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RESEARCH ARTICLE

Use of fecal and sawdust biochar as a new perfume delivery system

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Abstract

Human fecal matter mixed with pine sawdust was heated at 200, 300, 400, 500, 600, or 650°C in the absence of oxygen to generate black solid residues called biochars. These biochars were subsequently evaluated as a perfume delivery system for air care. The performance of biochar was compared to that of cellulosic material, which is commonly used for the release of perfume into the air, and to that of active charcoal, which is used for air purification. A perfume model system consisting of alcohols, aldehydes, alkanes, and terpenes was loaded onto these solid materials. Results showed that the cellulosic material had a good release profile, but that the aldehydes oxidized to some extent, which generates a rancid smell if no antioxidant is added. On the other hand, active charcoal strongly absorbed all volatiles such that no perfume release occurred and no smell was perceived. The biochar heated at 200°C showed good release performance (long lasting) but some fecal off-notes remained in the background. Biochar prepared at 300°C was the best material as a compromise between the release profile and the energy needed to produce the material. The goal of this work was to add value to biochar and in so doing empower toilet innovators, aid the circular economy, and propose a sustainable solution for malodor control.

KEYWORDS

air care, biochar, delivery systems, perfumes

1 | INTRODUCTION

Biochar, a combination of the words 'bio' and 'charcoal', is generally used to describe material resulting from heat treatment of any plant material in the absence of oxygen. Biochar is mostly used for agricultural purposes. This organic product stimulates soil activity by improving the retention of nutrients and the capacity of soil to retain water, among other things. With current concerns about climate change, the production of biochar is of interest in that it can transform agricultural waste material and reduce carbon dioxide (CO_2) emission generated by the decomposition of dying plant matter. Although only 12 papers dealing with the study of biochar were referenced in the SciFinder database in 2008, 1724 papers were published in 2016, emphasizing the growing interest of the scientific community in biochar over the past decade.[1-4]

The present investigation of biochar is a satellite study of a large project initiated in 2011 by the Bill & Melinda Gates Foundation called 'Reinvent the Toilet Challenge'.[5] Defecation in an open environment concerns more than 2 billion people around the world. Beyond the obvious problem of dignity, human waste is a vehicle for microorganisms and disease and represents a major risk for people exposed to these unsanitary conditions. To improve this situation, numerous toilets must be built and maintained in good condition, which implies investment and payback if they are privately owned.[6] Consequently, a large scientific and technical community is working on ways to improve the value of human waste. For example, urine contains the three most important nutrients that a plant requires: nitrogen, potassium, and phosphorus. Urine can be used as fertilizer, with 100 L of urine having a value of $1 in terms of nutrient content. Feces contain mainly organic compounds that can be composted to produce fertilizers as well, but fecal material is a microbiological hazard if not treated.[7-9] For example, *Ascaris* is a parasite worm of the human intestine. When released into the environment, its eggs can be ingested from contaminated vegetables or water, provoking a digestive disease known as ascaridiasis, which is responsible for several tens of thousands deaths every year worldwide, particularly among young

Abbreviations used: SEM, scanning electron microscopy; EtOAc, ethylacetate; GC–MS, gas chromatography–mass spectrometry

children. Ascaris eggs are extremely resistant, persisting over several years, and are also the most difficult fecal contaminant to eliminate, requiring heat treatment above 80°C.[10] The pyrolysis of toilet waste represents a solution to this problem. The biochar thus obtained can be used as a combustible or for soil amendment, although the value of this material is low.[11,12]

In line with the objectives of 'Reinvent the Toilet Challenge', we explore here the use of biochar for another purpose: perfume delivery. Using this sustainable delivery system could bring a significant added value to biochar and improve the value of the circular economy.

2 | EXPERIMENTAL

2.1 | Chemicals and material

Perfumery ingredients (octanal, decane, limonene, p-cresol, octanol, phenylethanol, decanal, dodecane, citronellol (3,7-dimethyl-6-octen-1-ol), citral (E/Z 7:3, 3,7-dimethyl-2,6-octadienal), caryophyllene, lilial ((+−)-2-methyl-3-[4-(2-methyl-2-propanyl) phenyl] propanal)) were obtained from in-house available raw materials (Firmenich S.A., Geneva, Switzerland). Tenax® was from Scientific Instrument Services (Ringoes, NJ, USA), active charcoal from Fluka cat. N° C9157 (St Louis, MO, USA), and BiVOC2 pumps from Umweltanalytik Holbach GmbH (Wadem, Germany). The biochar was obtained from Sanergy (Nairobi, Kenya), and the stainless steel rings (diameter 4 cm) to hold powders were obtained from Supelco cat. N° 58065 (Bellefonte, PA, USA).

2.2 | Biochar sourcing

The biochar was prepared from human waste made of human fecal material covered with sawdust from untreated cypress, pine, or cedar and cellulosic toilet paper. Typically, about one stool (about 200 g) was covered with 1 cup (about 250 mL) of sawdust and six sheets of toilet paper. The biochar process is a batch process. The biochar made at 200°C was more chunky compared with that made at 600°C. When the biochar was dispersed in water, the pH was about 7.5 for the 200°C batch, 7.8 for the 300°C batch, and 9.5 for the 600°C batch. Before use, the biochars were homogenized in a coffee grinder.

