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Characterizing the Hydrophobic Properties of Activated Carbon and the Factors Affecting VOC Adsorption

by

Steven M. Sheets

A Thesis

Presented to the Graduate and Research Committee

of Lehigh University

in Candidacy for the Degree of

Master of Science

in

Environmental Engineering

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Acknowledgements

Table of Contents

Abstract

Regeneration is vital to the life cycle of adsorbents such as activated carbon. Regeneration losses, in the forms of adsorbent mass and adsorption capacity, have long plagued the life-cycle of conventional adsorbents. Adsorption losses are compounded by the presence of moisture in exhaust gas streams during VOC treatment, due to the competition for adsorbent sites between water and VOCs. Since water vapor often out-competes the VOCs for these sites, the carbon's loss of adsorption capacity can be attributed to water's affinity to the carbon surface. The present research explores the hypothesis that selective organic phase adsorbents can be produced by designing the substrate material such that it exhibits hydrophobicity and selectivity for organic vapors. At the time of writing, this study is still in the design phase. An on-line apparatus, currently being developed for lab-scale use, is theorized for the continuous measurement of VOC concentrations under varying relative humidity conditions. This work aims to advance adsorption science for environmental applications, as it has the potential to provide a new class of gas phase adsorbents, advance polymer composite adsorbent manufacturing methods, and develop a novel adsorbent design approach using ground-up methodology rather than an empirical approach. Two additional research projects, to which the author provided support, are also described in brief.

Introduction

Volatile organic compounds (VOCs) are vapor phase organic compounds emitted from partial combustion, solvent use, vehicle exhaust, and various additional sources that remain a concern for their often adverse health effects, particularly in indoor environments, as well as for their contributions to photochemical smog. Further, VOCs can also be industrially-valuable solvents which need to be recovered from exhaust ventilation. Conventionally, VOCs are most often treated via activated carbon (AC) adsorption, a physical process that captures VOCs from air streams, after which they can be more easily remediated (U.S. EPA, 1999).

VOC-Water Competition

Polar Center Adsorption & Micropore Volume Filling

The task of treating VOCs is made more difficult when water vapor is also present in the air streams. The presence of moisture in exhaust gas streams is not favorable during VOC treatment because water also has an affinity for carbon adsorbents, and it will often out-compete the VOCs(Chou, 1997).Water vapor's affinity for carbon is in part due to the presence of functional groups naturally found on the adsorbent's surface, the most significant functional group being surface oxides (Boehm, 1994; Boehm, 2002; Qi, 2005).Water's electronegative oxygen atom maintains a high electron density and therefore a partial negative charge, resulting in partial positive charges on its two hydrogen atoms, which can then form hydrogen bonds with the partially negative oxygens found along the AC surface. This phenomenon can be referred to as polar center adsorption (PCA), and it is

the prevalent mechanism for water sorption to AC at low relative humidities (RH)(Foley, 1997).

It has also been observed that there are particular RH ranges in which capillary condensation will start to occur within carbon adsorbents, whereby water vapor condenses within the confined spaces of the pores, and as such, makes those pores unavailable for VOC adsorption; with seemingly few exceptions, the adsorption capacity for VOCs rapidly decreases starting at this RH threshold (RH_{th}) (Cal, 1996; Fastyn, 2005; Gawlowski, 1999; Gawrys, 2001; Gong, 1993; Haghighat, 2008). This phenomenon is commonly referred to as micropore volume filling (MVF).

Together, PCA and MVF are considered the two primary mechanisms for water uptake by AC. PCA, being limited to the adsorbent's surface and reliant on hydrogen bonding, is considered to be the weaker of the two and more easily managed, while MVF, which makes use of the adsorbent's vast pore network, can adsorb substantially larger amounts of water (Gawrys, 2001). But despite PCA's relatively lower water trapping ability, it remains a concern since it can itself contribute to MVF via a water-bridging effect(Foley, 1997; Muller, 1998; Qi, 2005). This occurs when water molecules build upon each other at the oxide adsorption sites, forming larger water clusters. Depending on how the adsorption sites are spread out, water clusters from neighboring sites may be close enough to connect, forming a bridge and increasing the amount of condensation that occurs within the pore walls. The formation of water clusters has been reported to occur within the 40-70% RH range, which is also the most commonly encountered RH range in real situations (Foley, 1997).

