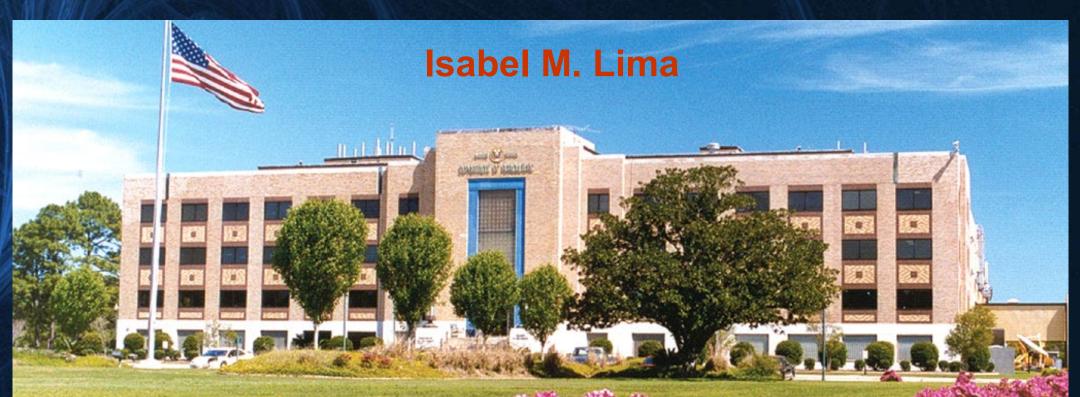
Going Full Circle: Biochars from Ag Waste as Adsorbents for Environmental Remediation



Hershey, PA May 25-26th, 2023 Using Carbon to Achieve Chesapeake Bay (and Watershed Water Quality Goals and Climate Resiliency: The Science, Gaps, Implementation Activities and Opportunities

Agriculture Residues - The Driving Force

How much is animal agriculture leaving behind?

Poultry, swine and cattle produce over 5 times the waste of the U.S. human population

~ 175 million tons of manure produced each year

129, 176 M DMT available from forestry & agriculture for bioenergy & bio-products





The leftovers of our Agriculture...

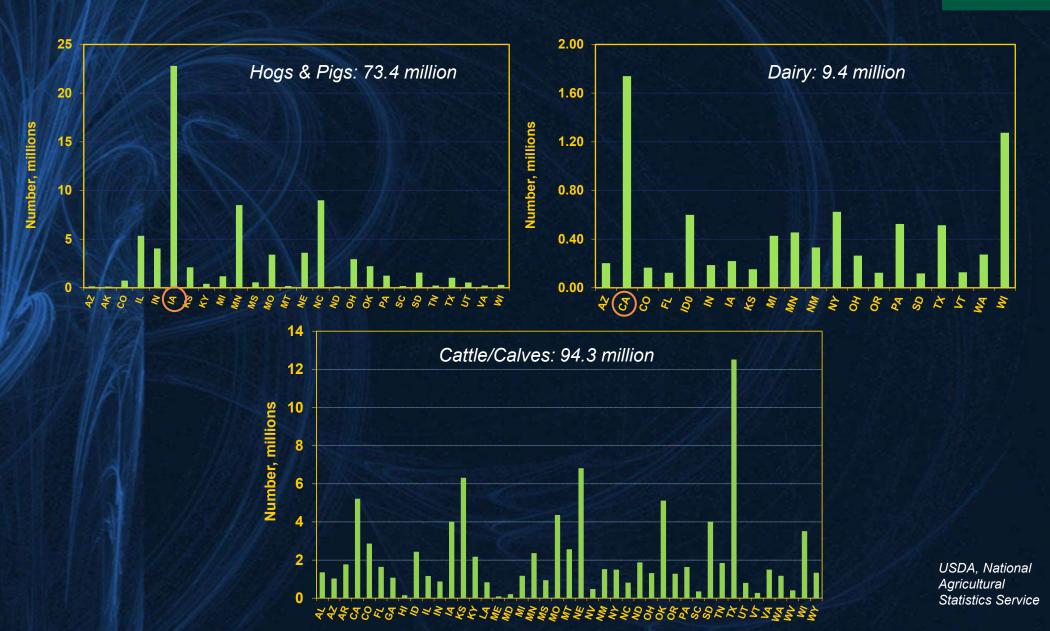
Out of 3.6 million miles of rivers and streams in the U.S., farming impairs water quality to some degree

Excess nutrients from fertilizing lawns, gardens, and farms, pollution from urban sources, wastewater, septic systems, and stormwater runoff all contribute to the Chesapeake Bay pollution

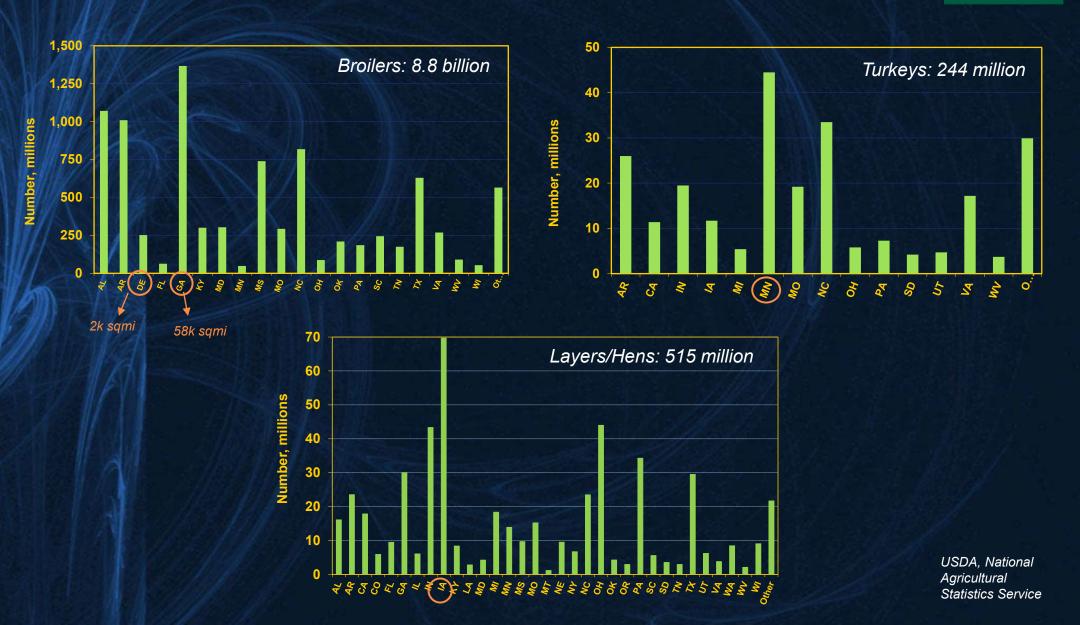
Increase in public and regulatory concern from the impact of animal waste on quality of life and the environment



