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Efficacy of Different Biochars in Removing Odorous Volatile Organic Compounds (VOCs) Emitted from Swine Manure

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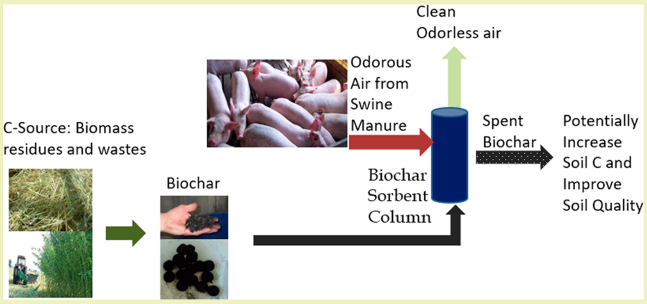
Supporting Information



ABSTRACT: The potential of various biochars to remove 15 odorous volatile organic compounds emitted from swine manure were investigated via laboratory sorption experiments. Nine biochars made from pyrolyzing poultry litter, swine manure, oak, and coconut shell at 350 °C and 500 °C and a commercial coconut-shell activated carbon were evaluated for their sorption capacities toward the odorous compounds. These 15 odorous volatile organic compounds (VOCs) consisted of reduced sulfur compounds, volatile fatty acids, phenolic, and indolic compounds. The sorption capacities of these biochars were investigated using a laboratory-scale sorption column system. Among the 15 targeted VOCs, acetic acid was the most predominant compound in the emitted gas from swine manure; however, its contribution to the complex swine manure odor mixture was minimal. Dimethyl disulfide (DMDS) and dimethyl trisulfide (DMTS) were the two most odor-causing VOCs in the swine manure emissions based on single compound odor active values. Livestock-manure-based biochars were poor sorbents for DMDS and DMTS. In contrast, plant-biomass-based biochars had considerably larger sorption capacity for DMDS and DMTS. Oak biochar pyrolyzed at 500 °C (OK500) showed high sorption capacities for both DMDS and DMTS. Although the sorption capacity of OK500 for DMDS is less than that of commercial activated carbon, it may provide additional income for users if the spent OK500 biochar can be sold as a soil amendment.

KEYWORDS: *Swine manure, Biochar, Odorous VOCs, Sorption*

■ INTRODUCTION

Malodorous emission from swine operations disrupts quality of life in rural and suburban communities. This disruption is exasperating in Korea where buffering distances between swine farms and nearby residents are relatively shorter than those typically found in the U.S. Because odor from swine farms caused a rise in the number of civil complaints, national regulation of malodor emission from livestock facilities had been enacted in Korea.[1] Since then, odor has become an important determinant for sizing and zoning of swine farms. Comprehensive lists of 300 or more potentially odorous VOCs emitted from swine manure and facilities were reported in the literature;[2,3] volatile organic compounds (VOCs) consisting of reduced sulfur compounds, volatile fatty acids (VFAs), phenols, indoles, amines, inorganic ammonia, and hydrogen sulfide were major odorous compounds. Both organic and inorganic sulfides, indoles, and phenols contributed to swine odor more than others because of their relatively low odor threshold values.[4] Emission of these odor-causing compounds from swine facilities must be reduced to improve quality of life in rural communities.

Current practices and technologies for reducing swine odor consist of diet modification, manure handling and treatment, and air treatment. Implementation of these available technologies is driven by economics, sustainability, social acceptability, and in some cases, regulation. Approximately 70% of the expenses associated with raising swine is due to feed costs. Therefore, technologies that can improve feed

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efficiency or lower nutrient excretion are often cost-effective odor mitigation tools as they increase producer profitability. Diet modification with lower crude protein and supplemental amino acid is a commonly used method to reduce odor by lowering nutrient excretions.[5] In Europe, the addition of fermentable carbohydrates to swine diets has been shown to reduce fecal pH and nitrogen excretion in urine as urea, resulting in less volatilization of ammonia.[6−8] However, due to the cost of availability and the cost of fermentable feed ingredients in the U.S., this dietary modification is not typically implemented. Manure handling and treatment is also used to reduce odors from swine facilities such as permeable and impermeable covers providing effective reduction of odor emission from manure storage tank and lagoon.[9] Air treatment technologies such as biofilters and wet scrubbers remove odorants directly from the air.[10] Biofiltration of exhaust air from swine facilities can reduce odor, ammonia, and hydrogen sulfide emissions by up to 90%.[10] Malodorous VFAs from swine manure have been reduced by 79 to 97% when anaerobic digestion is used.[11] In addition, manure additives such as microbes, enzymes, adsorbent and chemical can regulate production, decomposition and adsorption of odorous compounds.[10] A comprehensive list of technologies available to lower odor and gas emissions and the performance of each technology is available.[9] However, not all technologies that successfully lower odor and gas emissions at the lab-scale are implemented on the farm level due to cost and/or management challenges.

Recently, use of biochar as a soil amendment to improve soil quality has gained global interest. The biochar can also be used to remove pollutants from the environment. Biochar is a solid carbonaceous material obtained from the pyrolytic processing of biomass material, which can be used to improve soil quality and remove environmental pollutants.[12−16] Biochar can also be used to remove fugitive gas from air. The potential use of biochar as an air treatment medium was demonstrated by Ro et al.,[17] who reported that ammonia sorption capacities of nonactivated biochars were comparable to that of commercial activated carbon and natural zeolite. Maurer et al.[18] evaluated the effectiveness of manure surface application of nonactivated biochar in reducing swine odor. The biochar was produced from pyrolyzing pine at 495 °C to 505 °C. Ammonia emissions were reduced 13 to 23%; however, emissions of other compounds, such as VFAs, VOCs, and sulfur compounds, were not significantly changed. Although the pine biochar was found to be ineffective in reducing swine odor, the effectiveness of other biochars made from different feedstock materials and pyrolysis conditions has not been reported in the literature.