The preference for water vapors over organic vapors is a paradigm long plaguing organic vapor adsorbents. As has been addressed, AC's affinity for water vapor is due to oxygen-containing functional groups within the carbon's surface. But beyond the specific affinity for water vapor by AC, the adsorption of VOCs with respect to water vapor has also been well-documented; as a general rule, increased RH decreases VOC adsorption. Russell and LeVan investigated water vapor and organic coadsorption on activated carbon, finding that for low alkane partial pressures, a reduction of 60% of adsorption capacity occurs at 50% RH (Russell, 1997). In their work, they also point out that for certain compounds, like methanol, adsorption is actually enhanced by the presence of water. Further, work investigating the interaction of acetone-water on BPL carbon determined that miscible (water-soluble) compounds exhibit less degradation of capacity when mixed acetone-water vapors are present (Rudisill, 1992). In general, for most organic compounds, researchers have often decided to account for the effects of RH below 50% as being negligible (Haghighat, 2008).

Variation among Adsorbents

It is evident that the form of adsorbent used – granular (GAC) and powdered (PAC) activated carbons, activated carbon cloths (ACC), activated carbon fibers (ACF), graphitized carbon blacks (GCB), carbon molecular sieves (CMS), carbon composite membranes (CCM), or polymeric adsorbents – affects the RH at which micropore volume filling becomes the dominant water adsorption mechanism. Also important is that these different forms of carbon each trap different amounts of water by their natures, RH and other variables remaining the same; CMS have shown substantial water trapping abilities, whereas GCBs

and polymeric adsorbents have a naturally lower affinity for water (Fastyn, 2005, Gawlowski, 1999; Helmig, 1995). Water trapping data summarized from the available literature can be seen in Table 1:

Table 1:A summary of various carbon and polymeric resin adsorbent characteristics.

	SSA (m^2/g)	Water Loading (mg/g)	RH_{th} (%)	Adsorbents Tested
ACC	1000-1200	165-284	65	(brand not given)
GCB	100-110	< 30	N/A	Carbotrap, Carbotrap C
CMS	485-1200	400-450	32-45±3	Carbosieve SIII Carboxen 569 Carboxen 1000/1001
PPR	230-350 100-200	< 2-3	N/A	Porapak T, Porapak N Chromosorb 108
NPR	700-800 18-35	< 5	50	Chromosorb 106 Tenax TA, Tenax GR LC-1 (hypercrosslinked)

Notice that, in addition to carbon-based adsorbents, Table 1 includes data on polar and nonpolar polymeric resin adsorbents (PPR and NPR, respectively). Similarly to GCBs, the literature reports these materials as having a low water trapping ability, and also reports that the water that does sorb to them can be easily removed by purging the sorbent bed with a dry gas (Gawlowski, 1999; Helmig, 1995).

Adsorbent Properties& Production

Adsorbent materials are widely utilized for air phase applications, such as: industrial solvent recovery, pollution abatement, automotive or other transportation cabin air cleaning, indoor ventilation system air cleaning, and air purification. Activated carbon is the most widely utilized air phase adsorbent material, and is also the oldest technology available. To put this into perspective, consider that the development of the major carbon-

based vapor-phase adsorbents has been, in order: activated carbon, activated carbon fibers, polymeric adsorbents, and finally, polymer/graphene composites. Interestingly, the hydrophobicity of the adsorbents has developed over time from least (activated carbon) to most (polymeric adsorbents). Part of the research done herein focuses on the value in further exploring the potential of polymer/graphene composites, which will be shown to be the next likely step in carbon-based adsorbent technology. To make this point, a survey of the popular commercial adsorbents will first be considered.

