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Poultry manure as raw material for mercury adsorbents in gas applications

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Primary Audience: Agricultural Engineers, Poultry Managers, Researchers

SUMMARY

The quantity of poultry manure generated each year is large, and technologies that take advantage of the material should be explored. At the same time, increased emphasis on the reduction of mercury emissions from coal-fired electric power plants has resulted in environmental regulations that may, in the future, require application of activated carbons as mercury sorbents. The sorbents could be injected into the flue gas stream, where they could adsorb the mercury. The sorbents (now containing mercury) would be removed via filtration or other means from the flue gas. Our preliminary work has demonstrated that activated carbon made from poultry manure can adsorb mercury from air with good efficiency. In laboratory experiments, an activated carbon made from turkey cake manure removed the majority of elemental mercury from a hot air stream. Other activated carbons made from chicken and turkey litter manure were also efficient. In general, unwashed activated carbons made from poultry manure were more efficient in removing mercury than their acid-washed counterparts. The results suggest that the adsorption of mercury was mainly due to chemisorption on the surface of the carbon. Other potential uses for the activated carbons are the removal of mercury from air and natural gas.

Key words: activated carbon, poultry manure, mercury adsorption, gas application

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DESCRIPTION OF PROBLEM

In this manuscript, we describe the results of studies focusing on a technology that converts poultry manure to an activated carbon that can be used for removal of mercury from gas streams. Activated carbon can be produced from a variety of carbonaceous materials, such as coal and wood, and it has been suggested that coals with higher sulfur content may be better raw materials for the activated carbon targeting mercury uptake [1]. Poultry manure contains 0.15 to 0.6% sulfur on a wet basis [2] and may, for that purpose, serve as a potential raw material for an activated carbon. Based on preliminary experiments, the approach of making sorbents from poultry manure for mercury removal may be feasible [3, 4].

Approximately 8.9 billion broiler chickens and 262 million turkeys were raised in the United States in 2007 (Table 1), and the demand continues to increase [5]. As a result of raising these birds, the poultry industry produces a significant amount of manure in the form of cake and litter. Cake refers to the scraping of the top layer of bedding that occurs after removal of a flock, and litter refers to manure when the cake and the rest of the bedding material are removed all together.

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Table 1. Poultry meat and manure production data

Item	Broiler chicken	Turkey
Average size at slaughter, kg per live bird [5]	2.51	12.84
Annual production, no. of 1,000 birds [5]	8,898,000	261,960
Annual production, metric tons (t) of live birds [5]	22,320,800	3,569,500
Cake production, kg per kg of live birds sold [2]	0.18	0.30
Litter production, kg per kg of live birds sold [2]	0.56	0.91
Annual cake production, 1,000 t	4,018	1,071
Annual litter production, 1,000 t	12,500	3,248

Because the bedding material contains sawdust, wood chips, peanut shells, or other organic material, the litter is usually higher in organic (cellulosic) matter.

It has been estimated, based on the manure generated by poultry [2], that approximately 4 million metric tons (t) of broiler cake and 12.5 million t of broiler litter are produced every year (Table 1). In the case of turkey production, 1 and 3.2 million t of turkey cake and litter, respectively, are produced annually. Traditionally, manure waste from the chicken and turkey industry has been used for its value as a fertilizer because of the relative high content of potassium, phosphorous, and nitrogen. However, poultry litter usually contains more phosphorous than is required by most crops, suggesting that some phosphorous may wash away and pollute nearby rivers and lakes [2]. Additionally, the spreading of poultry manure is not without possible negative effects in the form of nitrate contamination [6], which is why other disposal options such as composting, anaerobic digestion, or direct combustion have been considered as alternatives [7]. The production of high-value products from manure has great potential, and our research group has shown that activated carbons made from poultry manure are very capable of removing metal ions from laboratory-prepared aqueous solutions [8, 9].