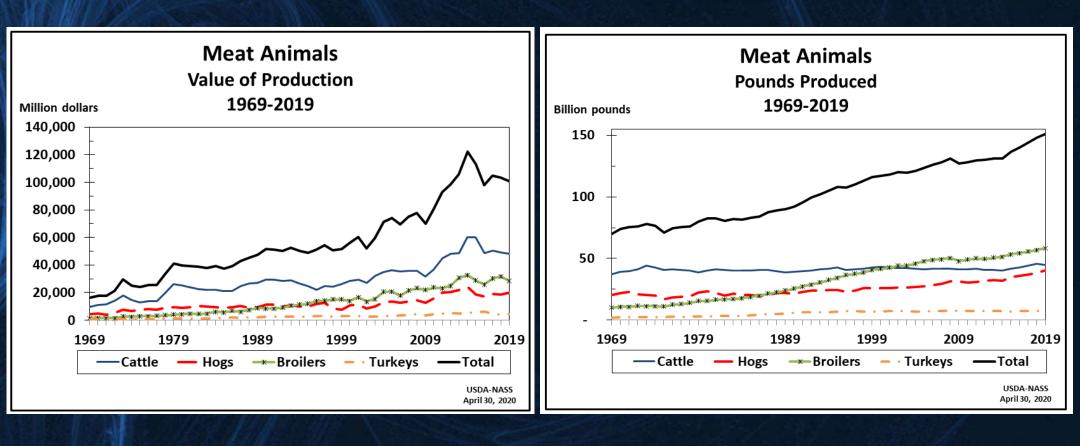
Production by States 2017-18



Production by States



Meat Animals: Production & Value by Year, US

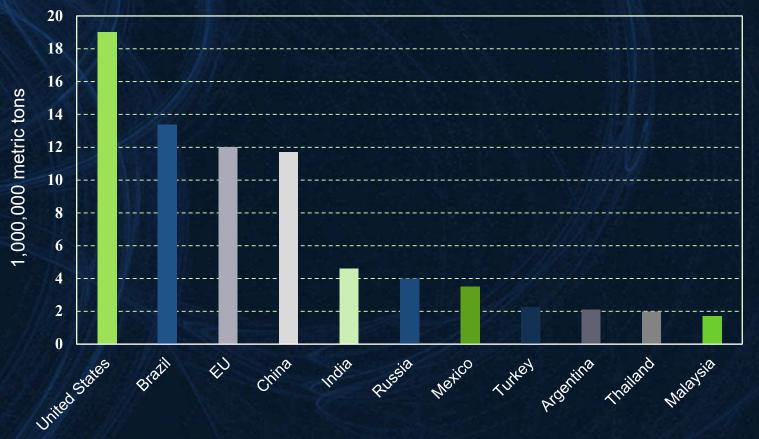




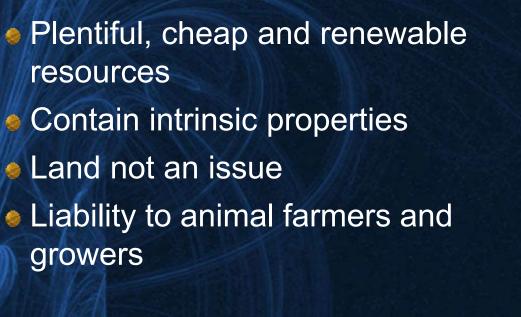
U.S. No1 Poultry Meat producer

World Total (2018): 92.5 M tons

Broiler Meat Production 2018



Agricultural Residuals





Adding value by transforming agricultural residuals into biochars

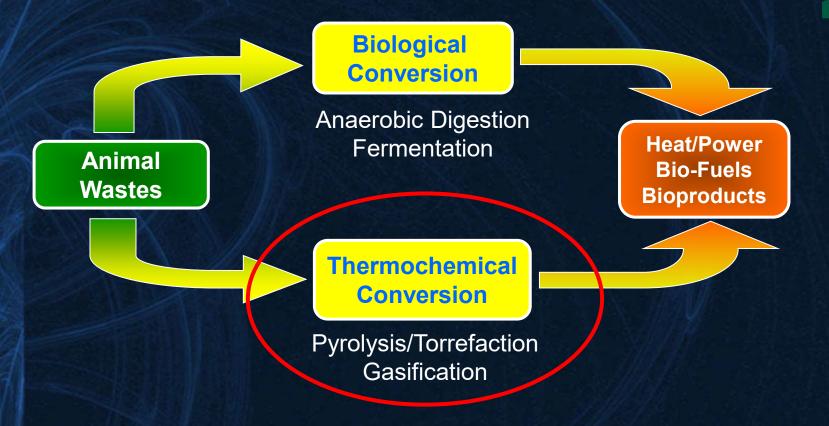
Value

Help protect the environment and public health

Solve a waste disposal problem

Adding

Energy Conversion Pathways



Thermal decomposition of feedstock: growth of aromatic structures and polymerization reactions

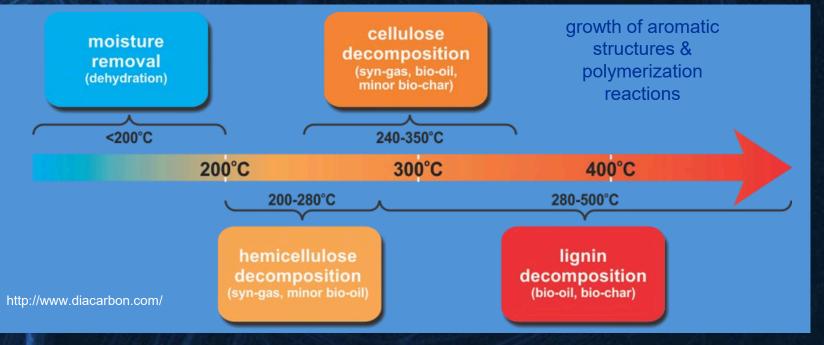
Pyrolysis (pyro = heat, lysis = breaking apart), fast or slow pyrolysis

- Gasification (conversion of solid into gas), dry or wet gasification
- Combustion (burning of gas with O_2 to make H_2O and CO_2)

Pyrolysis



- Carbonization: C enrichment, porosity development as VM is removed
- Used as amendment to improve soil properties or sorbent for environmental stressors
- Biochar properties and application depend on feedstock and processing conditions



- High heating rates > 200°C/s
- Endothermic reaction
- Maximize bio-oil production

Slow Fast

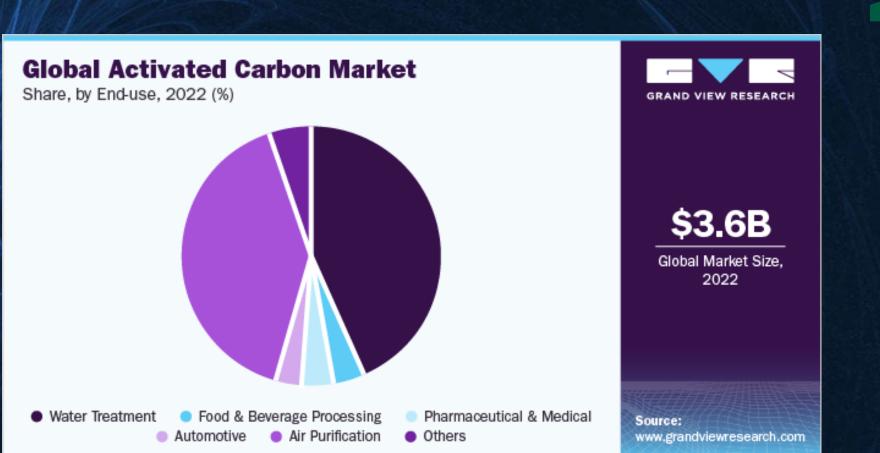
- Low heating rates, 0.01 to 2°C/s
- Exothermic reaction
- Maximize biochar production

Activated Carbon Market



- Common feedstock is coal, coconut shell, wood or peat.
- U.S. AC market estimated at 472,000 tons for 2022
- Global AC market estimated at 3 million tons, is predicted to double by 2030
- Total global market size valued at USD \$3.62 billion for 2022
- Compound Annual Growth Rate of 2.6%
- There are no carbons with good metals adsorbing properties
- High-quality activated carbons are commonly expensive

Activated Carbon Market



Applications range from water treatment, air purification, food & beverage processing, medical & pharmaceuticals production, automotive emission canisters, etc.