2.3 | Biochar characterization: Scanning electron microscopy (SEM)

SEM micrographs were collected by using a JEOL 6010 LA SEM. Samples were gold-coated before imaging with an SPI-Module™ Sputter Coater from SPI Supplies, the plasma current being created after controlling the vacuum with an SPI-ModuleTM control (Figures 1 and 2).

2.4 | Biochar characterization: Surface area measurements

Surface areas of biochars were measured by using a TriStar®II PLUS system from Micromeritics. Using a sample degas system (VacPrep 061), we pretreated solid samples at 90°C for 16 h by applying a vacuum to remove adsorbed contaminants from atmospheric exposure (water, CO_2). The solid was then cooled under vacuum to a temperature that depended on the adsorptive gas used, in particular, −195.8°C with liquid nitrogen (N_2) and 0°C in the case of CO_2. The solid was then exposed to doses of the adsorptive in controlled increments. After each dose, the pressure was allowed to equilibrate and the quantity adsorbed was calculated. The quantity adsorbed at each pressure defined an isotherm from which the quantity of gas required to form a monolayer over the surface of the solid was determined. The specific surface area was calculated by using the Brunauer–Emmett–Teller (BET) theory. The micropore surface was assessed with the t-plot model (N_2 adsorption). In the case of CO_2 adsorption, an equivalent surface area was calculated by using the Dubinin-Astakhov model.

2.5 | Thermal desorption-gas chromatography–mass spectrometry

Identification of compounds was performed on a 6890 N GC (Agilent, Palo Alto, CA, USA) equipped with a fused silica SPB-1 capillary column (30 m × 0.25 mm i.d., 0.25 μm film thickness). The initial oven temperature was held at 80°C for 5 min and then increased at 10°C/min to 250°C. The carrier gas was helium. The column was coupled to a 5975B Inert XL MSP MS from Agilent for identification. The mass spectra in electron impact mode were measured at 70 eV in a scan range from *m*/*z* 30 to 300. MS interpretation was based on authentic samples from the Firmenich data bank or Wiley/NIST libraries. The injector was a Thermal Desorber (PerkinElmer, Waltham, MA, USA) TurboMatrix 650

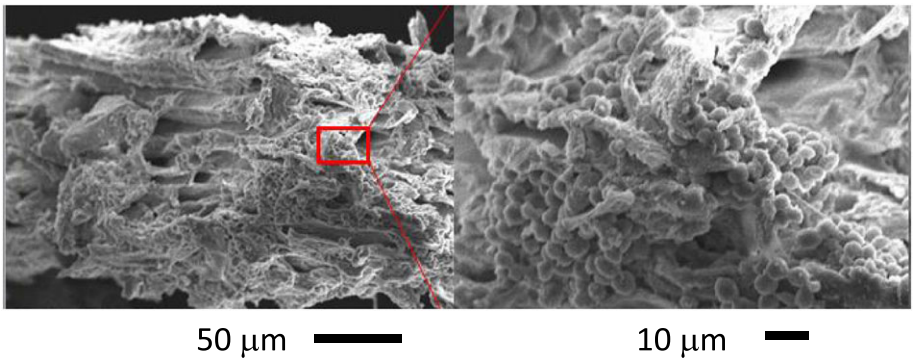

FIGURE 1 SEM images of fecal and sawdust compost from which biochar is obtained [Colour figure can be viewed at wileyonlinelibrary.com]

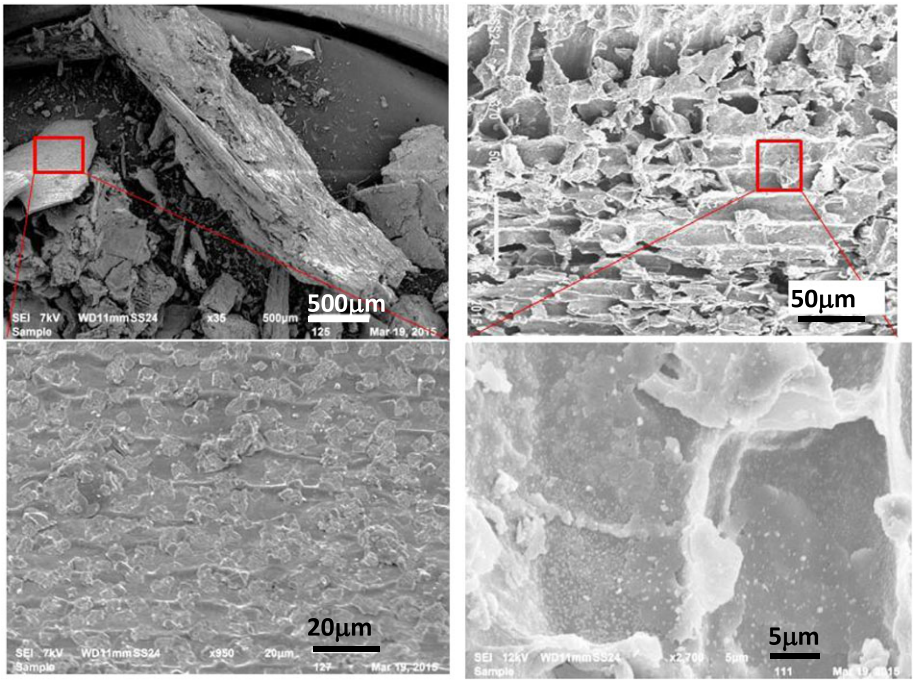

FIGURE 2 SEM pictures of biochar 200 [Colour figure can be viewed at wileyonlinelibrary.com]

with the following settings: valve 220°C, tube 250°C, transfer line 250°C, trap −30°C, and desorption for 5 min at 250°C under 30 ml/min helium flow. The outlet split was 50 ml/min.

