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Adsorption of 1,4 – Dioxane on Activated Carbon with Regeneration by Titanium Dioxide/Ultraviolet Light

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Approved By:

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Abstract

1,4 – dioxane is a commonly found recalcitrant organic contaminant that is of increasing concern around the world, causing contamination levels to be a recent concern for scientists and engineers. The objective of this project was to evaluate the adsorption effectiveness of several granular activated carbon (GAC) types in removing 1,4 – dioxane from water. Prepared 1,4-dioxane aqueous samples were contacted with various GACs onto which TiO_2 nanoparticles were embedded, and then evaluated for regeneration efficiency in an ultra violet (UV) light photocatalytic reactor. Results suggested that the use of GAC regeneration with a UV photocatalytic reactor and TiO_2 nanoparticles was very promising; however, further research should be conducted.

Acknowledgements

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Executive Summary

1, 4 – dioxane, a newly emerging contaminant, is an organic compound that has been classified as a probable human carcinogen. This organic compound is a known stabilizing agent for 1,1,1 – trichloroethane (TCA), causing these compounds to be common co-contaminants. 1,4-dioxane is also found in various household products (i.e. detergents, shampoos, cosmetics) (EPA; Zenker et al., 2003). Being completely miscible with water, common water treatment processes have low removal effectiveness of 1,4-dioxane (Zenker et al., 2003). In the early 1990s, the Environmental Protection Agency (EPA) set stringent regulations pertaining to the use of 1,4 – dioxane, causing the use of 1,4-dioxane in industrial applications to decrease. At this time, however, many groundwater sources had already been contaminated (Ellis, 1996).

The goal of this project was to research the treatment effectiveness of GAC adsorption for removing 1,4 – dioxane from water. Also, research was started into the adsorption and regeneration efficiency of GAC embedded with TiO_2, which utilized UV light to stimulate photocatalytic reactions. To complete this goal our project team completed a series of experiments showing promising results for the GAC adsorption of 1,4-dioxane and TiO2/UV photocatalytic regeneration of the GAC.

This bench-scale study also focused on determining the adsorption rate of 1,4 – dioxane to various GAC types through batch testing. Continuously flowing packed bed columns were utilized for the photocatalytic tests. The 1,4 – dioxane concentrations in the samples were then quantified with gas chromatography coupled with solid phase microextraction (SPME-GC). Results suggested that the GAC types vary in adsorption effectiveness due to variances in surface characteristics and activation. Also, the

photocatalytic regeneration process proved to be promising by increasing the uptake of 1,4 – dioxane when exposed to UV light.

It is recommended that further research be performed on the activated carbon adsorption of 1,4 – dioxane, the TiO_2 to GAC embedding process, and the photocatalytic reactor system for regenerating GAC embedded with TiO_2.

1.0 - Introduction

The age of industrialism is upon us and ever changing. The introduction of new chemical applications and removal of those proven to be inefficient or damaging to the environment is an ongoing cycle. One chemical that has been part of this cycle is 1,4 – dioxane, a chemical stabilizer used in many chlorinated solvent applications. While this is the primary use of 1,4 – dioxane, the chemical is also utilized as a stabilizer for various substances, primarily in the manufacturing sector such as: cellulose acetate, dyes, fats, greases, lacquers, pains, resins, and waxes among others (USEPA, 1995).

1,4 – dioxane, despite its need in many industrial processes, has been found to be a potential human carcinogen (Stickney et al., 2003). Contaminated sites are located in various regions globally, with industrialized countries such as the United States (US) and Japan having a higher occurrence of 1,4-dioxane contamination. In the US, as of October 2007, 1,4 – dioxane contamination had been identified in at least 31 of the 1,689 National Priorities List (NPL) sites. Meaning the EPA had deemed the area a serious hazardous waste site requiring long-term federal cleanup activity (ATSDR, 2007). As ground and surface water contamination occurrences are increasing, research into effective 1,4 – dioxane removal methods is of the utmost importance. Exposure studies in small mammals demonstrated an increased occurrence in nasal cavity and gallbladder carcinomas (Stickney et al., 2003). Likewise, epidemiological research in humans has shown potential for the development of carcinomas to those exposed (Stickney et al., 2003). In previous studies the chemical has shown to be resistant to common mitigation systems including: volatilization, sorption, and biologically mediated degradation, demonstrating the need to research new methods.

As a result of the potential carcinogenic nature of the contaminant and the need for mitigation processes, several methods have been analyzed. GAC, a commonly applied adsorption material for various treatment needs, represents a promising process for this problem in conjunction with a photocatalytic compound. Alone, GAC has a limited effectiveness in adsorbing contaminants, but with the addition of a photocatalytic compound for regeneration the process of adsorption has the potential to increase efficiency (Junghanel, 2007).

We conducted research on the effectiveness of GAC embedded with TiO_2 for the removal of 1,4 – dioxane from water. To test the effectiveness of the method we chose to run batch reactor laboratory experiments with various types of GAC and 1,4 – dioxane concentrations.

2.0 - Background

2.1 - 1,4 – Dioxane

1, 4 – dioxane, $C_4H_8O_2$, is a widely used chemical stabilizer for chlorinated solvents, including TCA. It is also a byproduct in the manufacture of polyester and various other polyethocylated compounds. 1,4 - dioxane is formed as surfactants, including polysorbates, sorbitol, and sorbitan, are synthesized with fatty acids and then introduced to ethylene oxide (Zenker et al., 2003). There is no strong attraction between 1,4 - dioxane and organic matter, allowing for easy transfer between surface and groundwater sources (Stickney et al., 2003). The introduction of the contaminant to water sources is attributed to 1,4 - dioxane being a byproduct to many domestic commercial products, improper disposal of industrial waste, and past solvent spills not completely remediated.

Due to 1,4 - dioxane's complete miscibility with water, most organic solvents, aromatic hydrocarbons, and oils, volatilization and sorption prove to be inconsequential mitigation mechanisms for contaminated sources (Zenker et al., 2003). The compound also proves to be resistant to abiotic and biologically mediated degradation, due to a heterocyclic structure with two ether linkages, as seen in Figure 1.

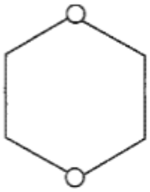

Figure 1: Chemical structure of 1,4 – dioxane (Zenker et al., 2003)

2.1.1 – History of 1,4 – Dioxane Use

In past applications, 1,4 - dioxane was primarily used as a solvent, stabilizing agent, and surfactant of polyester manufacture. The chemical also exists in many consumer products. Both applications allow for 1,4 - dioxane to ultimately be introduced to surface and groundwater sources.

2.1.1.1 – Production of 1,4 – Dioxane

Commercial production of 1,4 – dioxane in the US was first reported in 1951, though unreported production of the compound had been occurring in prior years. In 1971, 12 million pounds of 1,4 – dioxane were produced in the US alone, and roughly 15 million pounds in 1982. According to reports from the United States Department of Health and Human Services (USDHHS) 7.4 million pounds of 1,4 – dioxane were sold in the U.S in 1981. While there were only a small number of chemical plants in the US producing 1,4 – dioxane, in 1990 the total production volume was between 10,500,000 and 18,300,300 pounds. As of 1992 there were three producers of 1,4 – dioxane in the US: Ferro Corporation located in Zachary, Louisiana, Dow Chemical Corporation in Plaquemine, Louisiana, and Stepan Chemical Corporation in Elwood, Illinois. Dow Chemical Co. was also an importer of 1,4 – dioxane at this time (USEPA, 1995).

As of 1985, 90% of the production of 1,4 – dioxane produced in the US was used as a stabilizing agent for TCA and other chlorinated solvents. Degreasing formulations of TCA, used exclusively for metal cleaning operations, contained roughly 2.0 – 3.5% 1,4 – dioxane by volume. Due to more stringent regulations for TCA use set forth by the EPA, emissive uses of the compound are limited, causing the industrial use of 1,4 - dioxane to decrease. During the mid-1990s, as a response to these new regulations, various new methods were developed for synthesizing alkoxylate phosphate esters, producing less 1,4 - dioxane. One method, patented by Robert Ellis in 1996, removed 1,4 – dioxane in a water vapor stream by combustion. Through initial testing this methodology proved to be effective in 1,4 –dioxane removal during polyester production (Ellis, 1996). While efforts are being made in reducing 1,4 – dioxane emissions, many groundwater sources have already been contaminated (Zenker et al., 2003).

2.1.1.2 – 1,4 – Dioxane Contamination

As of 2003, the EPA had not yet established a maximum contaminant level for 1,4 – dioxane in water. Later, the EPA determined a 0.3 mg/L concentration in drinking water causes an estimated lifetime cancer risk, 1 in 10,000. Following this health advisory, many states adopted independent standards, ranging from 3 – 85 mg/L in groundwater and drinking water. In 2010, the EPA published an updated limit for 1,4 -

dioxane concentration in drinking water sources, 0.35 mg/L. This value is based on a 1 in 1,000,000-risk level for carcinogenicity (Zenker et al., 2003).

A surfactant is a compound able to lower the surface tension between two liquids or a liquid and a solid. Various types of surfactants contain 1,4 - dioxane and are used in consumer products, including detergents, shampoos, hand soaps, cosmetics, and even food. It was estimated that nearly one-third of cosmetics containing polyoxyethylene derivatives might contain 1,4 - dioxane as well. Contaminated water sources are not an issue limited to the confines of the US, as other industrial countries are also looking for ways to address 1,4 - dioxane contamination levels (Zenker et al., 2003).

In 2004, Japan set a contamination limit, 50 μg/L, and despite efforts set forth by the country there are still contamination levels up to 4,020 μg/L being reported in industrial effluent streams (Simonich, 2013). Japanese commercial compounds, including shampoo, liquid dish soap, detergents, were found to contain 0.2 – 56 mg/L of 1,4 - dioxane (Zenker et al., 2003).

2.1.2 – Studies of 1,4 – Dioxane Impacts

Upon discovery of increased levels of 1,4 - dioxane in water sources, various studies were performed to gain greater insight to the potential environmental and health effects that may arise due to exposure. Initially, studies of 1,4 - dioxane exposure were performed on mice, rats, and guinea pigs. These studies exhibited an increased occurrence of nasal cavity, gall bladder, and liver carcinomas; raising suspicion to potential carcinogenic properties of the compound.

In an effort to delve further into research of potential human health effects, a mortality study was performed by the USDHHS. This study, beginning in 1954, was comprised of 165 people potentially exposed to 1,4 – dioxane. Of these 165 people, two died due to cancer. Similarly, 74 German workers, between 32 and 64 years old, were exposed to various concentrations of 1,4 – dioxane, between 0.006 – 13.3 ppm, in a cross-sectional study. There was a range of exposure of 3 to 41 years with an average exposure time of roughly 25 years. At the end of this study, of the 74 workers, 24 were still working, 23 were no longer working, 15 had retired, and 12 had died. No person in the group showed evidence of kidney or liver damage or clinical effects of 1,4 – dioxane exposure. Of the 12 deaths, only 2 were attributed to cancer: a lamellar epithelial carcinoma in a 66-year old man and a myelofibrotic leukemia in a 71-year old man (Stickney et al., 2003). The results of these studies failed to validate the carcinogenic properties of 1,4 – dioxane, causing classification as a probable human carcinogen, Group 2B and Group B2, by IARC and the EPA, respectively. These classifications indicate inadequate evidence proving the carcinogenic effects of the compound in humans, though significant evidence has been shown in animals (Stickney et al., 2003). An in depth analysis of studies performed on oral exposure of 1,4 – dioxane contamination to guinea pig, rat, and human is listed in Appendix A.