Activated Carbon

Activated carbon production begins with selecting a high carbon content pre-cursor material. Among the most commonly used carbon pre-cursors are lignite coal, bituminous coal, anthracite coal, coconut shells, carbon fibers, walnut shells, wood, coke, agricultural by-products, and bones. The pre-cursor materials are first carbonized at temperatures around $700^{\circ}C$ in the absence of air. The carbonization process eliminates low molecular weight compounds, and begins to form the structural matrix for activated carbon. The next step is the activation process, which is performed by introducing a gas, such as steam, at high temperatures ($700-900^{\circ}C$) to the carbonized material. This process is a controlled oxidation that fully develops the final pore structure and distribution of the activated carbon. Following activation, there are optional post-activation treatment processes for obtaining specific functionality, for example silver impregnation for anti-microbial properties, addition of organic or inorganic functional groups to the carbon surface for targeted removal of specific compounds, or urea treatment to develop catalytic carbon. Since an array of pre-cursor materials, carbonization and activation processes, and post-

activation treatment are available to activated carbon producers, the producers can tailor the final adsorbent properties through several avenues: in the selection of the pre-cursor materials; in varying carbonization temperatures and residence times; in changing activation gas, time, and temperature; and in the selection of post-production chemical tailoring.

Together, activated carbon's porosity and tailorable surface chemistry provide the adsorbent with the mechanisms required to be a highly effective gas treatment technology. Specifically, activated carbon is non-polar (or slightly polar, due to surface oxide groups and inorganic impurities); this unique property provides the adsorbent with a few significant features: the ability to be used in air purification applications without stringent moisture removal; the ability to adsorb nonpolar and weakly polar organic molecules better than other sorbents, due to large internal surface areas and pore volumes; and a relatively low bond energy in its sorbed compounds, making removal of the compounds easier than it would be for other sorbents (Yang, 2003).

The sorption of water onto activated carbon increases as the vapor pressure of water increases. Once water begins to sorb to the surface, capillary condensation occurs, and the micropores fill with water. Despite the challenges of water vapor sorption, activated carbon is still widely used due to organic, nonpolar, and weakly polar compounds adsorbing preferentially compared to water vapor (Yang, 2003).

Chemical modification of activated carbon can alter the adsorption behavior of water vapor to the carbon. In general, minimal adsorption occurs at a P/P_o below 0.3 to 0.4, due to hydrogen bonding and electrostatic forces. As oxidation of the activated carbon surface increases, the threshold for P/P_o shifts accordingly. The surface groups that increase

with oxidation are generally acidic functional groups. Functional acidic groups increase with aging at mild temperatures and oxidation at elevated temperatures (Yang, 2003).

Other variables shown to affect water uptake by carbon adsorbents include the trap temperature, sampling volume, and initial VOC concentration. Sample RH has shown to be significantly decreased at elevated temperatures, leading to the development of a "warm trap" water management method that involves moderate heating of the trap (by 5-15°C) during sampling (Gawrys, 2001; Helmig, 1995). In regard to volume, water saturation in CMS has been shown to occur slowly and require large sampling volumes; collecting small sample volumes is therefore recommended (Helmig, 1995). Water trapping has also been shown to be generally more inhibiting at lower initial VOC concentrations (Cal, 1996; Haghighat, 2008).

Activated Carbon Fibers

Carbon fibers are typically derived from polyacrylonitrile (PAN), phenolic formaldehyde (Novalak), polyvinylidene chloride (Saran), cellulose, and pitch. They can be carbonized, and subsequently gas-activated, to form activated carbon fibers (ACF). ACFs can obtain BET surface areas of 1000 m^2/g to 2000 m^2/g. They can also be characterized by a narrow and uniform pore size distribution (for stronger interaction with sorbates), uniform fiber diameter (for faster sorbate uptake), graphitic properties (for higher conductivity and heat resistance), and high strength (for the ability to make clothes and papers) (Yang, 2003).