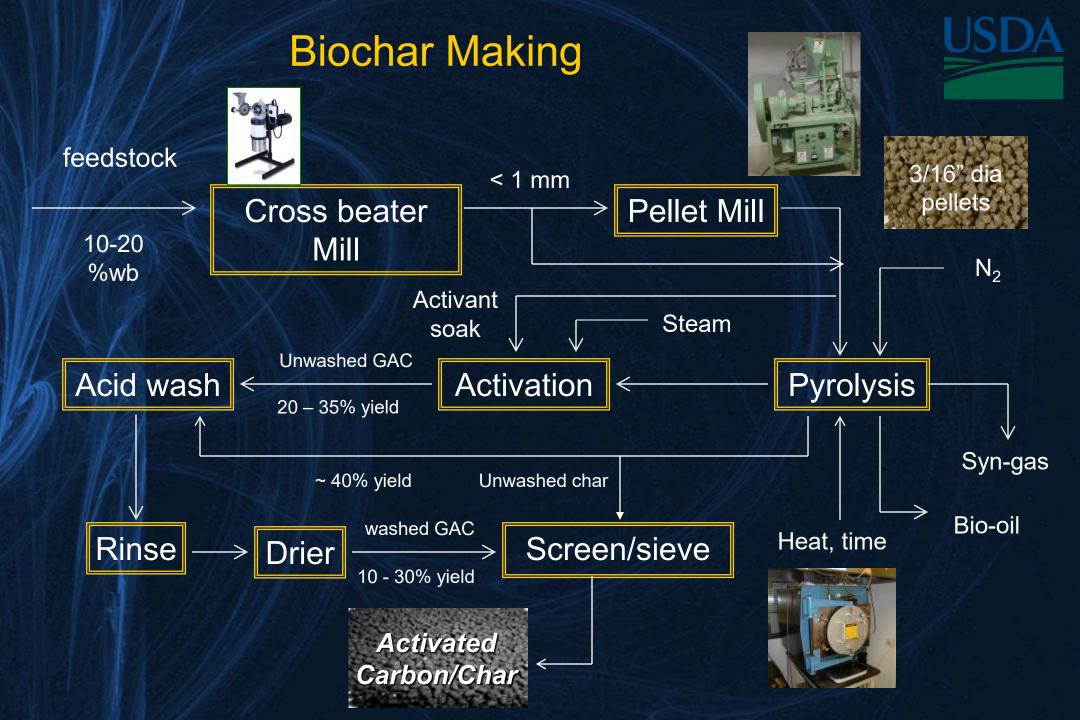
U.S. Activated Carbon History



Carbon in use for 1000's of years; impetus for large growth has been wartime uses with biggest launch of peace time use in the 70's – enactment of environmental legislation – CAA, CWA, superfund

Some growth since then with applications in water & waste treatment, remediation, pollution control & chemical operations

- Chinese sourced carbons in 90's led to severe drop in market, reversed with tariff protection
- Exponential growth expected through legislation leading to new water-air pollution laws, limitations on released contaminant levels and new applications



Biochar/Activated Biochar Characterization

USDA

Physical properties

 Carbon yields, surface area, attrition resistance, bulk density, particle size distribution, SEM characterization

Chemical properties

 Total surface charge, pH, compositional analysis, ash content, X-ray analysis, NMR

Adsorptive properties



 Adsorption isotherms, kinetic studies, batch/column, multiple adsorbates/compounds

Comparison with other carbons

Sample

Sample Description

Our carbons

Coal, coconut shell or wood based

PUR RF

Calgon F300

Norit Darco Hg

Made from pelletized manure, steam activated under N₂

Made from pelletized coal, ground coconut shells/sawdust, steam activated under N_{2}

Replacement Filter, coal derived, 10x20 mesh, originally in block form

Filtrasorb 300, GAC by Calgon Carbon for removal of organic pollutants from munic/indust wastewaters. Made from bituminous coal

Powdered (<45 µm) activated carbon made from lignite coal



Biochar Physical Properties

700C Sample	IY	FY %	Attrition %	BD g/cm³	BET, m²/g	PM %
Broiler cake	40	30	15.1	0.54	318	88
Broiler litter	41	34	14.4	0.60	238	90
Turkey cake	41	33	10.7	0.53	147	93
Turkey litter	42	35	9.2	0.57	179	93
Swine	38	31	21.3	0.59	92	40
Dairy	48	37	29.7	0.56	131	75
Coal	78	61	34.1	0.42	4	- 18-
Coconut shell	28	28	20.5	0.61	35	24
Wood	25	24	23.4	0.38	301	93

IY: initial yield before acid washing; FY: final yield after acid washing; BD: bulk density; BET: Brunner-Emmett-Teller Surface Area; PM: Percent of surface area in micropores.

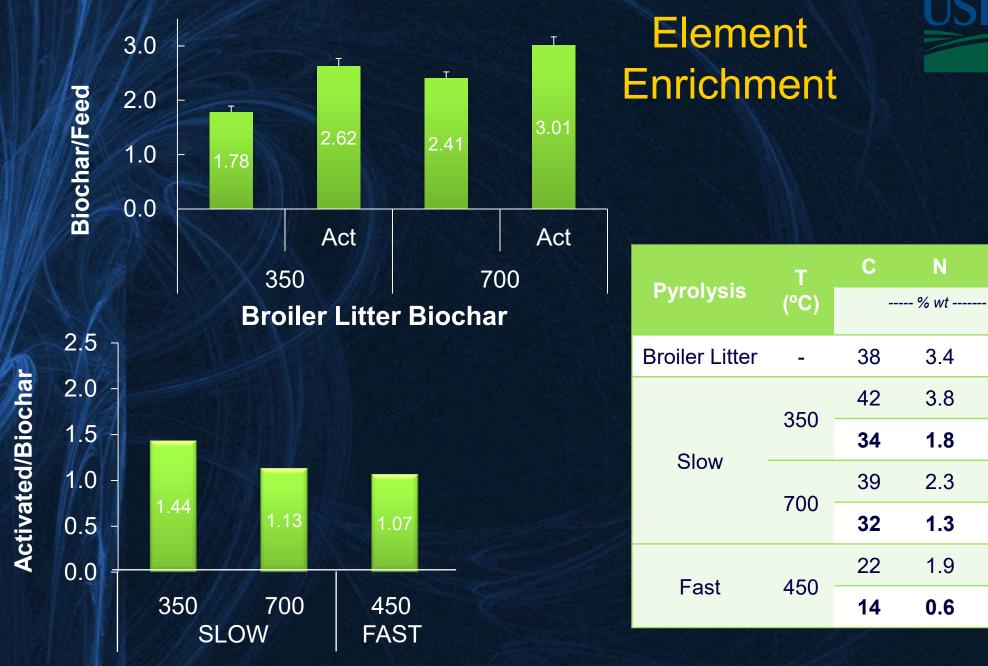
Biochar Physical Properties

700C Sample	рН	% Ash	% C	% H	% N	% S	C, af
Broiler cake	8.6	45.2	43.9	1.02	2.84	0.35	80
Broiler litter	8.1	49.2					
Turkey cake	9.2	40.4	39.9	1.05	3.43	0.37	67
Turkey litter	8.1	43.5					
Swine	6.8	56.9	31.4	0.33	1.80	0.01	73
Dairy	7.2	71.0	25.2	0.15	1.08	0.00	87
Coal	4.2	2.5	86.8	1.08	1.85	0.06	89
Coconut shell	6.6	1.8	82.1	1.33	0.19	0.09	84
Wood	5.1	1.4	85.1	1.76	0.31	0.22	86

C, af: carbon content (%), ash free basis.

