QUARTERLY PROGRESS REPORT
June 2020 – August 2020

PROJECT TITLE: ASSESSMENT OF LOW-COST ADSORBENTS FOR SILOXANES REMOVAL FROM LANDFILL GAS

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PROJECT WEBSITE: **http://www.eng.usf.edu/~jnkuhn/Hinkley2019.html**

Research Description:

Landfill gas (LFG) is increasingly used and researched as a feedstock for a variety of traditional and proposed Waste-to-Energy (WTE) technologies, which includes electricity generation, compressed natural gas, or liquid hydrocarbon fuels. In these various scenarios, contaminants in the LFG can have substantial economic and environmental consequences in the WTE processes.

Siloxanes are increasing contaminants of LFG as many consumer products being land-filled contain this compound. Siloxanes in biogas cause damage to machines if not removed because it thermally decomposes to silica. This leads to high maintenance cost of WTE technologies thereby serving as a disadvantage to the economics of the entire process. Current purification techniques available for siloxanes removal are expensive; it costs less to repair damaged engine parts than to adopt current siloxane purification techniques. In order to accelerate adoption of WTE processes, a need for more economical methods for removing siloxanes from LFG exists. The goal of this research project is to develop low cost strategies for siloxane removal from LFG. The study will be evaluating the economic potential and environmental impact of selected scrubbing technologies using low cost adsorbents.

Work accomplished during this reporting period:

For the period outlined in this report, crushed glass samples were obtained from the "Rosebud Continuum Sustainability Education Center." The crushed glass was made from waste bottles by crushing into smaller bits and grinding into pellets/powder using a garbage disposal unit (InSinkErator garbage disposal). The crushed glass samples obtained are displayed in Figure 1 below.

Figure 1: Crushed glass samples

N_2 physisorption analysis was conducted on crushed glass samples to determine its surface area, pore volume, and average pore diameter. The N_2 physisorption analysis results are displayed in Table 1. XRD analysis was conducted on the crushed glass samples to obtain information on its chemical structure. The XRD analysis profile as displayed in Figure 2 shows that the crushed glass samples are amorphous solids. CO_2 adsorption isotherm was generated for crushed glass samples in order to examine the competition of adsorption sites by this compound. The CO_2 adsorption capacity of crushed glass was calculated from the adsorption isotherm to be 0.03 mg CO_2/g crushed glass. Figure 3 displays the N_2 and CO_2 adsorption isotherm for crushed glass. L2 (hexamethyldisiloxane) vapor sorption experiment was conducted on DE (diatomaceous earth) samples and the adsorption isotherm generated is displayed in Figure 4. The L2 adsorption capacity of DE was calculated from the adsorption isotherm to be 0.013 mg L2/g DE. A static adsorption instrument (Autosorb; Quantachrome) was used in conducting the vapor sorption experiments.

Table 1: N_2 physisorption analysis result for crushed glass

Crushed Glass	**Specific Surface Area (m^2/g)**		**Pore Volume (cc/g)**	**Pore Diameter (nm)**
	S_{BET}	**S_{BJH}**	**V_{BJH}**	**D_{BJH}**
Pellets	0.08	0.08	<0.1	3.4

