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Removal of Estrone from Water by Adsorption on Zeolites with Regeneration by Direct UV Photolysis

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Abstract

Estrone is an endocrine-disrupting compound (EDC) that is suspected to have adverse effects on aquatic organisms. This work investigated the removal of estrone from water by adsorption onto hydrophobic molecular sieve zeolites followed by ultraviolet light (UV) photolysis to destroy the adsorbed estrone. A solvent-free analytical method employing solid phase micro-extraction (SPME) and gas chromatography (GC-FID) was utilized to analyze low estrone concentrations in water. Two types of zeolites, dealuminated Y (DAY) and silicalite-1, were evaluated for adsorption capacity and compared with Centaur[®] activated carbon (CAC). DAY showed the highest adsorption capacity, while silicalite-1 was the least effective in removing estrone. Moreover, DAY required four hours to reach adsorption equilibrium; much less than the eight days needed for CAC to reach equilibration. The Freundlich adsorption isotherm was found to best represent the data for adsorption of estrone on DAY. UV at $\lambda = 254$ nm degraded estrone in water much more effectively than long-wave UV ($\lambda = 365$ nm). Regeneration of the contaminant-saturated DAY was accomplished with $\lambda = 254$ nm UV light.

Key words: adsorption; estrone; endocrine disrupting compound; isotherm; UV; zeolites

Introduction

ENDOCRINE-DISRUPTING COMPOUNDS (EDCs) are suspected of causing adverse health effects in organisms by interfering with the normal function of hormones and the way hormones control growth. EDCs include natural and synthetic hormones, some industrial chemicals, and some pesticides. More than 160 compounds have shown some evidence of endocrine disruption (Commission of the European Communities, 1999). The early discoveries that certain compounds can mimic the endogenous hormones of animals can be traced back to the 1930s (Walker and Janney, 1930; Cook *et al.*, 1934). In 1946, Schueler explained that molecular configurations of natural and synthetic compounds influenced the degree of estrogenic and androgenic bioactivity in rodents (Schueler, 1946).

Three natural estrogens, estrone, 17 β -estradiol, and estriol, and one synthetic estrogen, 17 α -ethynylestradiol, display the strongest estrogenic effects according to many reports (Desbrow *et al.*, 1998; Snyder *et al.*, 1999; Snyder *et al.*, 2001; Tanaka *et al.*, 2001). This could be due to the common phe-

nol ring of these molecules that possibly interacts with estrogen receptors. Due to their extremely high biological potency, a number of experiments have shown that trace amounts of estrogens, as low as ng/l, are capable of exerting biological effects on aquatic organisms (Purdon *et al.*, 1994; Arcand-Hoy *et al.*, 1998; Kramer *et al.*, 1998; Panter *et al.*, 1998; Routledge *et al.*, 1998; Thorpe *et al.*, 2003). Through excretion, female and male mammals are the primary source for the natural estrogens (Adlercreutz *et al.*, 1986; Johnson *et al.*, 2000). Synthetic estrogens are present in contraceptives and other drugs used for treatment of cancers or hormonal disorders. They enter natural waters through discharges of wastewater, primarily from wastewater treatment facilities. Reports from the United Kingdom and the United States in the 1990s indicated that fish living below wastewater treatment plants had reproductive abnormalities (Purdon *et al.*, 1994; Bevans *et al.*, 1996; Folmar *et al.*, 1996; Harries *et al.*, 1996; Jobling *et al.*, 1998). Conventional wastewater treatment plants can remove about 85% of 17 β -estradiol and 17 α -ethynylestradiol and 70% of estrone on average (Johnson and Williams, 2004). However, the fraction that is not removed during treatment is still able to pose adverse biological effects in aquatic systems. In addition, part of the removed estrogens can accumulate in sludge from wastewater treatment plants, and may potentially cause contamination of soil and ground water if that sludge is used as soil amendments or

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TABLE 1. PHYSICAL AND CHEMICAL PROPERTIES OF ESTRONE

Molecular formula	Molecular Weight	Solubility (20°C) (Lai <i>et al.</i> , 2000)	Melting point	Molecular size (Wilcox and Vallieres, 2006)	Log K_{ow} (Yoon <i>et al.</i> , 2006)	pK_a (Lai <i>et al.</i> , 2000)
C ₁₈ H ₂₂ O ₂	270.4 g/mol	13 mg/l	255°C	4Å × 11Å	3.13	10.3

landfilled (Auriol *et al.*, 2006). Consequently, a variety of treatment technologies have been looked at for destroying or removing estrogens from water such as: ozonation (Nakagawa *et al.*, 2002; Ternes *et al.*, 2003), TiO₂/UV oxidation (Ohko *et al.*, 2002), UV/H₂O₂ oxidation (Rosenfeldt and Linden, 2004), UV/H₂O₂/Fe oxidation (Feng *et al.*, 2005), degradation with MnO₂ (Rudder *et al.*, 2004), adsorption on activated carbon (Fukuhara *et al.*, 2006), UV (Liu and Liu, 2004) and chlorination (Hu *et al.*, 2003). Effective treatment technologies are needed for removing EDCs from water.

In this research, estrone was removed from water by adsorption onto hydrophobic molecular sieves. Regeneration of the saturated adsorbent by UV photolysis was also investigated. Estrone was selected as the target compound for this research due to its presence in wastewater effluents, and because of the relatively low removal effectiveness of estrone in current treatment plants (Johnson *et al.*, 2000). The main physical and chemical properties of estrone are presented in Table 1 and the chemical structure is shown in Figure 1. A fast and solvent-free analytical method was utilized for quantifying estrone in water. It consisted of solid-phase microextraction (SPME) followed by on-fiber silylation for preparing the sample for gas chromatography (GC) analysis (Carpinteiro *et al.*, 2004).