Activated Biochar Physical Properties

	Yield %	Surface Area m² / g	Attrition %	рН
Broiler Litter	22.7	441	17.9	7.9
Broiler Cake	11.0	395	24.0	8.2
Turkey Litter	21.1	414	20.0	8.0
Turkey Cake	16.4	394	25.8	8.1
Swine	17.0	419	20.6	6.9
Dairy	26.8	318	22.1	9.0
PUR RF	-	474	32.0	6.4
Coal	70.0	0	13.8	4.9
Coconut Shell	22.7	843	22.3	3.1
Wood	17.9	849	15.6	2.9



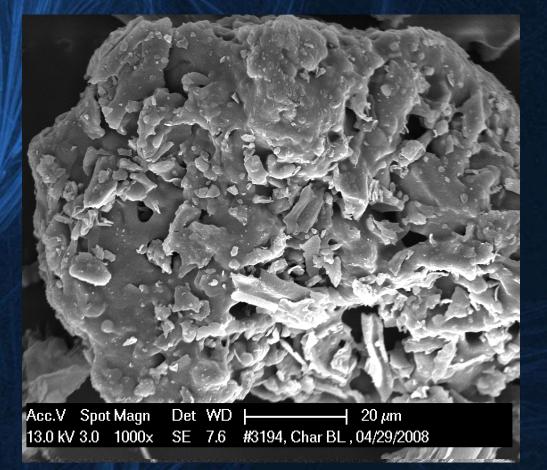
Bold numbers in rows indicate activated biochar

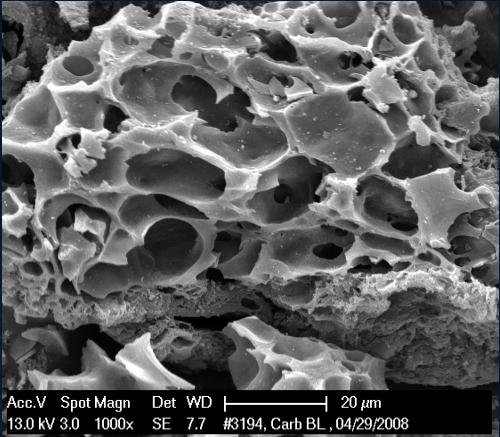


Broiler Litter Micrographs

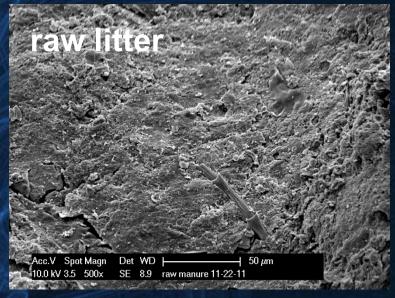
Biochar

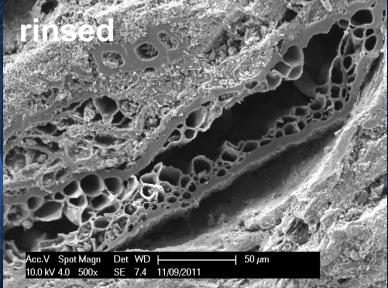
Activated Biochar





Broiler Litter Micrographs









Activated Biochar Metal Ion Adsorption



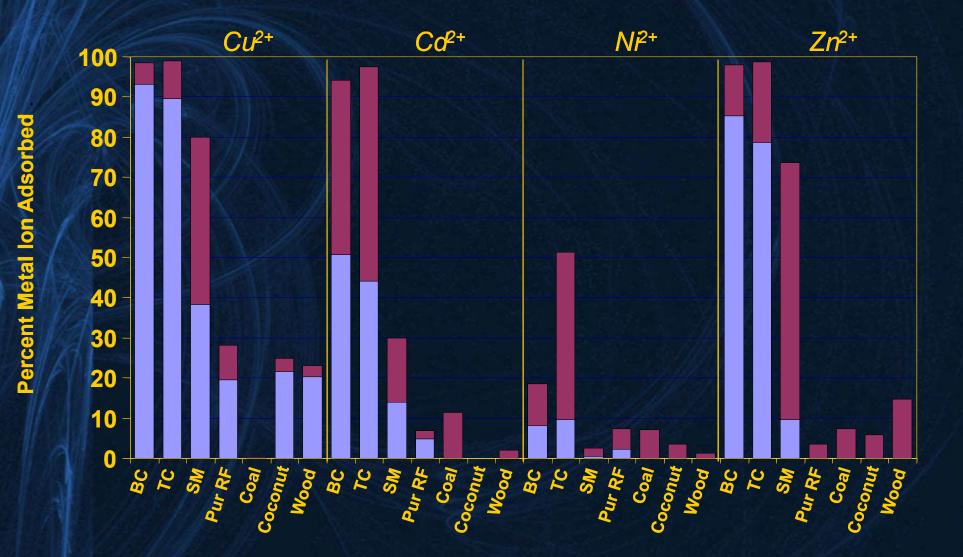
(mmoles/g)	Cu ²⁺	Cd ²⁺	Ni ²⁺	Zn ²⁺
Broiler Litter	1.20	1.09	0.06	1.33
Broiler Cake	1.90	1.33	0.42	1.94
Turkey Litter	1.65	1.44	0.86	1.73
Turkey Cake	1.42	1.48	1.34	1.67
Duck Manure	0.55	0.34	0.06	0.49
Swine	0.61	0.51	0.07	0.58
Dairy	0.33	0.12	0.07	0.15
PUR RF	0.28	0.15	0.00	0.15
Coal	0.08	0.30	0.05	0.04
Coconut Shell	0.29	0.02	0.04	0.06
Wood	0.26	0.00	0.02	0.14

Activation Comparison



(mg/g)	Cu ²⁺	Cd ²⁺	Ni ²⁺	Zn ²⁺		
BL carbon	77.0	122.9	3.7	86.9		
BL biochar	36.9	50.5	14.8	47.2		
BC carbon	123.8	149.8	26.5	126.5		
BC char	57.8	71.9	5.9	63.1	EPA disc	harge limits
TL carbon	110.4	161.9	32.2	113.4	Priority	mg/L
TL char	38.6	69.8	9.4	47.6	pollutant	daily avg/ max mo
TC carbon	99.0	165.9	78.7	109.3	Cu	1.00 0.23
TC char	21.1	51.3	14.5	40.6	Cd	0.73 0.16
Coal	0.0	6.0	7.7	2.0	Zn	1.20 0.27
Coconut Shell	0.0	4.8	7.9	6.4		
Wood	0.0	3.0	11.9	3.0		

