**FINAL REPORT**
**February 24, 2017**

# LACTIDE NANOPARTICLES FOR THE REMEDIATION OF RENDERING MALODORANTS


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**Duration of Project**: 21 months

**Lay Summary:** This project continues a sustained effort focusing on the development of new technologies to reduce odor emissions from the rendering industry. The main target of this work has been to develop engineered, biodegradable poly(lactic acid) nanomaterials whose surface is decorated with appropriate reactive sites (*i.e.* functional groups) that are poised to destroy 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. Alternatively, the offending odors will be chemically oxidized on the nanomaterial surface in order to generate less odorous byproducts. The malodorants will be chemically modified so as to both harness them onto the biodegradable materials for disposal, and to render them less odorous. This study will serve as a proof-of concept to demonstrate that functionalized biodegradable poly(lactic acid) nanomaterials have the potential to become a next-generation strategy for odor remediation in the rendering industry.

**Objective (s):** The following objectives were targeted during the course of this proposal:

> **Aim 1.** To explore and test an alternative, streamlined synthesis of multifunctional nanoparticles capable of sequestering or destroying aldehyde, carboxylic acid, and sulfurous malodorants.
>
> **Aim 2.** To field test our first generation amine-capped nanomaterials for the remediation of aldehyde and carboxylic acid malodorants at a rendering facility.
>
> **Aim 3.** To investigate the lifetime, leaching, degradation, and toxicity of spent and pristine nanoparticles.

**Project Overview:**

*Introduction:*

Odor Remediation in the Rendering Industry

The rendering industry invests significant efforts and capital into controlling odor emissions that result from processing unused organic matter from livestock production, meat and food processing, and the food service industry. The positive environmental impact of the rendering industry in terms of reducing the amount of landfill and biological waste from the aforementioned operations is often overshadowed by negative perceptions of the industry's environmental impact in terms of wastewater and odor emissions. Concerns over odor emissions often play a large role in community resistance to site selection for new rendering operations.[1] Indeed, *untreated* emissions from rendering operations can be detected up to 20 miles away from the source.[2]

Modern rendering facilities are equipped with sophisticated mechanisms for controlling odor and particulate emissions. Particulate emissions are controlled by filtering mechanisms called bag houses.[1] Malodorous vapors and contaminated air from the rendering process are controlled by means of several strategies. Common odor control methods include combustion/incineration, chemical oxidation, wet scrubbing, and biological scrubbing. Room air

emissions are often treated with packed bed scrubbers containing chemical oxidants. Cooking vapors are often treated in two stages. First, vapors are cooled and passed through a venturi scrubber. The vapor effluent of the venturi scrubber is then treated with packed bed scrubbers filled with chemical oxidants. Other methods for treating cooking vapors involve the removal of condensable vapors followed by incineration of the non-condensable vapors in the plant boilers.[1,2] Biological scrubbers remove plant odor emissions by passing odorous air through scrubbers containing bacterial biofilms that metabolize the odorous emissions.[1-4]

Despite their sophisticated nature, current odor remediation strategies in the rendering industry suffer from some drawbacks. Combustion and incineration strategies are energy intensive processes that also result in substantial venting of greenhouse gases. Chemical oxidation requires the use of strong oxidants. Spent chemical and biological packed bed scrubbers must be disposed of properly. Additionally, aqueous effluent from packed bed and venturi scrubbers contribute to the already substantial wastewater flow from rendering operations.[1]

There is a declared need for new means for controlling odor emissions from rendering operations.[5] This proposal seeks supplemental funding to continue efforts toward the development of a novel method for the chemical destruction of malodorous rendering emissions by employing an engineered poly(lactic acid) material that is biodegradable and non-toxic to both human and environmental health.

