RESEARCH REPORT

ENVIRONMENT

Title: Removal of Volatile Organic Compounds from Swine Facilities via Adsorption: Technical and Economic Evaluation - **NPB #12-072**

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Industry Summary: There is a significant interest in mitigating odors from swine operations. Considering the layout of a typical swine barn, a simple, inexpensive, and effective technology is needed. Biochar is one such material capable of adsorbing odors. In addition, due to intensification of biomass to energy processes, it is expected that large amounts of biochar will be available. Hence in this research we evaluated biochar derived from pinewood, swine manure, and coconut shell as an adsorbent for mitigation of *p*-cresol as a model odorous volatile organic compound from swine lagoons. Specifically we investigated how much *p*-cresol can be removed using biochar, how fast can biochar adsorb p-cresol, and how much will it cost to remove a gram of p-cresol. Our research indicated that biochars can potentially remove 6-30 mg/g of *p*-cresol within 100-1440 min depending on the type of char employed. Considering the fact that *p*-cresol and other VOC concentrations concentration in a swine lagoons are normally less than 5 mg/L, biochar based adsorption may be considered a viable alternative for treating swine wastewater. Based on the predicted production of biochar by bioenergy industry it is estimated that biochar treatment may cost around $0.79/Kg of biochar. Our research is important to swine industry because it provides a practical method to mitigate odors from swine operations and improve the quality of life facilities, and enhance the image of swine farming in the community.

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Scientific Abstract: The purpose of this research is to evaluate biochar as an inexpensive adsorbent for mitigation of odorous volatile organic compounds from swine lagoons. Biochar was synthesized from discarded pinewood, swine manure, and coconut shell via pyrolysis and gasification (two most popular) techniques, respectively. Briefly, pinewood was impregnated with K_2CO_3 (impregnation ratio: 2) and pyrolyzed at 266 °C for 2 h to obtain pinewood biochar. Surface characterization of pinewood biochar indicated that the acid value increased from 5.01 to 9.29 as a result of K_2CO_3 and pyrolysis. Batch experiments were performed in which, 1g of pinewood biochar was mixed with 100 mL of *p*-cresol solution (50- 1000 mg/L) at 15-45 °C. Samples were drawn periodically and analyzed via gas chromatograph equipped with a mass selective detector. The data indicated that a theoretical maximum adsorption capacity of 6.97 mg/g was possible at 25 °C for *p*-cresol). The thermodynamic analysis revealed that adsorption of p-cresol was exothermic ($\Delta H° = -2.11$ kJ/ mol) suggesting that lower temperatures favor higher adsorption capacities possibly due to p-cresol-char bond disruption at higher temperature. In addition presence of another VOC, 2 methylbutyraldehyde did not reduce or inhibit adsorption of either p-cresol or 2 methylbutyraldehyde, suggesting that pinewood biochar may adsorb VOC mixture simultaneously. In the second part of the research swine manure was used as raw material for preparation of biochar via gasification. Dried swine manure (40% moisture) obtained from NC State swine farm was gasified at 704 °C for 15 min using a mixture of nitrogen (25 parts) and air (1 part) to obtain swine manure biochar. Boehm titration analysis indicated that the biochar consisted predominantly of basic surface functional groups perhaps due to presence of ammonia in the manure. The swine manure biochar was tested for mitigation of *p*-cresol in batch experiments that were performed at 25, 35, and 45 °C to determine the kinetic, isotherm, and thermodynamic parameters. The data indicated that swine manure biochar may adsorb up to 14 mg/g of *p*-cresol irreversibly. Unlike pinewood biochar, the adsorption process of p-cresol on manure char seemed to be endothermic ($\Delta H° = 6.3$ kJ/ mol) suggesting that higher temperatures favor higher adsorption capacities, perhaps due to availability of higher pore volume and chemisorption rates at elevated temperatures. As the concentrations of *p*-cresol and other odorous VOCs are usually less than 5 mg/L, adsorption capacities obtained in our research are considered adequate for optimum mitigation of these aforementioned pollutants. But the biochar obtained from these thermochemical processes (pyrolysis and gasification) possess low structural integrity. Hence to be able to apply in lagoons, the biochar needs to be structurally stable. Hence we prepared biochar from coconut shell and tested its efficacy extensively. Our results indicate that coconut shell biochar can remove up to 30 mg of p-cresol per gram of biochar. In addition the biochar derived from coconut shell was extremely stable and was able to maintain its form even after several experiments. Our research is expected to have significant positive implications on air and water quality in and around swine facilities

Introduction: There is a significant interest in mitigating odors from swine operations. Considering the layout of a typical swine barn, a simple, inexpensive, and effective technology is needed. In this research biochar was evaluated as an adsorbent to mitigate *p*-cresol from water. It is expected that such adsorbents will reduce the concentration of pollutants in lagoons and improve the quality of air in and around the swine facilities, improve the image of swine industry, and make our swine industry competitive.