Materials and Methods

Water samples

Estrone-spiked water samples were prepared from powdered estrone (>99%, Sigma-Aldrich), stirred for 4–8 hr, and filtered through glass fiber filters (47 mm, 0.7 μm pore size, Pall Gelman Laboratory). The aqueous samples were stored protected from light at 4°C until use. Stock estrone solutions for GC standard curves were prepared by dissolving estrone in methanol (HPLC grade, Fisher Scientific). The estrone stock solution was stored at 4°C until use and diluted with purified water (Barnstead RO-Pure ST/E-pure system) to make standard solutions for SPME-GC-FID calibration. An internal standard solution, deuterated 17β-estradiol (d₄) (2,4,16,16 -D₄, Cambridge Isotope Laboratories), prepared by dissolving 5 mg in 50 mL methanol, was added to all samples before GC quantification.

Adsorbents

Dealuminated Y (DAY) (Zeolyst), silicalite-1 (Union Carbide), and a granular activated carbon made from bituminous coal (Centaur[®], Calgon Corporation) were used as adsorbents. The pores of the zeolites are uniform in shape and size as a result of the regular crystalline framework structure. The pore sizes of the zeolites are listed in Table 2. The

granular activated carbon has pore diameters between 5–40 Å, with most pores in the 5–20 Å range (Merenov *et al.*, 2000). All three of these samples were used in our prior studies with other organic compounds (Giaya *et al.*, 2000; Erdem-Senatalar *et al.*, 2004; Koryabkina *et al.*, 2007), thus providing a basis for comparison. The adsorbents were first dried in an oven at 120°C for 12–14 hr, and then stored in a desiccator containing a supersaturated solution of CaCl₂ in water. This approach was expected to produce moisture equilibrium in a saturated humidity atmosphere (Giaya *et al.*, 2000; Giaya and Thompson, 2002; Erdem-Senatalar *et al.*, 2004; Koryabkina *et al.*, 2007).

Adsorption tests

The adsorption data were obtained by using various adsorbent/aqueous solution ratios (10–315 mg adsorbent/L water). Subsequent to 5 hr mixing on an orbital shaker (Labline Instruments, Inc.), 40 mL solutions were transferred to 45 mL vials, and liquid-solid separation performed by centrifugation for 10 min at 2000 RPM (Eppendorf 5804 centrifuge, Eppendorf, Germany).

Solid phase microextraction/gas chromatography procedure

A solid phase microextraction (SPME) fiber with an 85 μm film thickness polyacrylate coating (Supelco) was used for extracting and concentrating estrone from the aqueous samples. The fiber was initially conditioned by baking in the injection port of the gas chromatograph (Agilent Technologies, Series 6890) at 300°C for at least 2 hr as recommended by the manufacturer (Supelco). Extraction was performed in 45 mL vials by immersing the SPME fiber in 40 mL aqueous samples containing the internal standard. The extractions were conducted at room temperature (20°C ± 2°C) for 1 hr with

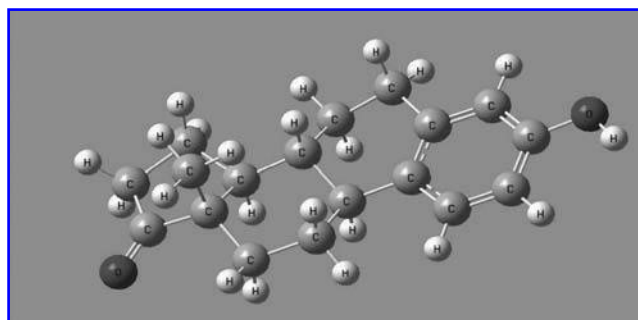


FIG. 1. Molecular structure of estrone (Wilcox and Vallieres, 2006).

TABLE 2. REMOVAL OF ESTRONE FROM WATER WITH 24 H ADSORPTION ONTO CAC, DAY, AND SILICALITE-1. INITIAL ESTRONE CONCENTRATION = 1130 $\mu\text{g/L}$

Adsorbent	Percent removal	Ave. largest pore dimensions, d_L (\AA) (Erdem-Senatalar <i>et al.</i> , 2004)	Specific surface area (m^2/g)	Total specific pore volume (m^3/g) (Erdem-Senatalar <i>et al.</i> , 2004)
CAC	69	7.8	1014 (Merenov <i>et al.</i> , 2000)	0.51
DAY	99	7.4	692 (Zhao <i>et al.</i> , 1998)	0.38
Silicalite-1	39	5.6, 5.5	371 (Zhao <i>et al.</i> , 1998)	0.21

stirring at 400 rpm. pH adjustment was not performed for these analyses as the samples were ca. neutral, and others had found that sample pH did not affect SPME extraction of estrogens (Carpinteiro *et al.*, 2004). After the microextraction 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 estrone to its silyl derivative (Carpinteiro *et al.*, 2004). Derivatization was carried out at 60°C for 15 min in an oven before each GC injection.

The GC was equipped with a flame ionization detector (FID), and an EquityTM-5 capillary column 12 m in length, 200 μm in nominal diameter with 0.33 μm film thickness. The inlet and detector temperatures were 280°C. Nitrogen was used as the carrier gas at a constant flow of 0.8 mL/min. Hydrogen gas and air at flow rates of 40 mL/min and 180 mL/min, respectively, were used for the FID flame. The flow rate of make up nitrogen gas was 19.2 mL/min. The GC oven was programmed as follows: 1 min at 80°C, ramped at 15°C/min to 260°C and held for 20 min. The SPME fiber was allowed to desorb in the GC inlet for 5 min at 280°C and was heated for an additional 5 min at the same temperature to avoid carry-over. The concentration of estrone in the sample was determined from a linear standard curve after adjusting for method sensitivity using the internal standard. Blanks were included in each run, as well as spikes of known concentrations within the standard curve concentration range. The method detection limit was 1 $\mu\text{g/L}$.