Pore sizes are uniform for nearly all ACFs. This uniform pore distribution is due to near-zero ash in the pre-cursor material, as ash materials act as catalysts during the activation process to open and enlarge pores during carbon gasification

(Goethel,1989).During gas activation of carbon fibers, the pores are elongated but are not widened; the pore is elongated between two graphitic sheets about 10 angstroms apart. These small pores provide strong interactions with absorbates due to strong overlap.

ACFs also contain micropores and small mesopores at their fiber cross-sections, and the pores are randomly-distributed and homogenous, leading to many long and winding tubes that twist their way throughout the adsorbent (Daley, 1996; Li, 1998). Their pores are also more interconnected than PACs and GACs, which have a larger amount of isolated pore entities than ACFs. As a result, the ACFs have a higher average specific surface area (SSA) than commercial PACs and GACs (averaging 1500m^2/g compared to 1000m^2/g). The significance here is that the higher SSA generally results in higher adsorption rates and greater micropollutant selectivity (Brasquet 1997; Foster, 1992).

There have been exceptions to this rule, where the ACF with the smallest SSA adsorbed more. In some cases this reversal is considered a result of the activation process, where micropores have been shown to widen with increasing activation times, leading to increased surface areas but decreased adsorption capacity (Foster, 1992). In other cases the reversal was related to the boiling point of the contaminant; in particular, ACFs have been shown to have a greater adsorption capacity for alkanes of lower boiling points than those of higher boiling points (Mangun, 1997).

In attempting to modify the pore sizes and adsorption properties of ACFs, studies have shown that oxidation and ammonia treatment can have adsorption enhancing effects. In a study comparing aqueous and nonaqueous oxidation techniques, aqueous oxidation resulted in reduced micropore volume (and surface area), while air oxidation resulted in

9

increased surface area; while this resulted in only a slightly higher adsorption capacity for acetone, the ACF's capacity for ammonia was shown to increase up to 30 times compared to untreated ACFs (Mangun, 2001). Ammonia-treated ACFs have also been shown to improve adsorption capacity for an acidic gas (HCl) compared to untreated ACFs. The significance is that ACFs offer a higher adsorption capacity than PACs and GACs, and, while still prone to the negative effects of water vapor competition, they have been shown to be tailorable for use on specific contaminants via modification of their pore structures.

Polymeric Resins

Polymeric resins are also known as macroreticular polymers. These porous polymers are produced by emulsion polymerization of monomers with a solvent that dissolves the monomers but is also a poor swelling agent. The polymers are typically produced with styrene crosslinked with divinylbenzene (DVB), and the resulting resins can be converted to carbonaceous polymeric sorbents by partially pyrolyzing the styrene/DVB polymer. Specifically, during polymerization, a solution of (poly)styrene, divinylbenzene, benzoylperoxide, diluents, and other additives are prepared in a water solution. The mixture is agitated until the round organic beads are formed. These polymeric resins can have functional groups attached to benzene rings to form ion exchange resins (Yang, 2003).

The polymer resins are composed of microgel particles 0.01 μm to 15 μm in diameter, also known as "microspheres", which agglomerate to form spherical beads. The pore structure is formed by porosity within the microspheres and by the pore space formed between the microspheres. A larger degree of cross-linking will translate to a higher surface area. These polymeric resins are by nature highly aromatic, as the surface is largely formed

by benzene rings. When the rings are unfunctionalized, these polymeric resins are hydrophobic. However, when the polymeric resins are functionalized for ion exchange applications, the resins lose hydrophobicity (Yang, 2003).

In general, the polymeric resins and carbonaceous polymers are significantly more hydrophobic than activated carbon; this is apparent when viewing the water vapor isotherms. In particular, studies have shown that the hydrophobic, hypercrosslinked polymer resin LC-1 is a promising adsorbent of VOCs from humid gas streams (Liu, 2009; Long, 2011). LC-1 is characterized by a poly(4-tert-butylstyrene–styrene–divinylbenzene) matrix, and it has shown good adsorption abilities for three chlorinated VOCs (trichloroethylene, trichloromethane, and 1,2-dichloroethene), with negligible effects on the VOC breakthrough times for RH ≤ 50%. When RH was increased to 90%, the breakthrough time decreased by less than 11% (Long, 2011).