There is a need to remove mercury from anthropogenic sources. Regulation of mercury from coal-fired power plants via the Canada-Wide Standards (in Canada) and the Clean Air Mercury Rule (in the United States) is under consideration. The Clean Air Mercury Rule went into effect in 2005, and it consists of a trading program that would set a maximum countrywide cap for mercury emissions from power plants. Current emissions have been estimated as 43.5 t of mercury per year [10], and the annual cap will be set to 34.5 t by 2010 and to 13.6 t by 2018 [11]. The Clean Air Mercury Rule was struck down in the District of Columbia Circuit Court of Appeals [12], but the US Department of Justice notified the court that the mercury from power plants would instead be regulated under the Clean Air Act, Section 112 (42 U.S.C. 7412) [13].

The existing pollution control devices on electric power plant boilers that target nitrogen and sulfur oxides and particulate matters also control mercury to some extent [14]. Their effectiveness is often influenced by the type of coal processed, fly ash properties, and gas treatment configurations. The use of activated carbon for the purpose of extracting mercury compounds from gases, including flue gases, is well documented [1, 15, 16], and activated carbon injection into the flue gas to enhance the sorption is perhaps the most promising approach to control mercury emissions when existing particulate removal systems are in place. The concentration of mercury in the flue gas varies but is in the range of 5 to 20 $\mu g/m^3$ of gas [15, 16].

Other fossil fuels contain mercury as well. Natural gas contains mercury in the range of 1 to 200 $\mu g/m^3$ of gas [17] and the concentration will vary depending on well location and age of the well, and has even shown oscillating changes over time [18]. Air emission of mercury from natural gas burning is minor [19] because care is taken to remove mercury from the natural gas to protect aluminum equipment and prevent material failure [20]. Many of the natural gas mercury removal systems that are used are in the form of an inactive support material (e.g., carbon) doped with sulfur or iodine compounds [19] but there is potential for the use of other sorbents.

Some of the chlorine in the nation is produced in chlor-alkali plants using mercury cells. Although many chlorine plants have been con-

verted to alternative technologies, the remaining plants are expected to release between 4.5 and 5.9 t of mercury per year until at least 2020 [11]. The air emissions mainly occur from the cell building, and in one study it was determined that the mercury concentration in the roof exhaust from this type of building was between 7.3 and 73 μg/m^3 of air, with an average of 24 μg/m^3 [21]. To estimate the feasibility of using activated carbons made from poultry manure as sorbents for gaseous mercury capture for a variety of applications, we conducted our studies using mercury-spiked air [22].

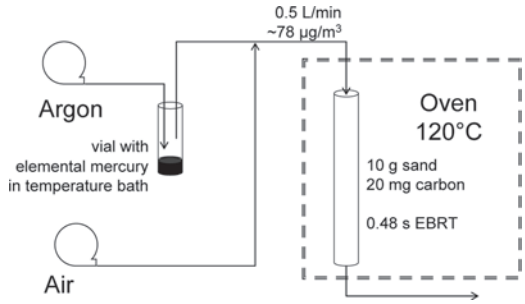

Figure 1. Experimental setup used for mercury adsorption testing. The empty bed residence time (EBRT) was calculated from the volume of the column divided by the gas flow rate.

MATERIALS AND METHODS

Activated Carbon Production

Commercial activated carbon used in previous mercury removal studies [3] was compared with activated carbons developed from various poultry manures. The commercial carbon was Norit Darco Hg [23]; this carbon was previously named Darco FGD [14] and is a powdered (<45-μm) activated carbon made from lignite coal. The experimental poultry waste-based activated carbons were made from chicken (broiler) and turkey manures.

The manure types were obtained as described previously [9]; briefly, chicken and turkey manures were collected as 2 fractions: litter and cake. The dried manure samples were milled to a uniform size, pelletized, and made into activated carbons by heating to 700°C for 1 h under nitrogen atmosphere and then activated via steam for 45 min at 800°C, with water being supplied into the furnace at 3 mL/min. The activated carbons were left unwashed or were washed with 0.1 *M* HCl and rinsed with water. The experimental carbons were ground and sized to less than 45 μm in particle size. Details of the pyrolysis and activation protocols were reported previously by Lima and Marshall [8, 9].