Degradation of estrone by ultraviolet light

Irradiation by UV light using a short wavelength UV lamp (Model 11SC-1 Mercury Pen-Ray lamp, 254 nm, 6650 $\mu\text{W}/\text{cm}^2$) and a long wavelength UV lamp (36-380 Spectronics Corp., 365 nm peak, 1000 $\mu\text{W}/\text{cm}^2$) was performed in an annular volume between a quartz tube (ACE-7506-10, ACE Glass Inc., approximately 13 cm long and 1.2 cm diameter with 5 mm wall thickness), and a glass outer tube (ACE Glass Inc., approximately 11 cm long and 2.5 cm diameter with 2 mm wall thickness). Due to the limited volume in this apparatus, 40 ml water samples were divided into 8 runs for irradiation. The contact times were 10 s, 20 s, 30 s, 1 min, 3 min, 6 min, and 30 min.

Thermogravimetric analysis

Three samples, pure dry estrone, wet DAY, and DAY saturated with estrone, were each subjected to thermogravimetric analysis (TGA). All samples were heated in the TGA (TA Instruments TGA 2950 Thermogravimetric Analyzer) from 30 to 500°C at a heating rate of 10°C/min under a purge of nitrogen gas. Weight losses as a function of sample temperature were recorded.

Results and Discussion

Screening experiments using zeolites and activated carbon

Initial screening experiments were conducted to compare the ability of the three sorbents to remove estrone from water. The results are listed in Table 2, and show that DAY had the greatest equilibrium removal of estrone (99%), while silicalite-1 was least effective (39%). The Centaur[®] activated carbon (CAC) removed 69%. Given that an estrone molecule has a width of about 3.8 \AA and length of about 10.8 \AA (Wilcox and Vallieres, 2006), it might be expected that estrone would

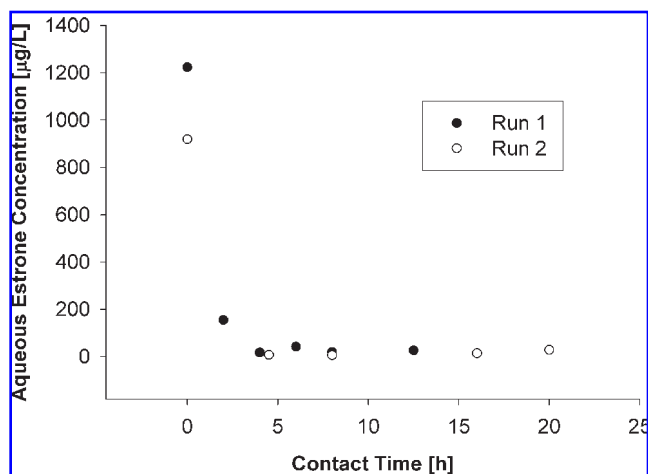


FIG. 2. Kinetics of adsorption of estrone on DAY (20°C); two symbols represent duplicate runs.

not be prevented from the pores in all three samples. However, DAY has a 3-D cage-like structure while silicalite-1 has a 3-D channel structure. It is uncertain if their structural differences contributed to their quite different adsorbability. BET surface areas also provide an indication of a sorbent's ability to remove contaminants. Higher BET surface areas usually provide for greater adsorbability, yet for estrone adsorption, CAC with a much greater surface area (Table 2) underperformed DAY. Silicalite-1 was eliminated from further study after the screening experiments due to its low equilibrium adsorption performance.

Kinetics of adsorption

Kinetics experiments were carried out with DAY and CAC by placing the adsorbents and estrone in 45 ml vials and sacrificing vials at predetermined times. The results of the kinetic studies for DAY and CAC are shown in Figures 2 and 3, respectively. The time for reaching adsorption equilibrium for DAY was approximately 4 hr, while it took more than one week for CAC to reach adsorption equilibrium. Due to the extremely long contact time for estrone to adsorb to CAC only DAY was studied in more detail in subsequent experiments.

DAY Adsorption Isotherm

The adsorption isotherm for estrone on DAY is presented in Figure 4. The data were fitted to the linearized Freundlich and Langmuir adsorption models.

The linearized Freundlich model is:

$$\ln q_e = \ln K + \frac{1}{n} \ln C_e$$

where q_e is the mass in μg of adsorbate (estrone) per mass in g of adsorbent (DAY), C_e is the equilibrium concentration of estrone in water in $\mu\text{g}/\text{L}$, and K and $1/n$ are Freundlich constants.

The linearized Langmuir model is:

$$\frac{C_e}{q_e} = \left(\frac{1}{b \cdot q_{\max}} \right) + \frac{C_e}{q_{\max}}$$

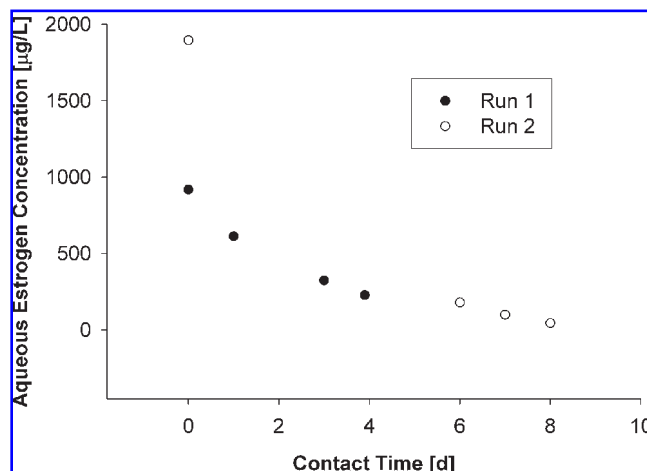


FIG. 3. Kinetics of adsorption of estrone on CAC (20°C); two symbols represent duplicate runs.