Malodorous Volatile Organics from the Rendering Industry

Van Langenhove *et. al.* conducted a comprehensive study aimed at identifying the specific volatiles that contribute to malodorous rendering odors that vent from cooking processes. In total, about 110 distinct volatiles were detected and identified, but just 26 of that number were confirmed to contribute to the unsavory odors of cooking processes. Chart 1 includes a comprehensive list of the offending odorants as well as a general depiction of their common functional group. The list contains ten short chain aliphatic aldehydes ranging from three to ten carbons in length. Carboxylic acids comprise the second most populous group, containing examples ranging from two to six carbons in length. Sulfur containing functional groups (including thiols, sulfides, disulfides, and trisulfides) comprise the third largest group of offending odorants. Additionally, a single alcohol and a single amine were identified.[6] Most of these volatile organics result from the thermal breakdown of protein and fats during the cooking process.[3]

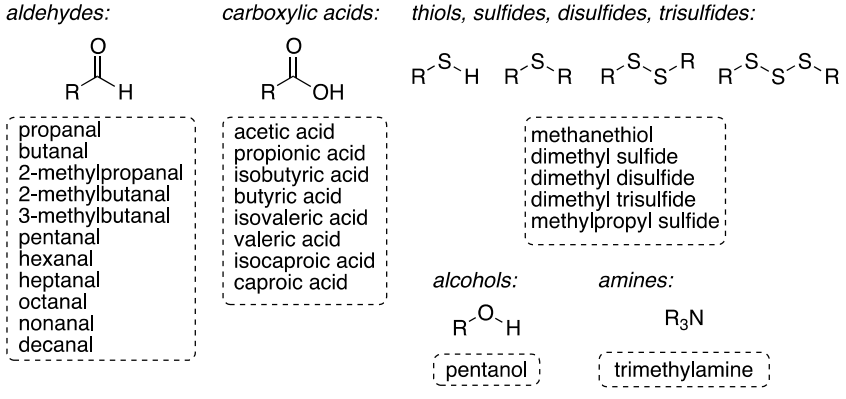


**Chart 1.** Volatile organics responsible for malodorant cooking emissions organized by functional group.

Other sources of odors in the rendering process include protein degradation products including amino acids and

peptides, most notably present during blood storage. Wastewater treatment produces several noxious emissions including hydrogen sulfide and ammonia. Evaporation processes and animal waste product storage also emit hydrogen sulfide and ammonia along with various other amines, aldehydes, carboxylic acids, and thiols. Finally, smokehouse operations emit various aldehydes, acids, and other organic constituents including cresol and acrolein.[3,7]

The large number of offending chemical entities as well as their ill-defined and often variable relative concentrations complicate approaches toward the strategic remediation of rendering plant odors. The situation is further complicated by the fact that the most offending odorants are not necessarily the major constituents of the emissions from rendering processes. For example, the human nose is capable of detecting odorants with thresholds as low as 0.1 parts per billion (v/v).[6,8]

Poly(lactic acid) (PLA) polymers and applications

Polymers of lactic acid (*e.g.* Figure 1) were first discovered in 1932, but their practical applications did not begin to emerge until the early 1970s when they found considerable use as dissolving sutures in surgical applications.[9,10] Fermentation technology developed in the late 1980s resulted in affordable means for the preparation of the requisite monomer for PLA synthesis from D-glucose obtained from corn. Cheaper monomer sources for PLA catalyzed a renaissance of its study, and numerous new applications of the polymer have recently emerged. Current applications include formulations for biodegradable trash bags and lawn care bags, water bottles, food storage containers, and various fiber products.[11,12] Recent applications in medicine include applications for drug-delivery and controlled drug release. PLA polymers are particularly exciting in this regard due to their biodegradability and toxicological safety.[10] PLA polymers can be engineered to degrade over a timeline of days, weeks, months, or even years depending on the specific formulation. Their non-toxic nature and tunable degradation properties make them excellent candidates as a medium for the remediation of environmental pollutants, including rendering odor emissions. Our approach to this end is detailed below.

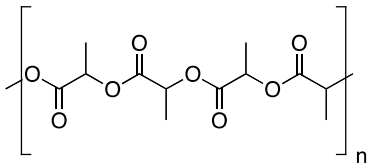

**Figure 1.** Polylactic acid (PLA)

Brief summary of accomplishments from previous ACREC/FPRF support

In previous efforts, spanning several years, we have:

1.) Successfully developed an efficient synthesis of polymeric nanoparticles comprised of the block co-polymer: poly(lactic acid)-poly(ethylene glycol)-poly(ethyleneimine) (*i.e.* PLA-PEG-PEI) (Figure 2).
2.) Rigorously characterized these materials with spectroscopic and other analytical techniques.
3.) Demonstrated that the materials are capable of capturing volatile organics associated with rendering odors including carboxylic acids, and aldehydes in the gas phase.