Objectives:

(1) Laboratory testing of pine-biochar as adsorbent for a mixture of *p*-cresol, acetic acid, and isovaleraldehyde

- Investigate the effect of mass, temperature, and pH on adsorption
- Determine the maximum adsorption capacity of char for *p*-cresol, acetic acid, isovaleraldehyde.

(2) Perform field scale testing of pine-biochar in an experimental swine facility

- Test the efficacy of pine-biochar for removing *p*-cresol, acetic acid, isovaleraldehyde in an anaerobic lagoon
- Estimate the mass of *p*-cresol, acetic acid, isovaleraldehyde adsorbed on pine-biochar via temperature programmed desorption.

Materials & Methods:

Nomenclature used in this report

C_e(mg/L): Equilibrium concentration of the adsorbate
q_e(mg/g): Adsorbate (p-cresol) adsorbed per unit mass of adsorbent at equilibrium
q_t(mg/g): Adsorbate (p-cresol) adsorbed per unit mass of adsorbent at equilibrium
Q_0: Langmuir constants for adsorption capacity
b: Langmuir constants for adsorption rate
K_F: Freundlich's adsorption constant
n: Freundlich's adsorption constant.
k_1 (1/min): First order rate constant
k_2 (mg/g min): Second order rate constant
α (mg/g min): Initial adsorption rate
β (g/mg): Initial desorption rate
C: intra-particle diffusion constant
Δ G° (kJ/mol): Gibbs free energy
ΔH° (kJ/mol): enthalpy change
ΔS° (kJ/mol): entropy change
R (8.3 J/mol/K): Universal gas constant
T (K): Temperature

Biochar synthesis: To synthesize pinewood biochar, pinewood samples were soaked in a solution of K_2CO_3 as described in Das et al. (2013). The optimum char was obtained by carbonizing samples (2 h) under the flow of nitrogen (2 L/min) at a temperature of (266 °C).

Characterization of biochar: The char so obtained was characterized via standard physical and chemical techniques such as specific surface area, acid value, and the strength of surface functional groups. The specific surface area was determined via nitrogen adsorption method. The

acid value of the char was estimated by soaking the char in DI water (pH:7) for 8 h followed by measuring the pH of the solution. Similarly, the strength of the surface functional groups was quantified by Boehm titration (Das et al., 2013).

Testing of biochar: The adsorption capacity of biochar was evaluated in batch experiments. Typically char samples (1 g) were mixed with p-cresol solutions (50-1000 mg/L) at various temperatures (15-55 °C). While mixing, samples were drawn periodically and analyzed for p-cresol concentrations using a gas chromatograph attached to a mass spectrometer. After equilibrium was reached, the adsorption capacity was determined via a mass balance

Isotherms: The data were analyzed using Langmuir (equation 1) and Freundlich (equation 2) adsorption isotherms to estimate the maximum adsorption capacity at a given temperature.

$$\frac{C_e}{q_e} = \frac{1}{Q_0 b} + \frac{C_e}{Q_0} \tag{1}$$

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \tag{2}$$

Kinetics: Pseudo-first order (equation 3), Pseudo-second order (equation 4), Elovich (equation 5), and intra-particle diffusion (equation 6) models were fitted to propose the mechanism and nature of adsorption.

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \tag{3}$$

$$\frac{t}{q_t} = \frac{1}{k_2 {q_e}^2} + \frac{1}{q_e} t \tag{4}$$

$$q_t = \frac{1}{\beta} \ln(\alpha\beta) + \frac{1}{\beta} \ln(t) \tag{5}$$

$$q_t = k_p t^{1/2} + C \tag{6}$$

Thermodynamics: Adsorption data obtained at various temperatures were combined with Gibbs modified free energy equation (equation 7) to estimate the enthalpy change to predict the nature of adsorption.

$$ln\ b = -\frac{\Delta\, G^\circ}{RT} = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \tag{7}$$

Effect of mixture: To investigate the role of competing pollutants on adsorption, additional experiments were performed using pine biochar and a mixture of p-cresol (500 mg/L) and 2 methylbutyraldehyde (500 mg/L).