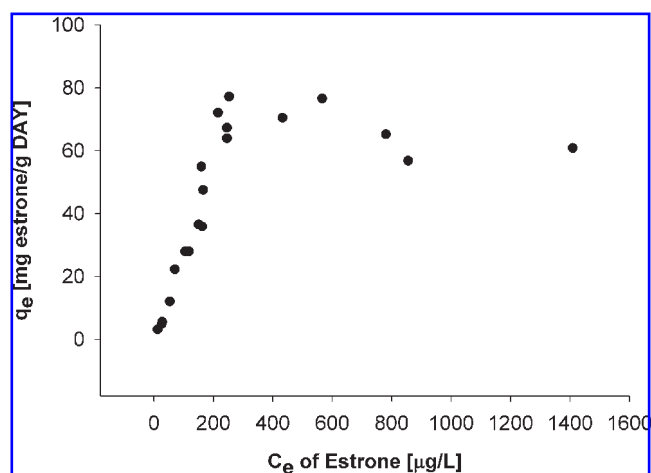


FIG. 4. Adsorption isotherm of estrone on DAY at 20°C.

where q_{\max} is the saturation capacity in mg/g, and b is a constant.

The fit of the data to the linearized Freundlich isotherm is shown in Figure 5. The high R^2 value establishes that there is a very good fit to the data. The R^2 value for the fit of the data to the linearized Langmuir model was 0.892, and is not shown here. However, it is worth noting that the saturation capacity parameter, q_{\max} , computed from the Langmuir isotherm analysis was 74 mg/g, quite close to the limiting value observed experimentally.

The values found for the Freundlich constants were $1/n = 1.10$, and $K = 0.163 \text{ (mg/g)} \cdot (\text{L}/\mu\text{g})^{1.10}$. The Freundlich constant K is thought to represent the adsorption capacity, and $1/n$ the adsorptive energy between the adsorbent and the adsorbate. The higher the value for K , the stronger the adsorption capacity; while the smaller the value for $1/n$, the stronger the adsorptive energy. Fukuhara *et al.* evaluated different types of activated carbons for estrone removal from water (Fukuhara *et al.*, 2006) (Table 3). They concluded that adsorption capacity increases with increases in specific surface area. This work is consistent with that observation as DAY has a smaller specific surface area than the activated carbons in Table 3, and performs less effectively from an equilibrium standpoint, yet has kinetics benefits over CAC (Figs. 2 and 3).

It was estimated that approximately 16% of the DAY pore volume was filled at saturation. This seemingly low level of pore filling, noted by the plateau in the isotherm, might be hypothesized to be due to estrone existing as pure, crystal or precipitated solid or quasi-solid estrone in the pore throats, blocking the potential for higher loadings. Note the rather high melting point for estrone (255°C), which is listed in Table 1. Thus, at room temperature, estrone can be expected to be a solid. Since prior evidence has suggested that these hydrophobic zeolites adsorb very little water (Giaya *et al.*, 2000; Giaya and Thompson, 2002), estrone might be assumed to adsorb with very little water, and thus be essentially pure in the adsorbed state. That being the case, one might expect it to behave as a solid or quasi-solid phase, making diffusion into the pores rather difficult. Secondly, Molecular Dynamics simulations of a single estrone molecule in a DAY cavity revealed that the hydrogen atom in the $-\text{OH}$ group (Fig. 1) hydrogen

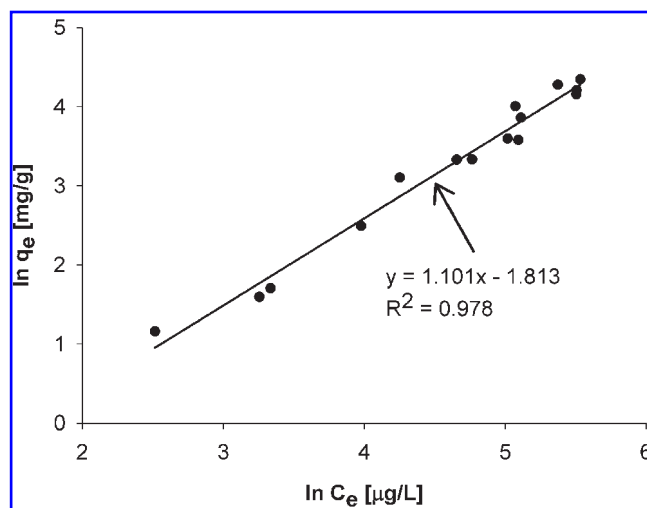


FIG. 5. Plot of estrone on DAY adsorption data to linearized Freundlich isotherm at 20°C.

bonded with oxygen atoms in the DAY structure, more or less anchoring it to the cavity (Yazaydin, 2007). The snapshot in Figure 6 shows very temporary and transient hydrogen bonds with three DAY oxygen atoms, which formed and broke very quickly. However, the estrone molecule was never observed to hop to an adjoining cavity in these simulations. Therefore, it is suspected that the relatively low loading was due to the isolation of estrone molecules to cavities near the external surfaces of the DAY crystals.