In this study, we determined the sorption capacities of various biochars made from different agricultural residuals and pyrolysis temperatures toward odorous VOCs commonly detected in swine facilities and estimated its production costs.

MATERIALS AND METHODS

Biochar Production. Biochar was produced from the following selection of biomass feedstocks: oak, solid-separated swine manure, coconut shell, and poultry litter. The swine manure samples were collected from a 5000-head finishing farm in North Carolina. The poultry litter samples were obtained from a broiler farm in South Carolina. Pelletized oak (6 mm diameter) was purchased (Alternative Heating Systems & Supply, Coward, SC). Coconut shell powder (NaturewithLove.com) was hydrated then used to make 6 mm pellets. Pelletizing the manures involved drying to 105 °C, grinding the dry manures to 2 mm particle size, rehydrating the manures, then creating 6 mm pellets. These raw feedstock pellets were pyrolyzed using a Lindburg electric box furnace equipped with a gastight retort (Model 51662, Lindburg/MPH, Riverside, MI). This particular furnace-retort was modified[19] to ensure precision regulation of the final charring temperature. The temperature schedule used for pyrolysis involved the following: (1) Hold for 60 min and purge using 15 L min^{-1} industrial-grade N_2 at 200 °C for equilibration; (2) Ramp up to the desired pyrolytic temperature while dropping N_2 flow to 1 L min^{-1} within 60 min (2.5 °C min^{-1} for 350 °C runs, 5.0 °C min^{-1} for 500 °C runs); (3) Hold for 120 min at the desired temperature for equilibration; and (4) Cool at 4.25 °C min^{-1} to below 50 °C then purge before withdrawing the pelletized biochar samples. In order to find the full potential of swine manure in removing odor, some of swine solid pellets were steam activated by first heating to 700 °C and held for 120 min before heating further to 800 °C and held for 1 h while introducing water (3 mL min^{-1}) into the retort. As an addition to the in-house biochar pellets, a commercial coconut-shell-based activated carbon sample (Dong Yang Carbon Co, Ltd., Cheonan-Si, Choongnam, Korea) was obtained. The abbreviations used to designate these biochar samples are shown in Table 1.

Table 1. Abbreviation Used to Designate Biochar Treatments

abbreviation	feedstock	pyrolysis temperature (°C)	steam activation temperature (°C)
laboratory-made biochar			
CS350	coconut shell	350	
CS500	coconut shell	500	
OK350	oak	350	
OK500	oak	500	
PL350	poultry litter	350	
PL500	poultry litter	500	
SM350	swine manure	350	
SM500	swine manure	500	
SM700	swine manure	700	800
commercial coconut-shell-based activated carbon			
KCS	coconut shell char shards	NA[a]	850

[a] Not available.

Laboratory Biochar Sorption Column System. A laboratory-scale continuous-flow sorption column system was fabricated to evaluate sorption capacity of biochar for odorous compounds generated from bubbled swine manure (Figure 1). A mass flow meter (Aalborg Instruments and Controls, #GFC17A-VAN6-DO, Orangeburg, New York) was used to control the flow of ultrapure N_2 gas into a sealed 19-L plastic pail containing 2.5 L of fresh swine manure. The N_2 gas agitated the swine manure by bubbling and promoted the emission of odorous VOCs from the manure. The headspace gas exited from the pail and entered to the top of the biochar sorption column. The sorption column consisted of a polyvinyl chloride (PVC) threaded pipe nipple (2.5 × 20.3 cm^2) with PVC caps at the top and bottom. A piece of stainless steel screen (18−8 mesh) was secured near the bottom of the column to support the biochar. The columns were loaded with 10 g of biochar.

Swine Manure Samples. Fresh swine manure samples were obtained from a 600-head finishing swine farm in Kentucky with a deep-pit manure management system. Two batches of the swine manure samples (about 24 L manure sample per batch distributed in three11-L buckets) were collected in July and September 2016. These manure samples were kept frozen (−5 °C to −25 °C) until use. Each bucket of manure was thawed and equilibrated to the laboratory temperature before using it for sorption experiments. For each sorption experiment, the batch and bucket numbers along with manure age (i.e., days after thawing and equilibration to laboratory temperature) were recorded. Table S1 of the Supporting Information