2.1.3 – Occurrence

The unique chemical properties of 1,4 – dioxane allow it to be very recalcitrant and mobile in the environment. Contamination of this compound can be observed in many ground and surface water sources due to the wide variety of industrial and commercial applications, high solubility, and low biodegradation, as shown in Table 1 (Zenker et al., 2003). In the US, 1,4 – dioxane has been identified in at least 31 of the 1,689 National Priorities List (NPL) sites as of October 2007. In order for a hazardous waste site to be considered a NPL site the EPA must identify the area a serious hazardous waste site requiring long-term federal cleanup activities (ATSDR, 2007).

According to the EPA, as of 1992, 1.13 million pounds of 1,4 – dioxane was released into the US environment. Of this 1.13 million pounds, 680 thousand pounds were released into the atmosphere, 450 thousand pounds into surface waters, and 33 hundred pounds into soil. As a result, 1,4 – dioxane contamination above 1 μg/L has been detected in US drinking water sources (USEPA, 1995).

Table 1: Physical and Chemical Properties of 1,4 - dioxane (USEPA, 1995).

Characteristic/Property	**Data**
CAS No.	123-91-1
Common Synonyms	1,4-diethylene oxide
Molecular Formula	$C_4H_8O_2$
Physical State	Flammable liquid Faint pleasant odor
Molecular Weight	88.10
Melting Point	11.80°C
Boiling Point	101.1°C at 760 mm Hg
Water Solubility	soluble in water
Density	1.0329 g.mL at 20°C
Vapor Density (air = 1)	3.03
K_{OC}	1.23
Log K_{OW}	-0.27
Vapor Pressure	30 mm Hg at 20°C
Reactivity	Tends to form explosive peroxides, especially when anhydrous
Flash Point	5-18 °C
Henry's Law Constant	4.88×10^{-6} atm • m^3/mol
Log Bioconcentration Factor	-0.44
Odor Threshold	9.8 mg/m^3 (2.7 ppm)
Conversion Factors	1 mg/m^3 = 0.278 ppm 1 ppm = 3.6 mg/m^3

The first documented occurrence of 1,4 - dioxane in US drinking water was noted as early as 1980. In this instance, four municipal water supply wells, located in Bedford, MA, were closed after 1,4 - dioxane levels of 2,100 μg/L were detected. 1,4 - dioxane is also reported as a frequent contaminant in the Mississippi River (Zenker et al., 2003). Contamination of 1,4 - dioxane is detectable in industrial wastewater up to 4,020 µg/L in Japan. Also, surface water sources of US and Japan contain up to 260 µg/L and 46 µg/L 1,4 - dioxane, respectively. In the US, groundwater levels up to 220 mg/L have also been detected (Sei, 2010).

Contamination of groundwater by 1,4 - dioxane is commonly seen in regions where TCA has also been released in the subsurface environment. Landfill leachate is also reported to contain significant levels of 1,4 - dioxane, presumably due to 1,4 – dioxane's presence in consumer products. The Army Creep Landfill in Willmington, DE, reported contaminant concentrations of 0.5 to 2.4 µg/L in 37% groundwater sources. Concentrations up to 500 µg/L have been reported in groundwater near Gloucester Landfill in Ottawa, Ontario. Some of the highest concentrations of 1,4 - dioxane contamination are reported from landfills that receive significant amounts of plastic residue from manufacturing plants. Trace 1,4 - dioxane levels have also been reported in landfill leachate from radioactive waste disposal sites in Maxey Flats, KY, and West Valley, NY (Zenker et al., 2003).

As 1, 4 – dioxane is a stabilizing agent to TCA, in many contaminated industrial sites the two chemicals are seen as co-contaminants. Seymour Recycling Corporation Hazardous Waste Site in Indiana is one example of the co-contamination of TCA and 1,4 - dioxane. In this instance 1,4 - dioxane was estimated to have traveled 2,000 feet farther through the soil than TCA, demonstrating the high transport rate of the compound. While 1,4 - dioxane is commonly seen as a co-contaminant, this is not always the case. Pall Life Sciences Corporation, located near Ann Arbor, MI, has one of the largest 1,4 - dioxane contaminations reported. However, this is not the only reason this contamination site is of interest to researchers. At this site the only contaminant present is 1,4 - dioxane. In this instance four separate contaminant plumes are located in this area, ranging from 3.2 to 6.44 kilometers in length at concentrations between 30 and 45 mg/L, as a result of the impregnation of cellulose acetate membranes (Zenker et al., 2003).

2.2 – Adsorption

Adsorption is the accumulation of atoms, ions, or molecules from a gas or liquid at surface, known as the adsorbent. This process is used to remove contaminants from aqueous solutions or purify contaminated air (Crittenden et al., 1998). There are two variations of adsorption, depending on the nature of the involved forces, chemisorption and physiosorption. Chemisorption is a process in which a single layer of molecules, atoms, or ions is attached to the surface of the adsorbent by chemical bonds. During physiosorption, weaker Van der Waals' forces hold adsorbed molecules to the adsorbent (Daintith, 2008). There are various adsorption applications, each having pros and cons, allowing this technology to become widely used throughout industry.

2.2.1 – History of the Application of Adsorption Processes

It was not until the early twentieth century when adsorption processes were more fully understood. However, as early as 1550 BC, carbon was recognized for its adsorptive qualities and used in the purification of medicine. In the early 1930s, granular carbon filters were introduced in water purification applications and have since become an established technology (Nyer, 2009). Classical experiments performed by scientists including Brunauer, Emmett, and Teller, shed light on basic adsorption principals, such as how adsorbents are able to remove contaminants from gases and liquids. From the discoveries made in the early twentieth century about adsorption practices many modern theories in regards to the technology have been developed. (Crittenden et al., 1998)

Early commercial practice of using carbons as adsorbents was for the removal of color and odor in a variety of material, including air and water. In early water treatment methods, non-potable water was percolated through beds of carbonaceous adsorbent or introduced to mixing tanks containing activated carbon. The treatment method was dependent on both extent and form of contamination (Crittenden et al., 1998).

Industrial adsorption processes became common following the widespread use of charcoal in gas masks during World War I for the protection of military personnel from poisonous gases. One of the first industrial applications of adsorption was dehumidification of air with high moisture content. Dehumidification by this application was accomplished by adsorption with silica gel. In 1927, the first industrial plant was documented using solid adsorbent as a dehumidifier. A factory near Glasgow installed adsorption units containing silica gel to act as dehumidifiers for an iron blast furnace. In this instance six silica gel units treated 1 million cubic meters of air per second. At any given time the most units in operation was five, allowing for continuous process operation. The sixth off-line unit was regenerating the adsorbent, as this unit would come back on-line another would begin the desorption process (Crittenden et al., 1998).

2.2.2 – Transport Mechanisms

The process of adsorption takes place through a series of steps: bulk solution transport, external resistance to transport, internal transport, and adsorption. There are many steps involved with the adsorption process, resulting in a rate-limiting step, the slowest step, which controls the rate of removal. Typically in many processes external resistance is the rate-limiting step, however, after adsorbate accumulates within the surface pore, pore transport may be the rate-limiting step.

Bulk solution transport refers to the transport of a bulk solution to the boundary layer of the adsorbent particle. Diffusion or turbulent mixing can carry out this step. In diffusion the adsorbent must be suspended in latent water, similar to a sedimentation basin. Turbulent mixing is the turbulent flow resulting as the fluid flows through a bed of GAC or when powder activated carbon (PAC) is mixed in a flocculator.

As external resistance to transport is occurring, the adsorbates are transported by molecular diffusion through the stationary layer of water surrounding the adsorbent particle as water flows around it. The time required for this step is dependent on distance of travel along with flow rate.

During internal steps of adsorption the adsorbates pass through the boundary layer of the adsorbent and travel through the adsorbent's pore structures to the potential adsorption sites. At this time in the adsorption process, particle transport may occur by intraparticle transport or by diffusion along the adsorbent's surface. Intraparticle transport, also known as pore diffusion, may occur by means of molecular diffusion through the solution in the pores. After adsorption takes place, diffusion along the adsorbent's surface, also known as surface diffusion, may occur.

Following the transport to an available site within the particle an adsorption bond is formed. This step takes place rapidly for physical adsorption and as a result a proceeding step has potential to control the rate at which molecules are removed from solution. The reaction may be slower than the diffusion step if adsorption is also accompanied by a chemical reaction that changes the nature of the molecule. This reaction may be slower than the diffusion process and, as a result, may slow the rate of adsorption.

Adsorbent particle size and molecular size have essential effects on adsorption rates. Particle size determines the length of travel to a potential adsorption site and diffusion coefficients decrease as molecular size increases resulting in a longer duration for adsorption. When adsorption rate is controlled by intraparticle diffusion, and the effective diffusion coefficient is constant, the time to equilibrium is directly related to the diameter of the particle squared (Snoeyink, 1990).

2.2.3 – Adsorption Applications

The use of activated carbon for removal of organic molecules from aqueous solution is one of the most common adsorption applications (Lehr et al., 2005). Many different adsorbents have been used for various other applications. Those intended for drying gases and vapors include alumina, bauxite, and silica gel, while bone char and other carbons were used in sugar and oil refining processes (Crittenden et al., 1998).

The use of thermal swing adsorption (TSA) became a dominant application of adsorption in the early twentieth century (Crittenden et al., 1998). This was due in part to TSA being the simplest way for regeneration of adsorbents in industrial applications. During this process the vapor pressure exerted by the adsorbed content increases with temperature, thus causing the molecules to desorb until a new equilibrium is established with the fluid phase. As described previously with the Glasgow factory, in this process there are at least two units containing adsorbents, allowing for one unit to be online at all times while the other regenerates (Richardson et al., 2002). A schematic for TSA is shown in Figure 2.

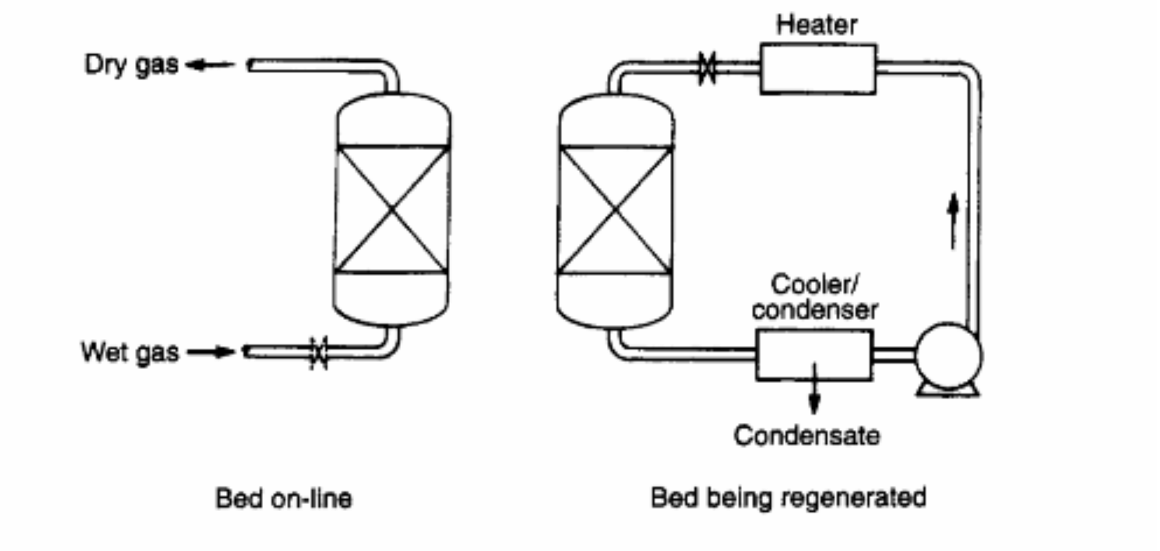

Figure 2: Thermal Swing Adsorption Schematic (Richardson et al., 2002).

