

**FINAL REPORT**  
**September 10, 2018**

**Modified Natural Materials for Rendering Applications**

**Principal Investigator(s):** Daniel C. Whitehead, Associate Professor  
dwhiteh@clermson.edu  
Department of Chemistry  
467 Hunter Laboratories  
Clemson University  
Clemson, SC 29634  
(864) 656-5765

**Collaborators:** Frank Alexis, Professor  
falexis@yachaytech.edu.ec  
School of Biological Sciences and Engineering  
Yachay Tech  
San Miguel de Urququí, Ecuador

**Date Submitted:** September 10, 2018

**Project Start Date:** May 5, 2016

**Duration of Project:** 16 months

**Lay Summary:** This project continued a sustained effort focusing on the development of new technologies to reduce odor emissions from the rendering industry. The main target of this work over the years has been to develop engineered poly(amine) functionalized nanomaterials that are poised to capture malodorous volatile organic byproducts of rendering processes. Briefly, by decorating the nanomaterials with appropriate reactive sites, offending volatile byproducts will be absorbed by the formation of either ionic or covalent bonds.

*This grant* continued and improved upon our 1<sup>st</sup> generation materials that were based on nanoparticles comprised of poly(lactic acid)-poly(ethylene glycol) copolymers decorated with a terminal poly(amine) motif. This project leveraged the lessons learned from our 1<sup>st</sup> generation approach to develop two new platforms based on natural materials: poly(amine) functionalized cellulose nanocrystals, and poly(amine) functionalized kaolinite clay materials. We have achieved both of the key objectives highlighted below and demonstrated that these new materials are highly effective at capturing malodorant molecules associated with rendering operations.

**Objective (s):**

- a.) to prepare and vet functionalized cellulose based materials for odor mitigation; and
- b.) to prepare functionalized clay materials for odor mitigation.

**Project Overview:** This project continued our prolonged efforts toward the development of new technologies to reduce odor emissions from the rendering industry. Early on in this endeavor, several years of ACREC/FPRF support was leveraged to develop engineered, biodegradable poly(lactic acid)-based nanomaterials whose surface is decorated with poly(ethylene imine) (i.e. PEI-PEG-PLA nanoparticles) that were capable of capturing volatile organic byproducts of rendering processes. This first generation approach culminated in the publication of two peer-reviewed manuscripts describing the design, preparation, evaluation, and malodorant capture performance of PEI-PEG-PLA nanoparticles.<sup>1-2</sup>

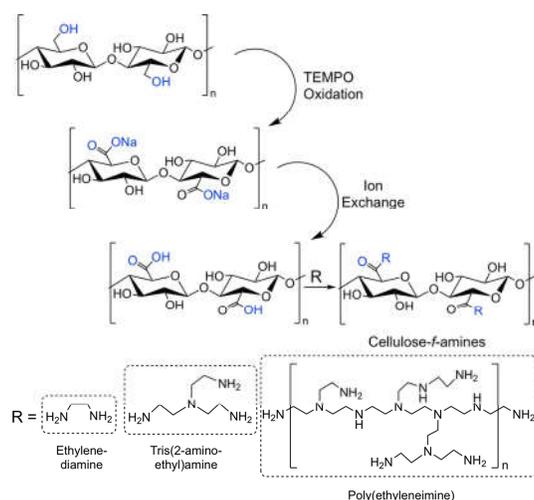
In *this study* we parlayed the lessons learned from our 1<sup>st</sup> generation approach into the development of two new poly(amine) functionalized materials that arise from natural materials, cellulose nanocrystals and kaolinite clay. The motivations for this objective were two-fold. First, we sought to utilize natural materials as the base platform for our technology in order to reduce fabrication costs. Both cellulose and clay are significantly cheaper than our first generation materials. Second, we sought a base platform for our technology that exhibited increased stability as compared to our first generation materials. This final report described the successful implementation of these objectives.

*Synthesis and Evaluation of Poly(amine) functionalized Cellulose Nanocrystals*

Amine-functionalized cellulose microcrystals (CMCs) and cellulose nanocrystals (CNCs) were synthesized for the capture of relevant aldehyde VOCs that were previously investigated using our first generation amine-functionalized synthetic polymeric nanoparticles. Cellulose is a natural polymeric material available worldwide and provides a more chemically and physically stable material when compared to the synthetic PDLA-PEG that was used as a platform in our previous study. Despite the fact that the base polymeric materials used to synthesize our first-generation materials are commercially available, their comparatively high cost may stymie

efforts toward economical scale-up. In contrast, cellulose crystals, arising from renewable sources, can be obtained at a much lower expense.

