moles of cavities per gram**	**Packing factor**
Zeolite Y1	$4.5046*10^{-5}$	0.53%
Zeolite Y2	$7.0072*10^{-5}$	0.34%
HISIV 1000	$4.00409*10^{-4}$	0.06%

The number of zeolite cavities occupied by estrone was found to be very low. This suggests that the estrone may only be sorbing into the cavities on the surface of zeolites and progressing no further into the crystal.

Hexane Solvent Flourecense

As can be seen in Figure 18 and Figure 19, hexane and estrone did not have a strong excitation at 325nm. Also, the hexane and estrone solution did not show a strong emission at 325m. This means that the estrone did not dissolve into the hexane solution. Therefore, hexane was not used as a solvent during estrone measurements. Perkin-Elmer was contacted to find another solvent which would allow for a clearer excitation and emission, but they did not respond.

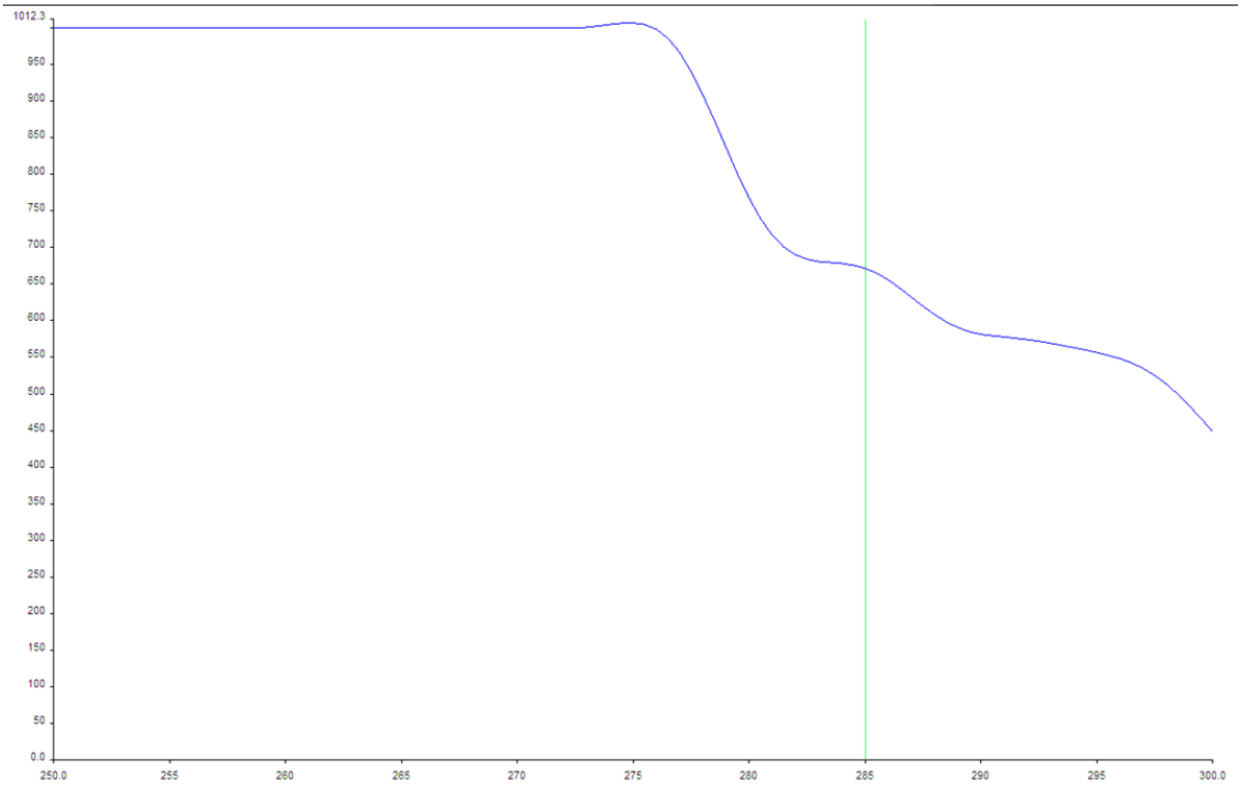


Figure 18: Hexane and Estrone Excitation

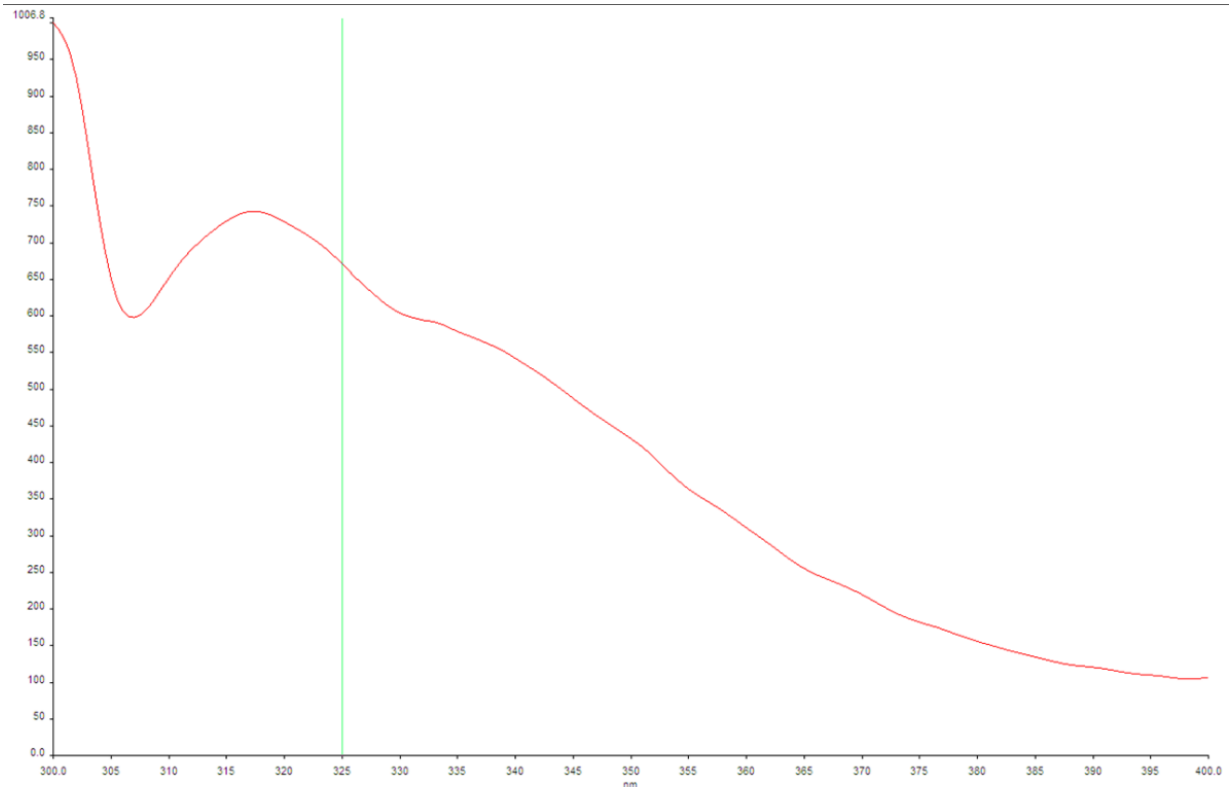


Figure 19: Hexane and Estrone Emission

The reason that estrone did not move into the hexane phase in appreciable amounts was most likely due to poor contact between the hexane and water phases. A shaker table was not an ideal way to bring two phases into contact. One alternative method that should be persued is bullbing the hexane through the estrone water solution. This should increase the contact area between the two solutions.

CHAPTER 5: CONCLUSION AND RECOMMENDATIONS

In this paper, HISIV 1000 was found to be the most effective at sequestering estrone. The reasons for this are two fold. First, Hisiv 1000 has a higher percentage of zeolite than the other two zeolites tested. Second, it has a larger micropore area.

Co-solvents adsorbed from the vapor phase were found to increase zeolite effectiveness in all cases. However, the best performing co-solvent varied between zeolites. Using zeolites pre-soaked with a co-solvent had mixed results. Zeolites with a large amount of binder preformed poorly when soaked in ethanol.