Pressure swing adsorption (PSA) is another application put in place, similar to TSA in practice. The primary difference in the two processes is the method the adsorbent is regenerated. In PSA processes desorption of contaminants is achieved by reducing the total pressure of the system (Crittenden et al., 1998). This process was successfully commercialized due to decreased cycle times required for regeneration. For TSA processes, desorption required hours to complete due to the required pressure increases, where as in PSA regeneration of adsorbent is achieved in minutes, as depressurization is a faster process.

The use of GAC as an adsorbent for contaminants present in drinking water is a common adsorption application. Prior to the introduction of GAC in industrial applications in the late-1960s, PAC was commonly used. The switch to GAC from PAC was made due to a decrease in effectiveness of the PAC technology. This reduction was caused by an increased chlorination of water causing undesirable taste, paired with an overall decrease in water quality unable to be addressed solely by PAC technologies. As GAC has a higher surface area, allowing for more adsorption of contaminants, many water treatment plants (WTP) changed the adsorbent in filtering beds from PAC to GAC. The use of PAC and GAC as an adsorbent is achievable in many ways. This includes simplified methods such as filtration beds as well as the use of water treatment columns. These applications can be seen in applications ranging from a household Brita® filter to large scale WTPs where large volumes of water are processed through gravity fed treatment beds and/or columns (Clark, 1981).

2.3 – Granular Activated Carbon

With its treatment methods originating from the adsorption process, GAC is one of the most commonly used water treatment processes to date. Manufactured from raw carbonaceous materials, GAC can be processed from a number of materials including coal, wood, walnut shells, and coconut shells (“Technology Information Sheet” 2004). The activated carbon process involves the passage of water over the carbonaceous surface where contaminants are then adsorbed to the carbon particles. Its use is suitable for household and commercial applications and can aid in the removal of many organic chemicals, natural organic matter (NOM), trihalomethanes (THMs), as well as improving taste and odor of water (Jurenka, 2010). Its cost effectiveness, ease of maintenance, and overall uses has propelled GAC around the world in both developing and developed nations.

2.3.1 – History

GAC’s uses, although increasingly found in modern treatment processes, was no stranger to human lifestyle throughout the past. Carbon has been activated and used as an adsorbent for centuries starting with the Egyptian times when powdered carbon was used for medical purposes, to charred interiors of whiskey barrels during the rise of human civilization (TIGG, 2014). The first wide use of GAC began during the 1910's at the height of World War I (WWI). WWI led the way for the use of granular vapor phase activated media for military gas masks. Shortly after this period, activated carbons predominant use was for solvent recovery systems (TIGG, 2014). In the late-1960's, GAC became a predominant use in many industrial applications. However, before that period PAC was commonly used. Both forms of activated carbon, the switch from PAC to GAC was due to the increased chlorination of water causing undesirable taste, and decreased water quality. The higher surface area and thus greater adsorption rate, of granular particles rather than powdered resulted in the transition from PAC to GAC (Clark, 1981). Currently, activated carbon is most commonly used to remove water contaminates, excess of chemicals used in other water treatment methods, unpleasant odors, and improve taste.

2.3.2 – Characteristics

The various characteristics of GAC particle surfaces allow for a range of effectiveness in adsorption rates of particular contaminants. These characteristics include the activation process, pore structure, the virgin carbon material, density, size, hardness, and much more. Each characteristic is vitally important in the adsorption capability for a specific contaminant and must be understood to predict the desired adsorption capacity for the unit.

2.3.2.1 - Activation

The activation process has been a vital aspect in furthering the development of carbon adsorption. Regardless of the activation source, the goal is to create an almost pure carbon structure that contains a high surface area. Commonly, the activation of the carbonaceous raw material is done through heating processes. Heating allows for an increase of surface area, giving contaminants a greater area to adhere to ("Technology Information Sheet" 2004). The heat from the process burns off some of the raw materials, producing microscopic pores. These pores increase surface areas that are able to contain the contaminate molecules through the process known as adsorption (*Carbonair*). The activation goals can also be accomplished through chemical processes (TIGG, 2014). The activation process does have drawbacks because it will remove a portion of the carbon content from the particles, but the total pure carbon remaining from the processes outweighs the lost material (TIGG, 2014). Once activated the carbon is then crushed into appropriate size in either the granular or powder form and then is suitable for adsorption processes (*Carbonair*).

Once activated, the resulting structure contains a network of carbon atoms that aid in the adsorption process. The structure can be a regular network of carbon atoms derived from the virgin materials molecular arrangement, or an irregular mass of crystallite platelets (TIGG, 2014).

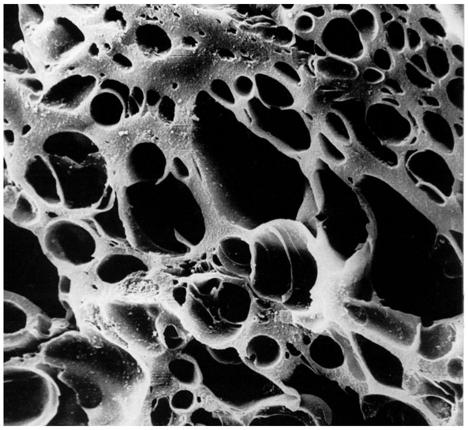

Figure 3: Electron microscope image of an activated carbon structure (Activated Carbon Pore Structure).

These structural arrangements under an appropriate microscope, commonly an electron microscope, contain laced openings, similar to a sponge structure (TIGG, 2014). Each microscopically arranged structure of the carbon aids in the particles total surface area, yielding the activity level of GAC (m^2/g) when divided by the unit weight (TIGG, 2014).

$$\text{Activity Level} = \frac{\text{Total Surface Area}}{\text{Unit Weight}}$$

Commonly, GAC materials are in the range of 600 – 1200 m^2/g. A visualization of this is one pound or one quart in volume of GAC has a surface area equal to roughly 125 acres of land (TIGG, 2014).

2.3.2.2 - Pore Structure

The resulting pore structure of GAC particles is the main characteristic behind the large surface area associated with the material. Even though the structures are commonly called pores, implying a cylindrical shape, the cavities on the particles can be in various shapes, depths, and diameters (TIGG, 2014). Practically every pore on the particle is unique even though most GAC perform the same if their surface area is similar amongst the other particles in the unit (TIGG, 2014).

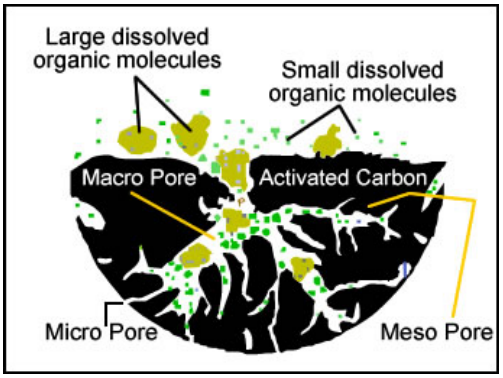

Figure 4: Imagine depicting the transport methods of molecules in regards to the pore structures of a particle (Representation of Activated Carbon Particle). (Sushrut Chemicals - Activated Carbon Powder)

The pore structures are broken up into three structure classifications: micropores, mesopores, and macropores. The micropores make up the smallest diameter pores on a carbon structure. Though small, these pores are the sites for the highest adsorption energy (TIGG, 2014). Generally the major part of the GAC internal surface area, micropores tend to have a diameter < 2 nm (Jurenka, 2010). These pores are helpful in adsorbing lower molecular weight, lower boiling point organic vapors, and removing trace organics in water to an almost non-detectable level (TIGG, 2014). The intermediate diameters on the activated carbon structure are mesopores are 2 – 50 nm in diameter (Jurenka, 2010). These pores as well as macropores, the largest possible pore diameters, are commonly regarded as the "highways" into the carbon particle since they are crucial for the movement of flow for the contaminants molecules (Jurenka, 2010). Macropores normally have diameters greater than 50 nm and are extremely useful when adsorbing large molecules and aggregates of molecules in raw sugar solutions (TIGG, 2014). These larger size pores also assist in the diffusion of fluids to adsorption sites within carbon particle (TIGG, 2014). The International Union of Pure and Applied Chemistry (IUPAC) define the knowledge of carbon pore sizes as crucial for any treatment application (Jurenka, 2010). The different carbon pore structures can be manipulated by combining the proper raw material and conditions during the virgin activation process (Jurenka, 2010).

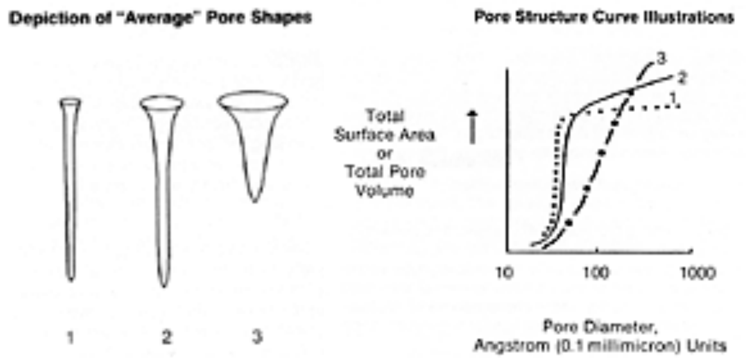

Figure 5: Relation of pore shape and diameter to available surface area (TIGG, 2014).

2.3.2.3 - Raw Material

GAC can be generated from a number of different carbonaceous materials. Each different virgin carbonaceous material gives unique properties to the GAC material (TIGG, 2014). Many of the commercially available carbon materials are commonly prepared from various nuts, bituminous and lignite coals, petroleum coke, sawdust, bark, and other wood products. The nutshells and petroleum coke will commonly produce an activated carbon material that is very hard with a characteristically porous structure. While the coals and certain wood materials normally lack hardness and abrasion resistance (TIGG, 2014). The activation of virgin material can result in a material with little resemblance to the original structure (TIGG, 2014). Currently, most carbon available in the U.S. is coal or coconut based due to availability and importation costs. Most of the other nut shell activated carbon is found outside the U.S. in the Eastern Hemisphere making them not economical. The raw materials ultimately result in the adsorption characteristics of the activated carbon and choosing the material and preparation techniques properly are crucial for the final products function.

2.3.2.4 - Density

The carbon's density aids in the adsorption process by allowing for a greater surface area of contaminant contact. The solid density of GAC is commonly between 2.0 – 2.1 g/cc (125 – 130 lbs/ft^3). However, at solid density there is minimal surface area for adsorption to occur (TIGG, 2014). The solid density is a representation of the solid carbon mass before it is broken into granular particles or powder form. GAC has a much lower density, known as apparent density (AD) than solid density (TIGG, 2014). This is due to the pores within the particles and the void space between the granular particles (TIGG, 2014). The typical AD for GAC is normally between 0.4 – 0.5 g/cc (25 – 31 lbs/ft^3). With a granular particle the density decreases and allows for a greater surface area to be in contact with the contaminant, increasing the adsorption extent and rate.

