PRODUCTION OF VALUE-ADDED CHARS AND ACTIVATED CARBONS FROM ANIMAL MANURE

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1 INTRODUCTION

The United States has a strong agricultural foundation that leaves behind large quantities of animal wastes. In the United States, an estimated 9 billion broilers, 256 million turkeys, 62 million pigs and 97 million dairy cows were produced in 2006 producing 5 times the waste of the U.S. human population. This substantial quantity of manure may pose a threat to public health and the environment (Bowman and Burnham, 2000). The potential hazard derives from repeated land disposal within a specific area leading to soil saturation of certain elements, such as phosphorus, and increasing pollution due to run-off from rainstorms and penetration into the groundwater. Solutions to the transformation of manure into valuable products are much more desirable than their current methods of disposal. Production of activated carbons can be an excellent reuse of these waste materials (Lima and Marshall, 2005a). Water quality and public health impacts of animal manure produced at large concentrated animal facilities prompted the need for viable solutions for their conversion and reuse. Our laboratory at the Southern Regional Research Center, SRRC, as part of the Agricultural Research Service, ARS of the U.S. Department of Agriculture, has shown that it is feasible to convert animal manure, particularly poultry litter into chars and granular activated carbons used for heavy metals remediation in waste waters, using laboratory prepared solutions. Pyrolytic products or chars are low porosity, lower surface area materials that are intermediate products in the development of activated carbons. Toxic metals contamination of various water sources is a significant problem in many parts of the United States. Neither chars nor activated carbons, which can be produced from a number of precursor materials including coal, wood and agricultural plant wastes, have been examined for remediation of this problem. We've been characterizing these chars and activated carbons for their physical properties and most importantly their ability to adsorb metal ions, ammonia and mercury.

2 MATERIALS AND METHODS

2.1 Char and activated carbon making (Figure 1)

Dried animal manures (less than 20% moisture w.b.) were milled to less than 1mm and pelletized to produce cylindrical pellets (4.76mm diameter). Pelletized samples were placed in a Lindberg bench furnace equipped with a retort and pyrolyzed at 700°C for 1hr under a flow of N_2 gas. Chars were allowed to cool overnight. For activated carbon production, the chars were steam-activated at 800°C by pumping water via a peristaltic pump into the N_2 flow entering the heated retort. Activated carbons were also allowed to cool in the retort to room temperature, overnight. Surface-ash was removed by washing samples with 0.1 M HCl and subsequently triple-rinsing to remove excess acid. Dried carbons were ground to specific particle sizes (Figure 2) depending on the test. Chars and carbons were tested for yield, surface area, pH, attrition, ash content and adsorption per methods described in Lima and Marshall (2005b).

2.2 Adsorption studies

Four metal ions considered environmental pollutants and commonly found in both drinking and wastewater streams and ponds were chosen: Cu^{2+}, Cd^{2+}, Ni^{2+} and Zn^{2+}. Metal ion uptake was determined using the methods of Lima and Marshall (2005). Mercury uptake was measured using the methods of Klasson et al (2009). For the ammonia adsorption, three columns filled with carbon were placed in series and effluent NH_3 concentration was monitored by a photo-acoustic gas analyzer and data converted into time to breakthrough. Isotherm curves for trihalomethanes adsorption were generated by exposing varying amounts of carbon to 10ppm-solutions each of chloroform, diclorobromomethane, dibromochloromethane and bromoform. Purge and trap and solid phase micro extraction methods coupled with mass spectrometric detection were used to measure the amount of trihalomethanes remaining in solution after 24 hr batch adsorption studies.

3 RESULTS AND DISCUSSION

Animal manure-based char yields were relatively consistent ranging between 38 to 41% and were highest for dairy manure and lowest for swine manure-based chars. Yields decreased with activation and were highest for dairy manure carbons and lowest for broiler cake carbons ranging between 11 to 32% (Table 1). Surface areas increased with activation as expected with highest observed for broiler litter carbon with 441 m^2/g (Table 1). Adsorption for metal ions far exceeded that of the reference sample (coal) with negligent to no adsorption observed, under the same conditions (Table 2). A feasibility analysis estimated the cost to produce these carbons at $0.65/lb (Lima et al, 2009). This compares favorably to alternative technologies that use ion exchange resins with typical retail costs of $9–22/lb for commercial, petroleum-based cation-exchange resins when purchased in bulk quantities (Marshall et al, 2001). According to Bailey et al. (1999), a sorbent is considered low-cost when it requires little processing, is abundant in nature or is a by-product or waste material and this is the case for animal manure-based carbons, when compared to those made from non-renewable and more expensive coal. In looking to different markets and uses for these manure based chars and carbons, our laboratory has been recently testing their use in remediating ammonia from poultry houses (Figure 3), removing organics such as trihalomethanes from drinking water (Figure 4), and removing mercury from air with promising results (Figure 5).