Encouraged by our results, biochar was also synthesized by gasifying swine manure (40% moisture) using 25:1 nitrogen:oxygen stream. The char was characterized and tested as described previously.

Results: Representative samples of pine biochar are presented in figure 1. The characterization of the char indicated that acid value of the char increased from about 5 to 9.29 suggesting that carbonization resulted in enhancement of surface basicity. Further Boehm titration also suggested that after carbonization, the acidic functional groups surface increased from 0.58 to 1.00 mmol/g and basic functional groups (0.05 to 1.58 mmol/g)

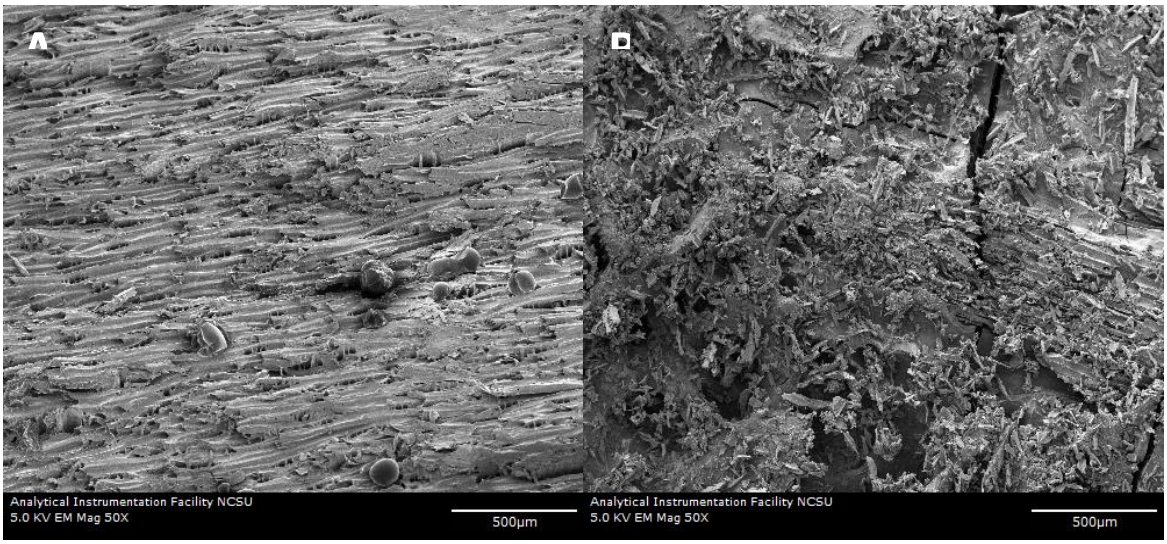

Figure 1. . Representative SEM micrographs of pine wood (control) (A) and pine-biochar (B) (Das et al. (2013), Industrial Crops and Products, 45, 215-222; Elsevier Publications, reused with permission)

When the batch adsorption data was analyzed using linearized Langmuir and Freundlich's models (Figure 2), it was found that pine biochar has a maximum adsorption capacity of 6.97 mg/g at 25 °C (Table 1).