Surface Area Measurements

The carbons were conditioned under vacuum at 200°C, and surface area measurements were obtained from nitrogen adsorption isotherms at –196°C by using a surface area analyzer [24]. Specific surface areas were taken from the adsorption isotherms by using the Brunauer-Emmett-Teller (**BET**) equation [25]. The micropore areas (<2-nm-diameter pores) were calculated using t-plots derived from the Nova 2000 software [26]. Similarly, with the Nova 2000 software, the mesopore areas (2- to 50-nm-diameter pores) were calculated using the density functional theory [27].

Experimental Setup for Mercury Sorption

The studies were conducted using 20 mg of powdered activated carbon mixed with 10 g of purified sand [28] (dried for 1.5 h at 150°C). The sand and carbon mixture was placed in a vertical column (14 mm i.d. × 35 mm height). The sand-carbon rested on a section of glass beads (acid washed, nominal 1 mm in diameter) supported by silanized glass wool. This type of study has been used in the past for evaluation of activated carbons in flue gas applications [15, 16]. The column was placed in an oven [29], which was held at 120°C for the entire experiment. All tubing to and from the column was made from Teflon, except for very short pieces of silicone tubing where unions were needed. The gas was preheated before entering the column by passing it through a long loop of Teflon tubing in the oven.

The gas passing through the column consisted of air, argon, and elemental mercury, and it was prepared as follows: a small stream of argon (1.47 mL/min at 1 atm, 21°C) was purged through the headspace of a vial containing mercury (kept in a constant-temperature water bath) and was then combined with a larger stream of filtered air (0.5 L/min at 1 atm, 21°C) before en-

Table 2. Summary of surface area analysis results

Activated carbon (AC)	BET[1] surface area, m^2/g	Micropore[2] surface area, m^2/g	Micropore volume, mL/g	Mesopore[3] surface area, m^2/g
Norit Darco Hg	480	238	0.112	61
Chicken cake AC, unwashed	83	65	0.030	12
Chicken cake AC, washed	246	179	0.083	25
Chicken litter AC, unwashed	262	179	0.083	40
Chicken litter AC, washed	452	323	0.151	58
Turkey cake AC, unwashed	174	138	0.060	14
Turkey cake AC, washed	343	262	0.124	20
Turkey litter AC, unwashed	224	174	0.084	11
Turkey litter AC, washed	378	330	0.159	24

[1]Brunauer-Emmett-Teller [25].

[2]Micropores were defined as having a diameter of less than 2 nm.

[3]Mesopores were defined as having a diameter of 2 to 50 nm.

tering the column. The gas flow rates were controlled with mass flow controllers [30] and the flows were equilibrated for at least 2 h before they were diverted to the column. The levels of mercury in the gas averaged 78 $\mu g/m^3$ of mercury and remained constant throughout an experiment. The empty bed residence time, calculated as empty bed volume divided by volumetric gas flow (at 120°C), was 0.48 s in all experiments. The experimental setup is shown in Figure 1.

Mercury Analysis

The concentration of mercury in the gas was determined by gold amalgamation and atomic fluorescence detection [31]. In this procedure, a known amount of gas (5 mL from the inlet or outlet of the column) was injected with a syringe into an argon gas stream that was passed over a short column packed with gold-coated sand. The column was then heated and the adsorbed mercury was released over a short time interval into an argon gas stream that was passed through the detector. Calibration of the procedure was performed by injecting a known volume (100 µL at a known temperature) of air saturated with elemental mercury.

RESULTS AND DISCUSSION

The BET specific surface area was measured to be between 83 and 480 m^2/g of carbon (Table 2), with the commercial carbon having the highest surface area. Unwashed carbons had less surface area compared with their washed counterparts. In general, activated carbons made from litter manure had a greater BET surface area than carbons made from cake manure. The majority of the surface area was found in the micropores of the experimental carbons, and only a small fraction was attributed to mesopores. In most cases, the extent of both BET surface area and the micropore volume exceeded that found by Cui et al. [4], who made activated carbon from chicken waste. Cui et al. [4] reported a surface area of 164.2 m^2/g and a total pore volume of 0.043 mL/g for activated carbon made from chicken waste. These values are similar to our unwashed activated carbons made from chicken and turkey cake manure. As noted in Table 2, the values for surface area and micropore volume were 83 m^2/g and 0.030 mL/g for unwashed activated carbon from chicken cake manure, and 174 m^2/g and 0.060 mL/g for unwashed activated carbon from turkey manure. It should be noted that Cui et al. [4] activated the carbon at 650°C, whereas in this study the activation was done at 800°C. The greatest BET surface area was found with the washed activated carbon made from chicken litter.