2.3.2.5 - Size

Sizing the activated carbon is performed for quality assurance and functionality during the adsorption process. GAC particle size is particularly important when designing the GAC contactor, as it impacts the energy loss in flow through the system. Sieving the carbon is done using a US Sieve range or Tyler Screen, allowing for the separation of the activated carbon by size (TIGG, 2014). There are many different customer applications for activated carbon; sizing is performed to comply with the specific customer requirements. Ultimately, the three major activated carbon groups have average particle sizes of the following: Powdered activated carbon 1 – 150 µm; Granular activated carbon; 0.5 – 4 mm; Extruded (cylindrical shape) activated carbon 0.8 – 4 mm (Table 2) (*Carbonair*).

Table 2: Common sizes of each GAC phase (TIGG, 2014).

Activated Carbon Phase Sizes	
Liquid Phase	*Vapor Phase*
4x6	8x30
4x10	12x20
6x16	12x40
12x30	20x50

Many adsorption characteristics can be altered simply by the size difference of each particle. For instance, the rate of adsorption will increase as the overall unit's particle size decreases (TIGG, 2014). In an adsorption unit, the increased rate of adsorption will require less adsorbent bed depth and contact time – saving on both time and money (TIGG, 2014). Smaller particle sizes can cause the potential risk of increasing flow resistance, carbon usage rate (CUR), and pressure drop, creating negative consequences for the flow system (Jurenka, 2010). Activated carbon particle sizes are selected to produce a reasonable balance between the benefits of rapid rate of adsorption and efficient removal, and avoid the hazards of flow resistance and pumping costs (TIGG, 2014).

2.3.2.6 - Hardness

The hardness and abrasion resistance characteristics are extremely beneficial for adsorption processes of large-scale and high use. Beneficial to any adsorption process, the GAC particles must be able to withstand the weight loads for the entire activated carbon unit, and hold up to the added pressure effects that are induced from the fluid flows (TIGG, 2014). Abrasion resistance and hardness are factors of importance when being applied in heavily used adsorption systems. Customers with sporadically used systems, that are unaffected by movement or vibrations, have less stringent requirements for hardness of the GAC particles (TIGG, 2014). Systems with high movement are frequently handled, or subjected to outside factors like vibration require the hardness of particles to be able to withstand these external forces (*Carbonair*). For example, an activated carbon system that is constantly used and backwashed will require particles that can withstand these procedures, so not to risk increased loss of carbon from reactivation procedures. Also, systems that use steam, another form of reactivation, can cause carbon particles to fracture into smaller size particles. Re-sieving or replacing the material can fix an accumulation of fractured carbon, but it results in a waste of resources (TIGG, 2014).

2.3.2.7 - Ash

One of the most noticeable results for the activation of carbonaceous material is ash. Ash can vary between 2 – 20 wt.% in commercially used GAC (*Carbonair*). The ash from wood and shells tend to be rich in alkaline metals whereas coal is largely oxides of aluminum, silicon, and iron (TIGG, 2014). Ash coexists with GAC and cannot be completely removed; however, most GAC types go through a "washing processes" after activation to cleanse the particles of the resulting ash. A portion of ash can be water-soluble, though normally a greater amount are acid soluble. The remainder of ash is deep within the skeletal structure of the carbon particle, making it insoluble (TIGG, 2014). Pre-washing the activated carbon will not completely remove every trace of ash within a particle, but overall it does have a profound effect on total ash level.

Natural ash tends to not deter from the effectiveness of the adsorption processes and is included in the efficiency calculations of the GAC. The main efficiency problem of ash within activated carbon systems is the microscopic ash dust blocks micropores of the particles. These pores, essential for the removal of organics and other contaminants, must be open for the activated carbon to function properly. When these pores are blocked the performance of the activated carbon is severely compromised and the lifespan for the unit is significantly shortened (TIGG, 2014).

2.3.2.8 - pH

The pH is determined from analyzing water extracts from activated carbon. Untreated GACs have a pH range of 6 – 10, coal carbons have a natural pH of 7, while nut shells and wood carbons are commonly basic, pH of 7 – 14 (TIGG, 2014). It is from these variances in pH that variances in adsorption occur. For instance, organic contaminants are best adsorbed from slightly acidic solutions at a pH around 5 – 7 (TIGG, 2014). It is these slight changes in pH that can considerably affect a unit's efficiency level for removing a particular contaminant

2.3.2.9 - Quality Assurance

Quality and uniformity can affect both adsorption capacity and the flow systems (TIGG, 2014). With such a crucial impact on the system, the activated carbon standards for assurance are set forth by a few organizations, one of which is American Society for Testing and Materials (ASTM). These standards are used to measure the characteristics of the activated carbon particles and to aid in production controls, which result in identifying the specifications that represent each product (TIGG, 2014). The test standards for activated carbon include tests of moisture, apparent density, particle size, and hardness or abrasion (TIGG, 2014). While all manufacturers must complete these tests for their products, not all companies publish the results. Manufacturers have withheld information for the adsorption specifications, which makes it difficult at times to find the activated carbon material with the right specifications for a company's requirements (TIGG, 2014). Though some information can be withheld from customers, the quality assurance standards completed on the activated carbon materials are effective assurance methods in assessing a products performance.

2.3.2.10 - Predicting Adsorption Performance

Practically all GAC applications are unique to each situation so it is hard to predict which will be best without testing (TIGG, 2014). One way for competitive analysis of predictions have been through computer modeling analysis. Companies such as TIGG Corporation have an Adsorption Predictive Technique computer service that can be available upon request to analyze the exact activated carbon needed depending on the customer's situation (TIGG, 2014). GAC tests usually produce adsorption isotherms from batch tests. These tests require special attention to predict the best possible GAC characteristics to peak the effectiveness. Also, column tests can be performed that range from small laboratory scale to semi-commercial size scale (TIGG, 2014). It is always important to recall that different GACs will end up having different efficiencies depending on the system requirements, which is why the ability and time spent on predicting its performance is critical.

2.3.2.11 - Price

There are numerous techniques that can be used to solve various types of water contamination, but price is a primary factor that restricts potential solutions. GAC is a cost efficient method of adsorption when compared to applications involved with other treatment processes. Variances in the cost of the GAC raw materials definitely affect the company's decision when designing the unit. Some materials are only accessible in select regions requiring transportation and refinery costs for the material. The availability and location factors do end up limiting the selection of the raw materials, but the overall use of GAC as an adsorption process is still favored over other more expensive methods.

2.3.3 – Treatment Technology

Carbon, in the virgin form, requires certain steps to be completed to adjust the overall adsorption performance and life span of the material. Prior to treatment there are numerous factors to be assessed, including: the amount of contaminates to be removed, other contaminates that can also be adsorbed through GAC, and the amount of time water is in contact with the GAC particles ("Technology Information Sheet," 2004).

Common treatment practices involve pretreatment, activation, contaminant removal, backwashing, and reactivation. Pretreatment is necessary for water with a significant amount of bacteria and total suspended solids (TSS), to avoid potential flow pressure issues, and optimize the GAC adsorption process (Jurenka, 2010). Pretreatment can consist of various methods including chemical treatment or treatment through coagulation. Activation, as previously described, is the process required to activate the carbon and allow use in adsorption processes. Activation processes include heating the carbon source in the absence of air in which high carbon content is then produced (Jurenka, 2010). With the activation process completed, the GAC can be used in the adsorption process and adsorption is able to occur. The adsorption process is the physical removal of the contaminant, which is done in the mass transfer zone (MTZ) of the carbon surface (Jurenka, 2010).

To ensure that the adsorption process is removing the contaminant at a proper rate there are a number of cleansing methods utilized. One is the backwashing practice, the flow of water in the reverse direction of what the adsorption unit was operating at. This is essential to break up the GAC particles that have become compacted together as well as allow for different points of the particles to become in contact with the contaminant. Reactivation is another process used to renew the GAC unit after use. The reactivation process involves volatilization and oxidization of the adsorbates on the spent carbon (TIGG, 2014). This process consistently produces a measurable change in the particle pore structure due to the oxidative sculpturing of the carbon surface. Although this is a method to prolong the life of the activated carbon particles it is not a permanent fix because it is impossible to clear the micropores of every activated carbon particle. These are ways to re-generate the activated carbon, however, are not perfect because the efficiency is significantly reduced when compared to that of virgin activated carbon.

Concluding with the general overview of the adsorption process involving GAC the focus can now be put on technologies that involve GAC. GAC is an ideal adsorption media as it is small in size and only requires that the contaminants pass over its surface. It can be used in small household applications with pour-through adsorption devices like a hand held Brita® filter or mounted to a faucet to have direct touch filtered water (Jurenka, 2010). Most of these filters are, as they appear, in-line filter units with one direct input and one direct output. For high-volume applications, like commercial community treatment, the GAC units are typically gravity fed or pressure driven. The can also be sequenced in parallel or in different adjacent series. Commonly, the GAC units are not the only media present in the unit but are combined with other media filters to provide services that are not applicable to GAC or more efficient than GAC (Jurenka, 2010).

Since the GAC particles are an adsorbent there is a point where the activated carbon will become saturated and require either regeneration or replacement. For household products this is fairly simple and consists of discarding of the small filter unit and installing another one; however, for large commercial size units this is not a probable way. The reactivation or regeneration of commercial units is primarily completed off site (Jurenka, 2010). Factors including activated carbon used, contaminant type, concentration, and rate of water flow decide the amount of times and frequency that the carbon system requires reactivation. In circumstances where the unit is offline for several days the activated carbon would require backwashing to break up the particles and prevent bacterial growth (Jurenka, 2010). However, under the circumstances when the activated carbon cannot be reactivated and requires disposal a contractor provides the replacement activated carbon. The spent activated carbon, once removed from the unit, is disposed of normally in either two manners: landfill or fuel, such as concrete kiln fire fuel (TIGG, 2014).

2.3.4 – Applicable Contaminants

The research on applicable contaminants that can be adsorbed through GAC has evolved over the past century with new findings on adsorption methods to control contaminant effluent concentrations. According to the Environmental Protection Agency’s (EPA) Best-Available Technology (BAT), GAC is a common adsorbent material for the following contaminants listed in Table 3.

Table 3: EPA BAT Contaminants for GAC (Jurenka, 2010).

Contaminant	Related Compound
Disinfection Byproducts (DBPs)	-
Mercury and Cadmium	-
Natural Organic Matter	-
Radionuclides	-
Synthetic Organic Chemicals	Benzo(a)pyrene
	Di(2-ethylhexyl)adipate
	Di(2-ethylhexyl)phthalate
	Hexachlorobenzene
	Dioxin

2.3.5 – Restrictions

GAC has proven to be a valuable adsorption material in today's world, but has various restrictions. First, the size of the activated carbon particles can cause issues in adsorption units. The particle pores need to be large enough to adsorb the contaminant and the particles must be an appropriate size for the unit as to not restrict water flow (TIGG, 2014). When considering water flows there are maintenance procedures required to ensure the proper function of the activated carbon. Back washing is the common maintenance procedure for GAC to break up the compacted particles and flush out the system ("Technology Information Sheet," 2004). Other physical restriction properties of GAC include the source of raw carbon and the activation procedure. The variances that can exist in activation procedures derive from the chemical and electrical properties of the virgin material. The hydrogen or oxygen content in material can account for variances in adsorbent rates and even water pH (Jurenka, 2010). Another restriction is the fact that the activated carbon particles cannot last forever and will inevitably become saturated. This then results in the replacement process and leaves the carbon as a solid waste. The spent carbon can then either be reactivated or disposed of depending on its hazardous characteristics (“Technology Information Sheet” 2004).