4.) Undertaken efforts to improve the technology by pursuing second generation materials that perform at the same level at reduced production costs.

5.) Undertaken efforts to optimize the synthesis of the materials at larger scale.

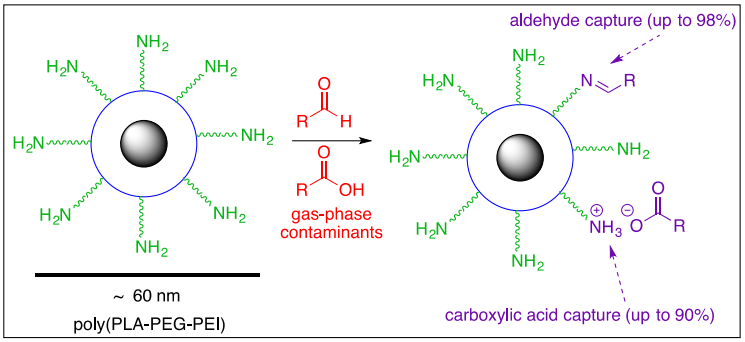


**Figure 2.** PLA-PEG-PEI NPs for rendering malodorants.

6.) Published a peer-reviewed manuscript describing our first generation materials.[13]

7.) File a patent protecting the intellectual property associated with our first generation materials.[14]

8.) Leveraged FPRF support to seek federal funding for the project and to obtain a grant for scale-up efforts from the Clemson University Research Foundation.

The current project sought to expand upon these initial discoveries to further develop the technology into a robust, affordable platform for the remediation of odors associated with rendering processes. Our progress to that end is described below.

*Aim 1: To explore and test an alternative, streamlined synthesis of multifunctional nanoparticles capable of sequestering or destroying aldehyde, carboxylic acid, and sulfurous malodorants.*

Our original proposal described a plan to carry out the selective oxidation of the tertiary amines resident in our first generation nanoparticles in order generate tertiary amine N-oxides capable of oxidizing and thus destroying sulfurous rendering malodorants. We made a number of attempts to oxidize the first generation materials with aqueous bleach (NaOCl), but the treatments always resulted in the decomposition of the starting nanoparticles.

Given the failure of our initially proposed oxidation strategy, we turned to an exploration of the capability of our first generation nanoparticles to capture sulfurous malodorants. In the event, we treated samples of our first generation PLA-PEG-PEI nanoparticles with gas-phase samples of three sulfurous materials: dimethyl sulfide (DMS), dimethyl disulfide (DMDS), and dimethyl trisulfide (DMTS) in the gas phase. These molecules have been detected previously in the off-gases associated with rendering operations and each presents a putrid, rotten egg odor. Upon treatment with our first generation materials, gas-phase samples of the malodorants were reduced by 90%, 82%, and 90% for DMS, DMDS, and DMTS,

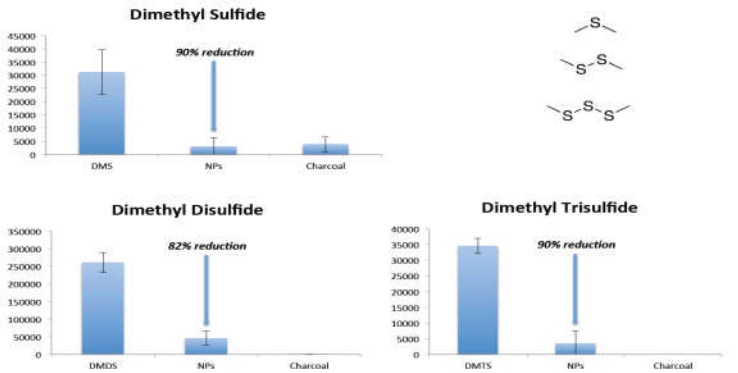


**Figure 3.** Gas phase capture of sulfurous malodorants with amine functionalized nanoparticles.

respectively (Figure 3). These results are on par with the performance of the common adsorbent, activated charcoal. Nevertheless, our materials are capable of capturing aldehyde and carboxylic acid VOCs as well.

