Application of Fly Ash as an Adsorbent for Estradiol in Animal Waste
Pauline Norris* ^a, Stephanie Hagan ^a, Martin Cohron ^b, Houying Zhao ^b,
Wei-Ping Pan ^b

- a. Advanced Materials Institute, Western Kentucky University. 2413
Nashville Rd. Bowling Green KY, 42101 USA
- b. Institute for Combustion Science and Environmental Technology,
Western Kentucky University 2413 Nashville Rd. Bowling Green
KY, 42101 USA

*Corresponding Author's Email Address: ami@wku.edu

Abstract

The contamination of agricultural ground with estrogen compounds through application of animal wastes is a present concern. At the same time, current uses for waste fly ash having high carbon content are limited. To help mitigate these problems, we examine using waste fly ash as a useful adsorbent for Estradiol in pig waste digests. In this study, Estradiol was added to vials containing water and fly ash from several different power plants. After an extraction process, the amount of Estradiol in the water was measured. Commercial activated carbon was also used for comparison purposes. Vials containing varying concentrations of Estradiol and no trapping material were used as a control. The results from this study indicate that fly ash can be used as a trapping material for Estradiol in water, but that commercially available activated carbon can trap about an order of magnitude more Estradiol than the fly ash and that the effects of the fly ash matrix can both inhibit and promote the solvation of Estradiol into water depending possibly upon pH and cation concentration effects. In addition, preliminary extraction studies using pig waste digest indicate that fly ash can be used as adsorbent for Estradiol present in pig waste.

Keywords: Fly Ash, Estradiol, Adsorption, Pig Waste

1. Introduction

This study examines the use of fly ash as an adsorbing media for Estradiol. The research presented here is intended to provide preliminary information towards the application of fly ash in the removal/capture of Estradiol in animal waste. The presence of Estrogen compounds in animal wastes has been an area of concern for some time due to the associated health risks. Estradiol is a known endocrine disrupting compound (EDC). Estrogen compounds in the environment can alter the normal functions of the endocrine systems of aquatic fauna, other wildlife and humans causing abnormalities in sexual development from exposure to even low concentrations. These effects are well documented and are summarized in a review by Tijani et al. (2013). Several studies have focused on measuring the quantities of Estrogen compounds in pig, cow and chicken waste. A study by Liu et al. (2012) measured the concentrations of steroid compounds in a typical swine farm and found detectable levels of Estradiol, among other steroids, in the animal waste as well as nearby water sources and fields. The research presented in this study concluded that typical lagoon systems do not effectively remove steroids. Raman et al. (2004) measured estrogen compound concentrations in dairy and swine waste and related them to macronutrient mass to clarify how much estrogen would ultimately be added to agricultural land as a result of trying to meet specific fertilization requirements. Additional research by Givens et al. (2012), measures concentrations of estrogen compounds in chicken manure at ppm concentrations. Some recent studies have focused on determining other factors, such as the degradation of estrogen compounds under simulated conditions and the effects of estrogen compounds on microbial activity in

soil. Hakk et al. (2014) reported that Estradiol would oxidize to estrone and adsorb to the solid portions of waste under anaerobic digestion conditions, resulting in a large decrease in estrogenicity. Another study examined Estradiol in poultry wastes under composting conditions over time and determined that composting could reduce, but not completely eliminate Estradiol (Hakk et al. 2005). Zhang et al. (2014) reported degradation of Estradiol and estrone within hours in soil with microbial activity and also reported stimulation of microbial activity by the presence of the estrogen compounds.

Despite research that shows degradation of estrogen compounds over time and under certain conditions, they are still detected in aquatic environments and can be harmful at low concentrations. Additional measures, such as the capture and removal or sequestration of estrogen compounds are needed to help further decrease the amount of estrogen compounds that ultimately make it into the environment. Some studies have focused on estrogen removal using mineral surfaces or activated carbon sorbents. A study by Shareef et al. (2006) reported successful adsorption of estrogen compounds onto montmorillonite as well as limited ability to desorb the estrogens from this material. This characteristic, of course, would be preferable when used for sequestration purposes. A study by Redding et al. (2009) examined lake water spiked with endocrine disrupting compounds in test columns filled with modified activated carbon demonstrating the material could adsorb to these compounds and determining the breakthrough point.