Molecular Dynamics simulations of estrone in silicalite-1 were also carried out (Yazaydin, 2007), but are not shown here. The observations in the silicalite structure were that estrone fit rather tightly in that pore system with little room for other estrone molecules, hydrogen bonding occurred frequently, and the estrone molecule seemed somewhat trapped in the pores. The estrone molecules did not move along the straight or zig-zag pores. The lower adsorption capacity of silicalite-1 observed in the experiments could be understood from these simulations to stem from the smaller pore volume in comparison to the larger DAY pore volumes.

Thermogravimetric analysis (TGA)

Thermogravimetric analysis was conducted to help understand the requirements for thermal regeneration of the saturated DAY, and to elucidate the behavior of estrone in the pores of the DAY with temperature increases. The results in Figure 7 show that the weight loss of pure estrone accelerated at about 300°C, i.e., slightly above its melting point of 255°C. A much slower weight loss continued to occur up to 600°C. A boiling point for estrone does not appear to have been reported, so this slower weight loss may have resulted from thermal decomposition in the nitrogen environment. Water in DAY started evaporating well below 100°C, and was essentially completely vaporized once the sample reached about 110°C. The carrier gas undoubtedly enhanced water vaporization at temperatures below its normal boiling point. The sample containing adsorbed estrone removed from water started losing weight as soon as heating began. Weight loss up to 75°C was most likely water adsorbed loosely on the external surface of the DAY, facilitated, as before, by the carrier gas. Subsequent weight loss due to estrone was revealed by a slow weight loss up to 600°C, as before.

Temperatures in the range of 250–400°C are typical for zeolite-catalyzed organic reactions, and the DAY sample is known to have small amounts of AlO_4^- T-sites, known to possess catalytic acidity that catalyzes some organic conversions. Thus, it is likely that the gradual weight loss noted here indicates that estrone experienced chemical degradation reactions in the DAY. This also would explain why weight loss of estrone in DAY began at lower temperatures than for the pure estrone.

Thus, using thermal regeneration to remove estrone from the DAY pores one would expect to have to raise the temperature to about 600°C for some period of time, an energy-intensive process. Incomplete removal of estrone from the DAY pores would be expected at lower temperatures.

Direct UV irradiation to destroy estrone in water

A 254 nm wavelength UV light (200 mJ/cm²) rapidly destroyed estrone in water as shown in Figure 8. A reduction of 89.5% was reached in 30 seconds. Further UV fluence did not degrade estrone to lower than 75 μg/L.

TABLE 3. COMPARISON OF FREUNDLICH CONSTANTS (C IN μg/L AND q IN mg/g) FOR ESTRONE ADSORPTION ONTO VARIOUS ACTIVATED CARBONS AND DAY

Adsorbent	K [(mg/g) · (L/μg) ^{1/n}]	1/n [unit-less]	R	Total specific pore volume [cm ³ /g]	Specific surface area [m ² /g]	Mean pore diameter [Å]	Reference
Activated carbon A-1	25.6	0.33	0.963	0.46	1038	17.7	(Fukuhara <i>et al.</i> , 2006)
Activated carbon A-2	73.5	0.40	0.996	0.839	1831	18.3	(Fukuhara <i>et al.</i> , 2006)
Activated carbon A-3	35.9	0.41	0.991	0.677	1514	17.9	(Fukuhara <i>et al.</i> , 2006)
Activated carbon B-3	47.2	0.51	0.998	1.149	1467	31.3	(Fukuhara <i>et al.</i> , 2006)
Activated carbon C-3	36.7	0.35	0.960	2.44	1187	24.4	(Fukuhara <i>et al.</i> , 2006)
DAY	0.163	1.10	0.989	0.38	692	<7.4	this work

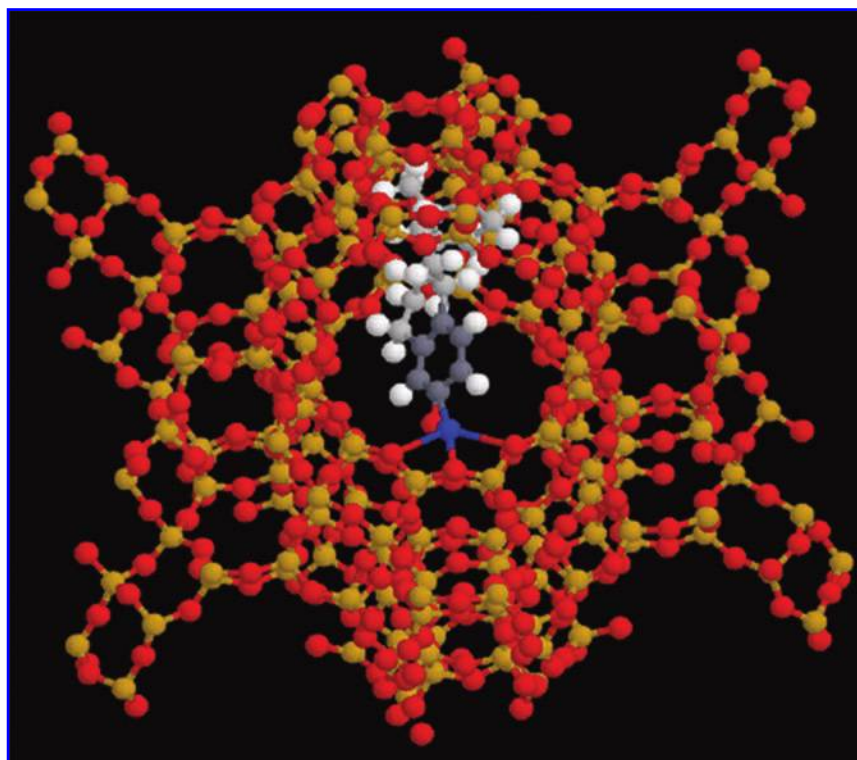


FIG. 6. Snapshot of estrone in a DAY cavity, based on Molecular Dynamics simulations (Yazaydin, 2007). The white atoms in the center cavity are the main hydrogen atoms of the estrone molecule. (Color image is available online at www.liebert-pub.com/ees)

UV irradiation may mitigate the estrogenic impact of estrogens (Ohko *et al.*, 2002; Liu and Liu, 2004). Ohko *et al.* (2002) concluded that the phenol moiety may be the origin of photocatalytic oxidation and they presumed that the estrogenic activities of the intermediate products lacking a phenol ring were negligible. Liu and Liu (2004) showed that photolysis of estrogens caused the breakage and oxidation of benzene rings to produce products containing carbonyl groups.