The results with Y1 and Y2 where they came to equilibrium without sorbing all the estrone suggests that the estrone was only sorbing into the surface cavities of the zeolite and not diffusing further. If there was significant diffusion deeper into the zeolite crystals the graphs of amount of estrone sorbed versus time would have a different shape. The expected shape would be a sharply increasing slope immediately, for surface sorption, changing to a shallower increasing slope when interior diffusion predominated. In all cases less than 1% of the zeolite cavities were filled with estrone as shown by the occupation calculations. This in turn provides evidence that it is not the chemical environment that limits the sequestration of estrone. The diffusion of estrone into zeolite is instead size limited. An estrone molecule can only fit through a zeolite pore in one orientation. Once it is inside the cavity the estrone molecule may not readily realign to pass to the next cavity. It is known that the environment when a material is encapsulated is different than when it is in solution. This is especially true when a molecule is capable of hydrogen bonding[27] as is estrone. Estrone's rotational freedom within a zeolite cavity would be limited by interactions with that cavity.

HISIV 1000 pre-soaked in an ethanol co-solvent is the preferred method of estrone sequestration. It quickly removes nearly all estrone and it is relatively safe. The concentration of ethanol in the treated water would be low enough that no organisms would be harmed. Many organisms have enzymes that can process ethanol.[28]

For further study, it is recommended that an experiment be designed to test if the method of using co-solvents remains as effective at higher packing factors, the percentage of zeolite cavities filled by estrone, of HISIV. Also, an experiment to determine whether fixing the maximum packing factor effects rate of adsorption should be conducted.