Most organic contaminates can be adsorbed through GAC; however, there is also a large portion of organic compounds that cannot be treated by GAC or ones that the GAC process has little adsorption effect on (*Carbonair*). Some of these organic compounds are vinyl chloride, methylene chloride, chloromethane, and chloroethane. Another restriction with GAC’s adsorption is that some contaminants have molecules that are too small or too large in size to effectively be adsorbed within the carbon particle (*Carbonair*). Small molecules are normally less restrictive than large molecules, like globules that are oils and greases, which are too large to enter micropores. Also GAC is not effective in removing some organic compounds, inorganic compounds, and metals. Inorganic compounds include manganese, sulfate, iron, and many more. These are difficult to adsorb because they are often present in water in an ionized form; separating these bonds from water molecules is difficult (*Carbonair*). In fact, the water temperature and pH can have a significant impact on adsorption rates, as adsorption rates are known to increase as temperature and pH decrease (Jurenka, 2010). Lastly, there are restrictions that can be related to design flaws rather than the GAC particles themselves. The unit design, flow rate, and exposure time of the contaminant to the GAC can restrict systems. However, lower contaminant concentration and flow rate allow GAC to operate longer before reactivation or removal activities (Jurenka, 2010).

In conclusion, there are number of restrictions that can limit the adsorption rates of GAC and the attention needs to be put towards limiting these factors in order to increase efficiency. The reactivation and removal or replacement activities can be costly for facilities, especially if they are doing these and are still inundated with effluent problems. Commonly, the effectiveness of GAC is critically based on contaminant type, concentration, flow rate, and carbon used (Jurenka, 2010). If special attention is put on these factors and the process is monitored closely to limit restrictions, then GAC can continue to be an efficient and practical adsorption method.

2.3.6 – Modified Activated Carbon

Conventional activated carbon has proven itself to be an extremely viable media for adsorption but a number of modified activated carbon techniques exist. A few common modifications that exist are through tailored carbon, biological growth, and impregnated carbon.

Tailored carbon involves manipulating the electrical charge of the particles. It positively charges the surface of each activated carbon particle, thus allowing a stronger attraction of negatively charged contaminates, like perchlorate ("Technology Information Sheet," 2004). This opposite charge attraction allows for the removal of a high volume of contaminants than the standard activated carbon. However, due to the constant flow of the system and interactions of water and contaminants with the particles, this attraction only lasts for a limited time before becoming exhausted ("Technology Information Sheet," 2004).

Biological growth is a beneficial modified version of activated carbon that aids in the removal of organic and biodegradable material. Commonly known as biologically active carbon (BAC), it is beneficial in the removal of assimilable organic carbon (AOC) and various other biodegradable compounds (Jurenka, 2010). An issue with the BAC is that it normally requires the organic matter to be in smaller assimilable form to be removed, raising the issue of including a prior process, like ozonation, if it is not in this form. Also, a disinfection system is highly recommended after the media filters, to prevent biological growth in the exit stream and achieve the highest removal of AOC from the system (Jurenka, 2010). When this process is at its ideal conditions it does enhance contaminant removal, but requires a higher level of maintenance than standard GAC to be at ideal conditions. The BAC normally needs to be backwashed at least every 5 days to ensure proper growth and function (Jurenka, 2010). If growth conditions are not maintained properly than anaerobic conditions may occur creating an alarming odor problem and the potential for undesirable organisms to grow in the system. Also, unmaintained biological growth can lead to a shorter filter life and head loss from the system (Jurenka, 2010).

The impregnated modified carbon form is one of the most common alternate forms of GAC. The high surface area of the GAC can make it an effective substrate for dispensing other materials or chemicals in manageable forms (TIGG, 2014). These impregnated forms will commonly act as catalysts for the adsorption process. Reactive chemicals are impregnated within the GAC to improve the rates of selectivity, adsorption rates, or capacity for certain contaminants (TIGG, 2014). A number of chemicals have been impregnated or embedded on in the GAC particles, such as titanium dioxide, which normally allows for the modified carbons to retain at least 75% of the physical adsorption capability of the base carbon (TIGG, 2014). However, the impregnation process used with GAC can be a costly process. The impregnation process is normally cost effective if the purpose is to remove one sole contaminant and not need multiple other systems to remove other contaminants, odors, etc. that the first system could not remove (TIGG, 2014).

2.3.7 – Health & Safety Concerns

The health & safety concerns related to the GAC adsorption results from the hazardous nature of the adsorbed contaminants. The used activated carbon may contain high levels of hazardous substances that require special treatment, in accordance with environmental regulations, before disposal (Jurenka, 2010). Also, the reactions and bi-products resulting from regeneration or maintenance procedures on the activated carbon can potentially emit toxic gases such as dioxins and furans (Jurenka, 2010). With the processing unit remaining fairly simple for GAC adsorption, concerns stem primarily from the contaminant being removed or the chemical outgases that can result from the systems process.

2.3.8 – Measuring Adsorption of Granular Activated Carbon

The adsorption of contaminants to GAC is commonly studied by graphical analysis. These graphs are known as adsorption isotherms and quantify the amount of adsorbate on the adsorbent as a function of contaminant concentration. Each type of GAC has its own specialized isotherm graph, which allows for comparison of adsorption efficiency between various GAC types (Amrita, 2014).

There are two common equations used to construct isotherm graphs, Langmuir and Freundlich equations. The Langmuir equation, shown below, has a rational basis.

$$q = q_{max} \frac{K_L C}{(1 + K_L C)}$$

For this equation to apply to adsorption applications it must be assumed: the system is operating under equilibrium, there is monolayer coverage, all adsorption sites are equally probable, and there is a second order reaction.

The second equation commonly used is the Freundlich equation shown below.

$$q_e = K_f C_e^{1/n}$$

For this equation the K_f and 1/n values are constant values. K_f is a measure of the adsorption capacity of the GAC in question and 1/n is a measure of the adsorption intensity. The Freundlich equation is an empirical equation that is commonly used in water treatment studies. For this equation monolayer adsorption is also assumed, represented as (Sime, 1990):

$$A + S \leftrightarrow AS$$

For the experiments performed in this study the Freundlich equation was applied to results for analysis of GAC adsorption efficiency.

2.4 - Titanium Dioxide Nanoparticles

Titanium dioxide (TiO_2) is a non-toxic, wide band gap semiconductor, commonly used as part of various processes including plastics, paint, air purification, water treatment, and printing (Jurenka, 2010). TiO_2 is also known as titania, titanic oxide, titanium white, titanic anhydride, or titanic acid anhydride. Several semiconductors, such as TiO_2, ZnO, Fe_2O_3, CdS, and ZnS, are available for photocatalyst reactions, however, TiO_2 is the most commonly studied due to its ability to break down organic pollutants and even achieve complete mineralization (Umar et al., 2011).

With regards to TiO_2 nanoparticles, two of the most extensively investigated research topics involved with this form are the decomposition of organic compounds and the production of H_2 as a fuel using solar energy (Minna et al., 2013). With constant effort currently being put into researching processes with high efficiency and renewable energy, TiO_2 is a compound that will continue to grow in use throughout the scientific and industrial community.

2.4.1 – History

Discovered around 1795, Martin H. Klaproth first identified this naturally occurring oxide form of titanium. Four years later, William Gregor formularized the discovery of the element titanium (*TiO_2-Titanium Dioxide*). However, it was Fujishima and Honda, in 1972, who pioneered the concept of TiO_2 photocatalysis (known as the "Honda-Fujishima effect") (Umar et al., 2011). Since then, TiO_2 has been used in a variety of household items, such as the compound that makes toothpaste white (*TiO_2-Titanium Dioxide*). The compound is non-toxic, allowing for a seemingly endless amount of opportunities for it to be used for human, food, and water applications. In the past few decades TiO_2 has been researched for its potent photocatalyst characteristics that are able to break down various organic compound when exposed to UV light. Companies have now started using this method to develop a variety of environmentally beneficial products such as self-cleaning fabrics and ceramic tiles able to breakdown nitrogen oxide from air into benign substance. As constant research today is being applied to efficiency and environmentally beneficial results, TiO_2 will remain as a compound to be studied.

2.4.2 – Characteristics

TiO_2 does not exist as one sole structure; there are a number of forms that TiO_2 may be present in, all of which affect the applications (Table 4).

Table 4: Forms of TiO_2 (Junghanel, 2007).

Form of TiO_2	**Crystallographic properties**	
	Space Group	**Symmetry**
Anatase	$I4_1/amd$	D_{4h}
Rutile	$P4_2/mnm$	D_{4h}
Brookite	Pbca	D_{2h}
TiO_2 II – “columbite”	Pbcn	-
TiO_2 III – “baddeleyite”	$P2_1/c$	-
TiO_2 (H) – “hollandite”	I4/m	-
TiO_2 (R) – “ramsdellite”	Pbnm	-
TiO_2 (B) – “bronze”	C2/m	-

Currently, the most relevant and widely used forms for titanium dioxide are anatase, rutile, and brookite (Table 4). The previous types mentioned and TiO_2 (B) are naturally occurring modifications; whereas the others are synthesized by high-pressure treatment of anatase or rutile in a laboratory (Junghanel, 2007).

The structure of TiO_2 is commonly made up of d^0 titanium ions (charge +IV) at the center of an octahedron of six O^{2-} ions. The most important modification that differentiates anatase and rutile is the distortion of the inside octahedron. Refer to Figure 6 for the unit cell of anatase and rutile. Anatase normally has a density of 3.8 – 4 g/cm^3, and rutile has a slightly greater density of 4.2 – 4.3 g/cm^{-3} (Junghanel, 2007). As well as having a lower density, anatase also has a smaller average distance between Ti^{4+} ions making it thermodynamically less stable than rutile. Anatase is commonly employed for photocatalysis activities because of its high photoreactivity (Junghanel, 2007). On the other hand, rutile is normally used for pigments due to its effective light scattering properties.

Table 5: Common Crystal structure data for TiO_2 (Minna et al., 2013).

Properties	Rutile	Anatase	Brookite
Crystal Structure	Tetragonal	Tetragonal	Orthorhombic
Lattice Constant	= 4.5936 = 2.9587	= 3.784 = 9.515	= 9.184 = 5.447 = 5.154
Space Group	$P4_2/mnm$	$I4_1/amd$	Pbca
Molecule (cell)	2	2	4
Volume/molecule	31.2160	34.061	32.172
Density (g/cm^3)	4.13	3.79	3.99
Ti-O bond length	1.949 (4) 1.980 (2)	1.937 (4) 1.965 (2)	1.87-2.04
O-Ti-O bond angle	81.2° 90.0°	77.7° 92.6°	77.0°-105°

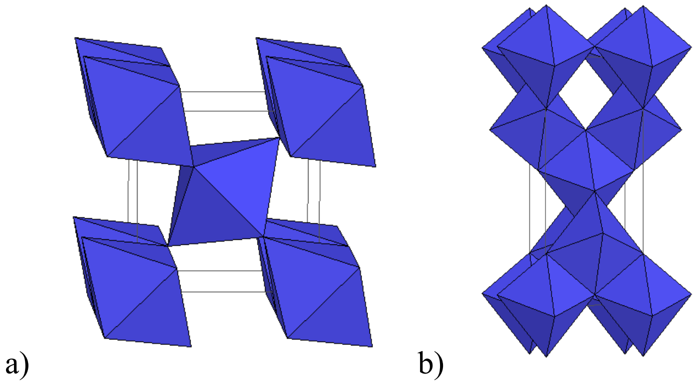

Figure 6: Physical Structures of rutile (a) and anatase (b) (University of Colorado).

Each structural characteristic of TiO_2 affects the suitability of the compound for certain applications. Fortunately, the compound can be manipulated on the molecular level to create the desired properties.