Thus, despite the failure of our initial strategy for addressing sulfurous malodorants via an oxidative strategy, we have successfully demonstrated that our first generation materials are effective at capturing sulfur malodorants through a non-specific adsorption phenomenon.

*Aim 2: To field test our first generation amine-capped nanomaterials for the remediation of aldehyde and carboxylic acid malodorants at a rendering facility.*

In a first attempt to assess the performance of our materials at a rendering facility, we fabricated small glass cartridges packed with ~1 g of amine NPs capped on both sides with small cotton plugs. Each end of the glass tube was sealed with a torch for transport to the rendering facility (see photos). Similarly, we prepared control cartridges filled with non-functionalized ($OCH_3$) capped NPs.

During the field test experiments, pumps were used to sample contaminated plant air through the NP-packed cartridges followed by a sample collection tube (plumbed in sequence via rubber tubing). The sample collection tubes were then subjected to malodorant isolation and GC identification/quantification (conducted by contract services). In this manner, we evaluated our amine capped NP cartridges for the capture of carboxylic acid and aldehyde/ketone malodorants in two independent experiments. Additionally, we collected data while passing the plant air through our unfunctionalized $OCH_3$ capped control nanoparticles. In each case, the results were compared to untreated plant air.

For the carboxylic acid capture experiments, the amine capped NPs performed excellently. The In untreated plant air, 12 distinct carboxylic acid malodorants were detected in concentrations ranging from 0.47 to 320 ppb. Treatment of plant air with our amine capped NPs effected an average reduction of 86% in the malodorant vapors (See Table 1). Importantly, the unfunctionalized control NPs were notably less effective, confirming that our functional materials are uniquely effective.

| Detected molecule | Non-treated (ppb) | amine NPs (ppb) | % reduction | OMe NPs (ppb) | % reduction |
|---|---|---|---|---|---|
| acetic acid | 320 | 46 | 86% | 260 | 19% |
| propanoic acid | 110 | 20 | 82% | 92 | 16% |
| isobutyric acid | 9.3 | 2.4 | 74% | 7.8 | 16% |
| butyric acid | 140 | 27 | 81% | 120 | 14% |
| 2-methylbutanoic acid | 8 | 1.7 | 79% | 6.7 | 16% |
| isovaleric acid | 8 | 1.7 | 79% | 6.5 | 19% |
| valeric acid | 9.5 | 1.7 | 82% | 7.4 | 21% |
| isocaproic acid | 5.9 | 0.98 | 83% | 4.3 | 27% |
| caproic acid | 5.5 | 0.84 | 85% | 3.7 | 33% |
| enanthoic acid | 0.67 | nd | 100% | nd | 100% |
| caprylic acid | 0.82 | nd | 100% | nd | 100% |
| pelargonic acid | 0.47 | nd | 100% | nd | 100% |

**Table 1.** Singleton volatile fatty acid capture experiment evaluation functional NPs at a rendering plant.

In the singleton experiment where we evaluated the capture of aldehydes and ketones from plant air, the results were strange. Some compounds were significantly reduced while some were observed to a higher extent as compared to untreated air samples (See Table 2). This result occurred after we encountered operational problems with the sample pumps that were utilized to collect the plant air samples. In short, we do not believe the data in the table below is an accurate reflection of the capability of our materials.

| Detected molecule | Non-treated (ppb) | amine NPs (ppb) |
|---|---|---|
| formaldehyde | 3.31 | 0.649 |
| acetaldehyde | 39.1 | 74.1 |
| acrolein | 0.661 | 0.602 |
| acetone | 54.3 | 56.1 |
| proionaldehyde | 6.97 | 6.11 |
| methacrolein | 1.73 | 1.82 |
| MEK & butyraldehyde | 60.4 | 58.5 |
| benzaldehyde | 0.682 | 0.477 |
| pentanal | 3.66 | 3.22 |
| hexanal | 5.58 | 5.09 |