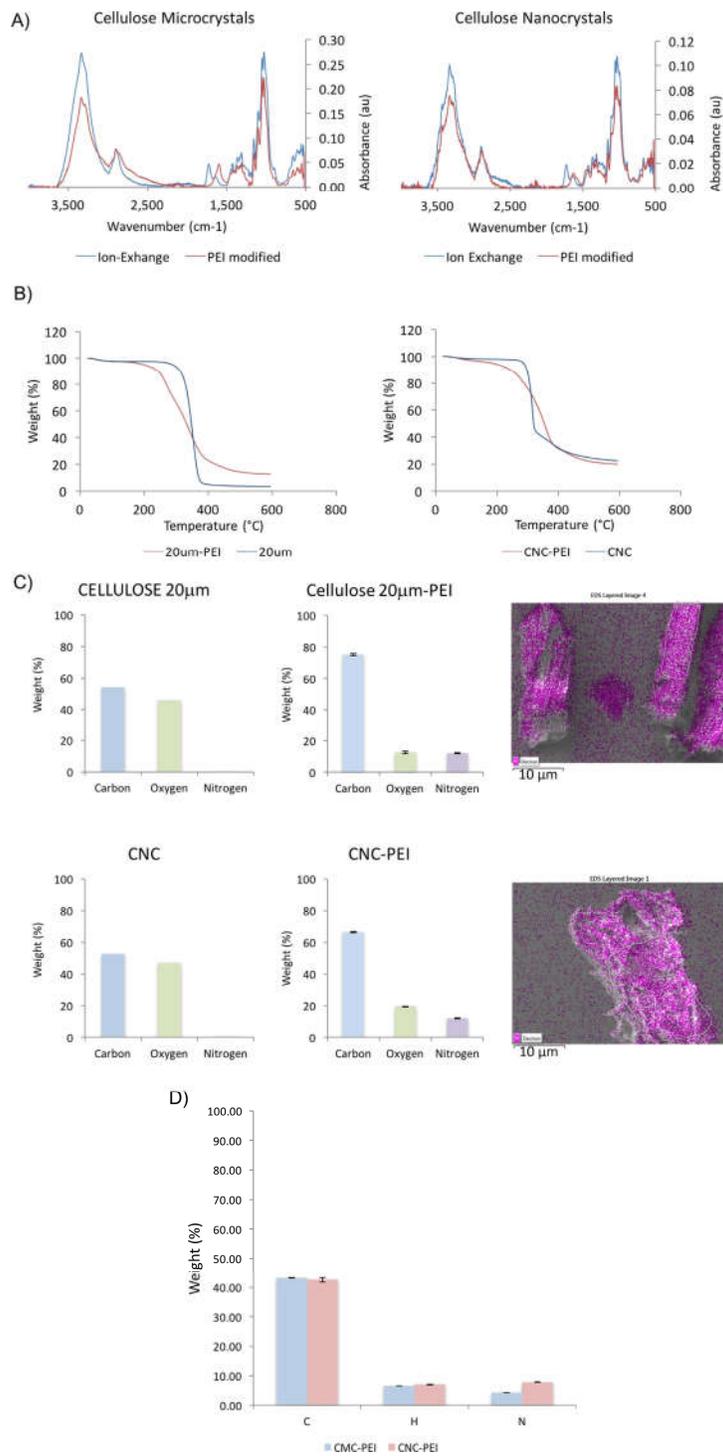
CMC and CNC materials were initially oxidized using (2,2,6,6-tetramethylpiperidin-1-yl)oxyl, commonly known as TEMPO. TEMPO-mediated oxidations are commonly used to promote the selective oxidation of primary alcohols to carboxylic acids in aqueous systems. Briefly, a suspension of the cellulose materials were oxidized at room temperature by action of 10% by weight of TEMPO and 1% by weight of sodium bromide utilizing bleach as the terminal co-oxidant. After the TEMPO reaction, the oxidized CNC and CMC samples were subjected to an ion-exchange treatment that acidified a 0.1% by weight suspension of the materials in water to pH= 2.5 upon addition of 0.1 M aq. HCl. This treatment converted the C6 sodium carboxylates in the oxidized cellulose materials to their corresponding neutral carboxylic acids. The conjugation reaction between the oxidized cellulose and the amine-bearing molecules was carried out at room temperature for 6 h in the presence of EDC, a water-soluble carbodiimide coupling reagent. **Figure 1** illustrates the steps of amine modification of cellulose structures. Initially, we focused on the preparation and evaluation of PEI-modified CMCs and CNCs as a direct analog to our first-generation polymeric nanomaterials.<sup>1-2</sup>



**Figure 1.** TEMPO-mediated oxidation of cellulose crystals and amino functionalization of the oxidized materials (amino-*f*-cellulose).

By modifying both CMCs and CNCs we were able to evaluate the necessity of operating at the nanoscale. Thus, the chemical modification of the cellulose materials to that end was conveniently followed by infrared spectroscopy by monitoring diagnostic changes in the carbonyl (*i.e.* C=O) stretching frequency (**Figure 2A**). The successful TEMPO oxidation of the C-6 carbinol was easily confirmed by the emergence of a strong C=O stretch at 1725  $\text{cm}^{-1}$ . (Note the absence of stretches in this region in unmodified cellulose.) While the amine N-H and  $\text{sp}^3$  CH stretches are obscured in the PEI-modified cellulose materials, the critical carbodiimide-mediated amide coupling that installed the PEI polymer was confirmed by the diagnostic shift of the carbonyl stretch to smaller wavenumbers. Namely, upon successful EDC coupling of the PEI onto the surface of the cellulose particles, the newly formed amides exhibit a C=O stretching frequency of 1600  $\text{cm}^{-1}$ . The diagnostic shift to smaller wavenumbers upon amide formation is

attributable to the larger extent of electron donation into the carbonyl moiety from the more electropositive nitrogen atom as compared to the carboxylic acid starting material.

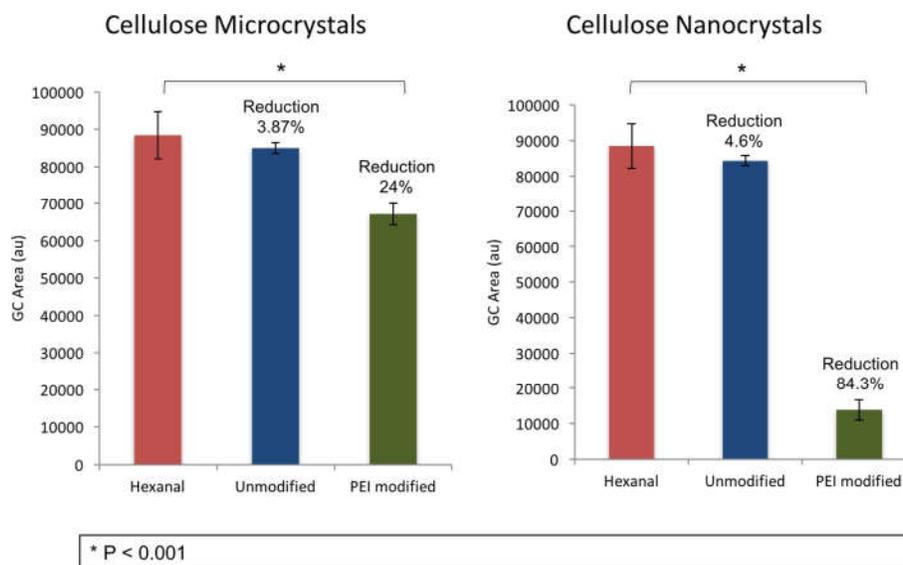


**Figure 2.** Characterization of cellulose crystals **A)** FTIR spectrum, **B)** TGA analysis, **C)** EDS analysis, and **D)** CHN Elemental analysis.