Competition Study – Activated Biochar



Legend: BC: broiler cake carbon; TC: turkey cake carbon, SM: swine manure carbon

Competition Study - Biochars

	Sample	Cu ²⁺	Cd ²⁺	Ni ²⁺	Zn ²⁺
	Broiler cake	95.4	83.2	6.6	89.8
	Broiler litter	95.0	82.3	5.1	90.9
Single	Coal	0.0	12.8	0.5	2.6
	Coconut shell	3.1	13.5	0.0	0.5
	Wood	6.3	13.3	0.0	1.8
	Broiler cake	71.1	18.8	3.8	23.7
	Broiler litter	66.1	18.1	3.6	25.2
Competition	Coal	0.6	0.3	0.7	1.0
	Coconut shell	0.2	0.9	0.7	3.8
	Wood	4.0	0.0	0.0	2.4



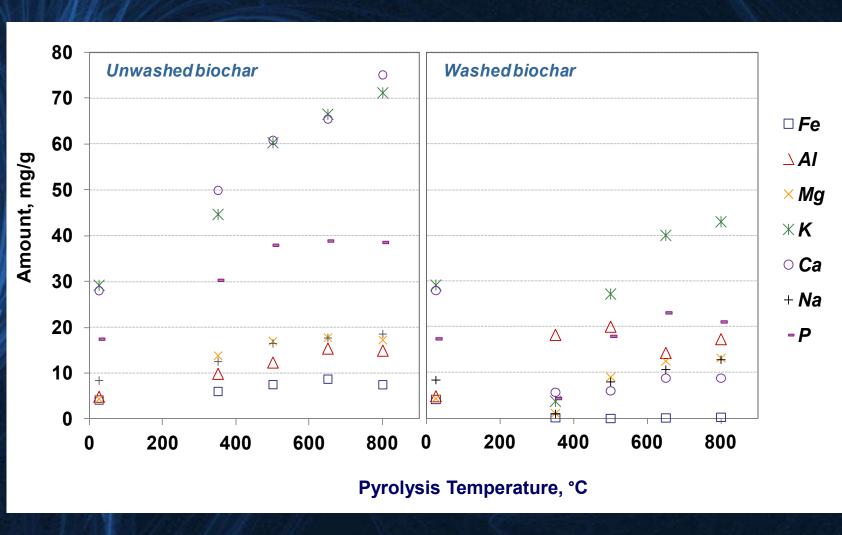
Comparison with other Adsorbents

Sample	Activation	Surface area	Cu ²⁺ ads.
	Method	(m²/g)	(mmoles/g)
Pecan shells	Steam	894	0.29
Pecan shells	Acid/air oxid	682	1.10
Broiler cake	Steam	481	1.90
Broiler litter	Steam	377	1.20
RO 3515	Steam	920	0.27
F-400	Steam	960	0.22



Elemental Composition (g/100g)

Manure						
Activated biochar	C	N	K	S	Р	
Broiler Litter	34.4	3.26	3.83	0.67	1.66 —	3.68
	25.8	0.75	3.00	0.64	4.80 -	+
	32.6	3.62	5.34	0.83	1.94 —	-
Broiler Cake	17.2	0.60	5.80	0.80	7.30 -	4.92
Turkey Litter	34.9	3.84	2.75	0.61	2.26	
	32.6	1.12	4.09	0.93	7.88	
Turkey Coke	35.4	4.82	2.88	0.66	2.04	
Turkey Cake	30.5	1.40	4.59	1.46	7.40	
Swine	41.5	4.21	1.81	0.42	1.85	
	39.9	1.48	1.67	0.27	5.20	
	30.3	3.01	1.46	0.50	1.29	
Dairy	28.8	0.69	0.83	0.50	2.70	



Elemental Composition Function of PT

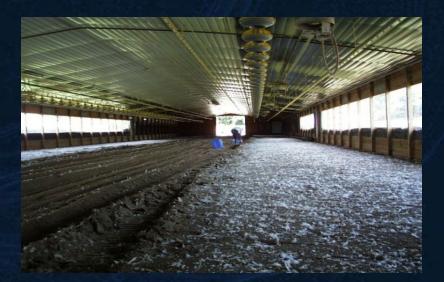
AW and RO: amounts removed by acid washing or rinse only treatments: selective element leaching

400 350 300 250 Na ■K Mg 200 Ca Fe 150 P 100 50 0 AW RO total

Feedstock: Forest versus Ag

- Pine wood shavings, broiler litter
- Pyrolysis at 250°C and 500°C
- Steam activation at 800°C, 45 min, 3ml/min flow rate
- Acid activation at 450°C under air, 30% H₃PO₄, 1:1 ratio
- Base activation at 450°C under air, 5M KOH, 1:1 ratio
 - Biochars and steam activated Biochars not rinsed
 - Acid and base activated biochars rinsed in hot water





Feedstock: Forest versus Ag

Source	Product	Act. yield %	BET m²/g	рН	Surf. charge meq H+/g
Wood shavings 250°C	Biochar Steam act Acid act Base act	36.0 36.8 45.8	0.03 573 851 27	5.3 8.8 2.5 6.7	1.57 0.00 3.00 0.36
Wood shavings 500°C	Biochar Steam act Acid act Base act	76.7 64.9 53.2	0.0 511 538 360	5.6 8.1 2.2 6.7	0.37 0.00 2.11 0.04
Chicken litter 250°C	Biochar Steam act Base act	31.8 58.6	0.5 592 122	8.2 10.5 -	1.28 0.06 0.70
Chicken litter 500°C	Biochar Steam act Base act	68.5 65.1	1.6 420 118	8.7 10.9 7.7	0.22 0.00 0.00

Proximate Analysis: Forest versus Ag (%)



Source	Product	MC	Volatile Matter	Fixed C	Ash
raw	Feedstock	4.6 41.4	56.9 70.6	40.0 17.8	3.1 11.6
250°C	Biochar Steam act Acid act Base act	 4.0 3.6 1.9 1.5 3.1 3.4 2.2 	59.1 59.5 6.0 7.3 35.8 19.9 22.1	38.3 27.0 88.4 44.7 57.8 77.6 55.7	 2.6 13.5 5.6 48.0 6.4 2.6 22.1
500°C	Biochar Steam act Acid act Base act	 7.7 4.4 1.6 1.1 2.4 3.3 4.8 	14.2 21.8 6.3 7.0 30.2 12.1 20.8	80.3 38.1 87.1 37.8 62.8 82.0 40.1	5.6 40.1 6.6 55.2 7.1 5.9 39.2