**Table 2.** Singleton aldehyde capture experiments at a rendering facility.

The following summer we returned to the same plants in order to carry out a larger scale evaluation of our nanomaterials. Thus, we prepared 18 filter cartridges for on-site field testing: a.) six cartridges packed with 1 g of PLA-PEG-PEI polyamine capped NPs, six cartridges packed with 1 g of PLA-PEG-OMe control NPs, and six cartridges packed with 1 g of activated charcoal. Each of these filter cartridges were plumbed in front of a sampling cartridge attached to a sampling pump and the plant air was assayed for either volatile carbonyl-containing compounds (*i.e.* aldehydes and ketones) or volatile fatty acids (VFAs). The sampling cartridges were then submitted for analysis to contract environmental sampling laboratories.

The motivation for this study was based on the favorable performance of the polyamine capped NPs (*i.e.* PLA-PEG-PEI NPs) in a previous singleton experiment on-site at a rendering facility (see Table X above). In that previous experiment, the PLA-PEG-PEI NPs effected on average an 86% reduction in the VFAs detected during the sampling run, which was consistent with the high levels of VFA capture that we demonstrated in the laboratory with the NPs. We elected to return to the same plant to collect similar sampling data in triplicate to further demonstrate the utility of our materials on-site at rendering facility using this particular assay.

Unfortunately, our efforts to collect similar data in triplicate yielded disappointingly inconsistent results (Tables 3 and 4). Upon analyzing the results, several confounding issues were apparent. First, the standard deviations for triplicate runs were unacceptably high. Second, in numerous samples, the concentrations of detected analyte were *higher* in treated samples than the baseline samples collected simultaneously. Third, our PLA-PEG-PEI NPs did not exhibit performance consistent with our more robust laboratory replicates. Fourth, activated charcoal appeared to out-perform our materials in the on-site assays, which is also completely inconsistent with our reproducible laboratory assays, which clearly indicate that charcoal does not capture target VOCs. There are several possible sources of the inconsistencies that were observed: 1. It is possible the unacceptably large standard deviations arose from pump-to-pump variations during the sampling period (18 pumps were used simultaneously to collect the data); 2. Batch-to-batch

| Carbonyls | Plant Baseline | PEI NPs | OMe-NPs | Charcoal |
|---|---|---|---|---|
| Compounds | Conc. (ppb) | % Reduction | % Reduction | % reduction |
| formaldehyde | 3.42 | 70 | + | + |
| acetaldehyde | 39.3 | + | + | + |
| acrolein | 0.871 | 44 | 34 | 74 |
| acetone | 66.6 | + | + | 10 |
| propionaldehyde | 6.35 | + | + | 52 |
| crotonaldehyde | x | x | x | x |
| methacrolein | 3.07 | + | + | 93 |
| MEK/butyraldehyde | 73.8 | + | 2 | 87 |
| benzaldehyde | x | x | x | x |
| valeraldehyde | 3.4 | + | + | 92 |
| m-tolualdehyde | x | x | x | x |
| hexanal | 6.16 | + | + | 96 |

**Table 3.** Triplicate sampling of carbonyl capture with NPs and charcoal. (Note: "+" indicates that detected concentrations were higher than those detected in the baseline, untreated sample, "x" indicates that the particular analyte was not detected in the assay.)

| Carbonyls | Plant Baseline | PEI NPs | OMe-NPs | Charcoal |
|---|---|---|---|---|
| Compounds | Conc. (ppb) | % Reduction | % Reduction | % reduction |
| acetic acid | 320 | 29 | 1 | 81 |
| propanoic acid | 140 | 30 | 2 | 91 |
| isobutyric acid | 11 | 22 | + | 91 |
| butyric acid | 160 | 37 | 6 | 94 |
| 2-methylbutanoic acid | 9 | 28 | + | 97 |
| isovaleric acid | 9.1 | 32 | + | 100 |
| valeric acid | 12 | 35 | 5 | 97 |
| 2-methylpentanoic acid | x | x | x | x |
| 3-methylpentanoic acid | x | x | x | x |
| isocaproic acid | 7.5 | 40 | 4 | 100 |
| caproic acid | 6.1 | 34 | 4 | 91 |
| heptanoic acid | 1 | 11 | 7 | 100 |
| 2-ethylhexanoic acid | x | x | + | x |
| cyclohexanecarboxylic acid | x | x | x | x |
| octanoic acid | 1.3 | 27 | 17 | 100 |
| benzoic acid | x | x | x | x |
| nonanoic acid | 1.3 | 0 | 13 | 100 |