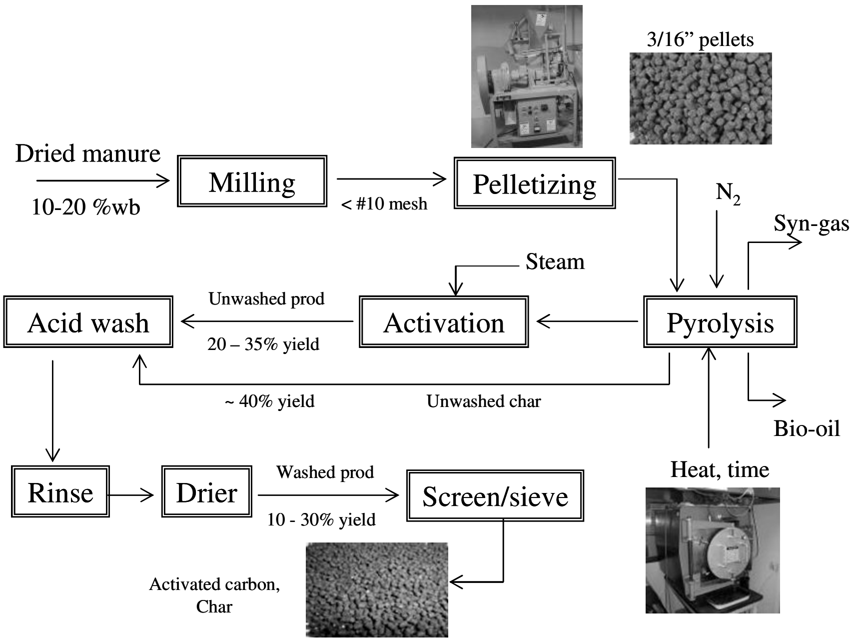

FIGURE 1 **Process of making chars and activated carbons from animal manure.**

TABLE 1 **Select physical properties for carbon and char samples (in parenthesis) from various animal manures as compared to those from coal: % yield, Y; surface area, BET; bulk density, BD, attrition, A and pH.**

Sample	Y %	BET m^2/g	BD g/cm^3	A %	pH
Broiler litter carbon (char)	22.7 (40.7)	441 (238)	0.54 (0.60)	17.9 (14.4)	8.8 (8.1)
Broiler cake carbon (char)	11.0 (40.3)	395 (318)	0.61 (0.54)	24.0 (15.1)	8.2 (8.6)
Turkey litter carbon (char)	28.1 (41.7)	414 (179)	0.58 (0.57)	20.0 (9.2)	8.0 (8.1)
Dairy manure carbon (char)	32.0 (40.4)	318 (131)	0.56 (0.57)	22.1 (29.7)	9.0 (7.2)
Swine manure carbon (char)	22.2 (38.2)	419 (91.5)	0.41 (0.59)	19.7 (21.3)	6.9 (6.8)
Coal carbon (char)	70.0 (78.3)	0 (0)	0.48 (0.42)	22.3 (17.4)	4.9 (4.2)

FIGURE 2 **Manure pellets (left) and their respective chars and activated carbons (right) ground into different sizes depending on end use.**

The high affinity of activated carbons toward metal ions is usually a function of their surface chemistry. Elemental analysis (data not shown) revealed that phosphorus concentrates in the char and carbon. The possibility exists that pyrolysis, followed by steam activation, entraps pre-existing phosphorus found in the manure to a certain degree, in the form of phosphate or polyphosphate anions, in the activated carbon matrix, thus improving the carbon's adsorption properties. The presence of covalently bound phosphorus in the form of phosphate ion can create centers of negative charge on the carbon that can readily adsorb or ionically bind positively charged ions such as metal ions. This inherent characteristic of poultry manures, coupled with their inexpensive and highly available status, can lead to the development of effective metal ion adsorbents as alternatives to existing commercial adsorbents.

TABLE 2 **Metal ion adsorption in mmoles/g (max. of 2 mmoles/g) for activated carbons and chars (in parenthesis) from various animal manures and carbons as compared to those from coal.**

mmoles/g	Cu^{2+}	Cd^{2+}	Ni^{2+}	Zn^{2+}
Broiler litter carbon (char)	1.20 (0.58)	1.09 (0.45)	0.06 (0.25)	1.33 (0.72)
Broiler cake carbon (char)	1.90 (0.91)	1.33 (0.64)	0.42 (0.10)	1.94 (0.96)
Turkey litter carbon (char)	1.65 (0.61)	1.44 (0.62)	0.86 (0.16)	1.73 (0.73)
Dairy manure carbon (char)	0.61 (0.16)	0.12	0.07	0.15
Swine manure carbon (char)	0.61 (0.27)	0.51	0.07	0.58
Coal carbon (char)	0.08 (0.00)	0.30 (0.05)	0.05 (0.13)	0.04 (0.03)