For comparison purposes, destruction of estrone was attempted with longer wavelength UV light. It was found that 365 nm UV light was not as effective at destroying estrone with only 10% destroyed in 6 min (360 mJ/cm^2). This observation is consistent with data presented by others. Liu and Liu found that long-wave light ($\lambda \geq 365 \text{ nm}$) was less effective than short-wave UV light ($\lambda = 254 \text{ nm}$) for photolysis of estrone in aqueous solutions (Liu and Liu, 2004). Rosenfeldt and Linden reported that bisphenol A, ethinyl estradiol, and

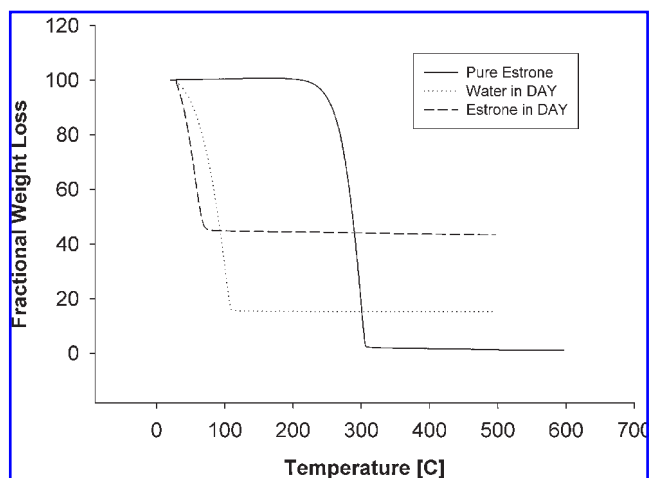


FIG. 7. Thermogravimetric analysis (TGA) results for pure estrone, DAY & water, and DAY & estrone.

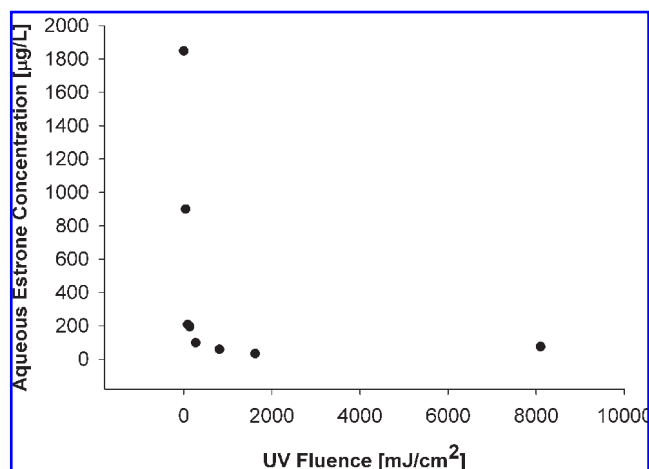


FIG. 8. Estrone degradation in aqueous solution with UV light irradiation ($\lambda = 254 \text{ nm}$).

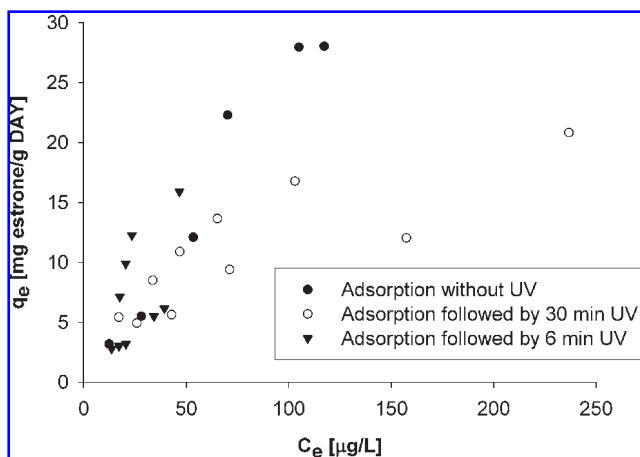


FIG. 9. Equilibrium capacity after adsorption/UV ($\lambda = 254$ nm) regeneration cycles.

estradiol only adsorbed UV radiation in the range of 200-300 nm (Rosenfeldt and Linden, 2004).

UV regeneration of estrone-saturated DAY

Irradiation with UV light at $\lambda = 254$ nm was used to regenerate the estrone-saturated DAY by mineralizing the entrapped estrone. A similar strategy was used to regenerate adsorbents containing chloroform and trichloroacetic acid in our previous work (Koryabkina *et al.*, 2007). Figure 9 shows adsorption equilibrium results for DAY regenerated using UV irradiated for 6 and 30 min. These data are the accumulation of nine cycles of adsorption, followed by regeneration with UV light. These results are compared to data from Figure 4, which represents DAY not previously exposed to estrone. While there is some scatter in the data for the regenerated DAY, the data suggests that UV light was successful in mineralizing estrone associated with the DAY pores. The small variations in the data are most likely due to small loss of the solid zeolite powder between cycles due to handling issues.