Outside of the field of zeolites, MOFs could potentially be used to sequester estrone. A metal organic framework has several advantages over zeolites. First, the organic ligands can be controlled to form pores and cavities of precise sizes. Second, MOFs can have much higher surface areas than zeolites. Third, the organic ligands can be tailored to chemically select a target molecule based on structure and functional groups.[29,30,31] The limiting considerations would be

---

27 Prins, L., Reinhoudt, D., Timmerman, P., *Noncovalent Synthesis Using Hydrogen Bonding*., Angew. Chem. Int. Ed. 2001, 40, 2382-2426.

28 Krook, M., Marekov, L., Joernvall, H., *Purification and structural characterization of placental NAD+-linked 15-hydroxyprostaglandin dehydrogenase. The primary structure reveals the enzyme to belong to the short-chain alcohol dehydrogenase family*.
Biochemistry, 1990, 29 (3), 738-743.

29 Snurr, R., Hupp, J., Nguyen, S., *Prospects for Nanoporous Metal-Organic Materials in Advanced Separations Processes*, AIChE Journal, 2004, 50, 6, 1090-1095.

30 Eddaoudi, M., Kim, J., Rosi, N., Vodak, D., Wachter, J., O'Keeffe, M., Yaghi, O., *Systematic Design of Pore Size and Functionality in Isoreticular MOFs and Their Applications in Methane Storage*., Science, 2002, 295, 469-472.

the cost of chemically modifying the MOFs, the ability of the organic ligand to survive the regeneration techniques used, and the fact that MOFs are only stable to about 400°C[32].

31 Eddaoudi, M., Moler, D., Li, H., Chen, B., Reineke, T., O'Keeffe, M., Yaghi, O., *Modular Chemistry: Secondary Building Units as a Basis for the Design of Highly Porous and Robust Metal-Organic Carboxylate Frameworks*., Accounts of Chemical Research, 2001, 34, 4, 319-330.

32 Czaja, A., Trukhan,N., Müller, U., Industrial Applications of Metal-Organic Frameworks., Chem. Soc. Rev. 2009 Metal-organic frameworks issue. 1284-1293.

REFERENCES

Baronti, A., Curini, R., D'Ascenzo, G., Gentili, A., Samperi, R., *Monitoring Natural and Synthetic Estrogens at Activated Sludge Sewage Treatment Plants and in a Receiving River Water*. Environ. Sci. Technol. 2000. 34, 5059-5066.

Belfroid, A.C., Van der Hors, A., Vethaak, A.D., Schafer, A.J., Rijs, G.B.J., Wegener, J., Cofino, W.P., *Analysis and Occurrence of Estrogenic Hormones and Their Glucuronides in Surface Water and Wastewater in the Netherlands*., Sci. Total Environ. 1999. 255, 101-108.

Chen, N., *Hydrophobic Properties of Zeolites*, Journal of Physical Chemistry, 1976,80, 1, 60-65.

Clipper Controls, *Dielectic Constants of Materials*, Retrived April 27, 2010, http://clippercontrols.com/info/dielectric_constants.html#W.

Czaja, A., Trukhan,N., Müller, U., Industrial Applications of Metal-Organic Frameworks., Chem. Soc. Rev. 2009 Metal-organic frameworks issue. 1284-1293.

Desbrow, C., Routledge, E.J., Brighty, G.C, Sumpter, J.P., Waldock, M., *Identification of Estrogenic Chemicals in STW Effluent. I. Chemical Fractionation and In Vitro Biological Screening*., Environ. Sci. Technol. 1998, 32, 1549-1558.

Eddaoudi, M., Kim, J., Rosi, N., Vodak, D., Wachter, J., O'Keeffe, M., Yaghi, O., *Systematic Design of Pore Size and Functionality in Isoreticular MOFs and Their Applications in Methane Storage*., Science, 2002, 295, 469-472.

Eddaoudi, M., Moler, D., Li, H., Chen, B., Reineke, T., O'Keeffe, M., Yaghi, O., *Modular Chemistry: Secondary Building Units as a Basis for the Design of Highly Porous and Robust Metal-Organic Carboxylate Frameworks*., Accounts of Chemical Research, 2001, 34, 4, 319-330.

Harris, D., Quantitative Chemical Analysis (Seventh Edition), 390-399, W.H Freeman and Company, 2007.

Harris, P., Liu, Z., Suenaga, K., *Imaging the Atomic Structure of Activated Carbon*., J. Phys,: Condens. Matter 20, 2008.

Krook, M., Marekov, L., Joernvall, H., *Purification and structural characterization of placental NAD+-linked 15-hydroxyprostaglandin dehydrogenase. The primary structure reveals the enzyme to belong to the short-chain alcohol dehydrogenase family*.
Biochemistry, 1990, 29 (3), 738-743.

Liney, K., Hagger, J., Tyler, C., Depledge, M., Galloway, T., Jobling, S., Health *Effects in Fish of Long-Term Exposure to Effluents from Wastewater Treatment Works*., Environ. Health Perspect. 2006, Apr; 114.

Marsh, H., Reinoso, F., Activated Carbon., Elsevier Science & Technology, 2006.