Results of the mercury uptake study are shown in Figures 2 and 3. As is noted in Figure 2, the commercial activated carbon (Norit Darco Hg) traditionally used for flue gas application removed some mercury in the incoming airstream during the initial 40 min of the experiment, after which the column appeared saturated. Very similar results were obtained in the case of unwashed activated carbons made from chicken cake. When this activated carbon was washed, it

performed worse. Similarly, unwashed activated carbon made from chicken litter performed better than its washed counterpart. In the case of unwashed activated carbon made from chicken litter, 60% of the mercury was initially adsorbed, after which the carbon slowly lost its capability for removing mercury. However, even after 2 h, the column was removing some (approximately 5 to 10%) of the incoming mercury and had not become saturated.

When the source of the activated carbon was turkey manure (cake and litter), the results were almost reversed (Figure 3). Whereas the unwashed activated carbons performed similarly to or better than their washed counterparts (as in the case of chicken manures), the activated carbon from turkey cake was better than the activated carbon from turkey litter. The highest removal efficiency for any of the carbons was noted for unwashed activated carbon made from turkey cake manure. This carbon initially removed approximately 80 to 90% of the mercury in the air (Figure 3). Not much difference was noted in performance between unwashed and

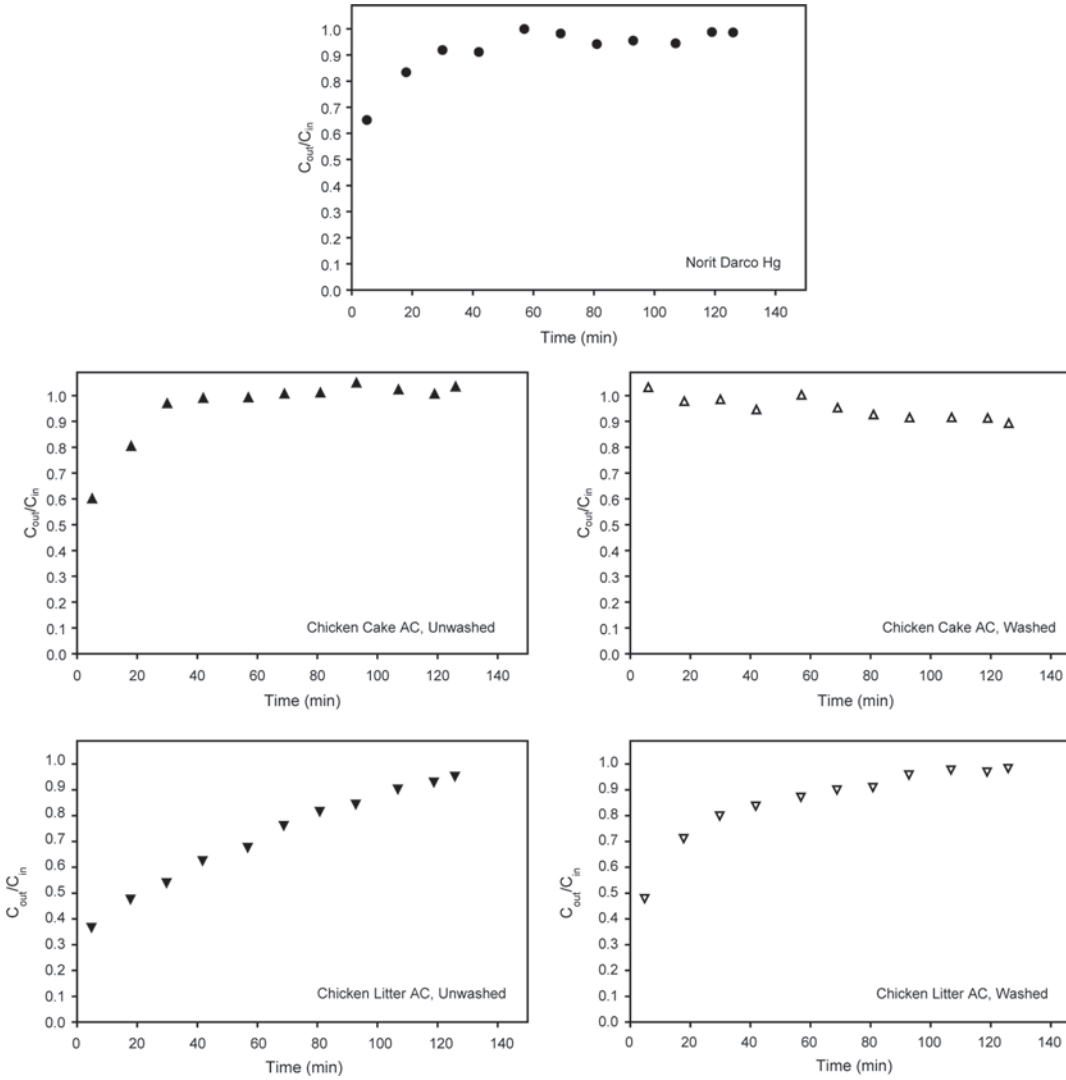

Figure 2. Results of packed-bed experiments with activated carbons (AC) from a commercial source or made from chicken manure. The data represent the fraction of the mercury in the incoming gas (C_{out}/C_{in}) that penetrated the carbon bed over time.

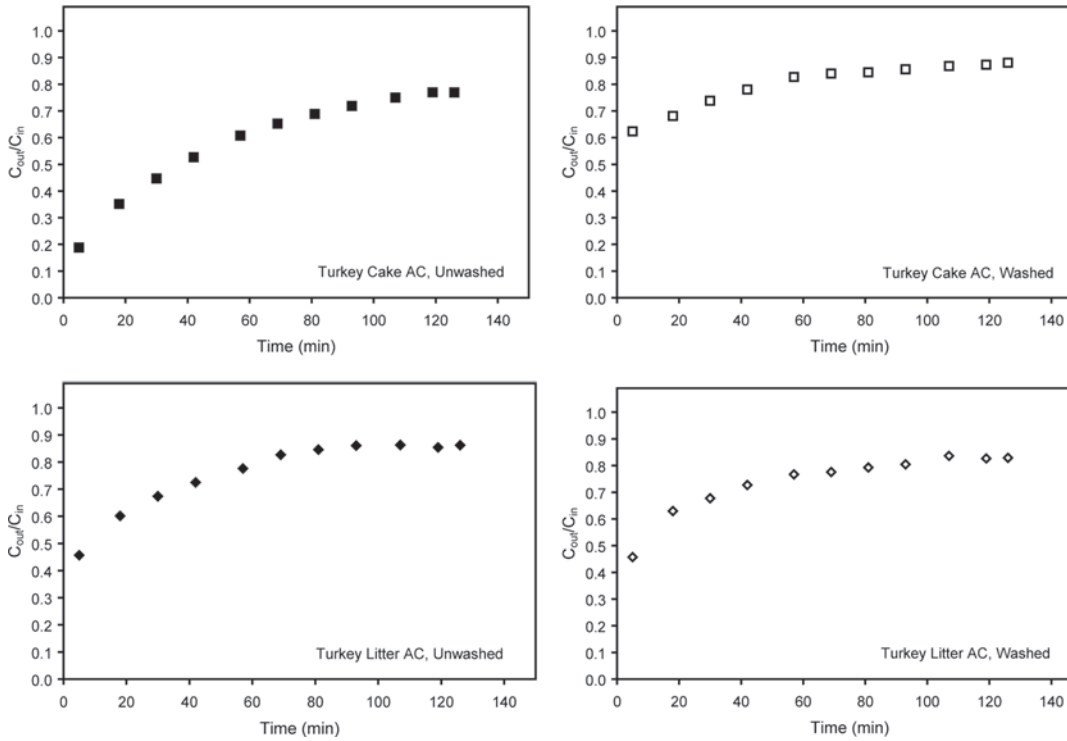

Figure 3. Results of packed-bed experiments with unwashed activated carbons (AC) made from turkey manure (cake and litter). The data represent the fraction of the mercury in the incoming gas (C_{out}/C_{in}) that penetrated the carbon bed over time.

washed activated carbon made from the turkey litter.