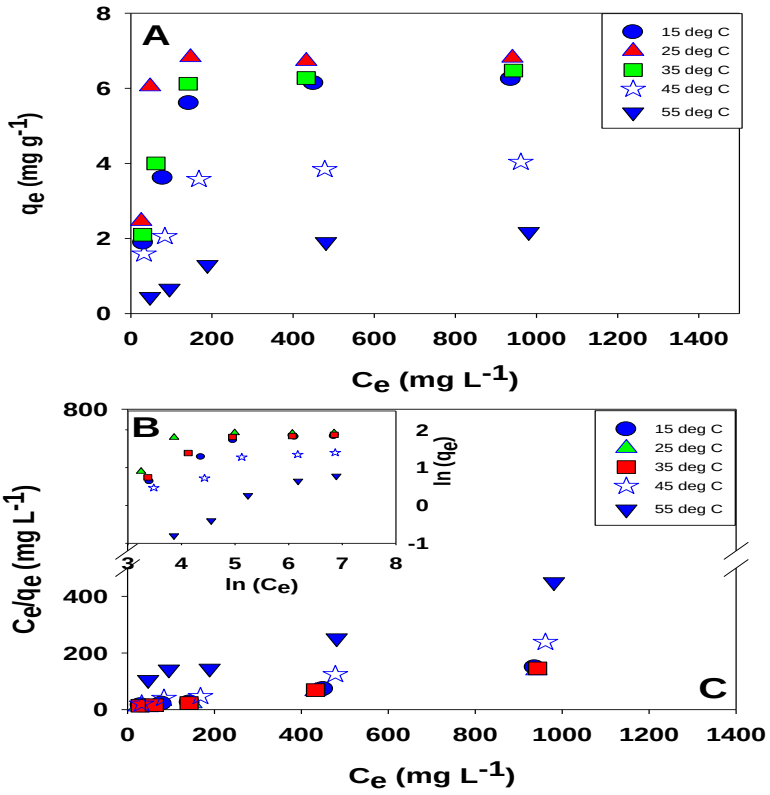

Figure 2. Adsorption isotherms of *p*-cresol on pine-biochar (A) using linearized Freunlich (B) and Langmuir models (C) (Das et al. (2013), Industrial Crops and Products, 45, 215-222; Elsevier Publications, reused with permission).

Table 1. p-cresol adsorption parameters of pine biochar ((Das et al. (2013), Industrial Crops and Products, 45, 215-222; Elsevier Publications, reused with permission).

Temp	**Langmuir**			**Freundlich**		
(°C)	Q_0	b	R^2	K_F	n	R^2
15	6.68	0.018	0.99	0.60	3.00	0.79
25	6.97	0.051	0.99	0.21	4.67	0.51
35	6.79	0.024	0.99	1.50	3.39	0.75
45	4.30	0.016	0.99	0.33	3.45	0.86
55	2.76	0.004	0.99	0.45	1.84	0.94

Kinetics: Representative plots (figure 3, below) illustrate the speed of removal of *p*-cresol when used with various biochars. Representative kinetic parameters are also presented in Table 2.

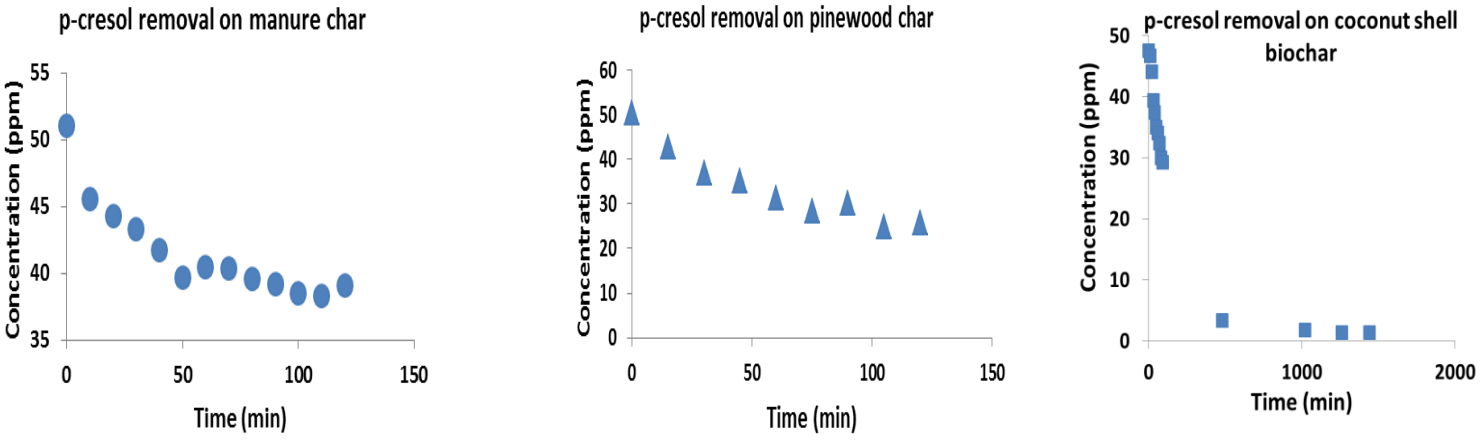

Figure 3. removal rate of p-cresol on various biochars tested.