Meshalkin, Y., Cherkasova, O., Fedorov, V., Samoilova, E., *Laser-Induced Fluorescence of Estrogens*, Optics and Spectroscopy, 2002, 92,1, 32-35.

National Institute of Environmental Health Sciences, *Endocrine Disruptors*, U.S. Department of Health and Human Services, June 2006,<www.niehs.nih.gov>.

Prins, L., Reinhoudt, D., Timmerman, P., *Noncovalent Synthesis Using Hydrogen Bonding*., Angew. Chem. Int. Ed. 2001, 40, 2382-2426.

Rahman, M., Hasnida, N., Wan Nik, W., *Preparation of Zeolite Y Using Local Raw Material Rice Husk as a Silica Source*., J. Sci. Res., 2009, 1(2), 285-291.

Shareef, A., Angove, M., Wells, J., Johnson, B., *Aqueous Solubilities of Estrone, 17β-Estradiol, 17α-Ethynylestradiol, and Bisphenol A*. J. Chem. Eng. Data 2006, 51, 879-881.

Sigma-Aldrich, *E9750 Estrone ≥99%*, Retrieved: April 27, 2010, http://www.sigmaaldrich.com/catalog/ProductDetail.do?lang=en&N4=E9750|SIGMA&N5=SEARCH_CONCAT_PNO|BRAND_KEY&F=SPEC>.

Sigma-Aldrich, *SAFTEY DATA SHEET*, Retrieved: April 27, 2010, http://www.sigmaaldrich.com/catalog/ProductDetail.do?lang=en&N4=E9750|SIGMA&N5=SEARCH_CONCAT_PNO|BRAND_KEY&F=SPEC>.

Snurr, R., Hupp, J., Nguyen, S., *Prospects for Nanoporous Metal-Organic Materials in Advanced Separations Processes*, AIChE Journal, 2004, 50, 6, 1090-1095.

Wen, H., Bergendahl, J., Thompson, R., *Removal of Estrone from Water by Adsorption on Zeolites with Regeneration by Direct UV Photolysis*. Environ. Eng. Sci., 2009, 26, 2, 319-326.

Wade, L.G., Organic Chemistry (sixth edition), Pearson Prentice Hall, 2006.

Wakeling, A.E., Bowler, J. *STEROIDAL PURE ANTIOESTROGENS*, Journal of Endocrinology. 1987, 112, R7-R10.

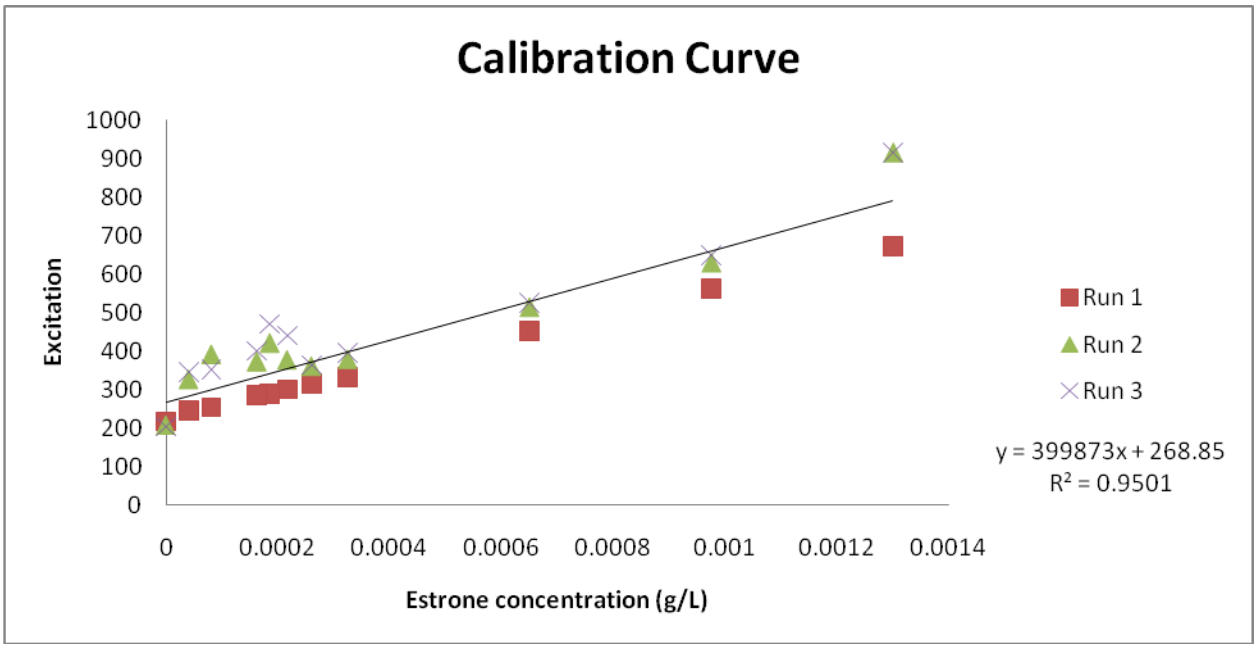
Yazaydin, A. O., Unpublished results from Ph.D. dissertation research. Chemical Engineering, Worcester Polytechnic Institute, 2007.