Further evidence for successful modification was apparent from thermogravimetric analysis (**Figure 2B**). The thermal degradation of the unmodified cellulose crystals occurs at approximately 260 °C. The presence of the PEI in the cellulose microcrystals causes the thermal degradation of the material to occur at approximately 145 °C, as represented in **Figure 2B**. The change in the thermal degradation of the cellulose material after PEI conjugation also confirms the modification of the cellulose crystals. Note that the lower degradation temperature upon PEI conjugation is consistent with similar results observed for our first generation PLA-based nanomaterials.<sup>1-2</sup>

In addition to TGA and FTIR, results from qualitative EDS analysis of the unmodified and the amine-functionalized cellulose crystals confirms the presence of nitrogen on the modified materials and highlights the absence of nitrogen on the unmodified cellulose (**Figure 2C**). The EDS analysis of the cellulose crystals was conducted by placing the solid material on a carbon tape. Due to the relatively larger size of the micro cellulose, it was possible to obtain data on individual crystals. However, due to limitations of the available EDS technique for accurate compound identification and quantification on the surface of nanomaterials, the EDS analysis of the nanocrystals was performed on aggregates of the nanocrystals, as shown in the electron microscopy image in **Figure 2C**. Nonetheless, quantitative CHN analysis of the nano and micro crystals was also performed. The results clearly show that CNC-PEI materials contain higher amounts of nitrogen, indicating a higher loading of PEI. The CHN analysis (**Figure 2D**) revealed that CMC-PEI contained  $4.26 \pm 0.05$  wt % of nitrogen and CNC-PEI contained  $7.85 \pm 0.10$  wt %.

After a thorough characterization of both unmodified and modified cellulose materials, an evaluation of the performance of the PEI-modified CNC and CMC materials in capturing a representative aldehyde VOC was conducted. In order to evaluate the reactivity of these new materials and to benchmark them with our first generation polymeric nanoparticles,<sup>1-2</sup> we initially conducted experiments with an illustrative VOC from the aldehyde functional group class, hexanal. The results from headspace analyses by means of gas chromatography revealed that the unmodified CMC and CNC materials were essentially incapable of capturing hexanal vapors upon a 30 min exposure of the gas to a 10 mg sample of the cellulose crystals (**Figure 3**).



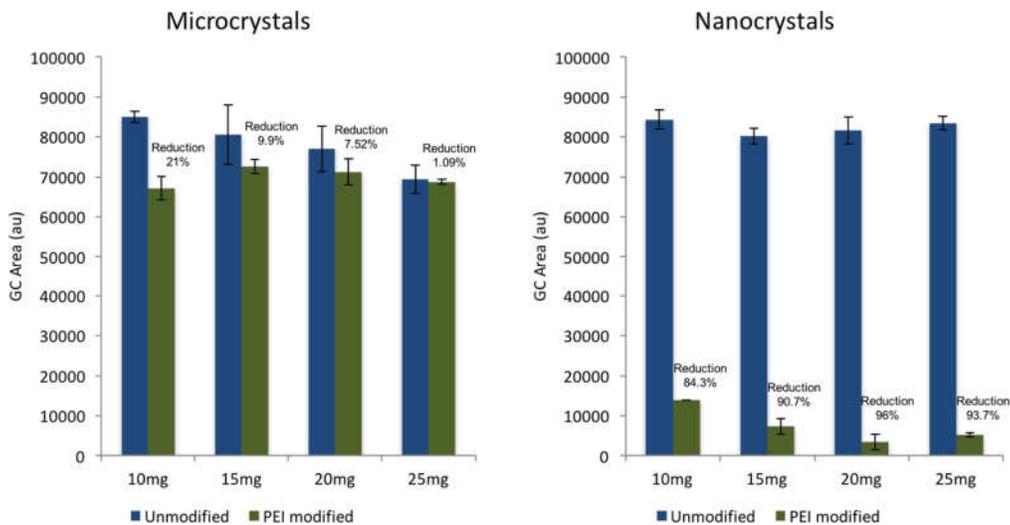
**Figure 3.** Gaseous capture of hexanal vapor using cellulose unmodified and PEI modified, micro and nano crystals.

Furthermore, PEI-functionalized CMCs were only capable of a  $24.04 \pm 3.27\%$  ( $p < 0.001$ ) reduction of hexanal vapors (as compared to untreated hexanal samples) within the 30 min capture experiment. In contrast, a 10 mg portion of PEI-functionalized CNCs exhibited a significantly better performance, resulting in a  $84.33 \pm 2.23\%$  ( $p < 0.001$ ) reduction of the hexanal vapors. A comparison of the results obtained for PEI-modified CMCs and CNCs highlights that while the microscale materials were not capable of significantly reducing hexanal vapor, a decrease in the size of the cellulose crystals to within the nanoscale range (90-300 nm) evidently facilitates the gas-capture event. It is well-described in the literature that nanomaterials present better efficiency when compared to micron-scale materials of the same kind due to their higher surface area to volume ratio. The BET multipoint method was employed to determine the surface area of the modified CNC materials prepared in this study. The results revealed that the surface area of 20  $\mu\text{m}$ -PEI crystals,  $18.397 \text{ m}^2/\text{g}$  that was approximately 3 times smaller than the surface area of the CNC-PEI crystals,  $60.625 \text{ m}^2/\text{g}$ .

We note that our first generation polymeric PEI-functionalized nano-materials<sup>1-2</sup> were capable of a slightly better reduction of hexanal vapors (*i. e.* 98% reduction over 30 min with 10 mg of PEI-polymeric NPs). We attribute the higher efficiency of gas-capture for our first-generation materials to the likely presence of more amine binding sites on the first generation materials as compared to the PEI-CNC material described herein. This situation could be attributed to either a more efficient EDC coupling during the synthesis of the former materials, or to the availability of fewer carboxylic acid coupling sites in the latter. Nonetheless, the PEI-cellulose materials are significantly cheaper and easier to prepare, especially when considering that the non-functionalized cellulose nanocrystals are commercially available and thus do not require nanoparticle synthesis and purification prior to surface modification.