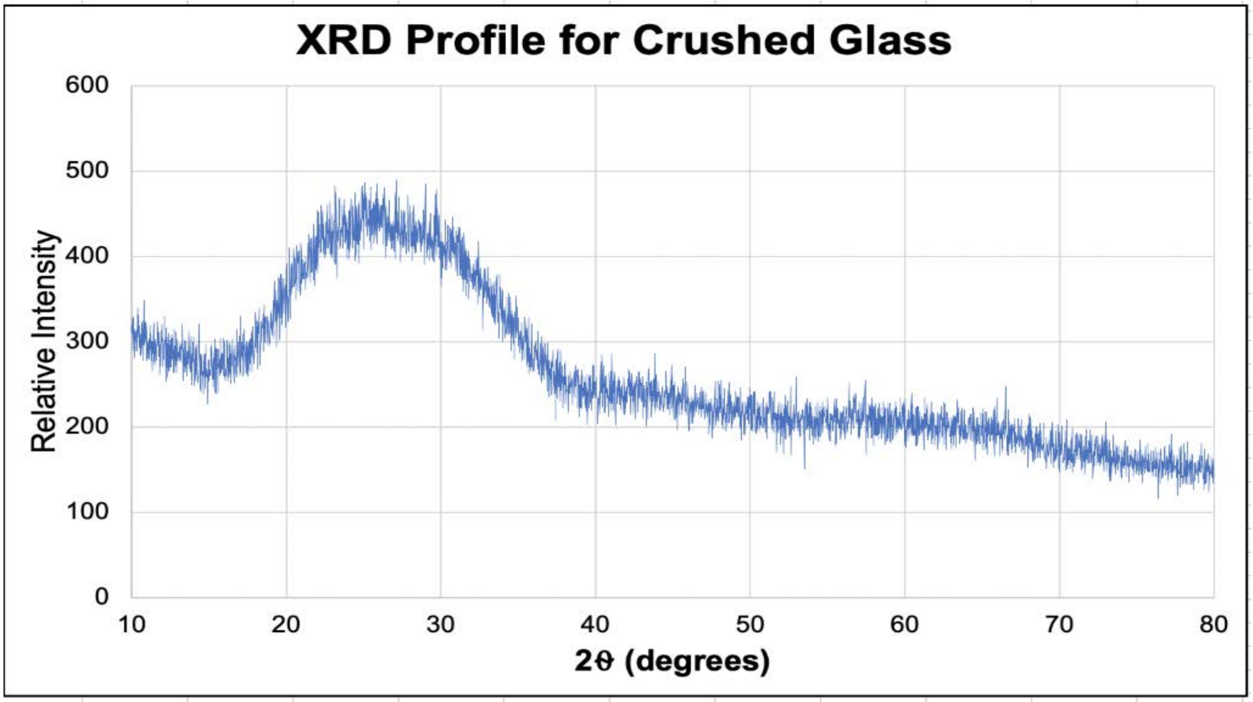

Figure 2: XRD analysis for crushed glass.