**Table 4.** Triplicate sampling of VFA capture with NPs and charcoal. (Note: "+" indicates that detected concentrations were higher than those detected in the baseline, untreated sample, "x" indicates that the particular analyte was not detected in the assay.)

variation in the NPs could contribute to large standard deviations; 3. Prolonged storage of the filter cartridges could result in reduced performance relative to laboratory samples, and 4. possible leaks in the plumbing connecting the sampling cartridge and the filter cartridge could contribute to sampling inconsistencies. The difficulties associated with this larger scale on-site

sampling endeavor led us to conclude that this particular method for vetting our NPs on-site at a rendering facility may not be ideal.

Despite these conflicting and somewhat disappointing results, we remain eager to pursue quantifiable methods to assess the performance of our functional materials. We may elect to return to the same plant in the future to evaluate the performance of our second and third generation materials that are more readily accessible in large, uniform batches. In this manner, we will be able to control some of the confounders described above as potential explanations for the observed variability in the data.

*Aim 3: To investigate the lifetime, leaching, degradation, and toxicity of spent and pristine nanoparticles.*

In pursuit of Aim 3, we sought to answer several key questions regarding the performance of our materials. The specific questions and associated data are described below.

a.) Do our materials leach captured malodorants after capture?

In this experiment, we sought to probe the propensity of our amine-capped nanoparticles (NPs) to release captured malodorants after sequestration. If the materials are to be useful for odor abatement, the capture event should be essentially non-reversible under ambient conditions. To probe this question, we treated a sample of amine NPs with a gas-phase sample of butanal in a sealed vial and then assayed the head-space over the course of six hours. In the event, we did not detect any appreciable amount odorant leaching after the initial capture event (Figure 4).

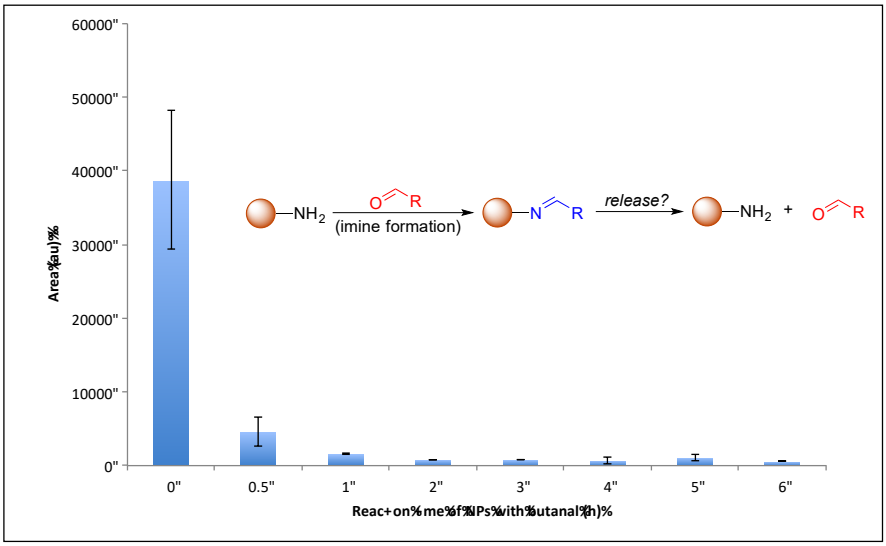


**Figure 4.** Leaching study with amine NPs

b.) Are our materials shelf-stable and storable?

In this experiment, we wished to evaluate the shelf-stability of our materials over an extended period of time. Prolonged shelf stability will be critical for our materials to be useful as a odor mitigation strategy. To probe the shelf stability of our materials we monitored the chemical composition of our functional nanomaterials over the course of one month both at 25 ˚C (77 ˚F) and 35 ˚C (95 ˚C). Based on comparative thermogravimetric analysis (Figure 5) at day 0, 3, 6,

14, and 28 days, there is no detectable change in the integrity of the amine capped NPs at either temperature.