Considering the present research examples demonstrating estrogen adsorption to mineral surfaces and activated carbon, it follows that the unburned carbon, iron and alkaline minerals present in fly ash may

provide excellent adsorption sites for estrogen compounds from animal waste.

Fly ash has been a material of interest for removing unwanted organic and inorganic contaminants from liquid streams for some time now. Examples of research using fly ash to remove dyes (Wang et al., 2005), herbicides (Neera, 2009), and heavy metals (Soco et al., 2013) are available in literature. Fly ash is a relatively cheap and extremely abundant coal combustion by-product (CCB) and consists mostly of the unburned, mineral portion of coal. A smaller portion of fly ash includes unburned carbon particles resulting from incomplete combustion of the coal material. This carbon can be used to remove selected analytes from liquid or gas streams, comparable to present uses for commercially produced activated carbon. The amount of unburned carbon in fly ash will vary depending upon the type of coal used, as well as the efficiency of the supplying power plant. This unburned carbon portion is undesirable when using fly ash in most applications; thus, it would be beneficial if this unburned carbon could be easily removed from fly ash and applied towards a different use.

Although the use of activated carbon as an absorbent is nothing new, unburned carbon obtained from and mixed in with fly ash is a far different matrix than commercially available “clean” activated carbon. Up to this point, there have been very few studies focused on the adsorptive capacities of unburned carbon in fly ash specifically for estrogen compounds. The goals for this study are to 1) confirm that the unburned carbon in fly ash can be used as an absorbent for Estradiol, 2) compare the capturing capacity with commercially available activated carbon, 3) compare fly ash capturing capacity from 5 different power plants, 4) Evaluate and discuss the effects of the fly ash matrix on Estradiol

solubility in water and 5) Tentatively evaluate the capturing ability of the fly ash when used as an adsorbent in a typical pig waste digest matrix. Estradiol is slightly soluble in water. Methanol can be added to increase solubility. For this study, it is assumed that for a mixture of Estradiol and fly ash in a 5% methanol in water solution, the Estradiol will be retained by the active carbon in the fly ash and will be absent from the water up until the point that the capturing capacity of the active carbon has been exceeded. At this point, the Estradiol will be detectable in the sample water. The concentration of Estradiol in the water will be dependent on the spiking concentration and solubility limitations. Using this approach, it should be possible to determine the capturing capacity of the fly ash by measuring the concentration of Estradiol present in the water. Even if the unburned carbon in fly ash can be used as an adsorbent, it may or may not be the best option when compared to commercially available activated carbon. Although commercially available activated carbon is more expensive, it also should have a much greater capturing capacity. In this study, two commercially available activated carbon materials were evaluated using the same spiking and extraction procedures used for the samples. If the unburned carbon in fly ash is found to be a suitable alternative to commercially available activated carbon, it is still very likely that some fly ash obtained from specific power plants, burning different kinds of coal under different conditions might be preferable over other types of fly ash. In this study, we look at fly ash from 5 different power plants and compare capturing capacity, Estradiol solubility and agglomerating characteristics. Finally, even if spiked Estradiol, obtained as a pure standard, is captured by fly ash in a simple water and fly ash extraction set up, that does not

necessarily conclude that the process would work in a practical application towards the removal of Estradiol in pig waste. Factors such as the pig waste matrix containing additional organics that might compete for adsorption sites and the possibility of the Estradiol already being bound to suspended solids present in the waste could prevent adsorption. In this study, the Estradiol is extracted from the pig waste to measure the initial Estradiol concentration. Separate portions of waste are then subjected to a fly ash extraction. The Estradiol is then extracted from these samples to determine the difference in Estradiol concentration from the initial concentration in the waste, which should represent the amount captured by the fly ash.

2. Material and methods

2.1 Description and Preparation of the Fly Ash

Fly ash was obtained from 5 different power plants. Descriptions of the power plants are provided below.

- Power plant A burns bituminous coal, with a high sulfur and volatile matter content and low moisture content
- Power Plant B burns a lignite coal, with a high moisture and volatile matter content and low sulfur content.
- Power Plant C burns bituminous coal with high volatile matter content and fairly low sulfur content.
- Power Plant D burns a low quality bituminous coal with a high sulfur and high volatile matter content
- Power Plant E burns a good quality bituminous coal with low volatile matter content, low moisture content and fairly low sulfur content. At the time of fly ash collection, the supplying power

plant was also injecting additives for mercury control. The exact nature of the additives was proprietary.