In addition, when all the kinetic models were fitted to the data, it was appeared that Elovich model and intra-particle model were able to describe the data better suggesting that adsorption was probably dominated via chemisorption.

Further analysis of intra-particle diffusion model indicated that adsorption is influenced by external and internal mass transfer. To verify that adsorption was indeed a chemical process, additional desorption experiments were performed using DI water. As most of the *p*-cresol was attached to the surface it was concluded that *p*-cresol was immobilized on the surface via chemisorption. Hence a plausible mechanism was proposed to describe the adsorption process (Figure 4).

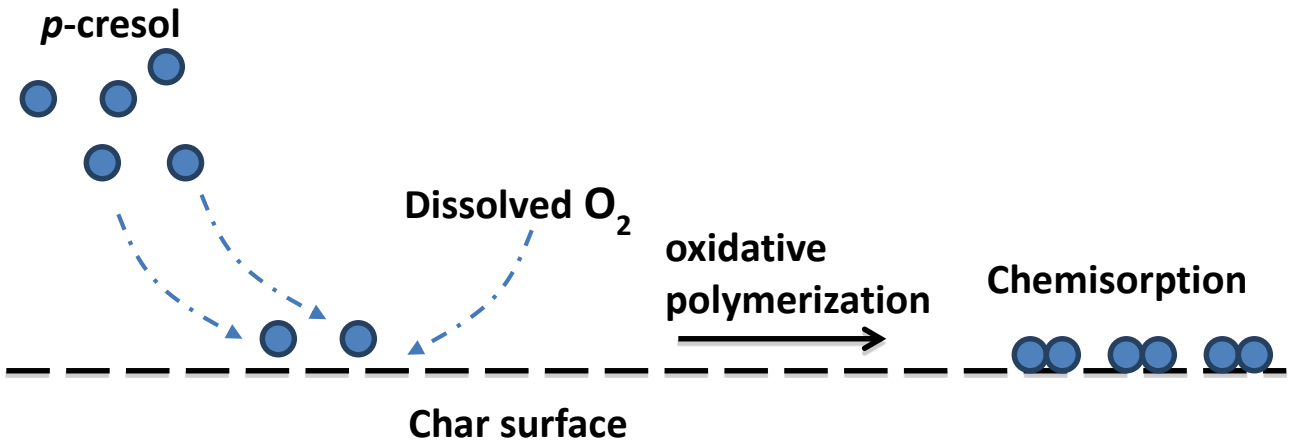

Figure 4. Proposed mechanism of adsorption of *p*-cresol on pine-biochar (Das et al. (2013), Industrial Crops and Products, 45, 215-222; Elsevier Publications, reused with permission).

Table 2 Kinetic adsorption parameters for *p*-cresol on pine biochar ((Das et al. (2013), Industrial Crops and Products, 45, 215-222; Elsevier Publications, reused with permission).

Experiment (Temp_Conc)	**Pseudo 1st order**		**Pseudo 2nd order**		**Elovich**			**Intra-particle**		
	R^2	K_1	R^2	K_2	R^2	α	β	R^2	K_p	c
15_50	0.523	0.038	0.960	0.027	0.960	0.479	2.396	0.967	0.180	0.106
15_100	0.289	0.161	0.650	0.001	0.970	0.830	1.238	0.883	0.331	0.533
15_200	0.815	0.017	0.650	0.004	0.800	1.633	0.927	0.895	0.496	0.053
15_500	0.307	0.023	0.987	0.015	0.972	1.390	0.726	0.904	0.571	0.837
15_1000	0.763	0.020	0.732	0.003	0.808	2.190	0.796	0.946	0.585	0.447
25_50	0.311	0.009	0.898	0.012	0.908	1.011	1.878	0.976	0.237	0.021
25_100	0.6	0.025	0.705	0.002	0.805	2.246	0.815	0.956	0.575	0.511
25_200	0.705	0.029	0.355	0.001	0.725	2.961	0.656	0.897	0.729	1.073
25_500	0.459	0.030	0.638	0.002	0.758	2.427	0.763	0.920	0.621	0.667
25_1000	0.697	0.019	0.790	0.005	0.838	1.691	0.797	0.916	0.564	0.059
35_50	0.010	0.001	0.994	0.143	0.950	0.535	2.128	0.786	0.184	0.513
35_100	0.545	0.023	0.790	0.011	0.843	1.594	1.218	0.948	0.374	0.163
35_200	0.827	0.018	0.778	0.003	0.832	1.983	0.852	0.961	0.542	0.305
35_500	0.448	0.033	0.678	0.002	0.803	2.408	0.774	0.953	0.650	0.606
35_1000	0.741	0.233	0.878	0.004	0.894	0.802	1.613	0.984	1.373	0.727
45_50	0.087	0.008	0.932	0.058	0.904	0.016	3.072	0.817	0.133	0.275
45_100	0.126	0.009	0.939	0.023	0.929	0.560	2.184	0.916	0.196	0.134