Zhang, Y., Zhou, J.L., Ning, B., *Photodegradation of Estrone and 17 β-Estradiol in Water*., Water Research, 2007, 41, 19-26.

Zhurova, E., Matta, C., Wu, N., Zhurov, V., Pinkerton, A., *Experimental and Theoretical Electron Density Study of Estrone*., J. AM. Chem. Soc. 2006, 128, 8849-8861.

APPENDIX A: CALIBRATION CURVE

Percentage Estrone	Excitation at 285nm			
	Run 1	Run 2	Run 3	Average
1	671.69	916.96	914.54	834.4
0.75	562.71	631.19	648.26	614.05
0.5	452.74	516	526.3	498.35
0.25	331.68	380.83	395.53	369.35
0.2	315.79	362.72	364.39	347.63
0.167	300.42	379.14	440.41	373.32
0.143	288.44	423.14	470.091	393.89
0.125	285.16	374.83	401.03	353.67
0.063	255.08	393.33	351.73	333.38
0.032	246.16	328.87	345.82	306.95
0	217.25	210.29	203.9	210.48



APPENDIX B: ZEOLITE Y1 DATA

Standard 1

Hour	Name on Vial	File Name of Scan	Excitation at 285 nm
1	D.1	ESTMQP-D06	715.59
2	D.2	ESTMQP-D05	617.73
3	D.3	ESTMQP-D04	587.8
4	D.4	ESTMQP-D03	586.64
5	D.5	ESTMQP-D02	560.82
6	D.6	ESTMQP-D01	552.75

Standard 2

Hour	Name on Vial	File Name of Scan	Excitation at 285 nm
1	G.1	ESTMQP-G10	605.13
2	G.2	ESTMQP-G09	629.01
3	G.3	ESTMQP-G08	583.21
4	G.4	ESTMQP-G07	588.91
5	G.5	ESTMQP-G06	569.92
6	G.6	ESTMQP-G05	560.72

Standard 3

Hour	Name on Vial	File Name of Scan	Excitation at 285 nm
1	J.1	ESTMQP-J23	639.41
2	J.2	ESTMQP-J22	631.38
3	J.3	ESTMQP-J21	620.94
4	J.4	ESTMQP-J20	635.02
5	J.5	ESTMQP-J19	618.55
6	J.6	ESTMQP-J18	999*

*Outlier, probably contaminated

Average Standard

Hour	Excitation at 285 nm	STD Between Runs	Amount Adsorbed (g)
1	834.40	140.91	1.18E-06
2	653.38	56.54	1.42E-06

3	626.04	7.29	1.68E-06
4	597.32	20.59	1.62E-06
5	603.52	27.30	1.80E-06
6	583.10	31.04	2.03E-06

Ethanol Soak

Hour	Name on Vial	File Name of Scan	Excitation at 285 nm	Amount Adsorbed (g)
1	M.1	ESTMQP-M07	652.42	1.19E-06
2	M.2	ESTMQP-M06	622.6	1.45E-06
3	M.3	ESTMQP-M05	602.33	1.63E-06
4	M.4	ESTMQP-M03	632.81	1.36E-06
5	M.5	ESTMQP-M02	651.85	1.198E-06
6	M.6	ESTMQP-M01	592.96	1.71E-06

Ethanol Desiccator

Hour	Name on Vial	File Name of Scan	Excitation at 285 nm	Amount Adsorbed (g)
1	P.1	ESTMQP-P06	456.75	2.91E-06
2	P.2	ESTMQP-P05	413.89	3.28E-06
3	P.3	ESTMQP-P04	413.96	3.28E-06
4	P.4	ESTMQP-P03	415.47	3.27E-06
5	P.5	ESTMQP-P02	437.37	3.07E-06
6	P.6	ESTMQP-P01	452.86	2.94E-06

Ethyl Acetate Soak

Hour	Name on Vial	File Name of Scan	Excitation at 285 nm	Amount Adsorbed (g)
1	S.1	ESTMQP-S06	523.96	2.32E-06
2	S.2	ESTMQP-S05	411	3.31E-06
3	S.3	ESTMQP-S04	395.18	3.44E-06
4	S.4	ESTMQP-S03	381.88	3.56E-06
5	S.5	ESTMQP-S02	372.46	3.64E-06
6	S.6	ESTMQP-S01	374.84	3.62E-06

Ethyl Acetate Desiccator

Hour	Name on Vial	File Name of Scan	Excitation at 285 nm	Amount Adsorbed (g)
1	V.1	ESTMQP-V06	471.24	2.79E-06
2	V.2	ESTMQP-V05	442.19	3.03E-06