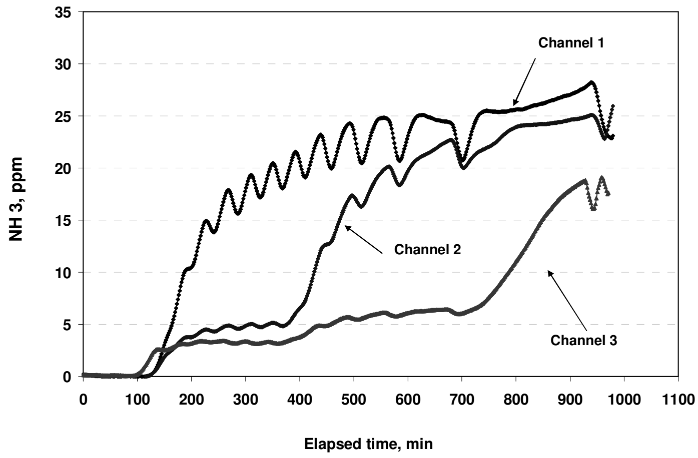

FIGURE 3 **Ammonia concentration in the effluent of a 3-chamber (in series) ammonia adsorption set-up with broiler cake carbons exposed to 34.8 ppm NH_3 gas at 3 LPM.**

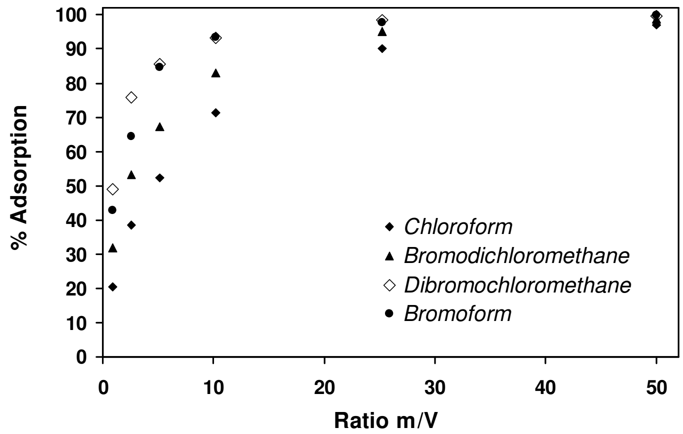

FIGURE 4 **Trihalomethane adsorption by a broiler litter carbon exposed to different carbon to volume (g/L) ratios of a solution containing 10ppm each of four different trihalomethanes.**

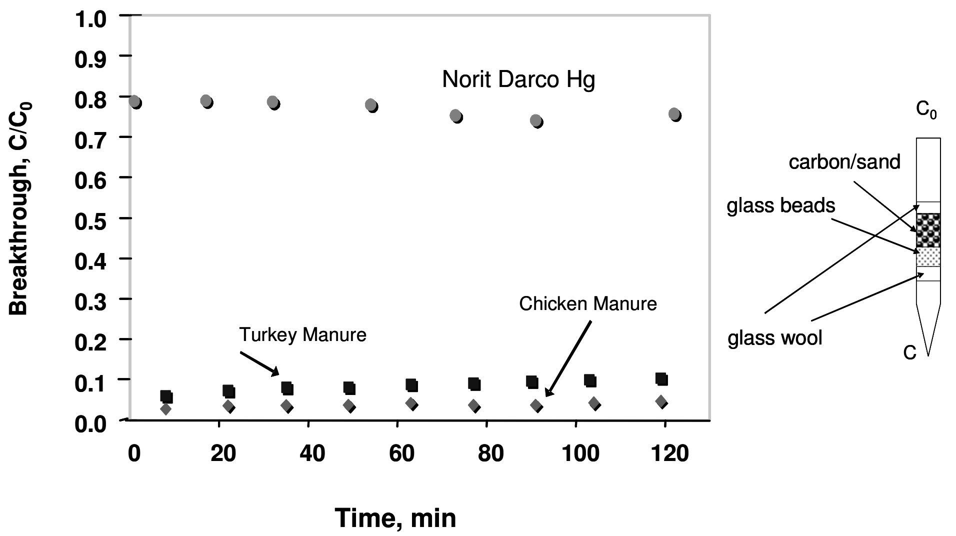

FIGURE 5 **Mercury adsorption by two types of manure based carbons as compared to a commercial carbon.**

4 CONCLUSIONS

The conversion of readily available and renewable animal manures into chars and activated carbons for environmental remediation might be an alternative to a serious disposal problem and at the same time create new markets for animal manures and new opportunities for animal farmers.

DISCLAIMER

The mention of firm names or trade products does not imply that they are endorsed or recommended by the U.S. Department of Agriculture over other firms or similar products not mentioned.

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