The fly ash from the power plants was separated using a sieve—greater than 75 μm , between 75 μm and 53 μm , between 53 μm and 45 μm , and less than 45 μm . The greater than 75 μm size fly ash was used for the Estradiol capture tests because the unburned carbon content was found to be largest in the larger particle size fly ash, as measured by a Leco TruSpec CHN analyzer.

The fly ash was not heat, steam or acid treated in any way prior to the Estradiol capture tests.

2.2 Description of the Estradiol Capture Testing Conditions

Two milliliter glass sample vials were filled with 400 milligrams of fly ash, varying weights of solid β -Estradiol (purchased from Sigma Aldrich), 950 milliliters of Optima LCMS grade water (purchased from Fisher) and 50 milliliters of Optima LCMS grade methanol (also purchased from Fisher). The sample vials were sonicated for 1 hour and then rotated for 18 hours in an end over end fashion using an ATR Model: RKVSD rotation device. The samples were allowed to settle and then the liquid portion was removed and filtered using a disposable syringe filter. For mass balance purposes, the solid fraction was removed from the vials and allowed to air dry overnight in a fume hood. Approximately 40 milligrams of the air-dried fly ash was removed and the Estradiol was extracted with 500 microliters of dichloromethane and 500 microliters of methanol using a sonicator. The dichloromethane/methanol solutions were filtered and diluted 1:100 and analyzed in the same manner as the water samples.

2.3 Description of the Commercially Available Activated Carbon

Two different types of commercially available activated carbon were tested in the same manner as the fly ash samples, one was a granular

activated carbon made from bituminous coal (GAC 250, hereafter referred to as GAC) purchased from Norit and designed for water treatment plant applications and the other was a powdered activated carbon made from lignite coal (Darco Hg-LH, hereafter referred to as PAC) also purchased from Norit.

The amount of unburned carbon in fly ash represents only a small fraction of the total 400 milligrams of sample used for the capturing tests; therefore, the amount of commercially purchased activated carbon used for the comparison test was decreased to 40 milligrams.

2.4 Description of the Pig Waste

Heritage Farms in Bowling Green, Kentucky was asked to provide a swine effluent sample that would be ready to pump onto soil for crop preparation. The system used at this location is a flushing type slatted floor system with two stages of holding ponds. The design of the system is suitable for 1500 female animals. Stage one is a solids collection area of approximately 1.5 million gallons storage and is lined with Hypalon (Hypalon is a trademark for chlorosulfonated polyethylene (CSPE) synthetic rubber (CSM) noted for its resistance to chemicals, temperature extremes, and ultraviolet light. It was a product of DuPont Performance Elastomers, a subsidiary of DuPont). The liner is also covered with 1.5 feet of clay soil. Stage one effluent transfers to stage two by way of a top of the berm pipe that only allows non solid material to flow into the second stage holding area. The flush system for the barns is supplied by the second stage holding area that is also lined and has a storage size of 7 million gallons. The flushing liquid is then returned to stage one. Material that is put onto fields is pumped from the second stage through underground pipe to each of the field areas. This is where the research samples were obtained.

2.5 Description of Pig Waste Extraction Conditions

The pig waste was centrifuged at 4000 RPM for 25 minutes to remove as much of the suspended solids as possible. This was necessary so that the liquid could be filtered through the extraction disk without plugging the filter. To determine the initial concentration of Estradiol in the pig waste, approximately 200 ml of the liquid pig waste was pulled, under vacuum, through a solid phase extraction disk coated with C18 absorbing material. The disk was then eluted with a mixture of dichloromethane and methanol. The solvent was evaporated to dryness and brought back up to 2 ml total volume with a 50/50 mixture of methanol and water prior to analysis. For the fly ash extraction tests, 200 ml of pig waste and 20 grams of fly ash were added to a 250 ml centrifuge container and gently agitated overnight. Following the extraction, the samples were centrifuged and extracted with a solid phased extraction disk as described previously for the initial sample.

2.6 Instrumental Analysis Conditions

Standards and samples were analyzed with an Agilent Ion-Trap LC-MS, using 0.02% ammonium hydroxide in water and 0.02% ammonium hydroxide in methanol as the mobile phase according to a modified EPA Method 539. The fly ash matrix added too much extra noise to run the instrument in full scan. The instrument was operated in MSMS mode with the ion 271 selected and the collision energy set low enough not to induce fragmentation. A stock calibration solution was prepared by spiking Estradiol into methanol and making subsequent dilutions of the stock solution into water.