2.4.3 – Photocatalytic Property

Photocatalyst compounds, such as TiO_2, are compounds involved in the chemical reaction when light strikes a compound that is light sensitive. As light, or ultraviolet (UV) light, strikes the TiO_2 compound a chemical reaction will occur and cause the breakdown of organic contaminants, odors, and more. The water purifying applications of TiO_2 can impact a number of organic chlorine compounds including tetrachloroethylene and trihalomethane.

Titanium dioxide is an ideal semiconductor for photocatalysis and has many benefits, especially for decomposition and treatment requirements. The ideal properties of TiO_2 stem from its high stability, low cost, and safety towards humans and the environment (Minna et al., 2013). Also, it is extremely beneficial for use with UV light, as TiO_2 does not photo-degrade upon excitement (Junghanel, 2007).

The TiO_2 tends to be embedded on materials and used in junction with UV to analyze its photocatalytic activity. The possible materials for embedding the TiO_2 commonly consist of glass beads, glass tubes, fiberglass, quartz, stainless steel, silica, and activated carbon (Rezaee et al., 2008). The base material choice is carefully chosen because it may have an effect on the process too. For instance, GAC has its advantages including high porosity, low density, natural abundance, absence of toxicity, and low price as a base material (Rezaee et al., 2008).

TiO_2 allows for a large improvement on treatment processes, and with the addition of nanotechnology this ability can grow immensely. Popularized in the 1980's by Eric Drexler, nanotechnology is the engineering of functional systems at the molecular scale (*CRN*, 2008). This allows for particle surface and interface alterations that results products of special functions with different physical and chemical features. With the advantages of nanotechnology, TiO_2's photocatalytic characteristics are enhanced. This alteration will not only increase the specific surface area of the TiO_2 particles, but also exhibit other benefits on optical properties and size quantization. Commonly, increasing the photocatalytic reaction is observed as redox potential increases and the particle size decreases (*TiO_2-Titanium Dioxide*).

The general sequence for photocatalytic reactions with TiO_2 involves the excitation by photons, which then lead to redox reactions. This heterogeneous photocatalysic reaction using UV and TiO_2 is the most common photocatalytic process. It is based on the adsorption of photons with energy greater than 3.2 eV, wavelengths lower than ~390 nm, resulting in excitation related to separation event (Umar et al., 2011). The excitation of higher-energy states of electrons and hole pairs occurs when the wide bandgap semiconductors. In this case, TiO_2 is irradiated higher than its bandgap energy. This then promotes an electron in the conductive band (e_{CB}^-) and the formation of a positive hole in the valence band (h_{VB}^+), represented by the reaction below:

$$\mathbf{TiO_2 + hv\ (< 387nm) \rightarrow e_{CB}{}^- + h_{VB}{}^+}$$

The h_{VB}^+ and e_{CB}^- are powerful oxidizing and reducing agents. The h_{VB}^+ products react with organic compounds that result in their oxidation that produces CO_2 and H_2O.

$$\mathbf{h_{VB}{}^+ + Organic \rightarrow intermediates \rightarrow CO_2 + H_2O}$$

This h_{VB}^+ can also oxidize organics by reacting with water to generate *OH.

$$\mathbf{H_2O + h_{VB}{}^+ \rightarrow *OH + H^+}$$

The *OH is electrophilic (electron preferring) in nature and can non-selectively oxidize all electron rich organic molecules which will eventually be converted into CO_2 and H_2O.

$$\mathbf{*OH + Organic \rightarrow intermediates \rightarrow CO_2 + H_2O}$$

The overall mechanism of the electron hole-pairing formation when TiO_2 is irradiated is displayed in Figure 7 below (Umar et al., 2011).

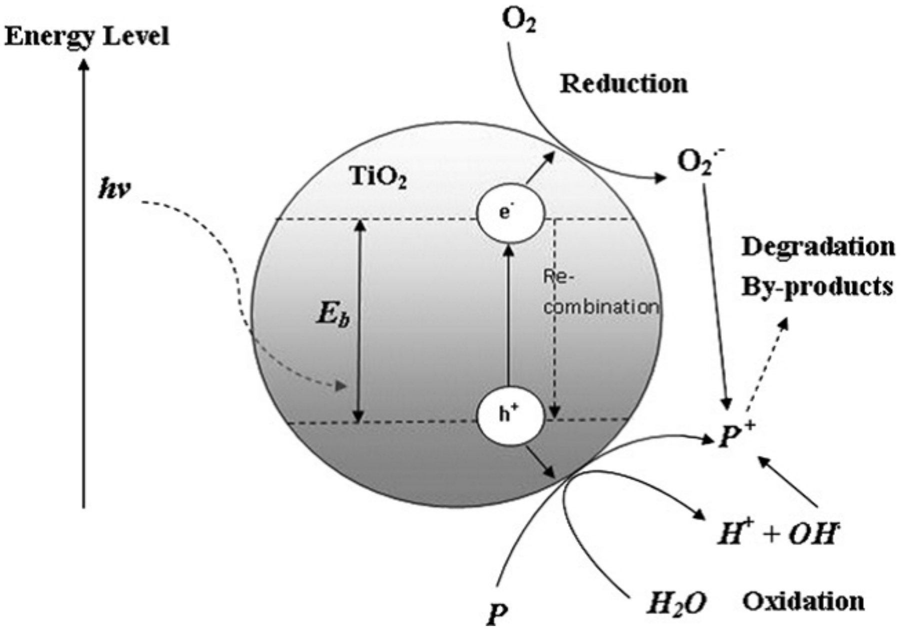

Figure 7: TiO_2 electron hole-pairing formation mechanism (Umar et al., 2011).

A number of factors help contribute to this mechanism such as the availability of dissolved oxygen (DO). DO levels allow for the recombination process on TiO_2 (e_{CB}^- /h_{VB}^+) difficult, allowing for the TiO_2 particles to be electroneutral. The reduction process plays a key role in the degradation of organics by allowing the process to proceed and avoid the accumulation of electrons in the conduction band zone, and thus the rate reduction of recombination of e_{CB}^- and h_{VB}^+.

TiO_2, after manipulation, can consist of multiple forms with, Degussa P25, being the most widely used. P25 is commonly synthesized by flame hydrolysis and is composed of 75% anatase and 25% rutile with an average surface area of 50 m^2/g. The effectiveness of this form is dependent on the inhibition of the recombination process on TiO_2. This is due to the smaller band gap of rutile in the form that absorbs photons and generates electron-hole pairs, and the electron transfer from the rutile conductive band to the electron traps occurring in the anatase phase of the particle (Umar et al., 2011).

2.4.4 – Availability

The properties of the two modifications result in a number of conflicts during synthesis, production, and sale. The single crystals of rutile are widely available and can be purchased from companies including: Kelpin Kristallhandel (Germany), Commercial Crystal Laboratory (USA), and Goodfewllos (UK). Anatase, on the other hand, is much more difficult to synthesize due to its instability which conflicts with company's capability to produce the product. The temperature during the reaction must not exceed a certain threshold to avoid a phase transition into a rutile synthesis (Jurenka, 2010). If exceeded, the product could no longer be sold as an anatase synthesis. The most commercially available TiO_2 modification is P25 from Degussa, which consists of TiO_2 powder with 25 nm particle diameter in average. It is difficult to find and synthesize a product that contains a 100% singular form (Junghanel, 2007).

3.0 - Methodology

This chapter is intended to outline the general laboratory procedures that will be used during the study and analysis of the adsorption of 1,4 – dioxane, using GAC and the photocatalytic regeneration procedures. We began experimentation using seven GAC samples donated by: Fisher Brand Company, Norit, TIGG, Genesis Water Technologies, Inc., and Omnipure Filter Co. All companies were able to donate at least one sample for experimentation. A detailed inventory of all GAC donated for our research is listed in Appendix B.

3.1 – Sample Preparation

Solutions of 5 ppm 1,4 – dioxane were prepared using pure 1,4 – dioxane and purified water for each treatment procedure, calculations for the dilution are listed in Appendix C. Solutions of 1,4 – dioxane were prepared weekly and kept in a temperature and light controlled environment at 20°C.

3.2 – Measuring Contaminant Adsorption to GAC

To measure 1, 4 – dioxane removed by adsorption, initial and final concentrations are measured using a gas chromatograph (GC), shown in Figure 8 below. The four GAC samples with the highest adsorption efficiency of 1,4 – dioxane were studied further. Determination of the highest adsorption efficiency was made based on the peak area detection of 1,4 – dioxane with the GC. Peak area is expected to range from roughly 1200 $pA * s$, for the 5ppm spike samples, to 100 $pA * s$, for samples tested with high GAC mass to 1,4 – dioxane proportions. These tests are conducted to conclude the mass of GAC needed for approximately 50% removal of 1, 4 – dioxane. After this GAC mass is found, further equilibrium testing was conducted to determine which GAC types demonstrated the greatest adsorbance of 1,4 – dioxane.

Figure 8: Gas Chromatography (GC) instrument

3.3 – Adsorption Treatment Experiments

Adsorption treatment experiments were first executed to analyze the removal efficiency of the GAC types. The GAC provided by TIFF was used for initial experimentation due to the recommendations from the company to use GAC derived from coconut shells during our preliminary data collection. This recommendation was made based on previous treatment success of 1,4-dioxane contaminated water with this form of GAC. In order to effectively analyze removal efficiency the adsorption was tested in a series of equilibrium trials.

For each experiment fixed amounts of GAC were weighed and added to 40-mL VOA vials. 20-mL of solution was added to each vial, capped, and placed into a mixer for 24 hours. Following treatment, each sample was removed from the mixer and placed into centrifuge to settle GAC particles and avoid carbon particles from being transported to the GC vials.

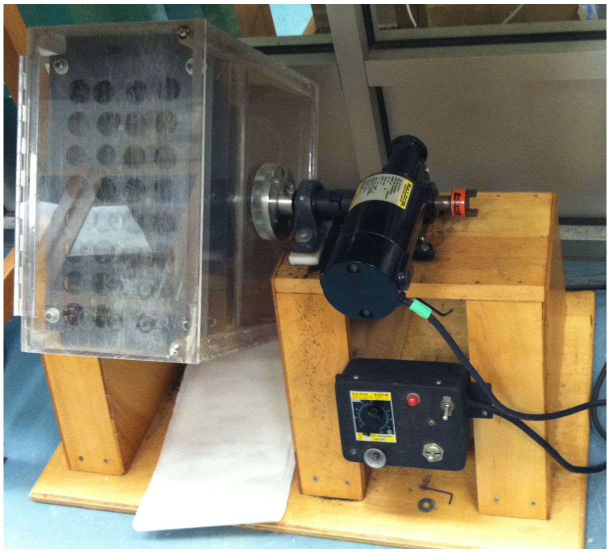

Figure 9: Sample Circular Rotating Mixer

In preparation for samples to be run through the GC, 10-mL of solution was removed from the VOA vial and placed in 20-mL SPME headspace vials, using an autopipet. Then, 4 g NaCl and 50 μL of 10mg/L chlorobenzene solution was added.

3.4 – 1, 4 – Dioxane Isotherm Study

From the adsorption treatments results, isotherm studies were conducted. These studies were able to quantitatively determine the efficiency of GAC adsorption of 1,4-dioxane. These isotherms were also able to graphically demonstrate removal of 1,4-dioxane GAC by adsorption to equilibrium, followed by continued removal after the regeneration of GAC using TiO_2 and UV.