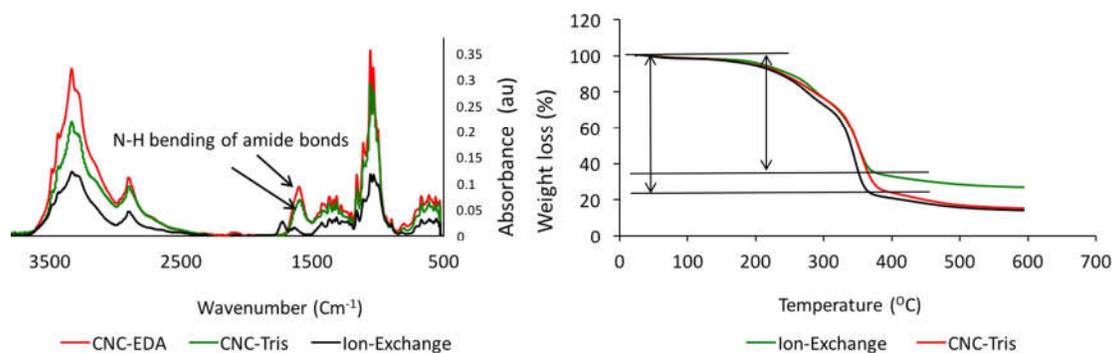
Thus, we investigated whether the more economical PEI-CNC materials would achieve a

comparable reduction percentage upon simply applying more material. The results presented in **Figure 4** confirms that a larger sample of the PEI-CNC material can achieve hexanal vapor reductions that are comparable to our first generation polymeric NPs. We were able to increase the hexanal reduction from  $84.33 \pm 2.23\%$  to  $96.07 \pm 1.16\%$  by increasing the mass of CNC-PEI applied to the sample from 10 mg to 20 mg. Notably, companion experiments using greater amounts of unmodified CNC did not demonstrate an increase efficiency of the gas capture. Further, experiments that increased the loading of the corresponding PEI-modified CMCs failed to increase the gas capture efficiency. This result further underscores the importance of the nanosized cellulose crystals in our design strategy.



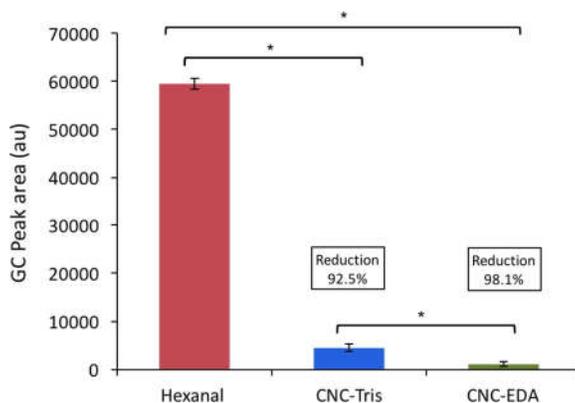
**Figure 4.** Vapor studies using increasing amounts of cellulose materials for the gaseous capture of hexanal.

In a second series of experiments, we sought to evaluate the effect of modifying the CNC material with smaller amine-bearing molecules in lieu of decoration with the PEI polymeric material. Thus we prepared CNC materials modified with the small molecules ethylenediamine (EDA) and tris(2-aminoethyl) amine (Tris), and then evaluated these materials for the capture of hexanal (see **Figure 1** for structures). The same procedures employed for the synthesis of CNC-PEI were followed to synthesize the new CNC-EDA and CNC-Tris materials. These new compounds were characterized by means of the FT-IR spectrum in **Figure 5a** that reveals new peaks at  $1587$  and  $1570$   $\text{cm}^{-1}$  corresponding to the formation of N-H bending of amide bonds in CNC-EDA and CNC-Tris materials, respectively (Again, the appearance of any new N-H stretching frequencies are obscured by the coincident O-H stretches from the cellulose backbone). Further a clear shift of the C=O signal of the carboxylic acid groups was noted after carbodiimide coupling. Further characterization was performed by TGA. **Figure 5b** illustrates approximately the same curve behaviors of modified samples (EDA and Tris) that exhibit a slight difference comparing with the oxidized cellulose (unmodified).



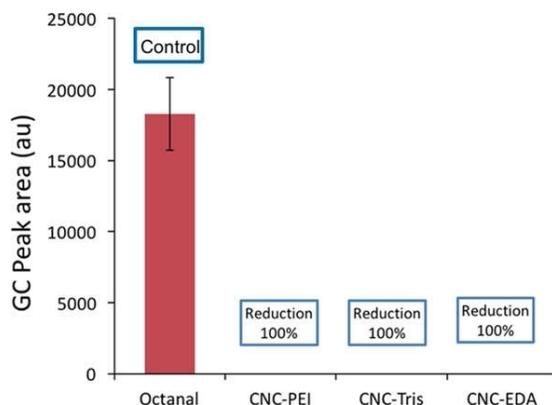
**Figure 5.** FT-IR Spectrum (a) and TGA analysis (b) of cellulose nanocrystals before and after modification by ethylenediamine and tris(2-aminoethyl)amine.

The CNC-EDA and CNC-Tris materials were then evaluated for their ability to capture hexanal vapors in the gas phase using our previously described method.<sup>1-2</sup> **Figure 6** clearly demonstrates that CNC-EDA and CNC-Tris materials are also capable of capturing hexanal vapors in the gas phase. Thus, the observed gas-phase hexanal peak area was reduced by  $92.5 \pm 1.29\%$  and  $98.1 \pm 0.76\%$  for 10 mg of CNC-Tris and CNC-EDA, respectively. These data indicate that CNC materials modified by small molecules bearing amine functionality slightly outperform CNC-PEI, modified by a polyamine (*cf.* **Figure 3**).



**Figure 6.** Gas Chromatography assay for evaluating hexanal capture efficiency for Tris- and EDA-modified cellulose nanocrystal by detecting the reduction percentage of the GC peak area of hexanal (control “untreated”) and with targeted materials (treated).

To ensure the targeting efficiency of all three synthesized materials to capture aldehydes by means of covalent imine bond formation,<sup>1-2</sup> we conducted similar gas capture experiments with a second aldehyde VOC, octanal. These experiments demonstrated 100% capture of octanal in the gas phase regardless of the amine-CNC formulation used (**Figure 7**).