2.6 | Perfume model system

Representative aldehydes used in perfumery (octanal, decanal, citral (E/Z 7:3, 3,7-dimethyl-2,6-octadienal), and lilial ((+−)-2-methyl-3-[4-(2-methyl-2-propanyl) phenyl] propanal)) were weighed at 1 g ± 0.01 each and mixed together. The same protocol was applied to the alcohols, p-cresol, octanol, phenylethanol, and citronellol (3,7-dimethyl-6-octen-1-ol), and to hydrocarbon decane, limonene, dodecane, and caryophyllene. The perfume model consisted of a mixture of 1 g of each class of compounds. Only the aldehyde mixture was used for the sensory analysis.

2.7 | Calibration curves

The perfume model was then diluted in a 100 mL volumetric flask with ethylacetate (EtOAc) for quantifications. The solution was further diluted stepwise by using a 100 mL volumetric flask to obtain calibration solutions containing 8330 ng/µL, 4165 ng/µL, 833 ng/µL, 417 ng/µL, 83 ng/µL, and 42 ng/µL of each compound. Calibration curves were obtained after injecting 1 µL of each solution on 50 mg Tenax cartridges. The cartridges were automatically thermally desorbed directly on the GC column coupled to the MS. The total ion current of peak areas were integrated and reported in an Excel table. The regression factors were between 0.98 for citronellol and 0.99 for the other compounds used.

2.8 | Headspace cell procedure for measurements

The sorbent (1 g ± 0.01) was impregnated with 25 mg of the perfume model system in a vial. The vial was vortexed for about 2 min. The powder was then placed between two stainless steel rings, wrapped in aluminum foil, and kept for 30 min. The headspace cells were designed according to the method of Herrmann *et al.*[13] (Figure 3). The cell volume was 1 L and the pumping flow rate applied was 200 mL/min. The headspace was measured at specific time points by inserting a Tenax cartridge for 5 min.

2.9 | Statistical analysis

Statistics were calculated by using the program R (http://www.r-project.org, 2014). The gas phase concentrations were log 10 transformed. The evolution of the gas phase concentrations over time was assessed by using piecewise linear regressions. For each compound, we obtained a linear model split into two segments: the first between time 0 and 6 h and the second between 24 and 94 h. To these models, we added the type of biochar (feces, a mixture of feces and sawdust, sawdust) as a categorical variable to evaluate whether the type of biochar significantly influenced the gas phase concentrations over time. The level of significance was set at 0.05.

2.10 | Extraction procedure

The perfume model (170 µL at 10% in EtOAc) was added to 500 ± 2 mg of biochar 300, active charcoal, or cellulosic material. The impregnated materials were placed in closed vials. These vials were stored for 48 h in an oven at 30°C. The powders were then dispersed in exactly 10 mL of EtOAc containing 1 mg ethyl octanoate (internal standard) and vortexed for 2 min. Prior to injection, the

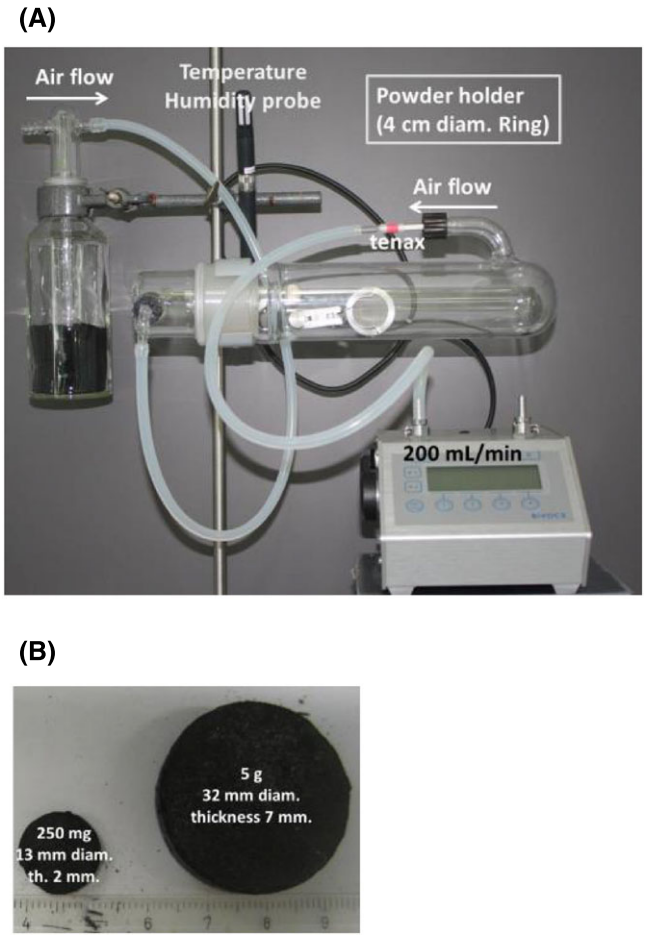

FIGURE 3 A: Setup to measure headspace concentrations. B: Pictures of biochar tablets. The small tablets were used for sensory analysis, whereas the large tablets were used for sorption profiles [Colour figure can be viewed at wileyonlinelibrary.com]