Graphene

Graphene is a two-dimensional (one-atom thick) material that was long considered no more than a theoretical material that could not exist due to thermodynamic instability. Despite this doubt, free-standing graphene was finally discovered in 2004, and it has since come to the forefront of materials science and physics research. Described as simply a thin sheet of sp^2-hybridized carbon with an extensive honeycomb lattice network, it has been called the thinnest known material in the universe, and it is also strongest ever measured. Graphene is also essentially the building block for graphitic materials of all dimensionalities; it can be wrapped into fullerenes, rolled into 1D nanotubes, or stacked into 3D graphite (Geim, 2007). Over the past decade, graphene has become popular for the wide array of

potential applications that result from its excellent thermal, mechanical, and electrical properties. In particular, it is a potential nanofiller that can dramatically improve the properties of polymer/based composites, owing to its large surface-to-volume ratio. It can also be easily derived from graphite precursors in large quantities and made available at low costs, which has made it attractive for both academic and industrial reasons (Allen, 2010; Du, 2012; Geim, 2007).

Particularly significant to the current research is the fact that graphene's single aromatic carbon layer has one of the strongest in-plane bonds among all known materials, and as such, it provides exceptional strength and exceptional porosity. With this in mind, consider that the value in combining the characteristics of polymeric adsorbents with those of graphene, to form polymer/graphene composites. Known to date, graphene has been successfully combined with epoxy, polystyrene, polyaniline, nafion, poly(vinylalcohol) (PVA), polyurethane (PU), and poly(vinylidene fluoride) (PVDF), among others. Also, future derivations of polymer/graphene composite adsorbents can be tailored for unique applications, considering that the conjugated graphene sheet can be readily functionalized through noncovalent π-π stacking or covalent C-C coupling reactions. By derivatizing graphene with different organic parts, the solubility of graphene can be tuned to suit different solvents needed for processing different composites. By combining graphene's strength with an infinite number of polymeric functional groups, the newly created polymer/graphene composite becomes what is potentially the strongest and most versatile adsorbent available (Bao, 2010; Carotenuto, 2012; Du, 2012; Kim, 2010; Kuilla, 2010; Luo, 2011; Potts, 2011).

Research Plan

Problem: Overcoming Humidity & Regeneration Losses

Important to the life-cycle of adsorbents is the ability to regenerate the adsorbents, particularly in the case of valuable industrial solvent recovery. Regeneration losses in both mass of adsorbent (due to mechanical degradation) and loss of adsorption capacity (due to loss of adsorption sites) has long plagued the life-cycle of conventional adsorbents. Further compounding these adsorption losses is the presence of moisture in exhaust gas streams during VOC treatment, due to the competition for adsorbent sites between water and VOCs. Since water vapor often out-competes the VOCs for these sites, the carbon's loss of adsorption capacity can be attributed to water's affinity to the carbon surface. For the present research, this culminates in the following.

Hypothesis:

> *Selective organic phase adsorbents can be produced by designing the*
>
> *substrate material such that it exhibits hydrophobicity and selectivity*
>
> *for organic vapors.*

As a result, the primary goal of this research is to produce a VOC adsorbent technology which overcomes both regeneration adsorption losses and humidity adsorption losses. This has led specifically to the investigation of the manufacturing process methods used for producing polymer/graphene composite adsorbent materials. The goal is to combine graphene's strength with the hydrophobicity of polymeric adsorbents. Investigating new techniques for preparing this relatively new composite material will also give insight into how manufacturing processes impact sorbent material performance.