**Figure 7.** Gas Chromatography assay for evaluating octanal capture efficiency of PEI-, Tris- and EDA-modified CNC.

Thus, we report an efficient preparation of amine modified cellulose materials that are capable of near quantitative or quantitative capture of gaseous aldehyde vapors. Full physicochemical characterization was conducted using FTIR, TGA, SEM, EDS, and elemental analysis to confirm their chemical structures. Thus we demonstrated that commercial CMC and CNC materials could be easily functionalized with PEI after TEMPO-mediated oxidation and ion exchange steps. While the resulting PEI-modified CMC material was not capable of significantly reducing gaseous hexanal samples within a 30 min experiment, the PEI modified CNC materials showed a successful reduction of the analyte. An initial 84% reduction of the gas was obtained for experiments conducted using 10 mg of PEI-modified CNC, but larger reductions were possible when larger loadings of the material was employed. Specifically, a 20 mg sample of PEI-CNC facilitated a gas reduction of 96%, on par with the reduction efficiency observed for our first generation materials.<sup>1-2</sup> The comparison between the results obtained for micro- and nano-scale cellulose crystals are in concordance with other remediation studies presented in the literature. The better performance of the modified CNC material is likely due to the higher surface-to-volume ratio that is obtained by operating on the nanoscale. This effectively translates to more reactive amine sites present on the surface per unit volume. These initial efforts then motivated the preparation of related amine-decorated CNC materials that were modified with EDA and Tris, respectively. The data demonstrated that the small amine caps, EDA- and Tris, generated materials that were as efficient at the capture of aldehyde VOCs as compared to the CNC-PEI material. Current efforts are now geared toward scale-up and validation of the CNC-poly(amine) materials in a plant setting.

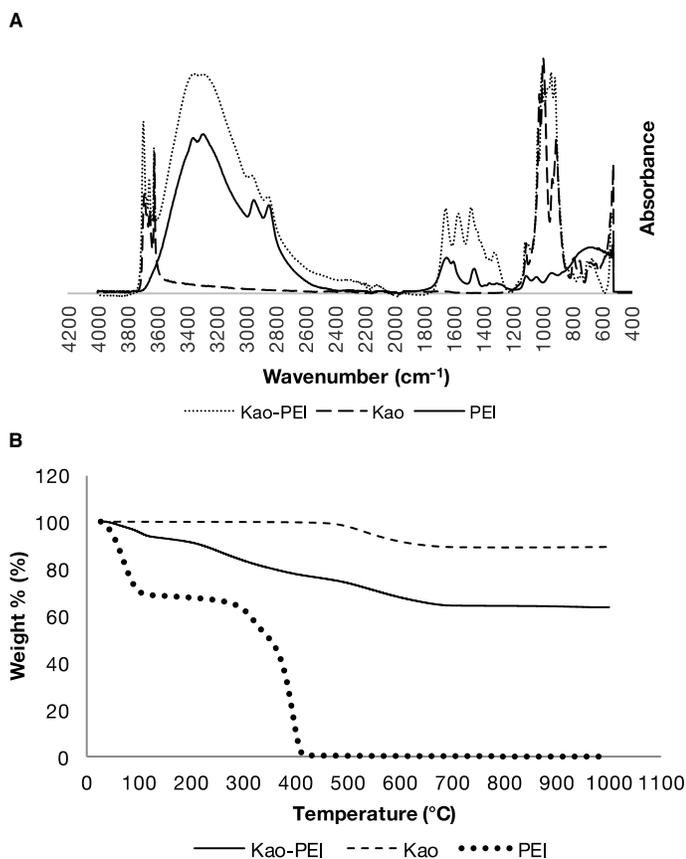
#### Synthesis and Evaluation of Poly(amine) functionalized Kaolinite Clay

In a parallel effort, we set out to functionalize kaolinite (Kao) clay with a poly(amine) in order to evaluate this material's potential to ameliorate malodorous VOCs emanating from rendering operations. Kao was functionalized with PEI following the wet impregnation technique wherein PEI is immobilized onto the porous clay substrate. Briefly, the clay substrate was suspended in a solution of PEI and methanol and allowed to stir for 3 h. The wet amino-functionalized clay was then dried *in vacuo* at 75 °C for 12 h. For evidence of successful modification, FTIR spectroscopy, TGA, TEM imaging, and energy-dispersive X-ray EDX analyses were performed.

FTIR spectroscopy was used to qualitatively confirm PEI impregnation onto kaolinite (**Figure 8A**). Three intense bands at approximately  $3650\text{ cm}^{-1}$  are attributed to the Kao hydroxyl stretching vibrations and can be observed in both the Kao and Kao-PEI spectra. Strong overlapping bands at approximately  $1000\text{ cm}^{-1}$  include vibrations credited to the silicon-oxygen bonds and the bending vibration of the hydroxyl groups present in Kao. The appearance of new bands in the Kao-PEI spectra corresponding to the immobilized PEI are diagnostic of successful modification. Specifically, the bending vibrations of  $\text{NH}_2$  resulting in bands at  $1600\text{ cm}^{-1}$  and at  $1470\text{ cm}^{-1}$  are evident. The broad N-H stretching bands at  $3280\text{ cm}^{-1}$  and bending bands at  $1650\text{ cm}^{-1}$ , the stretching vibrations for  $\text{CH}_2$  at  $2871\text{ cm}^{-1}$  and  $2943\text{ cm}^{-1}$  and the bending mode of the carbon-nitrogen bond at  $1330\text{ cm}^{-1}$  are all qualitative matches for PEI's experimental vibrational bands.

TGA profiles for the Kao-PEI also support the effective modification of the substrate (**Figure 8B**). Unmodified Kao shows little thermal degradation (*i.e.*  $< 20\%$ ) up to  $1000\text{ }^\circ\text{C}$ . Kao-PEI presents an altered temperature degradation profile. The thermal degradation of Kao-PEI is observed at approximately  $300\text{ }^\circ\text{C}$  showing a  $25\%$  mass loss until the amine is fully desorbed from the clay surface around  $400\text{ }^\circ\text{C}$ , which ultimately results in a total mass loss of  $63\%$  over the temperature gradient. TEM imaging and EDX analysis also provide additional evidence of successful PEI-clay modification.