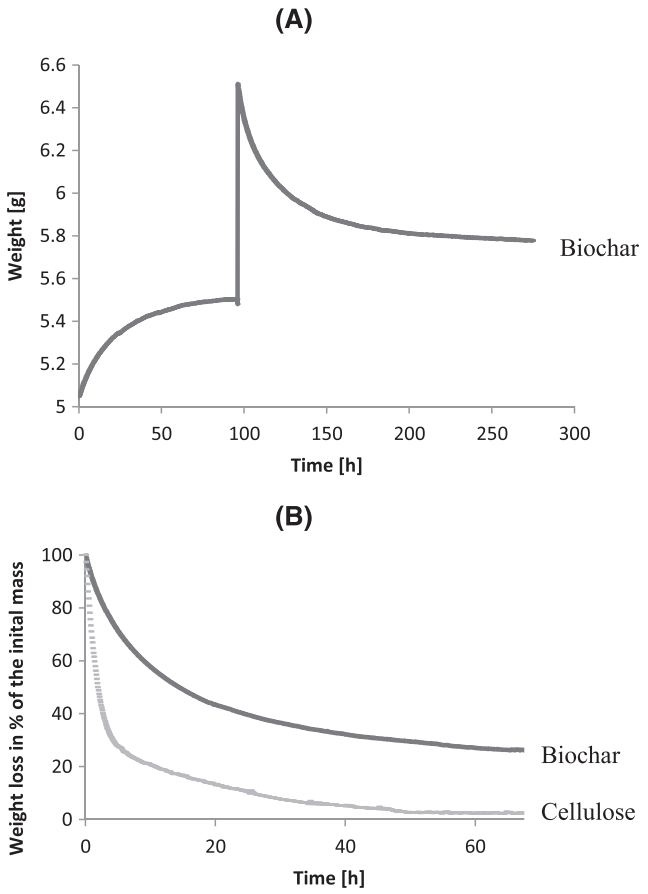

FIGURE 4 A: Weight monitoring of biochar 300 at 35°C and 70% humidity in a climatic chamber. The first part of the graph is the weight gain in humidity; the perfume model system was then added (1 g pure perfume model) and weight loss was monitored. B: Comparison of weight loss of cellulosic material with that of biochar at 25°C and 50% humidity. Equilibration time is 2 days prior to perfume loading

solvent was filtered. The perfume model (170 µL at 10% in EtOAc) was added to exactly 10 mL of EtOAc containing 1 mg ethyl octanoate. The ratio of the peak area compound/peak area internal standard, compared to that without powder, allowed us to determine a percentage recovery of perfume after a contact time of 48 h on solid supports. The procedure was repeated three times.

2.11 | Tablet preparation for weight-loss measurements in climatic chambers

Biochar or cellulose tablets were prepared prior to impregnation with perfume by using a IR Accessory hydraulic press (Bodenseewerk, Perkin-Elmer 800 GmbH) and applying a $1 \times 10^{+4}$ kg/cm^2 pressure force. As a reference delivery system, cellulosic air care pads (Orlandi, New York, USA) were ground to obtain a fluffy powder before being pressed into tablets with similar dimensions to those of our biochar samples. About 5 g of powder was compressed into 32 mm diameter tablets with a thickness of about 7 mm. The tablets were placed on an analytical balance (Mettler Toledo ML204T) controlled by BalanceLink Software, Version 4.1.0. and stored at 35°C and 70% humidity in a climatic chamber for 100 h before applying the perfume (Figure 4A). For the following study at 25°C, 50% humidity, the tablets were equilibrated for only 2 days before applying the perfume (Figure 4B).

2.12 | Tablet preparation for sensory analysis

About 247 mg and 262 mg of biochar 300 were compressed into 13 mm diameter and 2 mm thickness tablets and loaded with 25 ± 1 µL of aldehydes in the aldehyde mixture. Cellulosic tablets of the same dimensions were prepared by using a cookie punch and contained 117 mg or 113 mg of solid material. They were loaded with 12 ± 1 µL of the aldehyde mixture to keep a constant ratio of perfume/solid. A first sensory evaluation was performed on tablets freshly impregnated with the aldehyde mixture and deposited in a 500 mL glass jar. To prepare the aged tablets, we placed the freshly impregnated tablets in the jars the day before the sensory evaluation and kept them in a steam room at 30°C for 24 h. All jars were smelled at the same temperature.

2.13 | Sensory analysis

The method used was a 'difference-from-control test'. We presented to each subject and for each solid support: (1) the control sample consisting of the mixture of aldehydes applied to the support 1 h after deposition and (2) the sample consisting of the mixture of aldehydes

applied to the support 24 h after deposition. The blind control sample was the mixture of aldehydes applied to the support 1 h after deposition to measure the placebo effect. It is a measurement of the bias obtained in the answer when asking a subject to smell the difference between two identical samples. Each subject rated on a linear scale the amplitude of the difference between the blind control and the sample vs. the control sample (control and blind control = product applied 1 h before panel evaluation; sample = product applied 24 h before panel evaluation and which remained at 30°C); 0 = no difference; 10 = very different). Subjects were then asked to choose among attributes to describe the difference in intensity, quality, or both. The duration of the panel evaluation was estimated to be 1 h, and 28 internal panelists took part in this panel.