*c.) Can we fabricate cheaper-to-access micron-scale amine capped polymeric particles?*

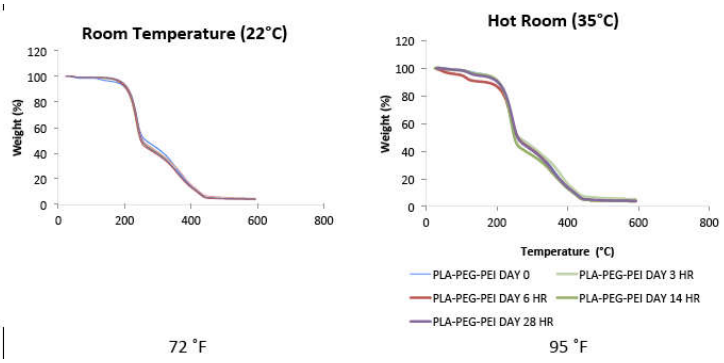


**Figure 5.** TGA analysis assessing shelf-life and stability of first generation polymeric NPs.

In this series of experiments, we sought to investigate whether or not we could prepare related micron-scale functional particles. We also wanted to assess whether these materials were effective at capturing malodorant VOCs associated with rendering operations. We were motivated to undertake this study because our current nanofabrication strategy requires a time consuming and costly filtration step to isolate the NPs. The fabrication of larger, micron scale particles would obviate the necessity of this onerous task. In the event, we found that larger particles were accessible ranging from 1.2 µm to 25 µm depending on precipitation conditions (Figure 6).

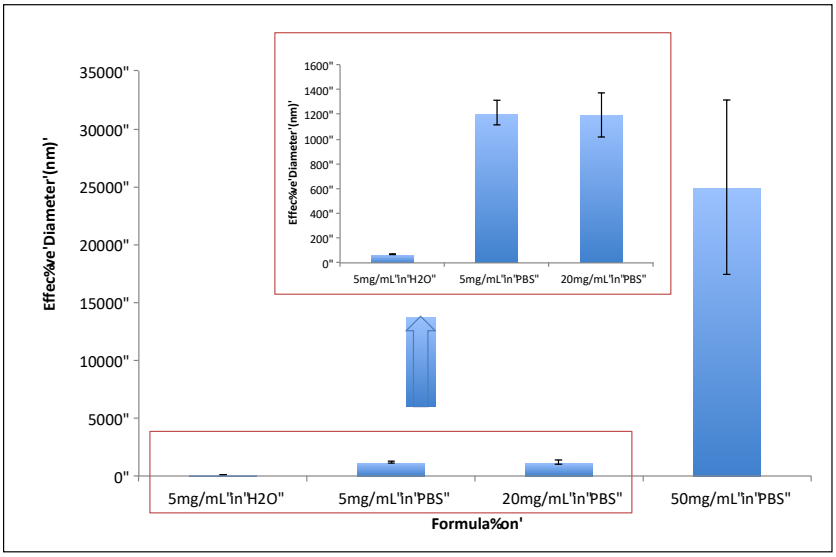


**Figure 6.** Fabrication of micron-scale functional particles.

Further, we were able to demonstrate the our larger functionalized microparticles are capable of sequestering malodorant VOCs with comparable efficiency as compared to our first generation functional NPs (Figure 7).