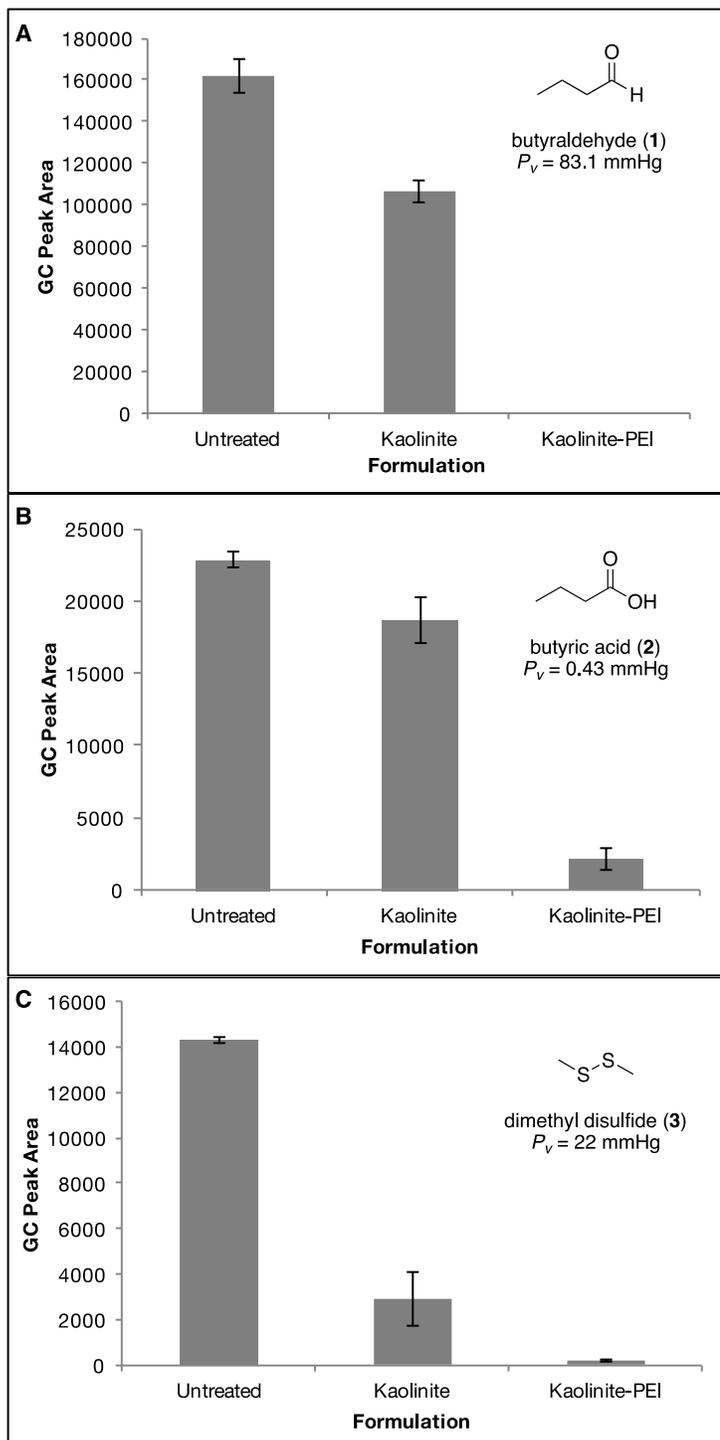
Next, initial investigations into the application of Kao-PEI for the remediation VOCs were conducted. Representative compounds from three malodorant functional group classes (*i.e.* aldehydes, carboxylic acids, and organodisulfides) were employed: butyraldehyde, butyric acid, and dimethyl disulfide, respectively (**Figure 9**). Treatment of each VOC with Kao-PEI was completed in sextuplicate and vapor reduction percentages were calculated by means of a previously established GC headspace analysis protocol.<sup>1-2</sup> Unmodified Kao was employed as a control.



**Figure 8.** A. Infrared spectra of PEI-modified kaolinite clay (Kao-PEI, dotted line), unmodified Kao (dashed line), and PEI (solid line). Successful PEI modification is indicated by the N-H stretching bands at  $3280\text{ cm}^{-1}$  and bending bands at  $1650\text{ cm}^{-1}$  present in the Kao-PEI spectra. B. TGA analysis of Kao-PEI (solid line), unmodified Kao (dashed line) and PEI (dotted line).

**Figure 9** highlights the percent reduction for each VOC after a 30 min exposure to either Kao or Kao-PEI. Butyraldehyde vapors were partially remediated in the presence of Kao with 33% ( $P < 0.0005$ ) vapor reduction observed (**Figure 9A**). When treated with the Kao-PEI, butyraldehyde was completely reduced with 100% ( $P < 0.0005$ ) vapor capture (**Figure 9A**). We surmise that the highly effective capture of aldehydes with Kao-PEI is driven by the rapid condensation of the aldehyde analyte with the poly(amine) to form imines, an observation that we confirmed spectroscopically with our 1<sup>st</sup> generation polymeric nanoparticles.<sup>1-2</sup> Unmodified Kao was somewhat effective at sequestering the butyric acid (18% capture ( $P < 0.0005$ ), **Figure 9B**). Nevertheless, Kao-PEI was successful in reducing 90% ( $P < 0.0005$ ) of the butyric acid vapors (**Figure 9B**) presumably through the formation of ammonium carboxylates via acid base reaction between the carboxylic acid vapor and the poly(amine) resident on the modified clay.<sup>1-2</sup>

Lastly, we probed the potential capture of dimethyl disulfide (DMDS). DMDS vapor was treated with Kao and Kao-PEI, with both materials performing as promising sorbents. Treatment of DMDS with kaolinite resulted in 79% ( $P < 0.0005$ ) reduction, while Kao-PEI was 99% ( $P < 0.0005$ ) effective (**Figure 9C**). While the unmodified kaolinite clay was poorly/moderately effective at remediating VOCs, the amine functionalized kaolinite was especially successful at capturing organics in the vapor phase. We hypothesize that possible electrostatic or ionic capture is enhanced compared to non-functionalized clay. These data clearly indicate