3	V.3	ESTMQP-V04	446.65	2.99E-06
4	V.4	ESTMQP-V03	497.81	2.55E-06
5	V.5	ESTMQP-V02	465.68	2.83E-06
6	V.6	ESTMQP-V01	427.71	3.16E-06

Diethyl Ether Soak

Hour	Name on Vial	File Name of Scan	Excitation at 285 nm	Amount Adsorbed (g)
1	Y.1	ESTMQP-Y06	455.6	2.92E-06
2	Y.2	ESTMQP-Y05	411.29	3.30E-06
3	Y.3	ESTMQP-Y04	394.07	3.45E-06
4	Y.4	ESTMQP-Y03	430.74	3.13E-06
5	Y.5	ESTMQP-Y02	397.86	3.42E-06
6	Y.6	ESTMQP-Y01	453.82	2.93E-06

Diethyl Ether Desiccator

Hour	Name on Vial	File Name of Scan	Excitation at 285 nm	Amount Adsorbed (g)
1	beta.1	ESTMQP-beta06	487.36	2.64E-06
2	beta.2	ESTMQP-beta05	441.22	3.04E-06
3	beta.3	ESTMQP-beta04	395.79	3.44E-06
4	beta.4	ESTMQP-beta03	438.56	3.07E-06
5	beta.5	ESTMQP-beta02	424.38	3.19E-06
6	beta.6	ESTMQP-beta01	425.67	3.18E-06

APPENDIX C: ZEOLITE Y2 DATA

Standard 1

Hour	Name on Vial	File Name of Scan	Excitation at 285 nm
1	E.1	ESTMQP-E07	653.98
2	E.2	ESTMQP-E06	630.55
3	E.3	ESTMQP-E05	621.15
4	E.4	ESTMQP-E04	617.6
5	E.5	ESTMQP-E03	620.69
6	E.6	ESTMQP-E02	602.58

Standard 2

Hour	Name on Vial	File Name of Scan	Excitation at 285 nm
1	G.1	ESTMQP-H06	686.8
2	G.2	ESTMQP-H05	645.9
3	G.3	ESTMQP-H04	621.45
4	G.4	ESTMQP-H03	631.71
5	G.5	ESTMQP-H02	621.7
6	G.6	ESTMQP-H01	611.94

Standard 3

Hour	Name on Vial	File Name of Scan	Excitation at 285 nm
1	K.1	ESTMQP-K06	646.53
2	K.2	ESTMQP-K05	608.63
3	K.3	ESTMQP-K04	594.75
4	K.4	ESTMQP-K03	596.54
5	K.5	ESTMQP-K02	644.75
6	K.6	ESTMQP-K01	613.65

Average

Hour	Excitation at 285 nm	STD Between Runs	Amount Adsorbed (g)
1	662.44	21.43	1.11E-06
2	628.36	18.73	1.40E-06
3	612.45	15.33	1.54E-06
4	615.28	17.70	1.52E-06

5	629.05	13.61	1.40E-06
6	609.39	5.96	1.57E-06

Ethanol Soak

Hour	Name on Vial	File Name of Scan	Excitation at 285 nm	Amount Adsorbed (g)
1	N.1	ESTMQP-N06	462.61	2.85E-06
2	N.2	ESTMQP-N05	410.96	3.31E-06
3	N.3	ESTMQP-N04	427.07	3.17E-06
4	N.4	ESTMQP-N03	421.28	3.22E-06
5	N.5	ESTMQP-N02	465.52	2.83E-06
6	N.6	ESTMQP-N01	504.36	2.49E-06

Ethanol Desiccator

Hour	Name on Vial	File Name of Scan	Excitation at 285 nm	Amount Adsorbed (g)
1	Q.1	ESTMQP-Q06	429.52	3.14E-06
2	Q.2	ESTMQP-Q07	447.79	2.98E-06
3	Q.3	ESTMQP-Q08	420.81	3.22E-06
4	Q.4	ESTMQP-Q09	422.92	3.20E-06
5	Q.1	ESTMQP-Q10	440.87	3.04E-06
6	Q.2	ESTMQP-Q11	473.65	2.76E-06

Ethyl Acetate Soak

Hour	Name on Vial	File Name of Scan	Excitation at 285 nm	Amount Adsorbed (g)
1	T.1	ESTMQP-T06	447.17	2.99E-06
2	T.2	ESTMQP-T05	400.43	3.40E-06
3	T.3	ESTMQP-T04	396.49	3.43E-06
4	T.4	ESTMQP-T03	380.31	3.57E-06
5	T.5	ESTMQP-T02	381.68	3.56E-06
6	T.6	ESTMQP-T01	393.5	3.46E-06

Ethyl Acetate Desiccator

Hour	Name on Vial	File Name of Scan	Excitation at 285 nm	Amount Adsorbed (g)
1	W.1	ESTMQP-W06	509.34	2.45E-06
2	W.2	ESTMQP-W05	427.37	3.16E-06
3	W.3	ESTMQP-W04	386.89	3.52E-06
4	W.4	ESTMQP-W03	386.81	3.52E-06