Strategy: Ground-Up Adsorbent Development

Adsorbent materials are conventionally developed by empirical approaches. For instance, researchers and manufacturers identify a readily available and low-cost material – such as coal, coconut shells, peat, wood, agriculture bagasse, etc. – and pyrolyze, then subsequently activate, the newly formed adsorbent. Based on the produced material, an application for the material's properties is assigned. In an effort to challenge this conventional practice, the present research aims to develop an adsorbent material production method that will produce a high performance adsorbent with targeted applications. Specific to this effort, the objective is to convert materials into high performance absorbents for the application of adsorption of organic vapors without the simultaneous sorption of water vapor.

Methods: Apparatus Design for On-Line GAC Column

To achieve the present research goal – creation of an adsorbent that resists water vapor and provides preferential adsorption to organic vapors – the first step was to design an on-line apparatus capable of continuously measuring VOC concentrations under varying RH conditions. Using this apparatus, various sample adsorbents would be prepared and appraised for ultimate loading during high humidity conditions. Specifically, ultimate loading will be monitored with respect to RH under the following conditions: (a) while utilizing various polymer/graphene blend ratios, (b) while using an array of cross-linking methods, and (c) while using an array of enhanced activation methods.

Upon its completion, the experimental apparatus will consist of source gases, mass flow controllers, photoionization detectors (PIDs), a gas humidifier, a computer, and a column which contains the adsorbent material. The source gases will provide a mixture of a single organic compound (e.g. benzene or acetone) with air. The source gas will be regulated by a mass flow controller and flow through a photoionization detector to measure the influent concentration. The source gas will then be humidified to various RH levels (e.g. 0%, 20%, 40%, 60%, 80%, and 95%).The humidity will be appraised in the influent and effluent. The source gas laden with water and organic vapors will flow through the adsorbent column, which is maintained at constant temperature. The effluent gas will be appraised with photoionization detection, so as to determine the concentration of organic vapors in the effluent stream. The data from the photoionization detectors, humidity detectors, and mass flow controllers will be automatically logged on the apparatus computer.

The same column test apparatus described above will also be utilized to assess organic vapor competitive sorption, for the purpose of understanding the dynamic loading nature of organic vapors onto the adsorbent material (polymer/graphene blended adsorbents will be of primary interest here). The only adjustment that would need to be made to the apparatus for this test would be a change in source gas. To appraise organic vapor competitive sorption, a mixture of two organic gases (benzene and acetone) will flow through the polymer/graphene adsorbent column. The experiments will seek to determine how different organic compounds compete for adsorptive sites on the polymer/graphene adsorbent. Specifically, the effluent concentrations will be monitored to detect when

acetone is desorbed by benzene, as benzene conventionally possesses a higher affinity for organic adsorbents than acetone.

Discussion

At the time of writing, the experiment described above is still in the design phase, and as such, data is not yet available for review. In its place, consider instead the expected significance and potential impact of the research.

Succeeding to validate the hypothesis herein would result in the advancement in technical capability of adsorbent materials for air phase applications, yielding significant improvements to both ambient air quality and specific-environment air quality (e.g. cabin space air) on a large scale. This research will also provide adsorbent material users the ability to purify air of organic vapors while providing air with ambient levels of humidity; in particular, consider that adsorbent manufacturers could utilize the resulting new technology to produce and distribute the improved adsorbent materials both within the U.S. and abroad.

In general, this work will act to advance adsorption science for environmental applications, and it has the potential to: (a) provide a new class of gas phase adsorbents, (b) advance polymer composite adsorbent manufacturing methods, and (c) develop a novel adsorbent design approach. Meeting these goals would be groundbreaking for future work with polymeric composite adsorbents.

Additional Research

Prior to beginning work on the project described in the preceding pages, support was given to Lehigh team members for various other research projects; the two primary contributions will now be briefly described.

1) Hydrophobic Foundry Core Binders

Project Title: "Low-Emission Core Binders Reduce Core Sand Dilution: TG-GC-MS Analysis of Core Sand Binders and Understanding the Hydrophobic Nature of Core Binder Condensates and Recycled Core Sand"

PI: John T. Fox, Ph.D.