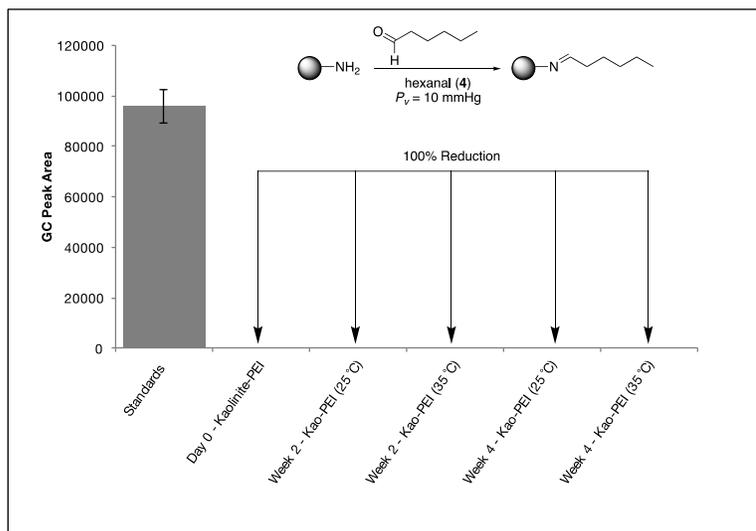


**Figure 9.** Vapor capture assays with Kao-PEI and Kao. A. butyraldehyde, B. butyric acid, C. dimethyl disulfide. Vapor pressures reported at 20 °C.

that Kao-PEI can serve as an effective sorbent for the mitigation of a selection of representative and relevant environmental VOC pollutants. It should be noted that montmorillonite (MMT) clay might also serve as a viable platform for PEI-functionalization considering its available interlayer space for sorption. However, due to the initial success of the Kao-PEI material as well as the cost difference between the two clays we opted to continue with the less expensive yet highly effective PEI-modified kaolinite clay.

Following the successful remediation of butyraldehyde, butyric acid, and dimethyl disulfide VOCs, we sought to follow the Kao-PEI vapor capture over a period of 6 h in order to glean information about the sorption kinetics. Additionally, the ability of the Kao-PEI to effectively retain the captured VOCs past the initial 30 min vaporization period was probed. Hexanal was chosen as a representative aldehyde for GC vapor capture analysis at 10 min, 20 min, 30 min, 1 h, 2 h, 3 h, 4 h, and 6 h time points. At 10 min a 49% reduction is seen, followed by a 65% reduction at 20 min, with complete hexanal vapor capture noted at 30 min. There is no evidence of hexanal vapor release from the modified clay at 1 h, as no hexanal vapor is detected via GC analysis. The Kao-PEI is able to retain the captured VOCs for at least 6 h with no hexanal vapor being detected at the remaining time points. Additionally, we evaluated the potential for the reuse of PEI-Kao material that had been previously treated with a target VOC. We found that a recycled sample of PEI-Kao was capable of capturing significant amounts (*i.e.* ~84%) of the target VOC in a second run.

Our final laboratory investigation using Kao-PEI probed the adsorbent efficiency of the material during the course of a one-month aging period where the material was stored at ambient temperature (25 °C) or at an elevated temperature (*i.e.* 35 °C). Treatment of hexanal vapors with Kao-PEI were conducted on day zero to establish the baseline adsorbent function directly after synthesis. Comparable to the results for butyraldehyde (**Figure 9A**), Kao-PEI demonstrated 100% capture of the less-volatile hexanal (**Figure 10**). The performance of another aliquot of the same Kao-PEI sample was also assessed following two weeks and 1 month of storage at both 25 °C and 35 °C, resulting in 100% reduction of hexanal vapors. These data clearly indicate that the Kao-PEI material is shelf-stable for at least 1 month and likely longer. Thus, the Kao-PEI material described herein is the result of an easily modified natural starting material and represents an inexpensive and stable sorbent material for VOC capture for industrial applications.



**Figure 3.** Kao-PEI Aging Study: Percent reduction for hexanal vapors after treatment with Kao-PEI stored over the course of one month at 25 and 35 °C. Complete capture of hexanal vapors was seen throughout the one month storage period.

As a final assessment of the

performance of Kao-PEI, we sought to investigate its potential to remediate VOCs in an industrially relevant setting at a rendering facility of an FPRF member company.

Briefly, we generated cartridges containing 0.75 g of Kao-PEI packed between two cotton plugs and sealed in a glass tube. Prior to the in-plant sampling runs, the ends of the sealed tubes were opened with pliers and the Kao-PEI cartridges were plumbed in front of a commercially available KOH-coated silica gel cartridge designed for sampling VFAs using a short length of tubing. The other end of the VFA sample cartridge was plumbed to a sampling pump and plant air was collected at a rate of 700 mL min<sup>-1</sup> over a 100 min sampling period. Thus, plant air was pumped first through the Kao-PEI sample cartridges prior to passing through the KOH-coated silica gel cartridge used to sample the VFA load of the sampling site. Sampling was conducted in this manner using three sampling pumps in parallel. Triplicate treated and untreated plant air samples were collected simultaneously. This sampling regime was then repeated on the next day. After the VFA sampling cartridges were treated with plant air for 100 min, they were sealed and sent to a commercial atmospheric analysis laboratory for VFA analysis using a standardized GC/MS protocol.

The results of this in-plant analysis show that the Kao-PEI material significantly reduces the VOC load of all detectable VFAs in comparison to the untreated plant air samples (**Table 1**). Untreated plant air samples revealed part-per-billion level concentrations of twelve fatty acids ranging from 233 ± 5.8 ppb for acetic acid to 1 ± 0.1 ppm for the less-volatile nonanoic acid. In comparison, the treated plant air, having passed first through the Kao-PEI cartridge prior to passing through the VFA sample cartridge, returned analyses below the limit of detection for all VFAs except for propanoic acid (1.9 ± 1.1 ppb), 2-methylpropanoic acid (0.9 ± 0.4), and butanoic acid (2.0 ± 1.7). Nonetheless, in the case of these three analytes, Kao-PEI treatment of the plant air reduced these constituents by 99, 95, and 99%, respectively. Ultimately, this study represents an important step in demonstrating the applicability of PEI-modified kaolinite clay and other functionalized naturally occurring clays in VOC mitigation in an industrial setting.