3. Results

3.1 Carbon Content

The percentage of carbon in the sieved fly ash samples was 7.8%, 2.3%, 45.8%, 7.4% and 11.25% for power plants A, B, C, D & E, respectively. Although unusually high, the carbon percentage for power plant C is correct; removal of the smaller particle size fly ash concentrated the carbon particles (which were larger in size) in the greater than 75 μm fraction of the ash.

3.2 Fly Ash Surface Area

The surface area was analyzed on an ASAP 2020 apparatus (Micromeritics, USA). The N₂ adsorption/desorption isotherms were obtained at -196 °C. The apparent surface area of the chars was evaluated by applying the Brunauer–Emmett–Teller (BET) equation in the relative pressure range of 0.05-0.30 (P/P₀). Power Plant C had the largest surface area with a value of 8.77 m²/g, then 6.29, 5.05 and 2.12 m²/g for plants A, B and E, respectively. Power plant D had the smallest surface area with a value of 1.37 m²/g.

3.3 Control Sample

In this study, a control (a series of vials spiked with increasing Estradiol concentrations in a 5% methanol in water mixture with no fly ash added) showed that under the conditions of the test, with no matrix interferences from the fly ash, Estradiol should be soluble in the methanol/water mixture at approximately 4 $\mu\text{g/ml}$.

3.4 Suitability of the Fly Ash as an Adsorbent

Figures 1 and 2 show the concentrations of Estradiol in the water fractions as a function of the μg of Estradiol added for fly ash from power plants A-D. The graphs clearly show that for each power plant, as the spiking concentration is increased, there is a point at which the unburned carbon in the fly ash fails to capture the available Estradiol and part of the Estradiol is dissolved into the water fraction. Therefore, the unburned

carbon in fly ash can be used as an adsorbent for Estradiol. The point at which the Estradiol was detected in the water fraction appeared to be at 200-400 µg of Estradiol spiked. Power Plant E, shown in Figure 3, did not show the same trend that was observed with the other power plants. The presence of the fly ash did seem to inhibit the solubility of the Estradiol into the water fraction, as evidenced by the fact that the concentration of Estradiol in the water fraction is less than what was observed for the control. However, this effect makes it difficult to determine the carbon trapping capacity for the fly ash from this power plant.

3.5 Comparisons between Fly Ash and Commercially Available Activated Carbon

Figure 4 shows the concentrations of Estradiol in the water fractions as a function of the µg of Estradiol added for both commercially available activated carbon materials. The graphs indicate that commercially available activated carbon is capable of capturing approximately 10 times as much Estradiol as the activated carbon in fly ash.

3.6 Effects of the Fly Ash Matrix

Figure 2 also demonstrates the effect of the fly ash matrix on the solubility of Estradiol in water; the concentration of Estradiol in the water is elevated past what was seen in the control samples. This indicates that some aspect of the fly ash matrix can increase the solubility of the Estradiol in water. The water samples for each power plant were tested for pH and cations concentrations to evaluate if there was any correlation.

The pH values for Power Plants A-E were 11.57, 10.55, 9.67, 11.65 and 6.15, respectively. The low pH observed for Power Plant E is likely related to the injection of additives. At the time of fly ash collection,

Power Plant E was injecting additives for mercury control studies.

Estradiol does not readily give up the hydrogen bound to the oxygen on the phenol ring to form an ion. A high pH value promotes the ion form of Estradiol. The pH values shown here indicate that the phenolate ion would be more readily available in solutions from power plants A-D. Cation chromatography also indicated increased sodium and potassium ion concentrations in the B & D power plants, see Figure 5, in comparison with the other power plants. The water extract from power plant B had a combined sodium and potassium concentration of 44.4 µg/ml. The water extract from power plant D had a combined sodium and potassium concentration of 60.2 µg/ml.

3.7 Agglomerating Characteristics

Only half of the water from the extraction test for power plant C was recoverable; the rest was soaked up by the fly ash, resulting in the particles agglomerating together. This would be undesirable in an application where the objective would be to pass water through the material, although might be beneficial if applied with agricultural wastes in situations where retaining moisture was ideal. The fly ash from the other power plants did not seem to have this issue.