3 | RESULTS AND DISCUSSION

3.1 | Biochar raw material

The raw material used to prepare the biochar came from toilets installed in a Nairobi slum. The pit latrines are a urine-diverted system, meaning that the urine and fecal material are separated. The users pay to use the pit and get a cup of sawdust (250 mL) with a few sheets of toilet paper. Solid and liquid human waste is collected daily into separate drums. The solid waste is composted on site and used for soil amendment for ornamental plants. However, some of this solid waste was heat treated, after 1 day to a maximum of 7 days of storage, in the central waste management area. This pilot artisanal process was set up to investigate the possibility of killing all germs in compost and adding value to the material. For our study, the sawdust alone and the fecal material alone were processed similarly.

3.2 | Biochar characterization

The observation of the composted fecal material by SEM showed the presence of tubular structures, common in vegetable waste materials (Figure 1). Zooming in to the surface of these tubular structures allowed observation of some small spherical objects, about 2 to 5 μm in size, probably corresponding to bacterial remains. Interestingly, all of these structures appeared to be well preserved after heat treatment at about 200°C (Figure 2).

The microscopic observations thus suggested that the heat treatment induced a 'freezing' of the structures of the organic compost, without major destruction of the macroscopic objects composing it. The surface area of biochar increases when it is pyrolyzed at a higher temperature: From N_2 adsorption, we measured a specific surface area of <1 m^2/g for biochar 300 and of about 4.60 ± 0.03 m^2/g for biochar 650 (Table 1). These values are low in comparison to that for activated carbon, which, for example, was measured in our case as 732 ± 2 m^2/g (BET). The surface area for biochar 300 made from sawdust appears to be about 4 times higher than that made from feces (Tables 1 and 2). With the N_2 adsorption method, however, no significant microporosity could be observed. With CO_2 adsorption, the corresponding equivalent surface area measured was significantly higher (50 to 70m^2/g), and the data reveal the presence of ultramicropores, i.e. pores of <6 Å. The difference is explained by the combined effect of the higher kinetic energy and a higher saturation pressure of CO_2 at 0°C compared to N_2 at −195.8°C, rendering the molecules capable of penetrating the narrow pores (ultramicropores) and condensing onto the highly energetic surfaces.[14] However no significant difference was measured between the samples from feces, sawdust, or the combination of the two.

More globally, we note that a higher pyrolysis temperature in the preparation of biochar induces a higher surface area in the solid powder.[15,16] The need to standardize the quality and properties of biochar is thus becoming critical.[17]

Resistance to biological decay in biochars is due to the formation of graphitic structures, which are rigid. In the present study, the starting biomass was elastic and adsorbent, as were the lower-temperature biochars. As the carbonization temperature increased, a greater fraction of the remaining solids became graphitized and contained less of the

TABLE 1 Specific surface area results (BET and t-plot analysis) obtained by adsorption of N_2 on biochar 300, biochar 650, cellulosic reference, and active charcoal samples

Sample	Specific surface area (BET) (m^2/g)	External surface area (t-plot) (m^2/g)	Micropore area (t-plot) (m^2/g)
Biochar 300 (sawdust)	1.14 ± 0.01	0.33 ± 0.01	0.81 ± 0.01
Biochar 300 (sawdust + feces)	0.68 ± 0.01	0.31 ± 0.01	0.37 ± 0.01
Biochar 300 (feces)	0.28 ± 0.01	0.18 ± 0.01	0.10 ± 0.01
Biochar 650 (feces)	4.60 ± 0.03	1.35 ± 0.01	3.25 ± 0.01
Cellulosic reference	1.54 ± 0.01	1.54 ± 0.01	---
Active charcoal	732 ± 2	287 ± 2	445 ± 2

TABLE 2 Micropore characteristics and equivalent surface area of biochar 300, biochar 650, and active charcoal samples, calculated by using the Dubinin-Astakhov model on CO_2 isotherms

Sample	Limiting micropore capacity (cm^3/g)	Limiting micropore volume (cm^3/g)	Equivalent surface area (m^2/g)
Biochar 300 (sawdust)	12.03	0.022	53.6
Biochar 300 (sawdust + feces)	15.96	0.029	69.7
Biochar 300 (feces)	11.87	0.022	49.8
Biochar 650 (feces)	44.3	0.080	223.8
Active charcoal	143	0.26	634

elastic biomass-like structures. The elastic structures may consist of unmodified biomass (cellulose, hemicellulose, lignin) or newly formed non-graphitic substances that may share many properties with bio-oils. While the pyrolysis temperature is the most dominant variable in biochar properties, carbonization processes vary in the extent to which they remove bio-oils as they form and the extent to which they deposit bio-oils into the developing graphitic structures, eventually modifying the internal porosity. As a consequence, the surface area, or the 'surface exposed by unit weight of solid material', is modified. A high value for the surface area means that more surfaces are exposed to interact with molecules in the air or in liquid and eventually develop higher adsorption efficiency. Similarly, the release of perfume molecules can be affected by the size of the surface area.

3.3 | Analytic approaches to assess biochar performance as a perfume delivery system

Solid perfume delivery systems that are widely used consist of cellulose. The biochar in the present study was composed of a mixture of chunks and coarse grains that were ground in a coffee grinder to obtain a more homogeneous powder. To compare the evaporation of organic compounds between the cellulosic pad and the biochar powder, we explored two approaches: one in which we made tablets with biochar 300 and one in which we grated the cellulose pad to make a powder. For the mass balance study, the cellulose pads were grated and then compressed into tablets. For the sensory analysis, the cellulose pad was cut into a disk and compared to biochar tablets.