Background:

Green sand is a mixture of silica sand, bentonite clay, bituminous coal, and water, and it is used by foundries in the form of cores, which provide the internal geometry required for cavities within various desired castings. Foundries and materials science researchers often face challenges with core sand dilution processes, wherein the condensates of the petrochemical core binders (largely sodium silicate, collagen, or phenolic urethane) form a hydrophobic coating on the sand and clay surfaces, inhibiting clay-water-green sand bonding. Hydrophobicity – the tendency of a material to repel water – can be quantified via contact angle measurements (CAMs) using a microscope-like instrument such as a goniometer.

Objective: To analyze pyrolyzed core binder residue for induced hydrophobicity.

Contribution:

Four groups of 10 glass slides were prepared, each treated with a different core binder: sodium silicate (NaSi), collagen, phenolic urethane (PU), and X-Link (a collagen-silicate hybrid). Each group was subsequently divided into 5 groups of 2, representing five different temperature regimes (50°C, 90°C, 130°C, 170°C, and 200°C). After pre-heating the oven to each target temperature, two slides per binding material were placed inside for 10 minutes. The oven was then cooled slowly to the next target temperature and held for 10 minutes, the process repeated until the slides eventually returned to room temperature; the reason for using this slow-cool method was to avoid cracking, particularly for the collagen-coated slides, which resulted from rapid thermal fluctuations.

Initial CAMs were then recorded on the slides using a Ramé-Hart analog goniometer. A single drop of DI water was applied per slide at a time, with analog CAMs being made by adjusting the goniometer dial to produce a line tangent to the droplet's base. These CAMs would later be verified by additional Lehigh team members via a second digital goniometer with a mounted webcam. Since the digital CAMs were similar to the analog CAMs, an average could be used. Data obtained from these measurements can be seen below.

Table 2: Average contact angles of heat-treated core binder samples.

Temperature	22.5 °C	50 °C	90 °C	130 °C	170 °C	200 °C
Collagen	84.3	87.7	101.6	104.0	69.8	63.6
Sodium Silicate	3.4	3.6	4.3	5.0	6.3	8.5
Phenolic Urethane	86.8	80.4	78.3	79.2	79.1	74.0
X-Link	97.6	85.5	73.9	84.4	60.5	31.3
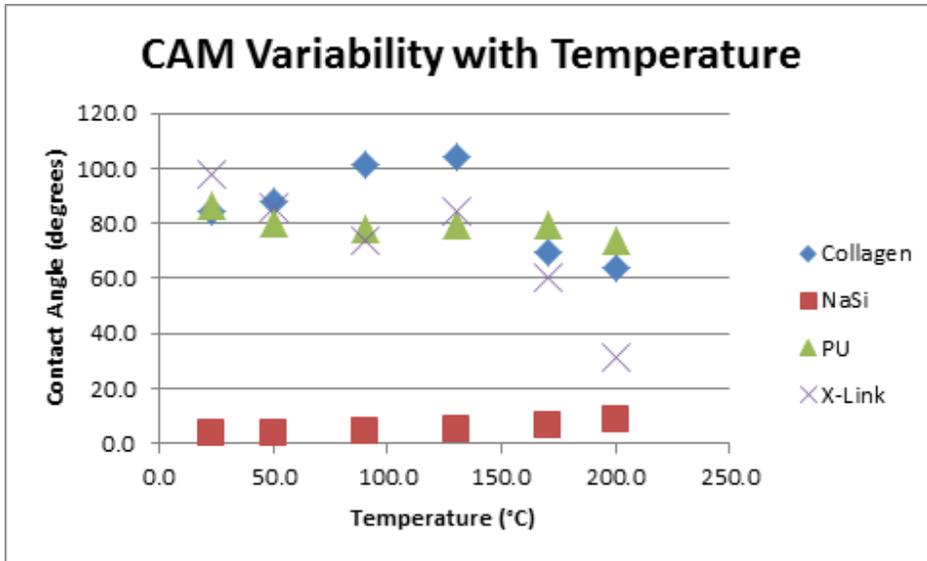
Figure 1: CAMs for core binder samples after thermal treatment.