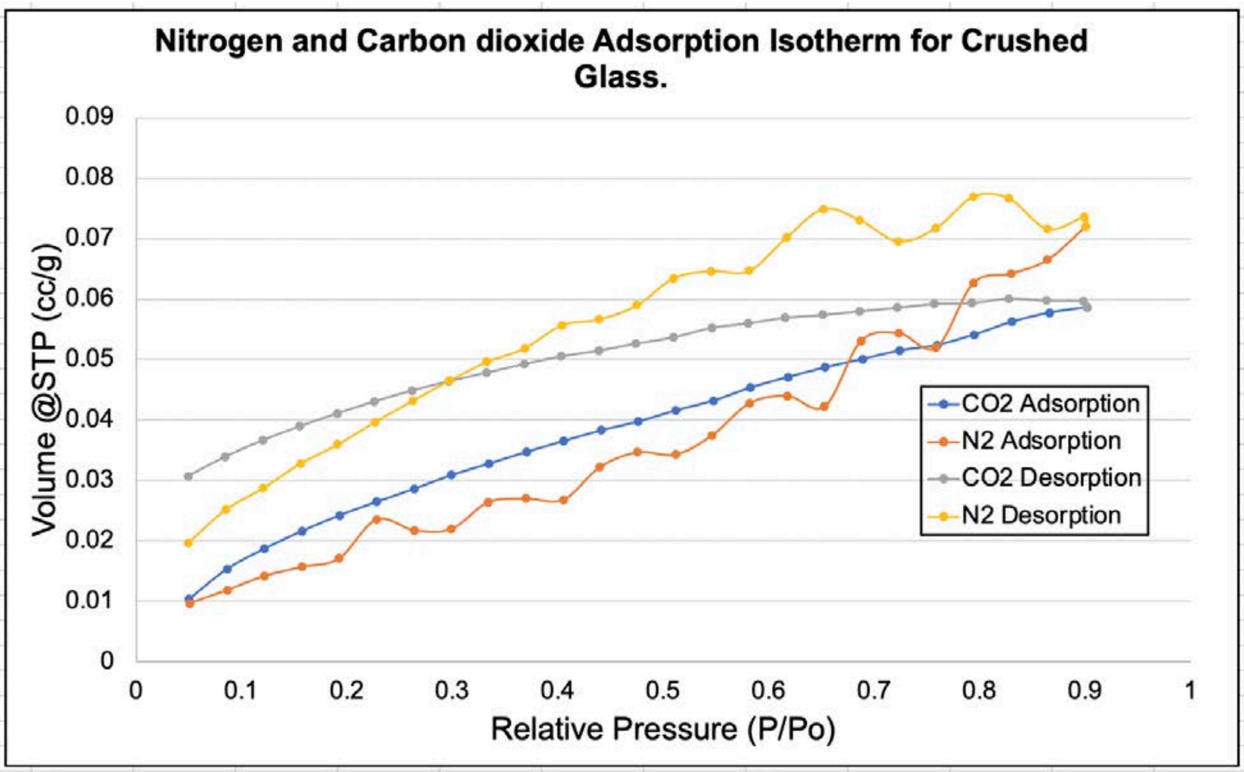

Figure 3: Nitrogen and Carbon dioxide Adsorption Isotherm for Crushed Glass at 77 K and room temperature, respectively.