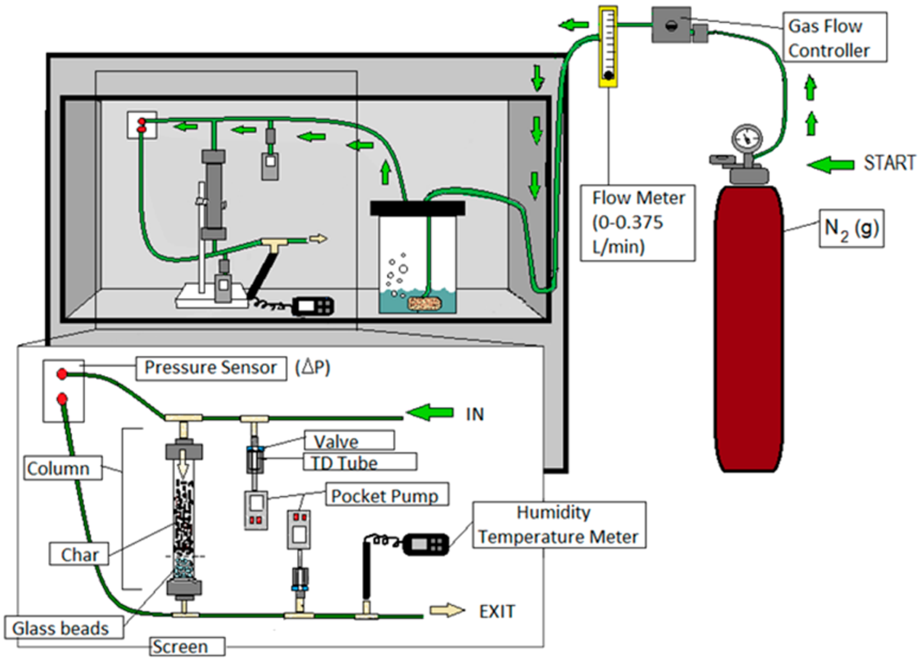

Figure 1. Laboratory continuous-flow sorption column system.

(SI) shows chemical characteristics (nitrogen species, pH and total solids) of the two batches of the swine manure sample (Ward Laboratories, Inc., Kearney, NE).

Analytical Methods. *Physico-Chemical Properties of Biochar.* The biochar proximate properties (volatile matter, fixed carbon, and ash) were analyzed using a thermogravimetric analyzer (TGA, Mettler Toledo International, Inc., Columbus, OH) to approximate the American Society for Testing Materials (ASTM) D3174 and ASTM D3175 standards.[20] Results for the ash tests were verified using a muffle furnace. The Nitrogen Brunauer−Emmett−Teller (BET) surface area was measured in accordance to the 2012 IBI standard with equilibrium over vapor pressure ratios consisting of five evenly spaced values between 0.05 and 0.1 (NOVA 4200e, Quantachrome Instruments, Boynton Beach, FL). The pH was measured in triplicate in deionized (DI) water at 20 g L^{-1} (0.4 g of biochar in 0.02 L DI water) after shaking for 24 h. The nonuniform biochar particle size was characterized with the Sauter-mean diameter[21] determined from fitting the scanned images of the 100−300 mg of biochar particle samples to ellipsoidal shapes and calculating the major and minor axes.

Analyses of Odorous VOCs. The concentrations of odorous VOCs in the influent and effluent stream were measured by sampling the gas stream at hour multiples using Thermal desorption sorbent tubes (Markes International, #C1-AAXX-5003, Sacramento, CA). Small pumps (SKC, #210−1002 pocket pump and #220−5000TC Airchek Touch, Eighty Four, PA) were used to pull the influent or effluent gas through the sorbent tubes at 75 mL min^{-1} for a duration of 20 min yielding a total sample volume of 1.5 L. The odorous VOCs collected on the sorbent tube samples were analyzed using a thermal desorption-gas chromatography−mass spectrometry (TD-GC-MS) system. The TD system consisted of a Markes Unity 2 thermal desorber with Ultra 2 autosampler (Markes International Inc., Wilmington, DE, U.S.A.). Samples were quantified with an Agilent 7890A GC with Agilent 5975C MS (Agilent Technologies, Inc., Santa Clara, CA, U.S.A.). In the TD system, samples were initially purged for 2 min (40 mL min^{-1}, 20 °C) to remove water and air. The tube was desorbed for 10 min at 280 °C with a carrier gas flow of 50 mL min^{-1} and trapped on the cold trap maintained at −10 °C. The cold trap was heated to 320 °C for 3 min with a carrier gas flow of 20 mL min^{-1}, and 1.4 mL min^{-1} was transferred to the column in the GC-MS. In the GC oven, the column was held at 40 °C for 3 min, ramped to 230 °C at 8 °C min^{-1}, then held at 230 °C for 5 min for a total run time of 31.8 min. The polar analytical column was an Agilent Innowax, 30 m × 0.25 mm ID capillary column (polyethylene glycol, 0.25 μm film thickness).

Samples were analyzed for eight VFAs (acetic, propionic, isobutyric, butyric, isovaleric, valeric, hexanoic, heptanoic), three phenolics (phenol, 4-methylphenol, 4-ethylphenol), two indolics (indole, skatole), and two sulfides (dimethyl disulfide, DMDS; dimethyl trisulfide, DMTS). Standard solutions were prepared by diluting known masses of pure chemicals with methanol. Standards were prepared using serial dilutions and injected onto clean tubes using a calibration solution loading rig (Calibration Solution Loading Rig or CSLR; Markes International Inc., Wilmington, DE, U.S.A.). The liquid calibration standard was introduced through the CSLR injector septum in clean bottled air carrier gas (75 mL min^{-1}) using a standard GC syringe. Within the linear range, standard curves were fit using linear regression with the curve forced through the origin. All sorbent tubes were conditioned with the Markes TC-20 tube conditioner system (Markes International Inc., Wilmington, DE, U.S.A.) and analyzed on the GC-MS prior to sampling to verify that clean tubes were used in the experiment.

Detection Limit and Minimum Concentrations. Detection limits (DL) of each of the odorous compounds were determined by multiplying three times of the noise levels generated from analyzing clean, unused sorbent tubes with the TD-GC-MS using the same method (Table 2). Because the clean biochar samples also emitted trace levels of odorous VOCs, the average VOC concentrations from passing ultrapure N_2 gas through the sorbent column filled with clean biochar samples (SM350, SM500, and Ok500) were measured and designated as baseline concentrations (BC). The minimum concentrations (MC) were selected from the higher of the DL or BC (Table 2). Only the data sets with higher than the minimum concentrations (MC) were used to calculate sorption capacity.