22.5°C PU e.g. CAM: 85°	170°C NaSi e.g. CAM: 7°
130°C Collagen **e.g. CAM: 107°**	**22.5°C X-Link** **e.g. CAM: 94°**
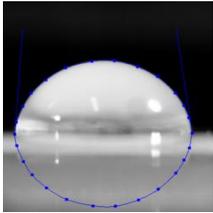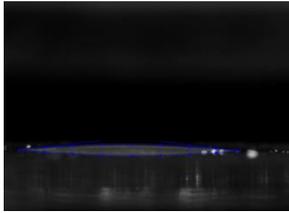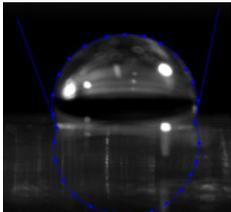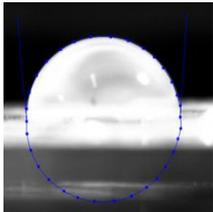
Image 1: Photos taken of example CAMs for PU, NaSi, collagen, and X-Link.

Results:

The CAMs recorded for the binder-treated slides showed that both the petrochemically-derived and collagen-based binders are innately slightly hydrophobic, and most become less-so with thermal degradation. Therefore, if phenolic urethane binders – which did not significantly change in contact angle – have minimal detrimental effects on green sand performance, it is unlikely that collagen-based binder residuals would have a direct impact on green sand due to core sand additions. Contact angles significantly decreased with thermal degradation for collagen-based binders, especially with the addition of alkali silicates. This may be evidence to the properties that make silicate addition to collagen suitable for core binder characteristics. Also note that both the collagen and the X-Link hybrid binders showed significant visual changes, possibly due to thermal degradation.

2) Antimicrobial GAC Properties

Project Title: "Benchmarking the Antimicrobial Nature of Granular Activated Carbon"

PI: Derick G. Brown, Ph.D., P.E.
Co-PI: John T. Fox, Ph.D.

Background:

Activated carbon may either intentionally serve as a biofilm host – the case with fluidized-bed bioreactors – or unintentionally serve as a host, the case when used for drinking water applications. At present, there is limited data on the innate antimicrobial tendencies of activated carbon. To better understand the factors affecting the adsorbent's antimicrobial nature, this project explores the hypothesis that increased positively charged surface functional groups will increase the antimicrobial properties of activated carbon.

Objective: To quantify the natural biological activities of different GACs.

Contribution:

Three primary GACs were used throughout the course of this study: (1) a virgin coconut-based GAC, (2) a urea-treated coconut-based ("catalytic") GAC, and (3) a quaternary amine-treated GAC provided by Siemens Water Technologies, LLC. The primary contribution to this project included keeping up with the high demand of activated carbon that needed to be prepared to continuously run isotherm tests, chemostat experiments, and respirometer experiments, in addition to acquiring data for adsorbent properties such as zeta-potential and point zero-charge measurements and slurry pH measurements. This preparation involved taking the stock activated carbons, provided by Siemens, grinding them to the desired size (200 x 325 U.S. Standard mesh), and rinsing the resulting product to remove any residual ultrafine particles. To perform the particle size reduction in way that was both cost-effective and bench-scaled for the laboratory setting, the only materials utilized were coffee grinders and a Retsch AS200 vibratory sieve shaker (rinsing would be done directly in the sieve plates, followed by drying in an oven overnight). Often, many iterations of grinding and rinsing would be required to achieve the desired uniform particle size, due to low percent yields achieved by the grinders.

Additional support given for this project included the daily taking and storing of samples from four GAC columns, and later IC analysis of the samples for acetate, which could be used as an indicator for bacterial presence on the carbon over time.

Results: Pending at the time of writing.

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24

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