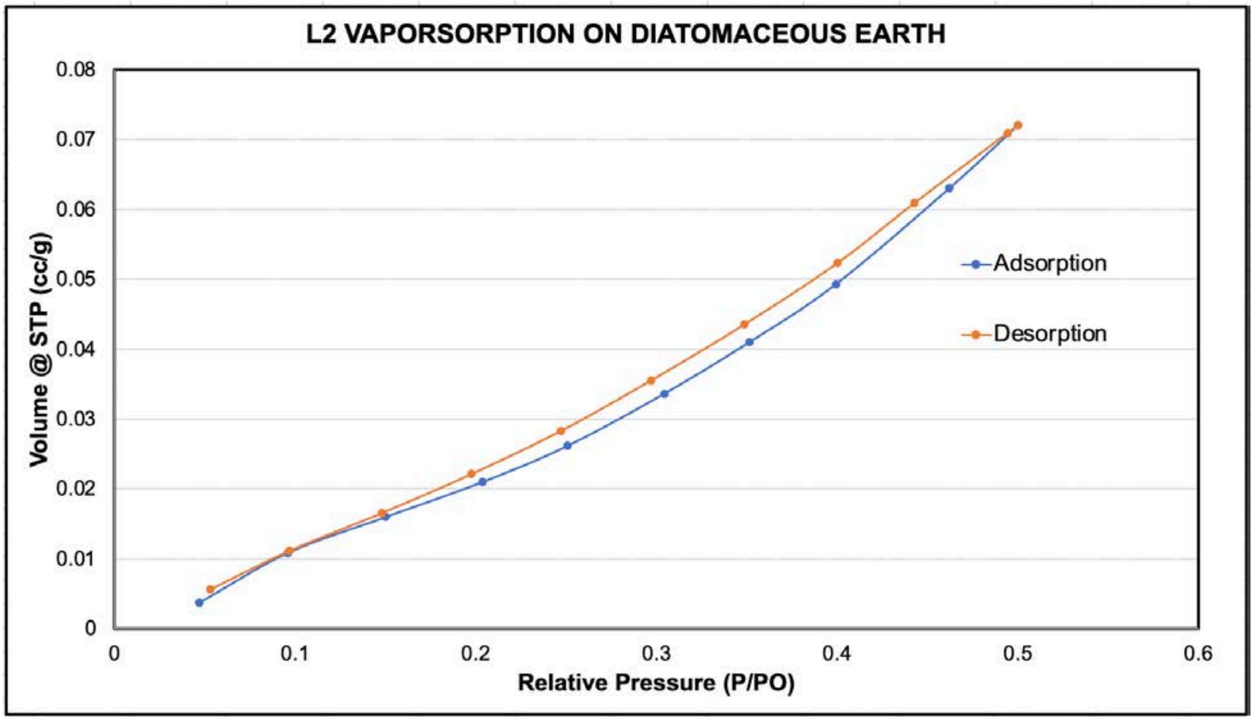

Figure 4: L2 Adsorption Isotherm for diatomaceous earth at room temperature.

The Agilent 5975C VL MSD Triple Axis Detector with 6890 GC will be used for the analysis of siloxanes concentration in inert and surrogate LFG during breakthrough experiment. The following conditions has been set up in the GC-MS for the analysis of siloxanes: The temperature of injector port and detector (MSD) was set to 230^{o}C and 150^{o}C respectively. The column being used for measurement is the Chrompack Capillary Column {CP-Sil 8 CB} (30m length, 0.25 mm inner diameter, 0.25µm film thickness). It is set to splitless mode. The carrier gas, Helium, is set to 2.0 ml/min. The temperature program starts at 80^{o}C for 3 mins, followed by ramping to 150^{o}C at a rate of 10^{o}C/min, then to 200^{o}C at a rate of 5^{o}C/min, and finally ramped to 280^{o}C at 30^{o}C/min. The MS acquisition mode is set to "scan" with a scanning mass range from 80 to 300 gmol.

The block diagram for the proposed breakthrough experiment is displayed in figure 5 below.

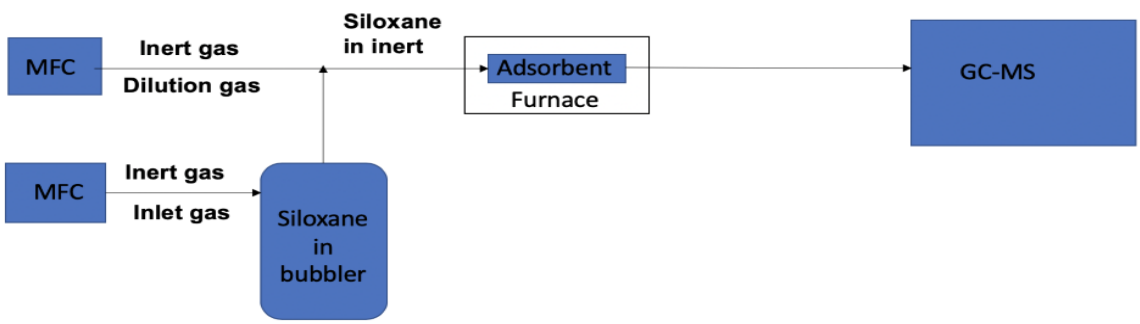

Figure 5: Block flow diagram for proposed breakthrough experiments of siloxanes.

Future Tasks:

The future work would be to:

- Characterize biochar and hydrochar.
- Generate hexamethyldisiloxane (L2) and octamethylcyclotetrasiloxane (D4) adsorption isotherms for selected adsorbents.
- Conduct breakthrough experiments on the selected adsorbents using siloxanes in inert gas, surrogate biogas and real landfill gas.
- Determine adsorption capacity and regeneration ability of adsorbents for selected siloxanes in inert and surrogate LFG.
- Test low cost/waste inorganic materials for thermal degradation performance of selected siloxanes in inert and surrogate LFG.
- Design a process flowsheet and conduct techno-economic analyses of the siloxane's adsorbents evaluated and the siloxanes thermal degradation process evaluated in this project.

TAG meeting:

The first TAG meeting occurred on March 4, 2020 (Video can be found here: https://youtu.be/bWuNFECMvTg). The second TAG meeting is estimated to occur in October 2020, though this may be pushed back due to the pandemic and associated project extension.