wood shavings

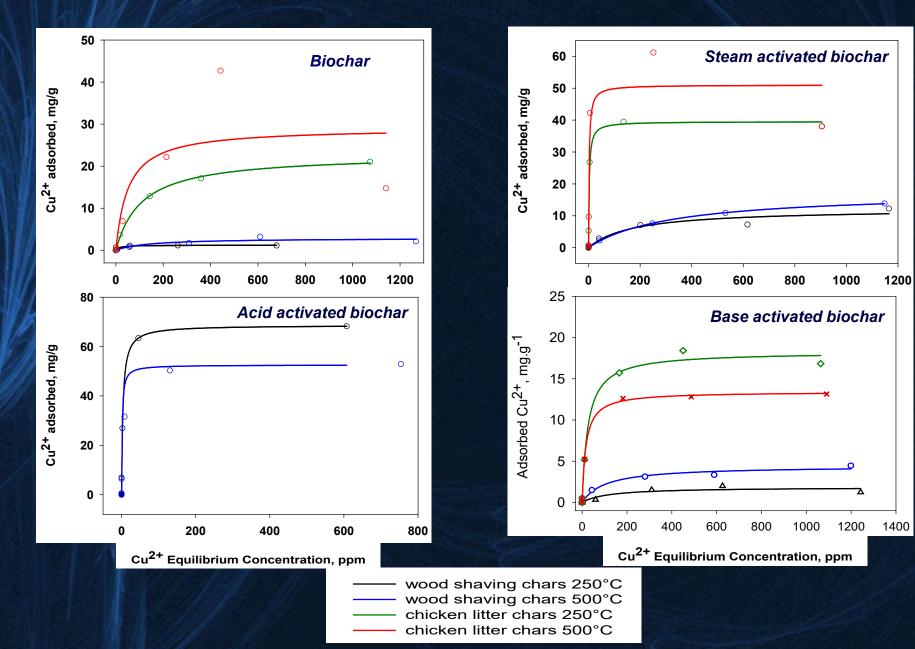
litter

Elemental Analysis, mg/g

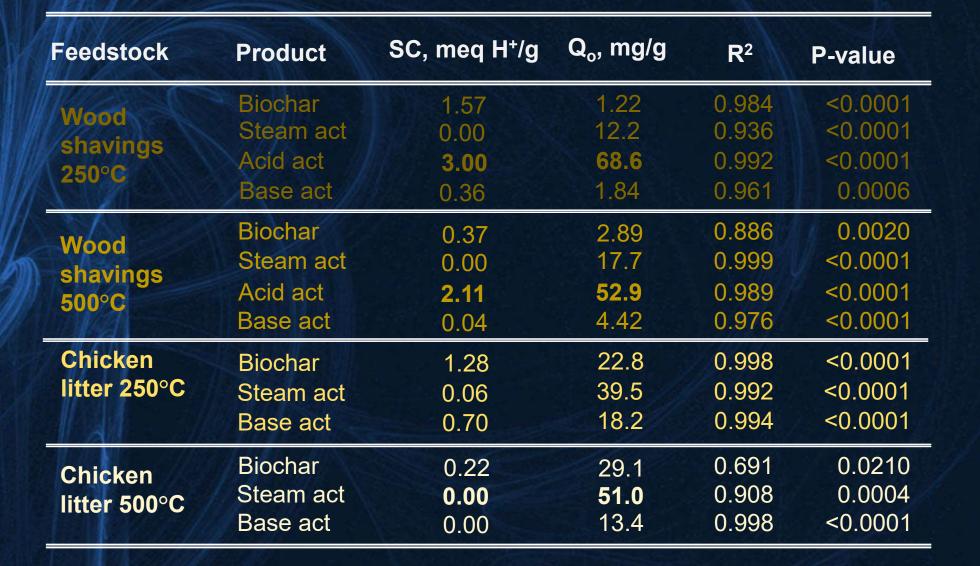


Isotherm Plots



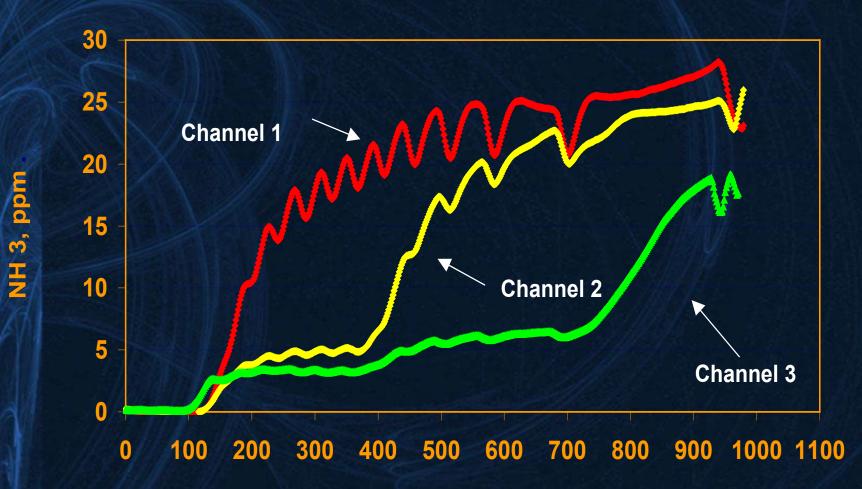


Isotherm Coefficients

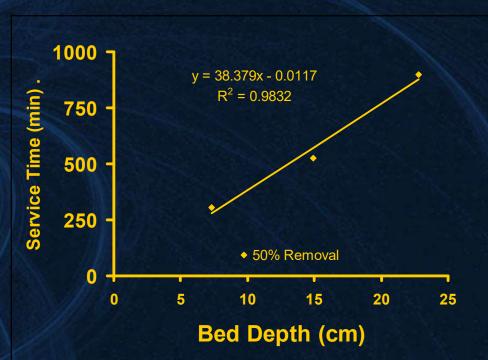




3-chamber NH₃ adsorption



Elapsed time, min





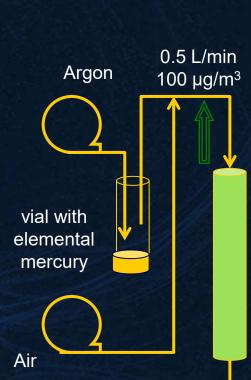
Column #	Cumulative bed depth	Service time (min) @	
π	(cm)	breakthrough	
1	7.3	303	
2	14.9	527	
3	22.8	897	

Hg Experimental Set-up

2021 U.S. mercury emissions at 16 metric t/yr

- Simulated flue gas with elemental Hg₀ at ~100 μ g/m³ flowing through bed of sand and pulverized biochar held in 150°C oven, samples taken from inlet & outlet and injected into mercury analyzer
- Feedstock: cotton seed hulls, broiler litter, lignin, nutshells
- 350-800°C, 150°C increments