Sorption Capacity. Sorption capacities of each biochar samples were calculated from the influent and effluent VOCs concentrations measured intermittently (every one or 2 h), biochar mass and gas flow rate while the manure tank headspace gas continuously passed through the biochar column for 6 h. The difference between cumulative masses of each VOC in the influent and effluent streams was assumed to be the odorant mass sorbed onto biochar. The sorption capacity was then calculated by dividing the mass of sorbed VOC by the mass of biochar (eq 1)

Table 2. Detection Limit, Baseline, and Minimum Concentrations[a]

compounds	DL (ng L^{-1})	BC (ng L^{-1})	MC (ng L^{-1})[b]
DMDS	0.3	0.1	0.3
DMTS	0	0.03	0.03
acetic	98	69	98
propionic	18	2.9	18
i-butyric	0.4	0.1	0.4
butyric	1.1	2.9	2.9
i-valeric	9.8	2.1	9.8
valeric	2.0	1.2	2.0
hexanoic	1.2	8.4	8.4
heptanoic	4.0	2.5	4.0
phenol	86	172	172
4-m phenol	2.2	0.4	2.2
4-e phenol	2.7	1.1	2.7
indole	0.1	0.01	0.1
skatole	0.1	0.01	0.1

[a]Represent the concentrations at room temperature and pressure (i.e., 23−25 °C and 1 atm). [b]DT or BC whichever greater.

$$q_{i,j} = \frac{\int_0^t (C_{\text{in},i} Q_{\text{in}} - C_{\text{e},i} Q_{\text{e}})\,dt}{M_{,j}} \tag{1}$$

.where $C_{\text{in},i}$ = influent odorant i concentration (ng L^{-1}), $C_{\text{e},i}$ = effluent odorant i concentration (ng L^{-1}), $M_{,j}$ = mass of biochar j (g), Q_{in} = influent flow rate (L min^{-1}), Q_{e} = effluent flow rate (L min^{-1}), $q_{i,j}$ = sorption capacity of j biochar for odorant i (ng g^{-1}) at time t, and t = flow time (min)

Typically, the mass of sorbed VOC monotonically increased with time and the largest sorbed mass occurred at the end of each run. However, the maximum sorption sometimes occurred before the end of experimental runs because the biochar became saturated with the odorants: Then, the sorbed mass achieves steady-state or decreases slightly to steady-state conditions due to desorption after the maximum sorption occurred. In addition, it was not clear whether the sorption capacity determined at the end of 6 h of the experimental runs was the saturation sorption capacity. Therefore, the Thomas kinetic model[22] was used to estimate the maximum sorption capacities based on observed ratios of the influent and effluent concentrations. The Thomas kinetic model is one of the most widely used kinetic models in column sorption studies.[23] The Thomas model assumes second-order sorption kinetics and an idealized plug flow with no axial dispersion. The ratios of the influent and effluent concentrations based on the Thomas kinetic model can be expressed as follows:

$$\frac{C_{\text{e},i}}{C_{\text{in},i}} = \frac{1}{1 + \exp\left(\frac{K_{\text{T},ij} q_{\text{e},ij} M_j}{Q_{\text{in}}} - K_{\text{T},ij} C_{\text{in},} t\right)} \tag{2}$$

.where $K_{\text{T},i,j}$ = Thomas kinetic constant for odorant i on biochar j (L min^{-1} ng^{-1}), and $q_{\text{e},i,j}$ = maximum sorption capacity of j biochar for odorant i (ng g^{-1}).

The Thomas kinetic constant (K_{T}) and the maximum sorption capacity (q_{e}) were determined by plotting $C_{\text{e}}/C_{\text{in}}$ against t for a given flow rate and the mass of biochar.

Statistics. The central tendency and precision of measurements were presented with arithmetic average and standard deviations (given as ± values). All the statistical parameters and analyses of variance (ANOVA) tests were obtained/performed using GraphPad Prism 7.03 (GraphPad Software, Inc., La Jolla, CA, U.S.A.).

■ RESULTS AND DISCUSSION

Biochar Properties. Table 3 shows the amount of biochar recovered as a percentage of the initial feedstock mass (i.e., yield) along with its physicochemical properties for different feedstocks and process conditions. Within each feedstock type, lower yields were observed for higher pyrolysis temperatures. The decrease in yield with pyrolysis temperature was due to the increase in devolatilization of volatile matter as manifested in the decrease in the volatile matter (VM) of biochar.[24] The biochar size also decreased with increasing temperature. The ash contents of animal manure and coconut shell were much higher than that of oak (less than 2.3%). The ash contents, fixed carbon (FC), and the pH increased with temperature, as observed in the literature.[24] The BET surface areas of nonactivated biochars ranged from 0.2 to 9.8 m^2 g^{-1}. In general, the BET surface area of nonactivated biochars slightly increased with the increase in pyrolysis temperature. The BET surface areas of nonactivated livestock-manure biochars are comparable to those reported in the literature (0.57 to 6.8 m^2 g^{-1}).[24,25,14] Steam activated swine-manure biochar (SM700) showed higher BET surface area with 164 m^2 g^{-1}. The commercial coconut-shell activated carbon (KCS) had the largest surface area with 488 m^2 g^{-1}.