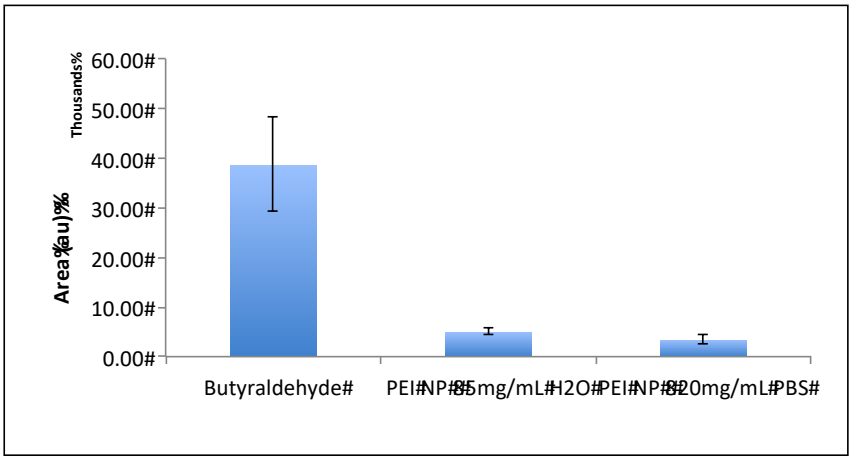


**Figure 7.** Efficient capture of butyraldehyde with micron-scale particles

Thus, by probing the questions outlined above, we have successfully demonstrated that our PLA-PEG-PEI polymeric amine capped nanomaterials: 1.) do not release captured contaminant, 2.) are reasonably shelf-

stable, and 3.) can be fabricated on the micron scale while maintaining their gas capture performance.

*Conclusions:*

This efforts arising from this proposal served to answer a number of important questions surrounding our previously published[13] first generation materials. In the first aim, this work allowed us to demonstrate that our materials can successfully address sulfurous malodorants in addition to the previously demonstrated capture of carboxylic acid and aldehyde VOCs. In the second aim, we obtained promising preliminary results indicating that our materials are capable of reducing the VOC load at a rendering facility in small scale experiments. Nevertheless, these efforts also revealed important confounding variables that make on-site validation difficult. Nevertheless, we remain committed to finding methods to vet our materials in quantifiable ways at a rendering facility. Finally, in the third aim, we answered important questions about the fabrication, stability, and leaching properties of our first generation materials. We have subsequently leveraged this data and our previous efforts from earlier years of ACREC/FPRF support toward the development of second and third generation materials that exhibit excellent performance at reduced cost. These efforts are described in the appropriate progress reports for those FPRF grants.

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**Impacts and Significance:** The technology that is being developed 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. The nanomaterials described herein might present several uses in an industrial setting. The formulations could be employed as a rapid-use odor adsorbent in an emergency or spill situation. Further, the nanomaterials might, 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 PLA nanomaterials that would compete with or ideally supplant existing odor elimination measures. One advantage of such an outcome includes the ability to landfill the spent scrubbing material without further processing. Indeed, PLA polymers are biodegradable and non-toxic. Additionally, since their means of neutralizing malodorants is based on chemical reactivity instead of thermal degradation, the implementation of this strategy should return significant cost savings in terms of reduced energy consumption and reduced greenhouse gas emissions. The general strategy of surface decoration of polymer matrices with reactive sites is not limited to PLA polymers. One could envision the development of similar strategies for the preparation of "smart" clothing or other materials that are equipped with an odor elimination mechanism. Finally, we are now poised to leverage what we have learned in order to develop other functional nanomaterials for rendering applications including, but not limited to, the development of microbicidal nanomaterials.

**Publications:** This proposal has not yet resulted in new publications, but we have two manuscript drafts that are in preparation for submission in the coming months. One manuscript will describe the our investigations into the optimal formulation of the materials and another will describe the preparation and evaluation of micron scale functional particles. These manuscripts will be submitted to the FPRF research board for review prior to submission.

**Outside funding:** We have attempted to leverage ACREC/FPRF support to obtain federal funding. Two $500,000 proposals were made to the USDA, and both were declined. Two proposals for $350,000 were submitted to the National Science Foundation. The first was declined, and the second one is still under consideration.

**Future Work:** Prior FPRF support and the support from this grant have allowed us to develop a workable first generation nanomaterial that is capable of capturing important malodorants associated with rendering operations. Nevertheless, the fabrication costs of our first generation materials are relatively high. Subsequent efforts (also supported by FPRF) have allowed us to leverage the knowledge gained during research for this grant into the development of two new

formulations based on functional clays and cellulose nanocrystals that perform well and at cheaper costs. Future studies will are also necessary to demonstrate quantitative efficacy on-site at a rendering facility. Also, efforts should be undertaken to demonstrate a scaleable synthesis of the materials.

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