In the case of active charcoal powder, it was not possible to make tablets because the samples lacked cohesion. For this reason, we used rings to hold together powders made of sawdust plus fecal biochar 300, sawdust plus biochar 300, and fecal biochar 300 (Figure 3A).

3.4 | Water and perfume sorption and desorption: Evaluation from weight variations

In a first step, the biochar 200 tablets were placed on a precision balance in a climate chamber with controlled humidity and temperature. The water absorption was monitored over time at 35°C and 70% humidity (Figure 4A). The measured weight increase was about 10%. In a second step, the tablets were impregnated with the model perfume, and their weight was monitored over time to evaluate the perfume release. The result showed a weight loss of the perfume of about 80% in 2 days (Figure 4A). A second experiment was performed at 25°C and 50% humidity conditions. The biochar 200 tablets were equilibrated for 2 days and then impregnated with perfume, and their weight was measured as a function of time and compared to the reference cardboard cellulosic material (Figure 4B).

After 5 h, about 30% of the perfume was released from biochar 200, whereas more than 70% was released from the cellulosic reference material. After 70 h of the experiment, about 25% of the perfume was still trapped in biochar 200, whereas no perfume was present in the reference. The result clearly indicates that under the same conditions, biochar 200 globally retains more perfume and delivers it more slowly than does the reference cellulosic material. To discriminate between the perfume molecules released, we performed headspace analysis.[13]

3.5 | Monitoring the perfume release

We monitored the release of volatiles in the headspace over time in the headspace cells. The headspace concentration was measured as a function of time for every compound, with the exception of the less volatile citronellol. The release profiles were similar between biochar prepared at 200°C, 300°C, 400°C, 500°C, and 600°C. With biochar 200, an off-note that smelled like cold ashes became perceivable after 72 h. In consideration of this parameter and the higher energy (i.e. cost) required for the preparation of the other biochars, we selected the biochar prepared at 300°C for further investigations. In addition, with a pH varying from 7.5 for biochar 300 to pH 9.5 for biochar 600, the stability of aldehydes would become critical in alkaline conditions.

The release profiles between cellulosic material, biochar 300, and active charcoal were monitored (Figure 5). The hydrophobic compounds decane, limonene, dodecane, and caryophyllene were no longer present after 1 h on cellulosic material, but were better retained on biochar 300. The active charcoal, as a strong adsorbent of organic molecules, did not release any volatile compounds. The aldehydes

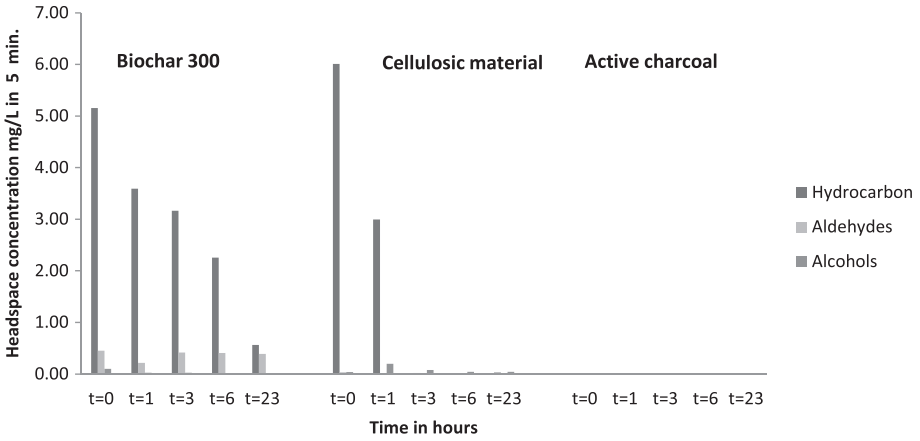

FIGURE 5 Comparison of release between cellulosic material, biochar 300, and active charcoal with the perfume model. The amounts of aldehydes, alcohols, and hydrocarbons in the headspace trapped for 5 min at 200 mL/min at different time points, expressed in mg/L, were summed

released from biochar 300 were surprisingly constant, whereas they were significantly affected by the cellulosic support. No significant differences were observed between the biochar and cellulosic supports with the alcohols.

3.6 | Solvent extraction of solid supports

When biochar 300 or active charcoal was extracted with an organic solvent, all aldehydes were recovered without significant differences between the two solid supports. With the cellulosic reference, however, parts of the aldehydes were lost. Instead, we recovered some octanoic acid or decanoic acid corresponding to the oxidized form of the corresponding aldehydes. The alcohols were more difficult to extract from the cellulosic material than they were with active charcoal and biochar 300. The alkanes were fully recovered from all solid supports (Figure 6).

The interaction of volatile compounds with biochar 300 and active charcoal was similar, the difference being that active charcoal did not release the volatiles into the air. The cellulose, probably because of oxidative treatments, transformed the aldehydes in acids, which should influence the odor profile.

3.7 | Comparison between biochar made of feces, sawdust, or both

One obvious question was: What is the impact of the biochar ingredients on biochar adsorption and release? To answer this question, we made different biochar batches in the same oven and under the exact same conditions with human feces only, sawdust only, or a mixture at 300°C. To measure the headspace, we used the headspace cell displayed in Figure 3A.