In an effort to normalize the data and quantify the overall performance, a pseudo distribution coefficient (**K_d**) was calculated at the end of the experiment (after 126 min of run time) as the adsorbed mercury on the carbon (in µg/g) divided by the average mercury inlet concentration (in µg/m^3). Although K_d is usually reported for batch studies (e.g., in shaker flasks), this pseudo K_d may be viewed as the volume of air that could be treated by 1 g of sorbent. The amount of adsorbed mercury was calculated from the inlet (C_{in}) and outlet (C_{out}) mercury concentrations throughout the experiment and from the known constant flow rate. The results of the calculations are shown in Figure 4. As is noted, the best performing sorbents were the unwashed carbons made from turkey cake and chicken litter, followed by the activated carbons made from turkey litter.

This finding is in contrast to other studies in which the Norit Darco Hg activated carbon usually performed better than, or as well as, other activated carbon types [1]. It should be noted, however, that the other studies never included activated carbons made from poultry manure

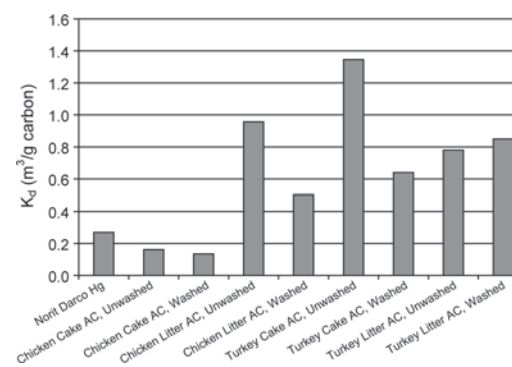

Figure 4. Overall performance of activated carbons. The pseudo distribution coefficient (K_d) value was calculated as cumulative adsorbed mercury (based on inlet and outlet concentration) per gram of adsorbent in the column, divided by the inlet concentration of mercury in air.

(or any other manure type). Another aspect to consider is that some of the earlier studies were often performed under simulated flue gas conditions, whereas the results from this study were obtained with air as the model gas. It should also be noted that Norit Darco Hg performs significantly better when used in gases containing small amounts of HCl [16]. Temperatures in flue gas can be considerably higher, up to 1,400°C [32]; however, in many of the previous studies, the temperatures were in the range of 121 to 177°C to simulate typical temperatures seen in the gas treatment systems after initial cooling [15, 33].

No correlation (data not shown) was found between overall mercury uptake (as described by K_d) and the BET, micropore, or mesopore surface areas. This finding is in contrast to other studies in which both elemental mercury uptake rate and sorbent capacity were affected by pore structure [34]; however, those studies were conducted with lignite-based carbons, and this could explain the different findings. It has been suggested that carbons inherently containing sulfur are superior for mercury uptake [1], and others have proposed that physisorption (pore structure dependent) predominantly takes place at below 75°C and chemisorption (surface chemistry dependent) takes place above that temperature [35]. Given that current studies were done at 120°C and that no correlation was found to link performance and surface pore structure, it is logical to assume that the majority of the mercury adsorbed was adsorbed via chemisorption.

The cost of activated carbon made from poultry manure is $1.44/kg [36]. This cost is slightly higher than the cost of $0.93 to 1.10/kg for the Norit carbon [37, 38]; however, it should be noted that the cost for the manure-based carbon was estimated by assuming that the carbons would be washed before use. In the present study, 2 unwashed manure-based carbons performed better than the others; thus, the cost for producing these unwashed carbons may be lower than $1.44/kg.

CONCLUSIONS AND APPLICATIONS

1. The activated carbon produced from poultry manure can remove elemental mercury from air.
2. The performance of the manure-based adsorbent was superior to that of an often-used commercial sorbent under the experimental conditions used.
3. On the basis of these findings, manure-based activated carbons may possibly be used in applications in which elemental mercury must be removed from a gas phase, such as in flue gas, natural gas, or air applications.
4. It is unknown how the manure-based carbons would perform in an actual flue or in natural gas applications; however, these preliminary laboratory results are encouraging.

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