Conclusions

The effectiveness of hydrophobic zeolites for removing estrone from water was investigated in this work. It was found through equilibrium adsorption experiments that dealuminated zeolites Y (DAY) outperformed silicalite-1 and Centaur[®] activated carbon (CAC). And kinetic testing illustrated that adsorption of estrone onto DAY was much faster than onto CAC. An adsorption isotherm for adsorption of estrone to DAY was obtained and the Freundlich isotherm model fitted to the experimental data.

Experiments were conducted with direct UV irradiation for the potential regeneration of estrone-saturated DAY. Regeneration of DAY with direct UV was found to be successful, and has the potential to reduce the energy required for regeneration when compared to regeneration by heating to 600°C. By using combined adsorption followed by UV regeneration, the estrone was first concentrated in the DAY pores, and then UV mineralized the compound. If UV alone

is used to treat wastewater, it generally requires a high consumption of UV energy due to continuous contact with a large volume of water with low concentrations of contamination. The combined adsorption/UV process may have advantages in treatment as the regeneration step can be performed with higher (adsorbed) contaminant concentrations.

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Author Disclosure Statement

No competing interests exist.

References

- Adlercreutz, H., Fotsis, T., Bannwart, C., Hämäläinen, E., Bloigu, S. and Ollus, A. (1986). Urinary estrogen profile determination in young Finnish vegetarian and omnivorous woman. *Journal Steroid Biochemistry* 24, 289.
- Arcand-Hoy, L. D., Nimrod, A. C. and Benson, W. H. (1998). Endocrine-modulating substances in the environment: estrogenic effects of pharmaceutical products. *International Journal of Toxicology* 17, 139.
- Auriol, M., Filali-Meknassi, Y., Tyagi, R. D., Adams, C. D. and Surampalli, R. Y. (2006). Endocrine disrupting compounds removal from wastewater, a new challenge. *Process Biochemistry* 41, 525.
- Bevans, H. E., Goodbred, S. L., Miesner, J. F., Watkins, S. A., Gross, T. S., Denslow, N. D. and Schoeb, T. (1996). Synthetic organic compounds and carp endocrinology and histology in Las Vegas Wash and Las Vegas and Callville Bays of Lake Mead, Nevada, 1992 and 1995, US Geological Survey, *Water Resource Investigations Report* 96, 4266.
- Carpinteiro, J., Quintana, J. B., Rodriguez, I., Carro, A. M., Lorenzo, R. A. and Cela, R. (2004). Applicability of solid-phase microextraction followed by on-fiber silylation for the determination of estrogens in water samples by gas chromatography-tandem mass spectrometry. *Journal of Chromatography A* 1056, 179.
- Commission of the European Communities (1999). Communication from the Commission to the Council and the European Parliament; Community strategy for endocrine disruptors. Brussels, Commission of the European Communities.
- Cook, J. W., Dodds, E. C., Hewett, C. L. and Lawson, W. (1934). Estrogenic activity of some condensed ring compounds in relation to their other biological activities. *Proc. R. Soc. Lond.* B114, 272.
- Desbrow, C., Routledge, E. J., Brighty, G. C., Sumpter, J. P. and Waldock, M. (1998). Identification of estrogenic chemicals in STW effluent. 1. Chemical fractionation and in vitro biological screening. *Environmental Science and Technology* 32, 1549.