**Table 1.** Pilot-scale capture of volatile fatty acids from a rendering facility by Kao-PEI cartridges

Entry	Volatile Fatty Acids	Untreated (ppb)	Treated (ppb)	% Reduction
1	acetic acid	233.3 ± 5.8	< 8	> 97%
2	propanoic acid	163.3 ± 5.8	1.9 ± 1.1	99%
3	2-methylpropanoic acid	17.0 ± 1.0	0.9 ± 0.4	95%
4	butanoic acid	180.0 ± 10.0	2.0 ± 1.7	99%
5	2-methylbutanoic acid	11.7 ± 0.6	< 0.6	> 95%
6	3-methylbutanoic acid	11.3 ± 0.6	< 0.6	> 95%
7	pentanoic acid	19.7 ± 1.2	< 0.6	> 97%
8	4-methylpentanoic acid	6.9 ± 0.5	< 0.5	> 93%
9	hexanoic acid	10.0 ± 0.9	< 0.5	> 95%
10	heptanoic acid	1.6 ± 0.2	< 0.5	> 69%
11	octanoic acid	1.7 ± 0.2	< 0.5	> 71%
12	nonanoic acid	1.0 ± 0.1	< 0.4	> 60%

Thus, the preparation and characterization of the Kao-PEI clay proved successful through FTIR, TGA, TEM, and EDX analysis. Further, Kao-PEI was demonstrated to be capable of capturing environmentally relevant VOCs from the carboxylic acid, aldehyde, and disulfide functional

group classes, with capture from the gas phase at or approaching 100%. Prepared cartridges packed with the Kao-PEI clay material were also successful in significantly reducing all detectable VFAs resulting from rendering operations during a small-scale in-plant field study, demonstrating reductions between 99-60% (most reduced below the limit of detection for the assay).

Ultimately, the ability to recycle or reuse the Kao-PEI clay would greatly improve its function and utility in an industrial setting. We have attempted to drive-off captured VOCs by heating previously used Kao-PEI clay at 65, 75, 85, and 100 °C for 24 h. This proved ineffective upon retreatment of the Kao-PEI with hexanal; no additional capture of vapor was observed. VOC capture was observed, however, when previously used Kao-PEI clay was subsequently reused in the hexanal vapor capture GC assay. As expected, when hexanal vapor was treated with fresh Kao-PEI a 100% reduction was noted. Upon reuse of the Kao-PEI to treat a second aliquot of hexanal vapor 82% reduction was still seen. Further efforts in our laboratory are focused on the development of a simple protocol in which adsorbed VOCs can effectively be desorbed from the modified clay while maintaining efficacy. These results will be reported in due course.

**Impacts and Significance:** The technology described in this proposal has the potential to be very beneficial to the rendering industry in terms of providing a next-generation alternative to established methods for odor remediation. We envision that the Materials described herein might present several uses in an industrial setting. The particles could be employed as a rapid-use odor adsorbent in an emergency or spill situation. Further, the particles could, in principle, be incorporated into existing odor remediation equipment as an added means for odor elimination. The obvious long-term goal would be to develop an appropriate formulation of functionalized nanomaterials that would compete with or ideally supplant existing odor elimination measures.

**Publications:** Three peer-reviewed manuscripts and one review article originated from the efforts described herein:

1. Guerra, F. D.; Smith Jr, G. D.; Alexis, F.; Whitehead, D. C. "A survey of VOC emissions from rendering plants" *Aerosol Air Qual. Res.* **2017**, 17,209-217.
2. Guerra, F. D.; Campbell, M. L.; Attia, M. F.; Whitehead, D. C.; Alexis, F. "Capture of Aldehyde VOCs Using a Series of Amine-Functionalized Cellulose Nanocrystals" *ChemistrySelect*, **2018**, 3, 5495-5501. (Cover feature)
3. Swasy, M.I.; Campbell, M.L.; Brummel, B.R.; Guerra, F.D.; Attia, M.F.; Smith, Jr., G.D.; Alexis, F.; Whitehead, D.C. "Poly(amine) modified kaolinite clay for VOC capture" *Chemosphere* **2018**, *in press*, DOI: 10.1016/j.chemosphere.2018.08.156.
4. Guerra, F. D.; Attia, M. F.; Whitehead, D. C.; Alexis, F. "Nanotechnology for Environmental Remediation: Materials and Applications" *Molecules*, **2018**, E1760, DOI: 10.3390/molecules23071760 (Review article).

**Outside funding:** We have been successful in leveraging preliminary data generated from FPRF/ACREC support to garner one additional grant to pursue similar objectives to the ones completed during the course of this project:

1. South Carolina South Carolina Research Authority (SCRA) - Academic Programs Maturation Fund Matching Grant: \$10,000 – PI: Daniel C. Whitehead “Accessing Kilogram Scale Quantities of Functional Nanoparticles for the Remediation of Industrial Environmental Contaminants”

**Future Work:** Leveraging current FPRF/ACREC support, we continue to aggressively pursue objectives geared toward scale-up and production cost reduction with the goal of commercializing the materials described herein. Our ultimate goal is to arrive at a commercially viable material that can be deployed for odor remediation in the rendering industry as well as other environmental applications.

**Acknowledgments:** Graduate Students Maria Swasy, Fernanda Guerra, McKenzie Campbell, and Beau Brummel contributed to the work described herein. Post-doctoral scholar Mohamed Attia also contributed to the goals of this project. Finally, we thank Ms. Kim Ivey (Clemson Materials Science and Engineering) for technical support.

**References:**

1. Campbell, M. L.; Guerra, F. D.; Alexis, F.; Whitehead, D. C. "Target-Specific Capture of Environmentally Relevant Gaseous Molecules with Functional Nanoparticles", *Chem. Eur. J.* **2015**, 21, 14834-14842.
2. Guerra, F. D.; Campbell, M. L.; Whitehead, D. C.; Alexis, F. "Tunable Properties of Functional Nanoparticles for Efficient Capture of VOCs" *ChemistrySelect*, **2017**, 2, 9889-9894.