5	W.5	ESTMQP-W02	377.06	3.60E-06
6	W.6	ESTMQP-W01	383.15	3.55E-06

Diethyl Ether Soak

Hour	Name on Vial	File Name of Scan	Excitation at 285 nm	Amount Adsorbed (g)
1	Z.1	ESTMQP-Z06	433.48	3.11E-06
2	Z.2	ESTMQP-Z05	470.94	2.78E-06
3	Z.3	ESTMQP-Z04	458.3	2.89E-06
4	Z.4	ESTMQP-Z03	459.1	2.88E-06
5	Z.5	ESTMQP-Z02	475.96	2.74E-06
6	Z.6	ESTMQP-Z01	441.86	3.04E-06

Diethyl Ether Desiccator

Hour	Name on Vial	File Name of Scan	Excitation at 285 nm	Amount Adsorbed (g)
1	gamma.1	ESTMQP-gamma06	434.24	3.10E-06
2	gamma.2	ESTMQP-gamma05	392.38	3.47E-06
3	gamma.3	ESTMQP-gamma04	444.32	3.01E-06
4	gamma.4	ESTMQP-gamma03	431.8	3.12E-06
5	gamma.5	ESTMQP-gamma02	485.48	2.65E-06
6	gamma.6	ESTMQP-gamma01	430.03	3.14E-06

APPENDIX C: HISIV 1000 DATA

Standard 1

Hour	Name on Vial	File Name of Scan	Excitation at 285 nm
1	F.1	ESTMQP-F06	431.93
2	F.2	ESTMQP-F05**	370.92
3	F.3	ESTMQP-F04	326.52
4	F.4	ESTMQP-F03	309
5	F.5	ESTMQP-F02	243.06
6	F.6	ESTMQP-F01	282.56

Standard 2

Hour	Name on Vial	File Name of Scan	Excitation at 285 nm
1	I.1	ESTMQP-I07	311.81
2	I.2	ESTMQP-I06	292.86
3	I.3	ESTMQP-I04	277.46
4	I.4	ESTMQP-I03	305.89
5	I.5	ESTMQP-I02	310.71
6	I.6	ESTMQP-I01	301.71

Standard 3

Hour	Name on Vial	File Name of Scan	Excitation at 285 nm
1	L.1	ESTMQP-L06	306.95
2	L.2	ESTMQP-L05	260.31
3	L.3	ESTMQP-L04	255.53
4	L.4	ESTMQP-L03	260.16
5	L.5	ESTMQP-L02	258.38
6	L.6	ESTMQP-L01	244.73

Average

Hour	Excitation at 285 nm	STD Between Runs	Amount Adsorbed (g)
1	350.23	70.76	3.84E-06
2	308.03	56.84	4.21E-06
3	286.50	36.35	4.40E-06
4	291.683	27.34	4.35E-06

5	270.72	35.47	4.54E-06
6	276.3333333	28.99583821	4.49E-06

Ethanol Soak

Hour	Name on Vial	File Name of Scan	Excitation at 285 nm	Amount Adsorbed (g)
1	O.1	ESTMQP-O06	217.61	5.00E-06
2	O.2	ESTMQP-O05	207.34	5.08E-06
3	O.3	ESTMQP-O04	210.4	5.06E-06
4	O.4	ESTMQP-O03	229.8	4.90E-06
5	O.5	ESTMQP-O02	227.65	4.90E-06
6	O.6	ESTMQP-O01	236.77	4.83E-06

Ethanol Desiccator

Hour	Name on Vial	File Name of Scan	Excitation at 285 nm	Amount Adsorbed (g)
1	R.1	ESTMQP-R06	320.02	4.10E-06
2	R.2	ESTMQP-R05	290.65	4.36E-06
3	R.3	ESTMQP-R04	260.24	4.63E-06
4	R.4	ESTMQP-R03	255.22	4.67E-06
5	R.5	ESTMQP-R02	256.39	4.66E-06
6	R.6	ESTMQP-R01	243.47	4.77E-06

Ethyl Acetate Soak

Hour	Name on Vial	File Name of Scan	Excitation at 285 nm	Amount Adsorbed (g)
1	U.1	ESTMQP-U06	256.07	4.66E-06
2	U.2	ESTMQP-U05	258.57	4.64E-06
3	U.3	ESTMQP-U04	247.48	4.74E-06
4	U.4	ESTMQP-U03	223.89	4.94E-06
5	U.5	ESTMQP-U02	239.79	4.80E-06
6	U.6	ESTMQP-U01	258	4.64E-06

Ethyl Acetate Desiccator

Hour	Name on Vial	File Name of Scan	Excitation at 285 nm	Amount Adsorbed (g)
1	X.1	ESTMQP-X06	229.58	4.89E-06
2	X.2	ESTMQP-X05	227.94	4.91E-06
3	X.3	ESTMQP-X04	236.16	4.84E-06
4	X.4	ESTMQP-X03	219.71	4.98E-06