- Erdem-Senatar, A., Bergendahl, J., Giaya, A. and Thompson, R. W. (2004). Adsorption of methyl tertiary butyl ether on hydrophobic molecular sieves. *Environmental Engineering Science* 21, 722.
- Feng, X., Tu, J., Ding, S., Wu, F. and Deng, N. (2005). Photodegradation of 17 β -estradiol in water by UV-Vis/Fe(III)/H₂O₂ system. *Journal of Hazardous Materials* 127:129.
- Folmar, L. C., Denslow, N. D., Rao, V., Chow, M., Crain, D. A., Enblom, J., Marcino, J. and Guillette Jr., L. J. (1996). Vitellogenin induction and reduced serum testosterone concentrations in feral male carp (*Cyprinus carpio*) captured near a major metropolitan sewage treatment plant. *Environmental Health Perspective* 104, 1096.
- Fukuhara, T., Iwasaki, S., Kawashima, M., Shinohara, O. and Abe, I. (2006). Adsorbability of estrone and 17 β -estradiol in water onto activated carbon. *Water Research* 40, 241.
- Giaya, A. and Thompson, R. W. (2002). Single component gas phase adsorption and desorption studies using a tapered element oscillating microbalance. *Microporous Mesoporous Materials* 55, 265.
- Giaya, A., Thompson, R. W. and Denkewicz, J., R. (2000). Liquid and vapor phase adsorption of chlorinated volatile organic compounds on hydrophobic molecular sieves. *Microporous Mesoporous Materials* 40, 205.
- Harries, J. E., Sheahan, S. A., Jobling, S., Matthiessen, P., Neall, P., Routledge, E. J., Rycroft, R., Sumpter, J. P. and Tyler, T. (1996). A survey of estrogenic activity in United Kingdom inland waters. *Environmental Toxicology and Chemistry* 15, 1993.
- Hu, J. Y., Cheng, S., Aizawa, T., Terao, Y. and Kunikane, S. (2003). Products of aqueous chlorination of 17 β -estradiol and their estrogenic activities. *Environmental Science and Technology* 37, 5665.
- Jobling, S., Noylan, M., Tyler, C. R., Brightly, G. and Sumpter, J. P. (1998). Widespread sexual disruption in wild fish. *Environmental Science and Technology* 32, 2498.
- Johnson, A. C., Belfroid, A. and Di Corcia, A. (2000). Estimating steroid oestrogen inputs into activated sludge treatment works and observations on their removal from the effluent. *Science of the Total Environment* 256, 163.
- Johnson, A. C. and Williams, R. J. (2004). A model to estimate influent and effluent concentrations of estradiol, estrone, and ethinylestradiol at sewage treatment works. *Environmental Science and Technology* 38, 3649.
- Koryabkina, N., Bergendahl, J., Thompson, R. W. and Giaya, A. (2007). Adsorption of disinfection byproducts on hydrophobic zeolites with regeneration by advanced oxidation. *Microporous and Mesoporous Materials* 104, 77.
- Kramer, V. J., Miles-Richardson, S., Pierens, S. L. and Giesy, J. P. (1998). Reproductive impairment and induction of alkaline-labile phosphate, a biomarker of estrogen exposure, in fathead minnows (*Pimephales promelas*) exposed to waterborne 17 β -estradiol. *Aquatic Toxicology* 40, 335.
- Lai, K. M., Johnson, K. L., Scrimshaw, M. D. and Lester, J. N. (2000). Binding of waterborne steroid estrogens to solid phases in river and estuarine systems. *Environmental Science and Technology* 34, 3890.
- Liu, B. and Liu, X. (2004). Direct photolysis of estrogens in aqueous solutions. *Science of the Total Environment* 320, 269.
- Merenov, A. S., Nelson, A. and Abraham, M. A. (2000). Support effects of nickel on activated carbon as a catalyst for vapor phase methanol carbonylation. *Catalysis Today* 55, 91.
- Nakagawa, S., Kenmochi, Y., Tutumi, K., Tanaka, T. and Hirasawa, I. (2002). A study on the degradation of endocrine disruptors and dioxins by ozonation and advanced oxidation processes. *Journal of Chemical Engineering of Japan* 35, 840.
- Ohko, Y., Iuchi, K.-i., Niwa, C., Tatsuma, T., Nakashima, T. and Iguchi, T. (2002). 17 β -estradiol degradation by TiO₂ photocatalysis as a means of reducing estrogenic activity. *Environmental Science and Technology* 36, 4175.
- Panter, G. H., Thompson, R. S. and Sumpter, J. P. (1998). Adverse reproductive effects in male fathead minnows (*Pimephales promelas*) exposed to environmentally relevant concentrations of the natural oestrogens, oestradiol, and oestrone. *Aquatic Toxicology* 42, 243.
- Purdon, C. E., Hardiman, P. A., Bye, V. J., Eno, N. C., Tyler, C. R. and Sumpter, J. P. (1994). Estrogenic effects of effluents from sewage treatment works. *Chemical Ecology* 8,275.
- Rosenfeldt, E. J. and Linden, K. G. (2004). Degradation of endocrine disrupting chemicals bisphenol a, ethinyl estradiol, and estradiol during UV photolysis and advanced oxidation processes. *Environmental Science and Technology* 38, 5476.
- Routledge, E. J., Sheahan, D., Desbrow, C., Brightly, G. C., Waldock, M. and Sumpter, J. P. (1998). Identification of Estrogenic chemicals in STW effluent. 2. In vivo responses in trout and roach. *Environmental Science and Technology* 32,1559.
- Rudder, J. D., Van de Wiele, T., Dhooge, W., Comhaire, F. and Verstraete, W. (2004). Advanced water treatment with manganese oxide for the removal of 17 α -ethynylestradiol (EE2). *Water Research* 38, 184.
- Schueler, F. W. (1946). Sex-hormonal action and chemical constitution. *Science* 103, 221.
- Snyder, S. A., Keith, T. L., Verbrugge, D. A., Snyder, E. M., Gross, T. S., Kannan, K. and Giesy, J. P. (1999). Analytical methods for detection of selected estrogenic compounds in aqueous mixtures. *Environmental Science and Technology* 33, 2814.
- Snyder, S. A., Villeneuve, D. L., Snyder, E. M. and Giesy, J. P. (2001). Identification and quantification of estrogen receptor agonists in wastewater effluents. *Environmental Science and Technology* 35, 3620.
- Tanaka, H., Yakou, Y., Takahashi, A., Higashitani, T. and Komori, K. (2001). Comparison between estrogenicities estimated from DNA recombinant yeast assay and from chemical analyses of endocrine disruptors during sewage treatment. *Water Science and Technology* 43, 125.
- Ternes, T., Stüber, J., Herrmann, N., McDowell, D., Ried, A., Kampmann, M. and Teiser, B. (2003). Ozonation: A tool for removal of pharmaceuticals, contrast media and musk fragrances from wastewater? *Water Research* 37, 1976.
- Thorpe, K. L., Cummings, R. I., Hutchinson, T. H., Scholze, M., Brightly, G., Sumpter, J. P. and Tyler, C. R. (2003). relative potencies and combination effects of steroidal estrogens in fish. *Environmental Science and Technology* 37, 1142.
- Walker, B. S. and Jarney, J. C. (1930). Estrogenic substances. II. Analysis of plant sources. *Endocrinology* 14,389.
- Wilcox, J. and Vallieres, P. (2006). Personal communication. Worcester.
- Yazaydin, A. O. (2007). Unpublished results from Ph.D. dissertation research. Chemical Engineering. Worcester, MA, Worcester Polytechnic Institute.
- Yoon, Y., Westerhoff, P., Snyder, S. A. and Wert, E. C. (2006). Nanofiltration and ultrafiltration of endocrine disrupting compounds, pharmaceuticals and personal care products. *Journal of Membrane Science* 270, 88.
- Zhao, X. S., Ma, Q. and Lu, G. Q. M. (1998). VOC Removal: Comparison of MCM-41 with hydrophobic zeolites and activated carbon. *Energy and Fuels* 12, 1051.

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