Table 3. Yields, Proximate Properties, Sizes, pH, and Surface Areas of Raw Feedstock and Biochar Samples[a]

samples	yield (%)	VM[b] (%db[c])	FC[b] (%db[c])	ash[b] (%db[c])	D[d] (mm)	pH[b]	BET (m^2 g^{-1})
raw oak		79.1 ± 1.5^{a}	19.5 ± 1.6^{a}	1.3 ± 0.5^{a}	8.1	4.9 ± 0.0^{a}	0.3
OK350	37.3	32.8 ± 0.8^{b}	65.4 ± 0.8^{b}	1.8 ± 0.0^{a}	8.0	3.7 ± 0.1^{b}	0.2
OK500	27.6	14.9 ± 0.3^{c}	82.9 ± 0.3^{c}	2.3 ± 0.1^{a}	7.7	6.5 ± 0.8^{c}	9.8
raw swine manure		59.5 ± 0.5^{d}	11.0 ± 1.6^{d}	29.5 ± 1.6^{b}	8.3	6.1 ± 0.1^{c}	0.7
SM350	51.8	31.7 ± 0.3^{b}	26.6 ± 0.4^{e}	41.8 ± 0.3^{c}	7.4	7.1 ± 0.1^{c}	2.2
SM500	41.9	17.1 ± 0.2^{c}	33.4 ± 1.5^{f}	49.4 ± 1.5^{d}	7.1	7.8 ± 0.1^{d}	5.5
SM700	31.8	7.9 ± 0.1^{e}	32.3 ± 0.2^{f}	59.8 ± 0.1^{e}	6.3	9.6 ± 0.0^{e}	164.3
raw coconut shell		62.5 ± 0.7^{f}	28.6 ± 1.2^{f}	8.9 ± 0.9^{f}	8.5	6.3 ± 0.1^{d}	2.2
CS350	52.7	28.6 ± 0.5^{g}	49.9 ± 0.7^{g}	21.5 ± 0.5^{g}	7.4	10.3 ± 0.0^{e}	3.6
CS500	50.2	16.7 ± 0.6^{c}	55.5 ± 0.7^{g}	27.8 ± 0.4^{g}	7.3	11.1 ± 0.2^{f}	3.6
raw poultry litter		40.3 ± 0.1^{h}	32.9 ± 5.8^{f}	26.8 ± 5.8^{g}	9.1	8.2 ± 0.3^{d}	1.0
PL350	45.6	33.5 ± 1.0^{b}	30.8 ± 1.4^{f}	35.7 ± 0.9^{h}	7.7	9.8 ± 0.1^{e}	2.4
PL500	37.6	20.3 ± 0.9^{i}	37.5 ± 1.2^{f}	37.5 ± 0.9^{h}	7.5	10.2 ± 0.1^{e}	3.3
KCS		3.9 ± 0.2^{j}	61.6 ± 3.2^{b}	34.5 ± 3.2^{h}	3.4	9.2 ± 0.1^{e}	488

[a]Acronyms: VM = volatile matter; FC = fixed carbon; Ash = ash content; BET = Nitrogen Brunauer−Emmett−Teller surface area. [b]triplicate samples expressed with mean ± standard deviation; Values followed by the same letter within each column category were not significantly different ($p < 0.05$, ANOVA). [c]dry basis. [d]Sauter-mean diameter.

Table 4. Odorous VOCs Emitted from the Swine Manure

	batch 1 manure sample		batch 2 manure sample				
compounds	C_1[a] ($ng\ L^{-1}$)	N_1[b]	C_2[a] ($ng\ L^{-1}$)	N_2[b]	overall average C ($ng\ L^{-1}$)	SCOT[26] ($ng\ L^{-1}$)	SCOAV
DMDS	132.2 ± 151.7	81	13.0 ± 14.9	58	82.8 ± 130	12	6.9
DMTS	52.0 ± 59.2	76	3.3 ± 4.4	43	34.4 ± 52.8	2	17.2
acetic	147 ± 50	25	107 ± 10	3	142 ± 49.2	578	0.3
propionic	BD[c]		BD		BD[b]	106	NA[d]
i-butyric	BD		BD		BD	38	NA
butyric	1.3 ± 0.1	8	BD		1.3 ± 0.1	6.9	0.2
i-valeric	BD		BD		BD	2.3	NA
valeric	BD		BD		BD	8.8	NA
hexanoic	BD		2.4 ± 0.5	6	2.4 ± 0.5	69	0.03
heptanoic	BD		BD		BD	60	NA
phenol	BD		BD		BD	206	NA
4-m phenol	3.2	1	BD		3.2	1.3	2.5
4-e phenol	3.5 ± 1.3	3	3.2 ± 0.4	3	3.2 ± 0.9	6.3	0.5
indole	0.3 ± 0.2	8	0.4 ± 0.3	8	0.3 ± 0.3	2.1	0.2
skatole	0.2 ± 0.2	16	0.3 ± 0.3	10	0.3 ± 0.2	0.48	0.6
			sum of SCOAV				28.3

[a] Average concentration ± standard deviation of batch 1 or 2 manure sample. [b] Number of samples above detection limit in batch 1 or 2 manure sample. [c] Below detection limit. [d] Not available.