5	X.5	ESTMQP-X02	274.04	4.50E-06
6	X.6	ESTMQP-X01	269.27	4.55E-06

Diethyl Ether Soak

Hour	Name on Vial	File Name of Scan	Excitation at 285 nm	Amount Adsorbed (g)
1	alpha.1	ESTMQP-alpha06	290.99	4.36E-06
2	alpha.2	ESTMQP-alpha05	246.42	4.75E-06
3	alpha.3	ESTMQP-alpha04	258.75	4.64E-06
4	alpha.4	ESTMQP-alpha03	221.28	4.97E-06
5	alpha.5	ESTMQP-alpha02	278.45	4.47E-06
6	alpha.6	ESTMQP-alpha01	302.1	4.26E-06

Diethyl Ether Desiccator

Hour	Name on Vial	File Name of Scan	Excitation at 285 nm	Amount Adsorbed (g)
1	mu.1	ESTMQP-mu06	315.44	4.14E-06
2	mu.2	ESTMQP-mu05	291.42	4.35E-06
3	mu.3	ESTMQP-mu04	239.68	4.81E-06
4	mu.4	ESTMQP-mu03	327.95	4.03E-06
5	mu.5	ESTMQP-mu02	275.25	4.49E-06
6	mu.6	ESTMQP-mu01	316.9	4.13E-06

APPENDIX D: ACTIVATED CARBON

Activated Carbon Standard

Hour	Name on Vial	File Name of Scan	Excitation at 285nm
1	Theta 1	J31	136.61
2	Theta 2	J32	162.82
3	Theta 3	J33	168.71
4	Theta 4	J34	160.85
5	Theta 5	J35	155.1
6	Theta 6	J36	141.88
7	Theta 7	J37	128.76
8	Theta 8	J38	69.5

Activated Carbon Ethanol Soak

Hour	Name on Vial	File Name of Scan	Excitation at 285nm

1	PHI1	PHI1	180.55
2	PHI2	PHI2	168.06
3	PHI3	PHI3	160.72
4	PHI4	PHI4	154.6
5	PHI5	PHI5	160.81
6	PHI6	PHI6	157.5
7	PHI7	PHI7	150.43
8	PHI8	PHI8	92.01

Activated Carbon Ethanol Desiccator

Hour	Name on Vial	File Name of Scan	Excitation at 285nm
1	PSI1	PSI1	179.77
2	PSI2	PSI2	170.26
3	PSI3	PSI3	166.01
4	PSI4	PSI4	231.82
5	PSI5	PSI5	163.92
6	PSI6	PSI6	161.49
7	PSI7	PSI7	138.55
8	PSI8	PSI8	104.88

APPENDIX E: CALCULATIONS

Mol Cavities

Mol Cavities Zeolite Y1

$$1g * 0.09\ \%\ zeolite * \frac{1cm^3}{1.92g} * \frac{1\ cavity}{1728Å^3} * \frac{1Å^3}{1.0 * 10^{24}cm^3} = 2.71 * 10^{19} cavites$$

$$2.71 * 10^{19}\ cavities * \frac{1\ mol}{6.022 * 10^{23} cavities} = 4.5 * 10^{-5} mol\ cavities$$

Mol Cativites Zeolite Y2

$$1g * 0.14\ \%\ zeolite * \frac{1cm^3}{1.92g} * \frac{1\ cavity}{1728Å^3} * \frac{1Å^3}{1.0 * 10^{24}cm^3} = 4.22 * 10^{19} cavities$$

$$4.22 * 10^{19} cavities * \frac{1\ mol}{6.022 * 10^{23}\ cavities} = 7 * 10^{-5} mol\ cavities$$

Mol Cavities HISIV 1000

$$1g * 0.80\ \%\ zeolite * \frac{1cm^3}{1.92g} * \frac{1\ cavity}{1728Å^3} * \frac{1Å^3}{1.0 * 10^{24}cm^3} = 2.41 * 10^{20}\ cavities$$

$$2.41 * 10^{20}\ cavities * \frac{1\ mol}{6.022 * 10^{23} cavities} = 4 * 10^{-4} mol\ cavities$$

Moles Estrone

$$\frac{1.3mg}{L} * \frac{1g}{1000mg} * \frac{1L}{1000ml} * 50ml * \frac{1mol}{270.366g} = 2.40 * 10^{-7} mol\ estrone$$

Packing Factor

Zeolite Y1 Packing Factor

$$\frac{2.40 * 10^{-7} mol\ estrone}{4.5 * 10^{-5} mol\ cavities} = 5.3 * 10^{-3} = 0.53\%$$

Zeolite Y2 Packing Factor

$$\frac{2.40 * 10^{-7} mol\ estrone}{7 * 10^{-5} mol\ cavities} = 3.4 * 10^{-3} = 0.34\%$$

HISIV 1000 Packing Factor

$$\frac{2.40 * 10^{-7} mol\ estrone}{4 * 10^{-4} mol\ cavities} = 6.0 * 10^{-4} = 0.06\%$$