45_200	0.784	0.012	0.538	0.002	0.780	2.073	1.175	0.923	0.393	0.395
45_500	0.385	0.006	0.484	0.002	0.735	2.132	1.265	0.915	0.379	0.510
45_1000	0.778	0.016	0.070	0.003	0.788	2.175	1.213	0.938	0.387	0.470
55_50	0.045	0.004	0.234	0.131	0.612	0.013	11.41	0.784	0.042	0.063
55_100	0.001	0.006	0.354	0.126	0.514	0.787	8.045	0.514	0.535	0.038
55_200	0.039	0.005	0.910	0.034	0.880	0.303	3.305	0.888	0.130	0.454
55_500	0.542	0.011	0.660	0.009	0.796	0.998	2.754	0.933	0.169	0.138
55_1000	0.463	0.309	0.299	0.003	0.618	1.594	2.232	0.774	0.216	0.300

The data was also analyzed to estimate the enthalpy change ($\Delta H°$ (kJ/mol), which was found to be -2.11 kJ/mol. It is theorized that reaction between p-cresol and biochar surface was exothermic reaction (lower temperature favors adsorption over high temperature).

When a mixture of *p*-cresol and 2 methylbutyraldehyde was tested, there was no significant difference between adsorption capacities a single component and a mixture ($P = 0.97$), suggesting that pine biohcar can work equally well when other pollutants are present along with *p*-cresol.

Similar results were found when swine manure was used as feedstock for preparation of biohcar via gasification. The surface was found to be basic and favored adsorption of *p*-cresol. Based on the analysis of the data via Langmuir and Freundlich's models the maximum adsorption capacities were between 7.5-14 mg/g (Fitzgerald et al., 2014). As expected the adsorption was found to occur via chemical reaction between p-cresol and manure char surface. However, unlike pine biochar, the enthalpy data for swine biochar suggested that adsorption was endothermic ($\Delta H° = 6.3$ kJ/ mol).

Field testing of biochar: For this portion of the objective, we have experienced several practical difficulties with using adsorbent directly in lagoon water. The char obtained from pinewood and swine manure, although effective, has very limited structural strength, and hence disintegrated in water. Hence the char has to be strengthened to maintain its form or use new precursor to prepare structurally stable char.

Based on a thorough literature review, we investigated coconut shell as precursor and synthesized biochar using zinc chloride treatment followed by thermal activation at 1000 °C (Zhu and Kolar, 2014). When we tested the biochar in the laboratory to remove *p*-cresol, we found that biochar obtained from coconut shell has substantially high adsorption capacity up to

30 mg g^{-1} at 20 °C (Table 3). In addition the char was structurally very stable. To test the stability the char was continuously agitated (200 rpm) for 24 h. It was encouraging to note that the char was still stable and maintained its form.

Table 3: Isotherm parameters for adsorption of *p*-cresol on coconut shell biochar

T(C)	Freundlich isotherm			Langmuir isotherm		
	K_F (mg g^{-1}) (L mg^{-1})$^{1/n}$	1/n	R^2	K_L (L mg^{-1})	Q_0 (mg g^{-1})	R^2
20	6.376	0.293	0.906	0.119	30.226	0.999
30	5.711	0.318	0.905	0.089	31.568	0.992
40	5.888	0.321	0.877	0.099	32.768	0.984
T(C)	Redlich-Peterson isotherm				Temkin		
	A (L g^{-1})	B (L mg^{-1})	β	R^2	α (L g^{-1})	ϕ (J mol^{-1})	R^2
20	3.591	0.119	1	0.999	2.218	4.875	0.982
40	2.815	0.089	1	0.992	1.456	5.339	0.978
50	3.241	0.099	1	0.984	1.312	5.78	0.967

However due to limited time we were not able to try coconut biochar in actual lagoon. But noting the fact that the char was very stable under intense mixing conditions in the laboratory for extended periods of time (24-48 h), we are confident that the coconut char will maintain its form when applied in the lagoons.