Table 5. DMDS Adsorption Capacities of Biochars

biochar[a]	mass (g)	Q[b] ($L\ min^{-1}$)	C_{in}[c] ($ng\ L^{-1}$)	q[d] ($ng\ g^{-1}$)	contact time (h)	manure batch/bucket	manure age (day)
				livestock-manure biochar			
SM350	10.0	1.1	0.6	0	1	1/1	4
	10.1	1.2	62.8	0	1	1/3	21
SM500	10.0	1.1	1.6	19	6	1/1	7
	10.0	1.2	66.2	893	6	1/3	22
SM700	10.0	1.1	6.8	150	6	1/3	9
	10.1	1.2	275	1,312	2	1/3	14
PL350	10.0	1.1	18.9	0	1	2/2	7
	10.0	1.1	276	0	1	1/3	8
PL500	10.0	1.0	18.8	0	1	2/2	9
	10.0	1.1	44.2	0	1	1/2	1
				plant-biomass biochar			
CS350	10.0	1.0	14.5	153	6	2/1	6
	10.0	1.2	445	13,368	6	1/3	2
CS500	10.0	1.0	3.5	113	6	2/2	2
	10.0	1.1	364	9,770	6[e]	1/3	1
KCS	10.0	1.0	33.2	1,497	6	2/2	20
OK350	10.0	1.1	10.5	141	6	2/1	1
	10.0	1.1	84.5	2,962	6[e]	1/3	7
OK500	10.0	1.0	18.9	448	6	2/1	5
	10.0	1.1	202	5,748	6[e]	1/2	2

[a] Biochar acronyms are defined in Table 1. [b] Flow rate. [c] Influent concentration. [d] Sorption capacity. [e] These concentration profiles were fitted to the Thomas model equation.

Odorous VOCs Emitted from the Swine Manure. Table 4 shows the average concentrations of the odorous VOCs emitted from the two batches of the swine manure samples. The total number of manure headspace gas samples taken before introducing into the biochar column was 139; however, only DMDS was detected in all 139 samples while other VOCs were either below their detection limits or detected only in some samples. Of the 15-targeted compounds, acetic acid, DMDS, and DMTS represented most odorous VOCs detected in the swine manure headspace gas. To assess the relative impact of each of these compounds contributing to the total mixture of odor, single compound odor active values (SCOAVs) were calculated. The SCOAV is the ratio of a mass concentration (i.e., ng/L) normalized to the single compound odor threshold (SCOT) for the compound (i.e., SCOAV = mass concentration/SCOT).[26] Table 4 shows the values of SCOT used in this study to calculate SCOAVs. The compound with higher SCOAV value was assumed to more likely contribute to the overall odor of a complex odor mixture. Although this approach does not account for hedonic tone and synergistic or antagonistic interactions of many odorous compounds in the air, it still infers a rough estimation of relative concentrations of each odorous VOCs emitted from the swine manure by dividing by the sum of SCOAV for all measured compounds.

Table 6. DMTS Sorption Capacity of Biochar

biochar[a]	mass (g)	Q[b] (L min^{-1})	C_{in}[c] (ng L^{-1})	q[d] (ng g^{-1})	contact time (h)	manure batch/bucket	manure age (day)
livestock-manure biochar							
SM350	10.0	1.1	0.2	0	1	1/1	4
	10.1	1.2	25.3	0	1	1/3	21
SM500	10.0	1.1	0.5	18.6	6	1/1	7
	10.0	1.2	25.8	0	1	1/3	22
SM700	10.0	1.1	1.1	10.9	6	1/3	9
	10.1	1.2	1.2	34	1	1/3	14
PL350	10.0	1.1	99.0	0	1	1/3	8
PL500	10.0	1.1	22.7	89.7	4	1/2	1
plant-biomass biochar							
CS350	10.0	1.0	5.0	102	6	2/1	6
	10.0	1.2	173	4,528	6	1/3	2
CS500	10.0	1.0	0.7	22	6	2/2	1
	10.0	1.1	134	3,374	6[e]	1/3	1
KCS	10.0	1.0	8.9	386	6	2/2	20
OK350	10.0	1.1	4.5	56	6	2/1	1
	10.0	1.1	44.1	1,427	6[e]	1/3	7
OK500	10.0	1.0	4.8	107	6	2/1	5
	10.0	1.1	61.9	1,427	6[e]	1/2	2

[a] Biochar acronyms are defined in Table 1. [b] Flow rate. [c] Influent concentration. [d] Sorption capacity. [e] These concentration profiles were fitted to the Thomas model equation.

Table 7. Thomas Model Parameters

biochar[a]	flow (L min^{-1})	mass (g)	C_{in}[b] (ng L^{-1})	Thomas model parameters: K_T[c] (L min^{-1} ng^{-1})	Thomas model parameters: q_e[d] (ng g^{-1})	Thomas model parameters: R^2
DMDS						
CS500	1.1	10.0	364	4.11×10^{-5}	10 999	0.92
OK350	1.1	10.0	84.5	8.38×10^{-5}	4375	0.96
OK500	1.1	10.0	202	1.55×10^{-5}	15 274	0.95
DMTS						
CS500	1.1	10.0	136	3.46×10^{-4}	3583	0.95
OK350	1.1	10.0	44.1	1.17×10^{-4}	3318	0.66
OK500	1.1	10.0	61.9	7.22×10^{-5}	3579	0.89

[a] Biochar acronyms are defined in Table 1. [b] Influent concentration. [c] Thomas kinetic constant. [d] Maximum sorption capacity.

The VOC with the highest concentration was acetic acid with an average concentration of 142 ng L^{-1} (52.5% of the sum of all concentrations) followed by DMDS (82.8 ng L^{-1}) and DMTS (34.4 ng L^{-1}). However, the contribution of acetic acid to the overall odor was minimal with SCOAV of 0.3, representing only 0.9% of the sum of SCOAV (Figure S1). In contrast, DMDS and DMTS contributed to the odor mixture significantly with the SCOAVs of DMDS and DMTS were 24.4 and 60.8% of the total SCOAV, respectively. Other VOCs with minor contribution to the odor mixture were butyric acid, hexanoic acid, 4-methyl phenol, indole, and skatole with their SCOAVs representing 0.7%, 0.1%, 8.7%, 1.9%, 0.6%, and 2.0% of the total SCOAV, respectively.