We did not find any significant difference in the respective linear parameters for all compounds tested (Figure 7). Our results demonstrated that biochars containing fecal material released all compounds more slowly (Figure 7). The para-cresol illustrates the trends observed with other alcohols such as citronellol, octanol, and phenylethanol. Their concentration in the headspace increased during the first few hours and then the evaporation from the biochar made from sawdust was much faster than that from biochar containing fecal material. The equilibration time between alcohols and the headspace was longer compared to that for alkanes. Decanal is also representative of aldehydes that behave in a manner that is in between that of hydrocarbon and alcohols. The limonene was released quickly during the first hour, as were decane and caryophyllene. Limonene was not retained on any solid, but the faster evaporation from sawdust biochar was significant and even more obviously observed with caryophyllene (not shown in Figure 7).

No clear correlation was found between the characterization of the solid (micropore volumes, specific surface area) and the release of volatile compounds. A complex interplay between surface area, adsorption/impregnation, microporosity, and capillary effects in the solid seems to determine the final release characteristics.

3.8 | Sensory analysis

To verify whether the transformation of aldehydes in acids affected the flavor profile, we loaded cellulosic pads and biochar 300 tablets (Figure 3B) with only the aldehyde mixture from the perfume model. Tablets freshly impregnated or aged were placed in jars and presented to panelists. The two blind control samples had a score of about 2 on a scale of 10, demonstrating an important placebo effect (Figure 8). This could be explained by the fact that we did not mention to the panelists that the products might not be systematically different from the reference. Nevertheless, the two placebo effects did not differ from each other (two-tailed paired study, test not significant). Furthermore, the comments related to the differences measured were balanced between the three choices (quality, intensity, and both). Some panelists found that the difference for the blind control cellulosic material versus the control was due to intensity rather than quality. The cellulosic sample was very different from the blind control sample (two-tailed paired student test, significant at 99.9%) (Figure 8), which was clearly attributed to both quality and intensity and not to intensity only. The

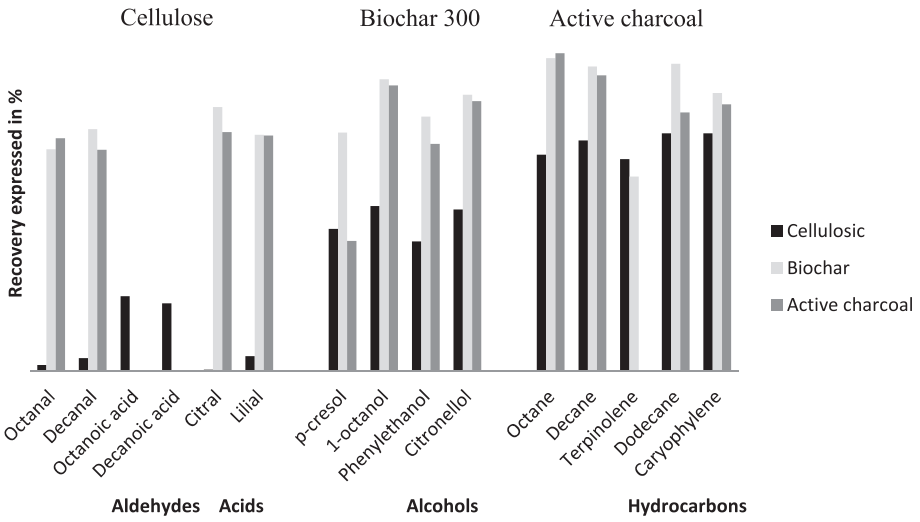

FIGURE 6 Liquid extraction of organic volatiles from different solid carriers: biochar, cellulosic cardboard reference, and active charcoal. The results are expressed as the remaining wt % from the initial amount of volatile loaded. The acids are expressed as the wt % of the total aldehyde conversion