Additionally, we are in the process of pelletizing the char obtained from swine manure and pinewood using biooil (from pyrolysis) as binder. Considering the physico-chemical properties of biochar, we expect that pelletized biochar will maintain its integrity in water.

Economic analysis: Treating swine wastewater via adsorption is expected to be a passive approach. As the process involves no equipment or moving parts, the major costs associated with adsorbent, transportation, and its storage. As reported by Kulyk (2012) the cost of production of biochar may be taken as $0.35/Kg (although the range is between $0.10-0.50/Kg). Transportation of biochar is perhaps one of the most expensive components of the entire process as the costs fluctuate based on weather and geopolitical stability. Assuming a 300-mile trip to pick up and deliver biochar to the site, the cost of transportation is estimated to be about $0.31/Kg (including rent, fuel, and driver wages and per diem). In addition broadcasting char in the lagoon was estimated as $0.1/Kg resulting in an overall cost of using biochar to be about $0.76/Kg. It may be noted that although spent adsorbent might have return value as fuel, its economic value was not considered in this analysis.

Discussion: Our data analysis showed that biochar could serve as an effective adsorbent for mitigation of *p*-cresol and VOCs from swine wastewater. We tested biochar obtained from both pyrolysis (carbonization with nitrogen) and gasification (with limited oxygen) as an adsorbent. In both cases it was found that char was able to absorb p-cresol (one of the most malodorous compound found in swine lagoons). Pine-based biochar could absorb a maximum up to 6.97 mg/g within 120 min (at 25 °C), while manure char was able to adsorb a maximum of 7.63 mg/g within about 100 min (at 25 °C). To address the structural weakness of manure and pine biochar, we also prepared and tested coconut-based biochar and found that it can remove as much as 30 mg/g (within 8-24 h) at 20 °C and still can maintain its form after several experiments. Considering that *p*-cresol and other volatile organic compounds are present in the range of 1-5 ppm, efficiency of biochar is considered adequate.

As the adsorption was found to be irreversible, there may not be any leaching of *p*-cresol back to water. In addition pine biochar was equally effective in removing *p*-cresol even in presence of other volatile organic compounds. Considering the expected production of biochar in the near future, we estimated the initial cost of using biochar to be about $0.79/Kg.

To illustrate the effectiveness of adsorption and put our research in perspective, we attempted to provide design calculations to treat 1,000 L of wastewater with 10 mg L^{-1} *p*-cresol and a target goal of removing 50% with 24 h. From our recent data on coconut biochar we determined that Langmiur's adsorption isotherm fits well. Hence we combined Langmuir's model (equation 1) with adsorption mass balance equation to obtain the following equation:

$$W = \frac{VX[(1+K_L C_o(1-X)]}{Q_o K_L(1-X)}$$

where W (mg) is the mass of the activated char (needed), V (L) is the volume of the wastewater, X (%) is the target fractional removal, C_0 (mg L^{-1}) is the initial *p*-cresol concentration Q_0 (mg g^{-1}) and K_L (L mg^{-1}) are Langmuir parameters.

From our data we estimated the values of Q_0 and K_L (at 20 °C) as 30.226 mg g^{-1} and 0.119 L mg^{-1} respectively. Assuming a liquid volume of 1000 L and an initial concentration of *p*-cresol of 10 mg L^{-1}, equation 1 is reduced to:

$$W = \frac{[1000X(1+1.19(1-X)]}{3.59(1-X)}$$

From the above equation, the mass of adsorbent can be estimated for any targeted fractional removal. For example, if 50% removal is targeted, the mass of adsorbent needed will be 444 g, which translates of about $350. The following simulation (Figure 5) may be used to estimate the mass of adsorbent needed for various targeted fraction removal of *p*-cresol from the system.