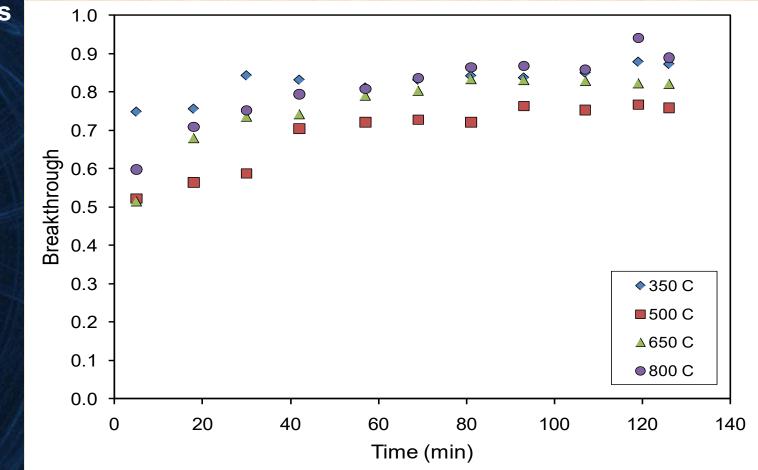




10 g sand 20 mg carbon 13 mm ID x 47 mm L 0.5 s EBRT



Unwashed cotton seed hull chars



AA

C_{out}

BF=C_{out}/C_{in}

C_{in}

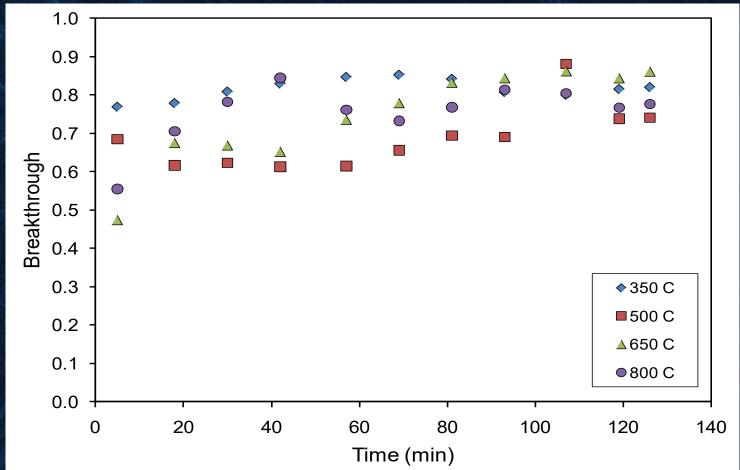
Results of Mercury Removal

<u>Washed</u> cotton seed hull chars

C_{in}

C_{out}

BF=C_{out}/C_{in}

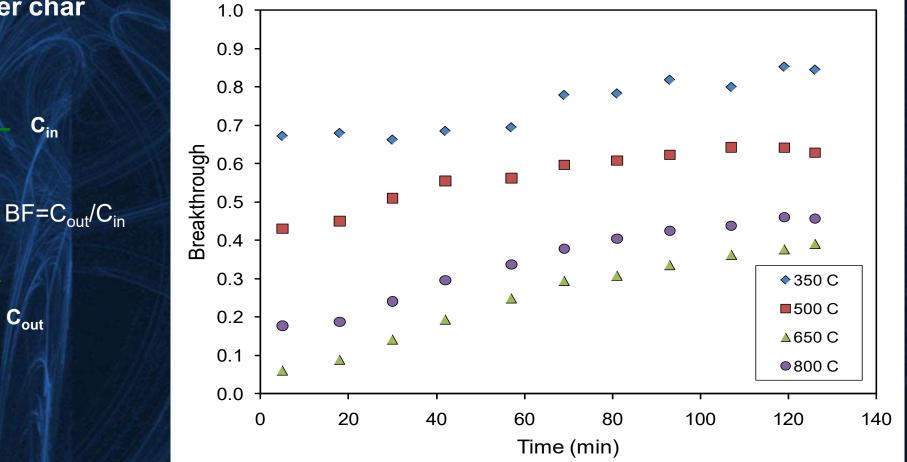


Results of Mercury Removal

Unwashed broiler litter char

C_{in}

C_{out}



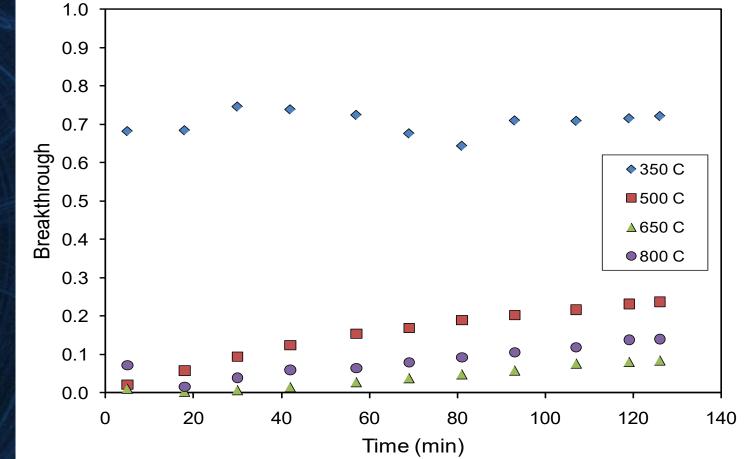
Results of Mercury Removal

<u>Washed</u> broiler litter char

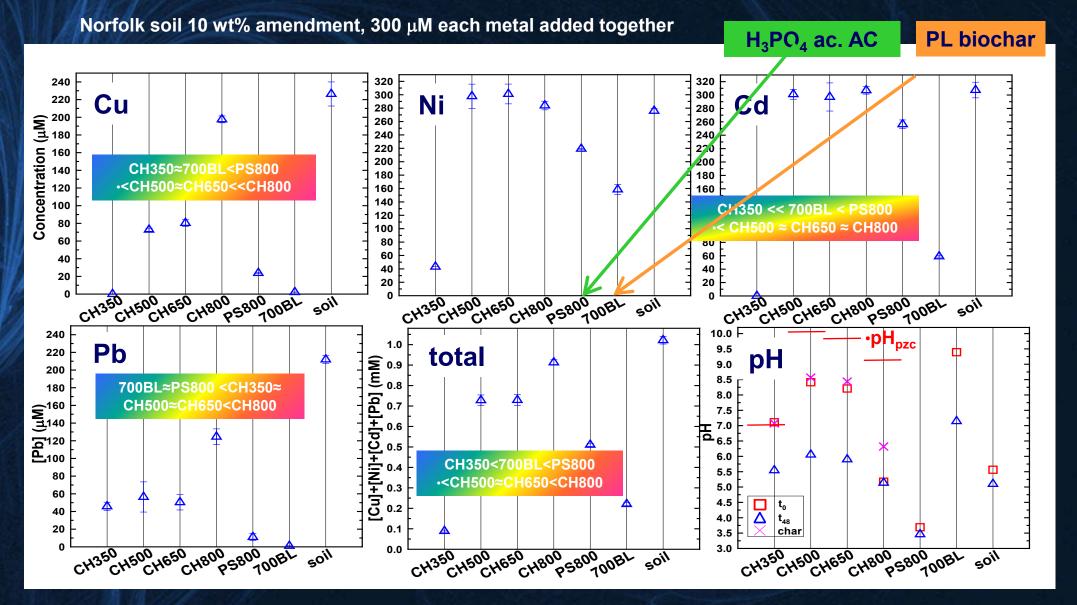
C_{in}

C_{out}

BF=C_{out}/C_{in}



Poultry litter char: among the most effective for Cu, Ni, Cd, Pb retention in soils



BIOMASS AND BIOENERGY 32 (2008) 568-572



Activated carbon from broiler litter: Process description and cost of production $\stackrel{\mathcar{\sim}}{\sim}$

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ARTICLE INFO

ABSTRACT

Article history: Received 31 May 2006 Received in revised form 30 October 2007 Accepted 24 November 2007 <u>Available online 21 February 2008</u> *Keywords:* Activated carbon Broiler litter Copper ion remediation Cost of production Animal manure continues to represent a significantly large and problematic portion of the US agricultural waste generated yearly. Granular activated carbons made from pelletized poultry litter have been shown to adsorb various positively charged metal ions from laboratory-prepared solutions. The objective of this study was to develop a conceptual capital and operating cost estimate using the Superpro Designer process simulation program. In the study, it was assumed that the activated carbon manufacturing facility obtains the poultry litter from various farmers at a cost of \$5.50 and \$27.50 t⁻¹ for transportation. The carbon manufacturing facility processes 20 t of poultry litter per day and converts it into granular activated carbon for a final carbon yield of 21.6% (dry basis). This facility operates continuously, 330 days of the year. Several parameters were incorporated in the study including equipment sizing, capital costs and operating costs, such as labor, utilities, maintenance and equipment depreciation. The largest contributor to the cost of producing the activated carbon is the \$1,200,000 equipment cost of the combined pyrolysis/activation furnace, which contributes about \$0.47 kg^-1 to the production cost. This study indicates that activated carbon can be produced by this method at a cost of about \$1.44 kg⁻¹.