To determine the mass of GAC needed for this amount of reduction further adsorption studies were completed and 1,4 – dioxane isotherms were studied. The Freundlich equation, $q_e = KC_e^{1/n}$, and the linearized form of this equation, $log q_e = log K + \frac{1}{n} log C_e$ was used in constructing the isotherm graph for the TIGG GAC. From the charts and graphs produced by these formulas we were able to determine the ideal mass of GAC for the adsorption applications of interest to this project scope.

3.5 – Optimal Granular Activated Carbon Type

Once the mass of GAC needed for desired contaminant reduction is known further adsorption testing was completed with all GAC types of interest to determine the four most promising types. The final GAC type that used for further testing was based on susceptibility of the GAC to embedding with TiO_2 particles. Once this was determined further adsorption and isotherm studies were conducted like those preformed with the TIGG GAC.

Once the optimal GAC type is known further adsorption testing, as described previously, was completed to determine the mass needed for 50% contaminant reduction with the specific GAC.

3.6 – Titanium Dioxide Coated Granular Activated Carbon

To further explore the adsorption efficiency of 1,4 – dioxane, TiO_2 was embedded on the GAC particles. This was performed with TiO_2 nanoparticles, P25 Degussa. The procedure includes steps for both cleaning the GAC and embedding it with TiO_2.

The cleaning preparation began by weighing the desired amount of GAC to be embedded. The GAC was then placed in a beaker and filled with distilled water to 200 mL. This mixture was then stirred for 5 minutes and then distilled with a filter vacuum unit as shown in Figure 10. The apparatus consisted of a 1000 mL filter flask, filter unit, and KNF vacuum pump. The cleaning process was to ensure that the particles were free of as much ash as possible. After distilling, GAC was placed in a beaker, covered with aluminum foil, and placed in an oven at 100°C until completely dry. This dry period duration continued overnight, as necessary, to ensure that the particles are dry. Once dry, GAC was removed from the oven and left to cool for 30 minutes.

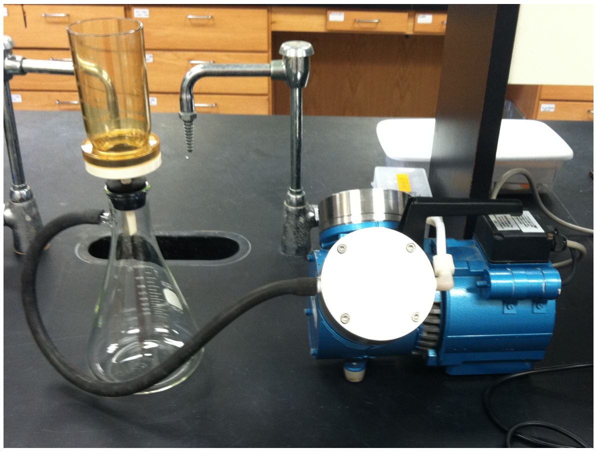

Figure 10: Filter Vacuum Apparatus

TiO_2 preparation was be started at this time. A ratio of 1:5 was used for TiO_2 to GAC respectively. The coating process was completed by mixing the desired mass of TiO_2 with distilled water, measuring 200 mL in total, stirring for 5 minutes. After mixing, the desired mass of GAC was added and then stirred for another 5 minutes, as shown in Figure 11 below.

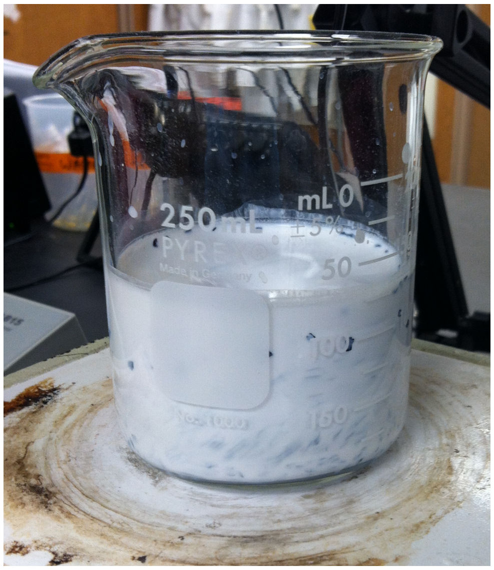

Figure 11: GAC and TiO_2 Solution Mixing

The TiO_2 and GAC solution was mixed vigorously to ensure that the GAC particles were fluidized in the solution. This was to reduce settling and to keep the TiO_2 solution passing through the particles pores. The mixture was then placed in an oven at 100°C until completely dry. Once dried the beaker containing the GAC and TiO_2 mixture was filled with 200mL of distilled water. The solution was then stirred slowly for 3 minutes to clean the GAC of non-embedded TiO_2. After being stirred, the solution was filtered with a sieve or water pump with a filter attachment. As shown in Figure 12 the filter was used to filter the TiO_2 solution from the embedded GAC. Repeat and refill with distilled water as needed to reduce the amount of non-embedded TiO_2 powder. The embedded GAC beaker was then placed back in the oven at 100°C overnight again to dry the remaining particles.

The embedded TiO_2 GAC was then removed from the oven, cooled for 30 minutes, placed in a screw-cap vial, and stored at room temperature.

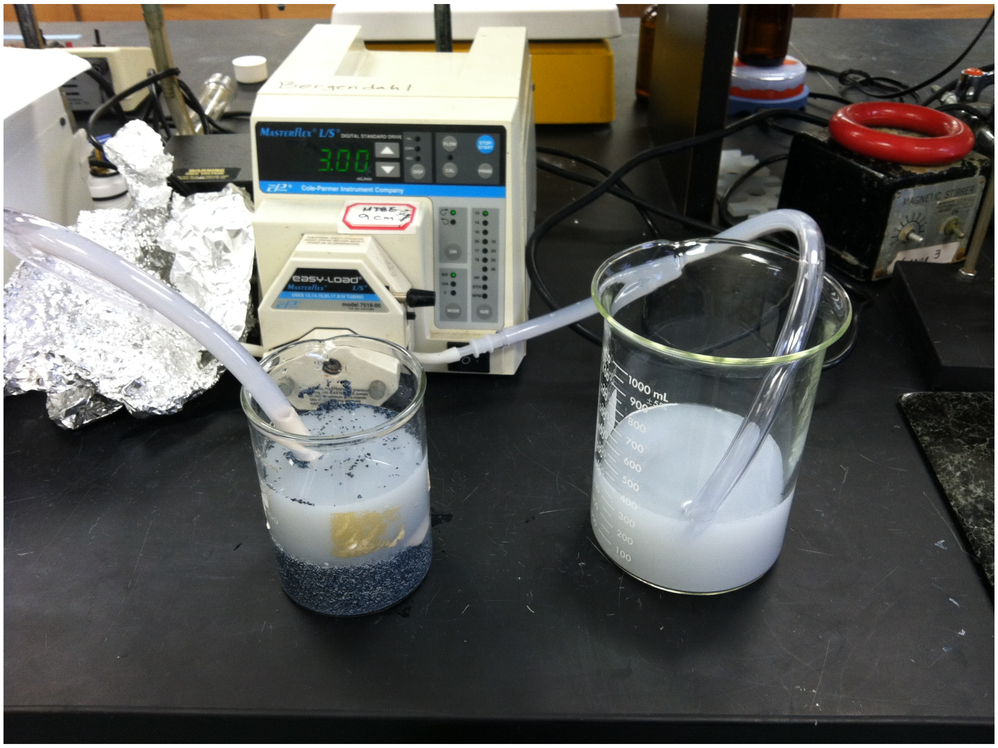

Figure 12: TiO_2 Filter Apparatus to Remove Non-Embedded TiO_2 (Master Flex L/S Pump)

3.7 – TiO_2 & UV adsorption tests

The combinations of adsorption and photocatalytic reactions were explored using a UV reactor apparatus and the previously made TiO_2-embedded GAC. The apparatus consisted of a 5 mL ACE glass incorporated UV reactor; UVP 5.5 watt UV light, a Masterflex L/S Cole-Parmer Instrument Company pump (Model # 7518-00), a 500mL filter flask, and connecting tubes of various diameters. Figure 13 shows a schematic for the system.

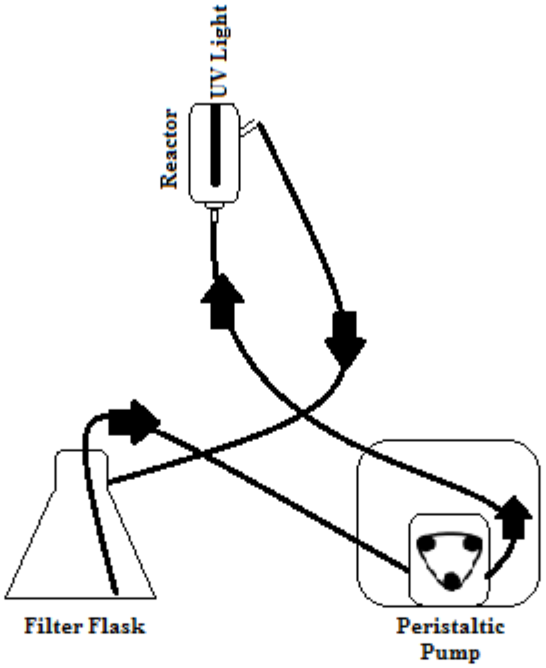

Figure 13: System Schematic

The system influent is from a filter flask that is capped air tight to ensure that no air flow with the atmosphere is occurring. A tube was fed from the filter flask to the systems pump. Connectors were used to allow different diameter tubes to be used throughout the process as well. The exit tube from the pump was attached to the reactor that sits perpendicular to the lab bench, as seen in Figure 14. The reactor includes a quartz center tube, which houses the UV light. This center tube screws to the reactor's outer core and the 5 mL volume between the two. The outflow tip on the reactor was then capped with a rubber stopper that housed a small diameter tube. This tube then flowed from the reactor and back into the filter flask to complete the process. All of the tubes diameters were determined by trial and error. To reduce the amount of atmosphere present in the system we had to reduce the diameter of the tubes as much as possible without restricting flow.

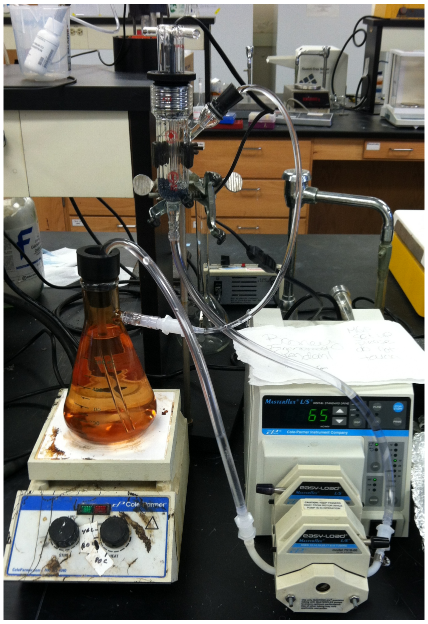

Figure 14: GAC and TiO_2 Reactor System

The desired 1,4 – dioxane concentration, 5 ppm, was mixed and 580 mL was poured into the filter flask. A large solution of 1,4 – dioxane was not required as long as there was enough to fill the system and reactor, while still allowing for the collection of 10 mL samples for GC testing. The key to the UV reactor was to spread the embedded GAC evenly amongst the reactors housing to allow for an even contact time with the UV light. The mass of GAC to be placed in the UV reactor depends on the optimum mass used during the batch equilibrium trials. In our experiment, we had a ratio of 0.05 g of GAC to 20 mL of water; thus, 1.45 g of GAC for the 580 mL in the UV reactor. The flow rate for the entire system was determined by the amount of fluid that can be optimized in the reactor without overflowing it. With the GAC in the reactor, the flow rate was set to 85 mL/min because the particles in the reactor were restricting the flow into the reactor.