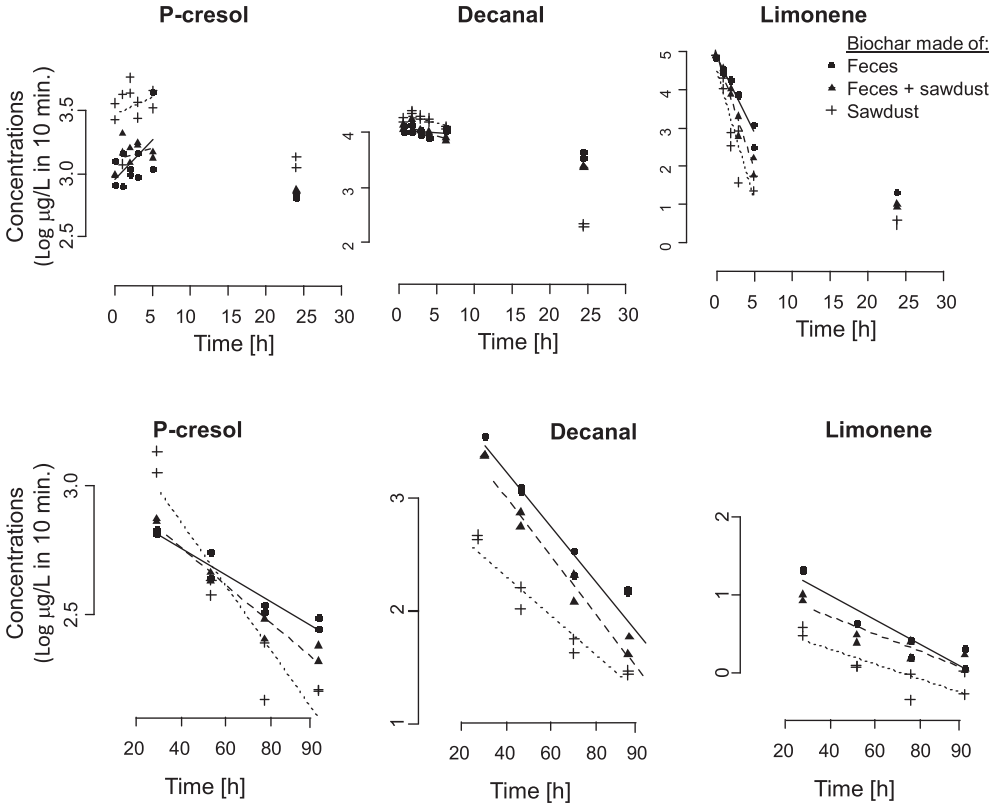

FIGURE 7 Gas phase concentrations as a function of time for all compounds tested and released from biochar 300 made of feces only, a mixture of feces and sawdust, and sawdust only. The lines show the piecewise linear models used to assess the difference between each biochar for each compound. The concentration is expressed as the log of mg/l trapped for 5 min at a 200 ml/min flow rate at different time points

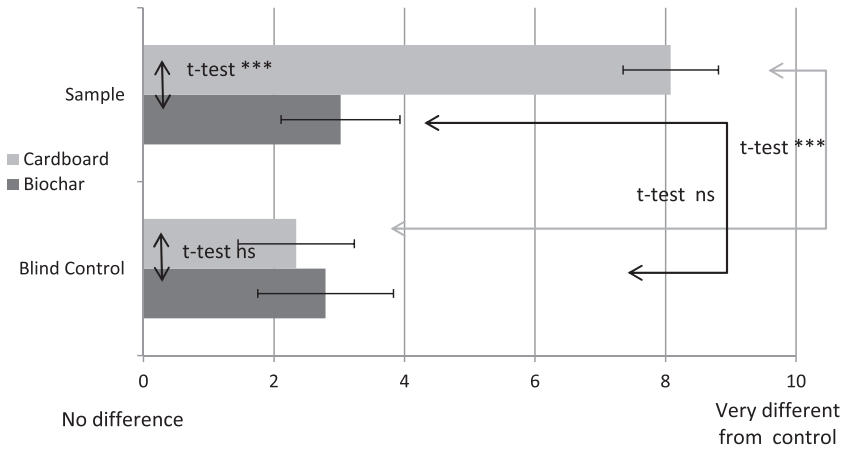

FIGURE 8 Sensory comparison of the delivery system performance of reference cellulosic cardboard vs. biochar 300 over time with a confidence interval of 95% (n.S. = not significant; *** = P value <0.001

quality difference perceived between 1 h and 24 h after perfume deposition demonstrates the evolution/degradation of the aldehyde mixture. Biochar 300 was not significantly different from the blind control (two-tailed paired student test, not significant) and here again the comments on the type of difference were balanced. No evolution of perfume quality was shown 1 h or 24 h after deposition, which demonstrates the stability of aldehydes on this substrate. The sensory evaluation with active charcoal as a substrate was not performed because of its strong absorbance of volatiles and the consequent lack of perceivable odor.

The aldehyde mixture on biochar 300 had a difference rating of about 3 and was therefore not perceived as significantly different from the blind control (two-tailed paired study test, not significant). This again shows the excellent stability of the compounds on this support. On the other hand, on the cellulosic support, the difference rating was above 8, and the aldehyde mixture was perceived to be significantly different from the blind control (two-tailed paired study test, significant at 99.9%) (Figure 8).

The sensory analysis confirmed the analytical results (Figure 6), reflecting the aldehyde degradation on the cellulosic reference. This is probably due to the presence of hydroperoxides in cellulose.[18-21] The perfume changed with this carrier in terms of intensity and quality. On the other hand, aldehydes were stable when deposited on biochar 300. The perfume profile was preserved and the benefit of using such a carrier as a delivery system was demonstrated.

3.9 | Thermal desorption on GC–MS of biochars

Biochar 300 made of sawdust, sawdust plus fecal material, or fecal material alone was thermally desorbed to ensure the absence of benzopyrenes or the other potentially most common harmful aromatic compounds such as benzene, napthalene, anthracene, and pyrene. The detection limit was evaluated by spiking Tenax with the pure standard compounds (benzene, napthalene, anthracene, and pyrene). None of these compounds were detected and if present, they would be at a concentration lower than 0.1 mg/kg. The main difference is the detection of short chain fatty acids and C16 and C18 fatty acids in biochar 300 containing feces; in sawdust only, methyl or methoxy alkyl phenols can be detected. The toxicity and properties of different biochar types is a topic that is becoming documented more frequently.[22-24]

This work demonstrated that biochar made from human waste, pure or blended with sawdust, performed better than biochar made with sawdust alone. Therefore, using biochar as a delivery system to deliver perfume may be a good opportunity to develop a sustainable delivery system, to add value to the biochar, and in this respect to help the circular economy.

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