Sorption Capacity. Although some minor VOCs were detected, DMDS and DMTS were the major compounds among the 15 VOCs (Table 2) emitted from the swine manure that were above the minimum concentrations. Tables 5 and 6 show the sorption capacities of biochar samples for DMDS and DMTS, respectively. Because the DMDS and DMDT concentrations in the influent (i.e., headspace gas from the plastic pail containing manure in Figure 1) varied considerably from day to day experiments (Figure S2), it was not possible to quantitatively compare the sorption capacities of these compound on different biochar samples.

The livestock-manure-based biochars were poor sorbents for removing DMDS or DMTS with their sorption capacities ranging from 0 to 1312 ng g^{-1} for DMDS and 0 to 89.7 ng g^{-1} for DMTS. The poultry-litter biochars both made at 350 °C and 500 °C (PL350 and PL500) showed no sorption capacity for DMDS. For DMTS, PL500 showed a small sorption capacity (89.7 ng g^{-1}) while PL350 did not have any. Swine-manure biochars without activation (SM350 and SM500) did not have any sorption capacity for DMTS. For DMDS, the sorption capacity for SM500 was 893 ng g^{-1}, while SM350 showed no sorption capacity. The sorption capacities for DMDS of the steam-activated swine manure biochar (SM700) were only slightly higher than that for SM500 at higher influent concentrations of 275 ng L^{-1}. Although the BET surface area of SM700 was almost 2 orders of magnitude larger than that for SM350 and SM500, the DMDS and DMTS sorption capacities of SM700 did not increase significantly. Although VM, FC, ash contents, and pH of the livestock-manure biochars varied widely, their sorption capacities toward DMDS and DMTS were mostly insignificant. This suggested that the BET surface area, VM, FC, ash contents, and pH of the livestock-manure biochar did not significantly affect the adsorption of these compounds.

In contrast, most plant-biomass biochars showed considerably higher sorption capacities than that of livestock-manure biochars. As with the SM700, the influent concentration strongly influenced sorption capacity for both compounds: Higher influent concentration resulted in higher sorption capacity. This influence on sorption capacity by influent concentration was probably due to the fact these biochars did not reach their saturation sorption capacity after 6 h of contact time.

To estimate the maximum/saturation sorption capacities, the influent and effluent concentration profiles were fitted to the Thomas kinetic model. Concentration profiles of only three biochars (CS500, OK350, and OK500) with higher influent concentrations fitted reasonably well with $R^2 > 0.66$ (Table 7 and Figure 2). Among the three biochars, OK500 showed the highest DMDS (15,274 ng g^{-1}) and second highest DMTS (3,579 ng g^{-1}) saturation sorption capacities. Although the sorption capacity of OK500 for DMDS is about 35% of commercial activated carbon's sorption capacity,[27] it may offer additional economical advantage to use OK500 for removing DMDS if the spent OK500 biochar can be applied to soil as a soil amendment. The potential soil application of spent biochar is currently under investigation.

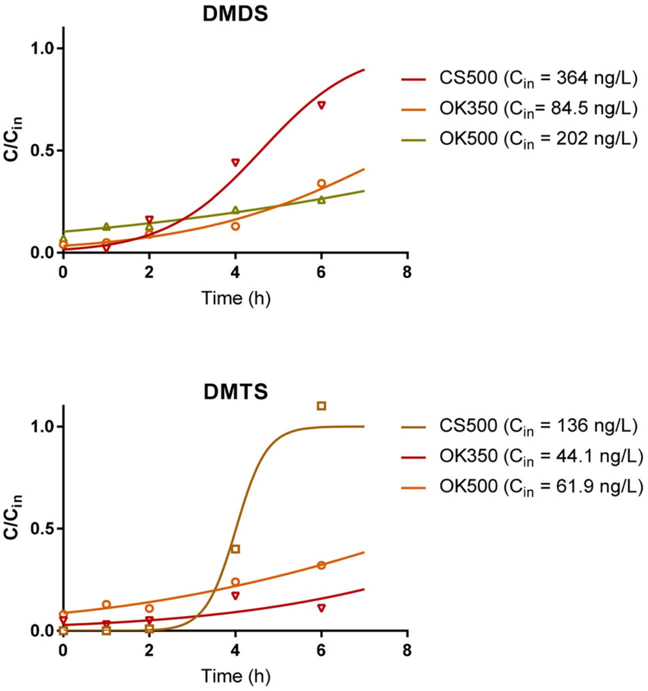

Figure 2. Concentration ratios fitted to the Thomas kinetic model equation.

The DMTS sorption capacities of CS500 and OK500 were similar, yet their pH values differed considerably with 6.5 and 11.1 for OK500 and CS500, respectively. This suggested that the pH of biochar did not play a significant role on DMTS adsorption. The FC and the ash contents for OK500 and CS500 were also significantly different, yet the DMTS sorption capacities of the two biochars were similar, suggesting both FC and ash contents of biochar did not play a significant role.

Figure 3 shows the effects of flow rate and influent concentration on breakthrough curves for OK500. These breakthrough curves were simulated using the Thomas kinetic model parameters determined previously. The effect of flow rate on the breakthrough curve is shown in Figure 3a. As the flow rate increased from 0.3 to 1.0 L min^{-1}, breakthrough time reaching saturation was significantly shortened. Similarly, as the influent concentration increased, the breakthrough time for saturation also decreased (Figure 3b).