3.8 Mass Balance Calculations

Finally, for determining a mass balance, some fly ash samples were selected for additional extraction by a 50/50 mixture of dichloromethane and methanol. For the majority of extractions, Estradiol recoveries were between 80-110% of the expected value.

3.9 Removal of Estradiol from Pig Waste

The initial Estradiol concentration in the pig waste was 2.5 ng/ml. The exact Estradiol concentration in the waste after the fly ash extraction was difficult to measure because the peaks were mostly buried with baseline

noise, but the concentrations were definitely less than 1 ng/ml. A chromatogram of the control sample, showing the area related to the initial Estradiol concentration in the pig waste with overlay chromatograms of the fly ash extracted pig waste is provided in Figure 6. Clearly, the fly ash was able to remove a very significant portion of the Estradiol in the pig waste. The fly ash from Power Plant E was not included in the pig waste extraction test due to the poor capturing ability that was observed in the initial tests

4. Discussion

This study demonstrates that there is a detectable portion of Estradiol present in liquid pig waste digests that are routinely applied to agricultural lands and that this portion of Estradiol can be effectively removed through extraction with fly ash. This study also provides useful information as to how much fly ash would be needed to capture a given concentration of Estradiol; although, ultimately, this would be a function of how much time the waste spent in contact with the fly ash and the specific mixing conditions. For this study, components were well mixed and extractions were allowed to proceed overnight, assuming that extraction would be complete in that time period. Subsequent tests using extraction conditions that could be duplicated in an actual pig farm setting would be useful. This study also determined that the effects of the fly ash matrix could either promote Estradiol solubility or decrease the fly ash capturing ability. Fly ash materials obtained during injection of some additives might not effectively capture Estradiol due to adsorption sites already being consumed, or the altered pH might decrease Estradiol solubility in water. Some of the fly ash materials clearly promoted Estradiol solubility in water, which would encourage movement of the compound through the environment. This study indicates that care

should be taken when selecting fly ash for its capturing ability and that not all fly ashes are equally applicable for this purpose.

5. Conclusions

The results of this study indicate that fly ash can be used as an adsorbent for unwanted Estradiol present in contaminated water, but that the capturing capacity of the fly ash is much less than what is observed for commercially purchased activated carbon. This could simply be a matter of the active sites on the fly ash already being consumed or a function of the additional pH changes and cations present in the fly ash matrix that promote or inhibit Estradiol solubility in water. It is difficult to estimate with certainty the economic benefit of using fly ash instead of activated carbon. The cost of commercially activated carbon will vary depending on the type, supplier and the amount purchased and would be expected to increase over time as the need for activated carbon increases. In addition, it is unclear at this point if the fly ash utilized in the pig waste clean-up could be regenerated and reused. If the material could not be regenerated and reused, then the cost of disposing of the waste fly ash after clean-up would have to be considered. Further research might also discover additional co-benefits to using fly ash as a capturing media. Fly ash has the potential to increase the pH of soils and possibly contribute valuable minerals to the soil.

Although results from this study show that fly ash can be applied towards removing Estradiol in pig waste digests, ultimately further research would have to be done to determine the overall benefits and the potential risks before this strategy could be put into practice. In addition to valuable minerals such as calcium, fly ash also contains various hazardous elements. Before fly ash could be used as a capturing media, testing

would have to conclude that the potential for the hazardous elements entering the water supply and/or being absorbed by plants was slight.

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Figure 1. Estradiol Conc. in Spiked Water Extracted With Power Plant A and Power Plant C Fly Ash

Figure 2. Estradiol Conc. in Spiked Water Extracted With Power Plant B and Power Plant D Fly Ash

Figure 3. Estradiol Conc. in Spiked Water Extracted With Power Plant E Fly Ash

Figure 4. Estradiol Conc. in Spiked Water Extracted With GAC and PAC

Figure 5. Cation Chromatograms from Water Spiked with Fly Ash (Power Plant A is in blue, Power Plant B is in green, Power plant C is in pink, Power Plant D is in brown and Power Plant E is in black)

Figure 6. Pig Waste Extraction Chromatograms (Pig Waste Control is in Red, Power Plant A is in blue, Power Plant B is in green, Power Plant C is in pink, Power Plant D is in brown)

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