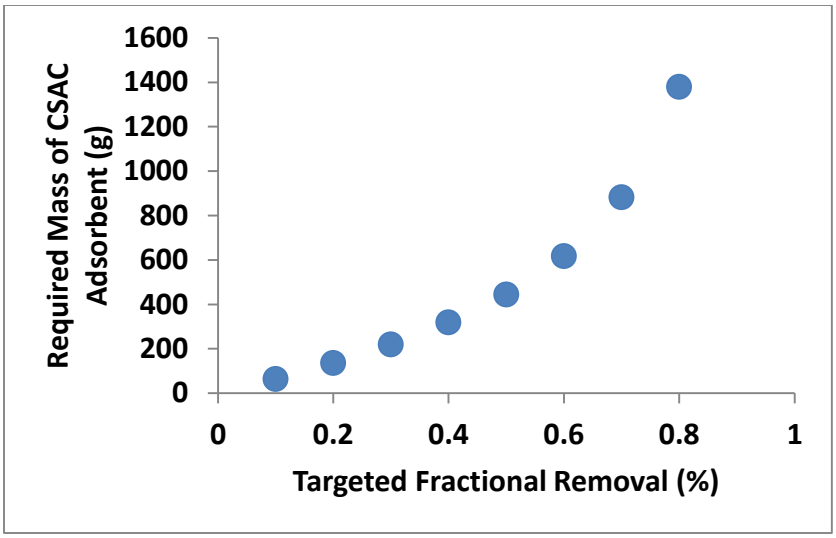

Figure 5. Sample simulation for predicting the mass of adsorbent needed for a given fractional removal of 10 mg L^{-1} of *p*-cresol in 1000 L waste water at 20 °C.

In addition the following table (table 4) provides quick summary of the adsorption parameters for all types of biochars tested.

Table 4. Efficacy of various biochars for removal of *p*-cresol.

Biochar type	Temperature (C)	Theoretical maximum amount removed (mg g^{-1}) based on Langmuir's model	Adsorption time (min)
Coconut shell-based (commercial)	15	43.7	25-30
	25	68	25-30
	35	52	25-30
Pinewood-based	15	6.68	100-120
	25	6.97	100-120
	35	6.79	100-120
	45	4.3	100-120
	55	2.76	100-120
Swine manure-based	25	7.63	100
	35	14.99	100
	45	14.84	100
Coconut-shell based	20	30.2	480-1440
	30	31.6	480-1440
	40	32.8	480-1440

Although gasification will result in slightly acidic chars, the adsorption capacities are still high enough to immobilize basic VOCs including *p*-cresol. Our research is expected to beneficial to the swine producers in the future. As there is significant interest in thermochemical renewable energy processes involving pyrolysis and gasification, abundant quantities of biochar is expected to be available as a byproduct. Hence from an economic standpoint, using biochar as a water treatment media appears feasible as the major expense will be associated with transportation of char from the site. In addition, as a passive treatment process, adsorption does not require machinery or constant manpower for monitoring. After the adsorption process if completed, the spent char may either be land applied to cropland or burnt for energy.

Summary

Objective 1: Estimate the amount of the VOCs removed from anaerobic lagoons

Biochar type	Temperature (C)	Theoretical maximum amount removed (mg g^{-1}) based on Langmuir's model
Coconut shell-based (commercial)	15	43.7
	25	68
	35	52
Pinewood-based	15	6.68
	25	6.97
	35	6.79
	45	4.3
	55	2.76
Swine manure-based	25	7.63
	35	14.99
	45	14.84
Coconut-shell based	20	30.2
	30	31.6
	40	32.8

Objective 2: Determine how fast the VOCs will be removed from anaerobic lagoons

Biochar type	Time needed for adsorption (min)
Pinewood	100-120
Swine manure	100
Coconut shell	480-1440

Objective 3: Predict how much does adsorption technique cost to the producers

About $0.76/Kg to remove approximately 30 grams of *p*-cresol.

Note: This research has resulted in the following manuscripts:

1. Das, L., P. Kolar, J. J Classen, and J. A. Osborne. 2013. Adsorbents from pine wood via K_2CO_3-assisted low temperature carbonization for adsorption of *p*-cresol. *Industrial Crops and Products*, 45, 215-222.

2. Fitzgerald, S., P. Kolar, J. J Classen, and M. D Boyette. 2014. Swine manure char as an adsorbent for mitigation of *p*-cresol. *Environmental progress and Renewable Energy* (*In press)*

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Das, L., P. Kolar, J. J Classen, and J. A. Osborne. 2013. Adsorbents from pine wood via K2CO3-assisted low temperature carbonization for adsorption of p-cresol. Industrial Crops and Products, 45, 215-222.

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