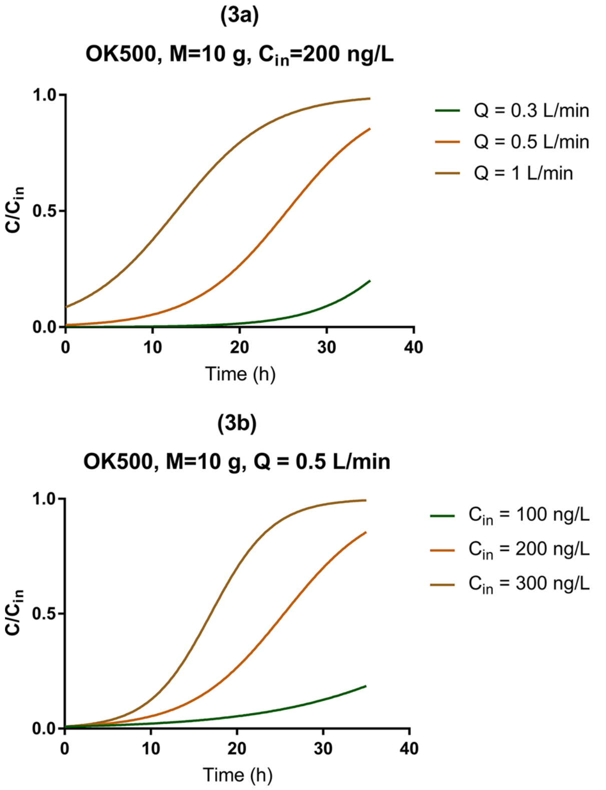

Figure 3. Breakthrough curved simulated for OK500 using Thomas kinetic model.

Estimation of Production Cost. There are multiple aspects of biochar that make it valuable as a soil amendment depending upon the condition and the needs of soil. Several possible needs include maintaining soil organic carbon for a longer period of time, increasing cationic exchange capacity, improving water retention capacity, and reducing nutrient leaching and environmental pollutants. Therefore, assigning an economic value to biochar depends on the needs and the condition of the receiving soil. Although comprehensive economic analysis of spent biochar as a soil amendment provides valuable information for potential users, it would be well beyond the scope of this study. Instead, we estimated approximate production costs of OK500 with the cooperation of private pyrolysis and wood pelleting companies in the U.S. and Korea. Table 8 shows the costs that potential users would pay for a tonne (i.e., metric ton) of OK500 delivered to the site of biochar application. The total OK500 costs ranged from \$1626 to \$1660 per tonne. These prices are on the lower end of the literature reported biochar market price (\$220 to \$6615 per tonne[28]). It is also lower than the currently available commercial biochars in the U.S. that are made from switch grass (\$1870/tonne FOB) but more expensive than biochar made from poultry litter (\$880/tonne FOB). Poultry litter biochars are less expensive than OK500 probably because chicken litter is substantially less expensive than pelleted wood. Therefore, if the spent OK500 is as effective as other virgin biochars in improving soil quality, it may be economically

Table 8. Production Costs of OK500 Biochar

item	costs in the U.S. (US $)	costs in Korea[b] (US $)
oak wood pelleting (4 tonnes)[a]	1146	1120
shipping pellets to pyrolysis company[c]	120	120
drying and pyrolyzing 4 tonnes of wood pellets to produce 1 tonne of OK500 biochar with an yield of 25%[d]	330	390
shipping biochar to users[c]	30	30
total costs	1626	1660

[a] Including the costs of oak wood scrap delivered to the pelleting company. [b] Currency conversion of US $1.00 = 1150 Korean Won. [c] Assumed shipping distance of 10 mi (16 km) and the cost of US $ 3 per mi (1.6 km). [d] Price of 1 tonne of produced biochar.

advantage for a farmer to use the virgin OK500 to reduce DMDS and DMTS emission and sell the spent OK500 as a soil amendment. However, more in-depth study is needed for the feasibility of using spent OK500 as a soil amendment.

■ CONCLUSIONS

Sorption capacities of 15 odorous VOCs emitted from the swine manure on different biochars were determined via laboratory sorption column experiments. Although acetic acid was the most predominant compound in the emitted gas, its contribution to the complex odor mixture was minimal based on its SCOAV. DMDS and DMTS were the two most odor-causing compounds tested and also the only compounds with high enough concentrations enabling us to estimate the sorption capacities of different biochar samples. Livestock-manure biochars were poor sorbent for DMDS and DMTS. Poultry-litter biochars did not have any sorption capacity toward DMDS, while PL500 showed a small sorption capacity for DMTS. In contrast, plant-biomass biochars had considerably more sorption capacity toward DMDS and DMTS. It appeared that the biochar properties (VM, FC, ash content, pH, and BET surface area) did not play any significant roles in adsorption of these compounds on biochar. Comparing saturation sorption capacities of three biochar samples (OK350, OK500, CS500) estimated from the Thomas kinetic model, OK500 might be the most promising sorbent among the three. Although the sorption capacity of OK500 for DMDS is less than that of commercial activated carbon, it may provide additional income for users if the spent OK500 can be sold as a soil amendment. Although other technical challenges, such as pressure drop requirements across biochar filters, must be addressed before successful implementation of biochar odor removal technology, the findings of this laboratory-scale study favorably suggest the potential of using biochar for swine operations.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acssuschemeng.8b02881.

> Chemical characteristics of swine manure (Table S1), relative contribution of odorous VOCs in terms of their concentrations and SCOAVs (Figure S1), and sorption column inlet concentrations of DMDS and DMTS from the two batches of manure samples (Figure S2) (PDF)

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Notes

The authors declare no competing financial interest.
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