Estimated cost of production for a broiler litter-based adsorbent

Based on a feed rate of 44,000 lbs/day (22 t).

Based on a product yield of 21.6% or a daily output of 3,360 kg (7,390 lbs) of product.

 Poultry litter is obtained from various farmers at a cost of \$5.00/ton. Litter is transported for 10 miles to the processing facility at a cost of \$25.00 per ton.

Processing facility converts poultry litter into activated carbon on a continuous basis 24 hr/day and 330 day/yr.



Estimated cost of production for a broiler litter-based adsorbent

Based on equipment costs and operating expenses.

- Production costs include utilities, operating & maintenance, labor & supplies, facility overhead charges, & amortization of the cost to build the manufacturing plant over a 10-yr period.
- Costs do not include profit. Profit would have to cover sales and marketing expenses, distribution costs and interest on the capital investment.
- Facility dependent costs included depreciation (total capital costs spread over 15 years), maintenance, and several overhead charges calculated as a function of the projects capital cost.

Equipment Specification and Cost



Labor, raw materials & utilities Cost

Labor Type	Unit Cost (\$/hr)	Amount (hr)	Cost (\$/yr)	%
Plant Workforce	23.47	8,320	195,000	70.12
Supervisor	40.00	2,080	83,000	29.88
TOTAL	X III	10,400	278,000	100.00
Bulk Raw Material	Unit Cost (\$/kg)	Amount (kg/yr)	Cost (\$/yr)	%
Water	0.001	30,601,979	22,000	24.56
Poultry Litter	0.006	6,597,360	36,000	41.08
HCI	0.100	304,040	30,000	34.36
TOTAL		37,503,379	88,000	100.00
Utility	Amount/yr	Ref. Units	Cost (\$/yr)	%
Electricity	3,532,117	kWh	176,606	63.53
Nat Gas	342,103	kg	98,868	35.56
Water	35,999,952	kg	2,520	0.91
TOTAL			277,993	100.00



Annual Operating Cost Breakdown (%)

Raw Materials (5.6%) \$88,000

Transportation (11%) -\$181,000

Labor-Dependent (18%) -\$278,000 Facility-– Dependent (48%) \$762,000

Utilities (18%) \$278,000

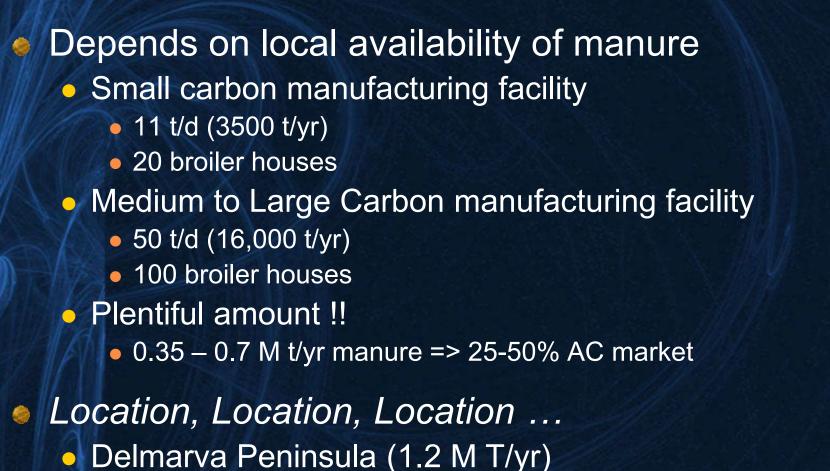


Estimated cost of production for a broiler litter-based adsorbent

Excluded from the capital costs were charges for environmental controls, land acquisition and site development, working capital and the cost of capital during construction.

1	Treatment	Cost / Ib	Yield, %
Carbon	washed	\$0.65	21.6
Carbon	unwashed	\$0.43	30.0
Biochar	washed	\$0.38	33.5
Biochar	unwashed	\$0.32	40.5

Potential Market Size



- Perdue Agri-recycle, Seaford, MD (2500hp mills, 30 T pellets/hr)
- GA, AL, MS => 1/3 U.S. broilers supply

Summary

- Biochars and activated biochars produced by thermo-chemical conversion of organic feedstock such as animal manures proved to be excellent candidates for remediation applications (wastewater, air, soil).
- Carbons made from animal manure are extremely versatile in their use, possibly due to their high organic content and apparent intrinsic qualities.
 - High adsorption for Cu²⁺, Cd²⁺, and Zn²⁺ observed for the poultry and swinebased carbons.
 - Poultry litter biochars also performed well in Hg and NH₃ adsorption studies.
- Pyrolysis conditions, activation strategies and pre- and post-treatments can be manipulated to affect the properties of the resulting biochars and activated biochars.
- Biochar properties are feedstock dependent: surface area and surface charge play a role in adsorption; significant differences in metal uptake between plant versus manure-based biochars.

Summary

- Manure biochars, without being subjected to subsequent activation were able to adsorb up to 58 mg/g of Cu²⁺, with a metal ion sequestering ability exceeding that of biochars from traditional feedstocks.
- Acid activation significantly improved metal ion adsorption for wood based biochars making them as effective as their chicken litter biochar counterparts.
- Copper ion uptake is affected by surface functionality via oxygen bearing groups added via acid activation.
- Functionality as measured by surface charge is not sufficient to explain why broiler litter biochars and steam activated biochars are superior to wood shavings in metal ion adsorption; for this feedstock, functionality could be related to phosphate containing groups.
- In Hg removal experiments, BL650°C biochar was the best performing by far, amongst other feedstocks (lignin, cotton seed hulls and nutshells).
- Ash significantly higher in manure biochars,40 to 70% as compared to 1.4 to 2.5% for plant biochars, selective elemental reduction via acid-wash.

Conclusions



A cost analysis revealed that manure biochars can be produced for 32-38¢/lb (\$0.65/lb for activated biochar), considerably lower than the purchase cost for comparable commercial materials and could be part of an attractive solution for farmers to dispose of their waste and the manufacturer in terms of profit.

- Key areas would include regions of concentrated poultry production close to sensitive environments such as the CB with explosive suburban development.
- Establishment of this product in the marketplace will benefit not only the manufacturer in terms of profit, but also the farmer by establishing a steady market for their waste.
- The key is the profitable reuse of wastes for which farmers are liable and for which, the waste could be almost as valuable as the meat,

- a true Value-Added Product.

Its success will ultimately depend on the economic viability, environmental sustainability and consumer acceptance & the need for legislation.

Multi-purpose