To analyze the effects of the embedded GAC adsorption and photocatalytic properties the system must first reach equilibrium. After starting the pump the system is run for three hours to reach equilibrium. Samples are taken at 0 and 1.5 hours to ensure that the system has reach equilibrium. Upon reaching equilibrium, the UV light is turned on and subsequent samples will be taken at 0, 1, 2 hours to analyze the effects of the photocatalytic reaction on the system. Samples are taken by using a 10mL micropipette with a 10mL tip. 10mL of the 1,4 dioxane solution was taken from the filter flask, placed in the GC vials, and properly labeled and stored in a dark area until it was analyzed.

4.0 – Results & Discussion

The goal of this project was to evaluate the treatment efficiency of a reactor that utilized TiO_2 nanoparticles embedded on GAC in a fixed bed UV reactor configuration. The degradation of the organic contaminant 1,4-dioxane was evaluated with gas chromatography. The data was used to carry out a full-scale system design as well as to make recommendations for future research.

4.1 – 1, 4 – Dioxane Adsorption Isotherm Experiments

The seven GAC samples chosen for study were run through a series of 24-hour equilibrium testing. To determine the proper mass to complete experimentation with all GAC samples first extensive equilibrium testing was completed with the TIGG GAC. To determine the appropriate isotherm equation to use in analyzing the collected data points linearized forms of both the Landmuir and Freundlich isotherms were plotted. From these linearized plots we are able to see which the data points best fit by looking at the R^2 values. Below in Figures 15 and 16 the linearized plots are shown.

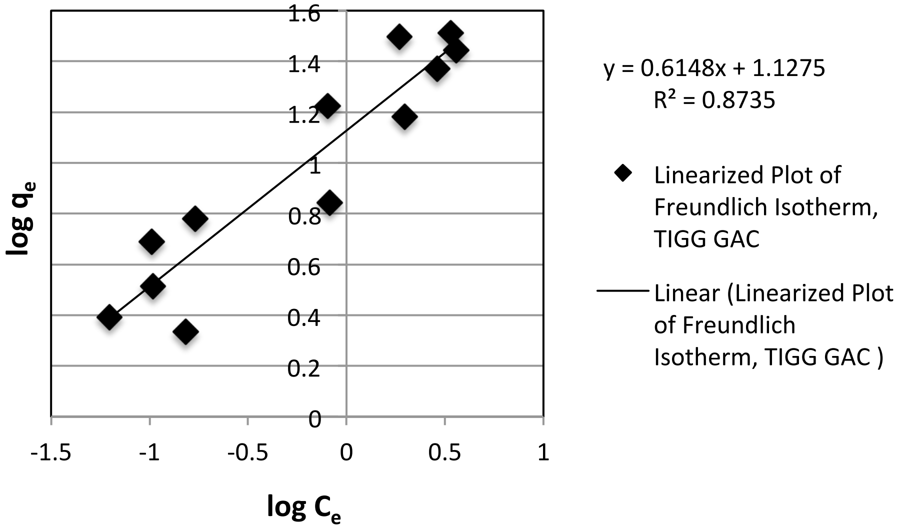

Figure 15: Linearized Plot of Freundlich Isotherm, TIGG GAC

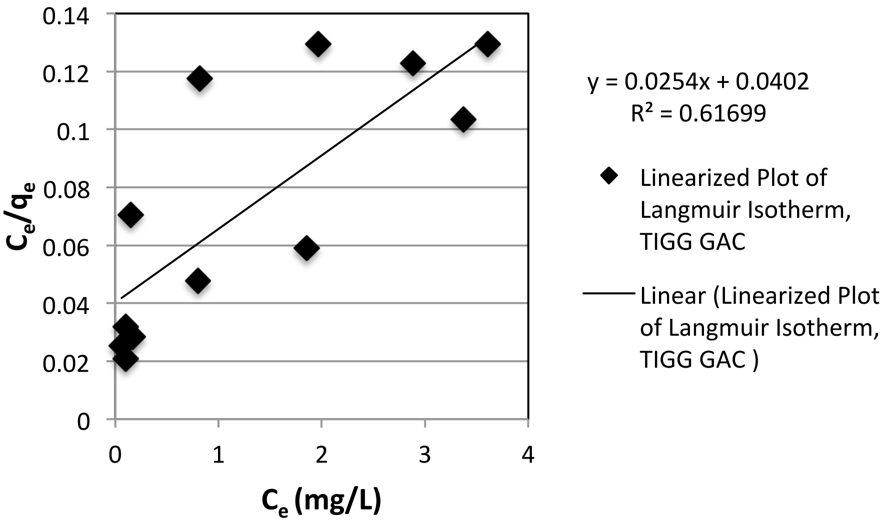

Figure 16: Linearized Plot of Langmuir Isotherm, TIGG GAC

As shown above, the linearized Freundlich isotherm plot yielded a larger R^2 value, 0.87, compared to the linearized Langmuir isotherm R^2 value of 0.620. For this reason the Freundlich isotherm was chosen to analyze the data points shown below in Figure 17.

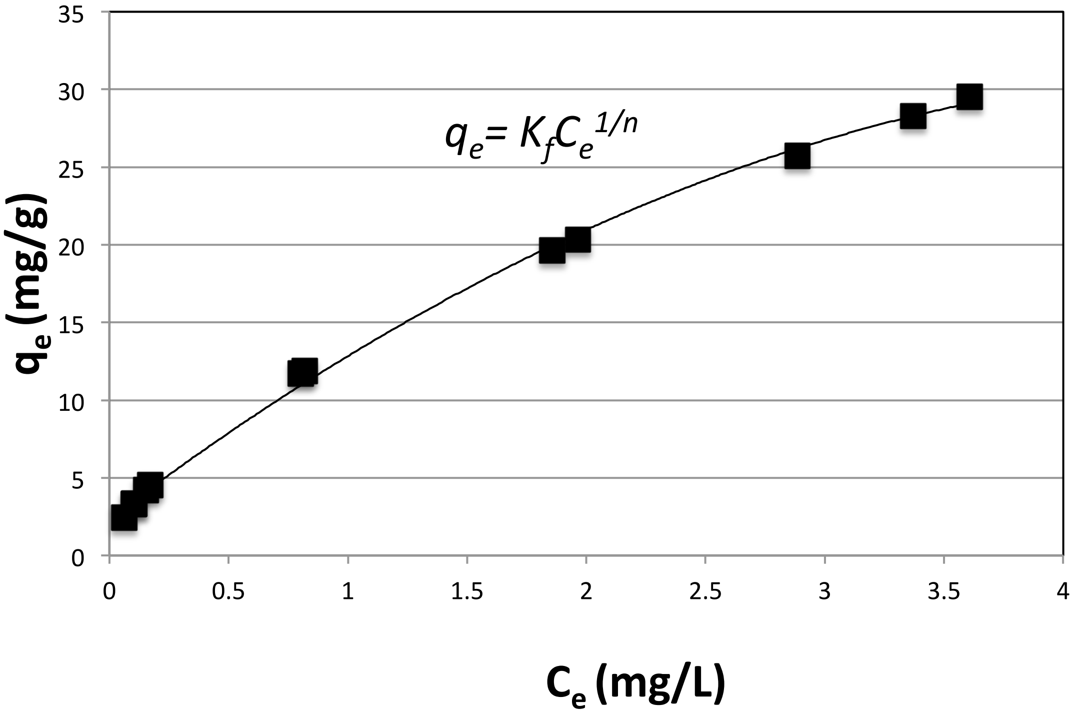

Figure 17: Isotherm with TIGG GAC

With the appropriate isotherm equation for this data, $q_e = K_f C_e^{1/n}$, we were able to determine the mass of GAC needed for the desired removal rate, shown in Table 6.

Table 6: Determining Desired GAC Mass

C_e (mg/L)	Q_e (mg/L)	Mass GAC (g)
1.00	12.84	0.31
1.50	17.20	0.20
1.75	19.15	0.17
2.00	20.97	0.14

The mass chosen for further testing was found to be 0.20 g.

4.2 – Granular Activated Carbon Adsorption Efficiency Testing

All GAC samples were run in a 24-hour equilibrium experiment to determine which would be most suited for additional experimentation. These GAC types were determined to be: Genesis, Fisher Brand, Calgon, and Omnipure 12x40, shown in Table 7. These results indicated the GAC samples would be ideal to show the removal at equilibrium followed by possible increased removal of the TiO_2 embedded GAC when exposed to UV light.

Table 7: GAC Contaminant Removal at Equilibrium

GAC Type	C_f (mg/L)	Mass of Contaminant Adsorbed (mg/L)
Omnipure 12x40	1.78	3.22
Genesis	1.85	3.15
Calgon	1.96	3.04
TIGG	2.08	2.92
Fisher Brand	2.16	2.84
Norit	2.51	2.49
Omnipure 20x50	3.17	1.83

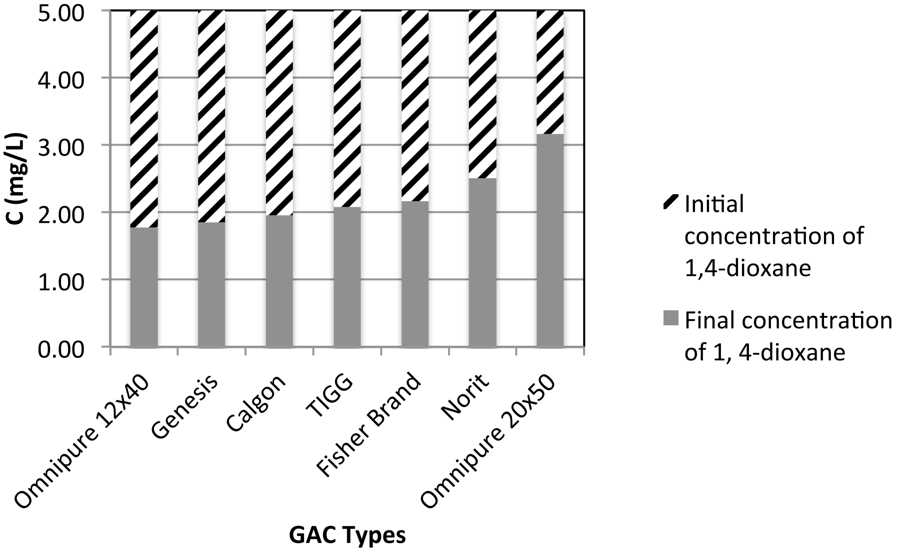

Figure 18: Graph of Contaminant Removal at Equilibrium with .2 g GAC

4.3 – TiO_2 Embedding

Each type of GAC adsorbed different amounts of 1,4 – dioxane and would then react differently to being embedded with TiO_2. Three samples were chosen for TiO_2 experimentation: Genesis, TIGG, Calgon, and Omnipure 12x40. Each GAC type was embedded using the same process as explained in the methodology section. Ultimately, the results were based on visual observations of the carbon particles and not quantitative. The characteristics that were analyzed through the observations were:

1) If the carbon particles maintained their size and were not broken down in the embedding process

2) Particle coverage by the TiO_2. i.e. how much TiO_2 was present on each particle

3) Quantity of GAC particles that had TiO_2 on them.

After testing each GAC type it was determined that Omnipure 12x40 showed the best TiO_2 embedding results. It had efficient coverage on each GAC particle and also had a large quantity of particles with TiO_2 attached as shown in Figure 19 below.

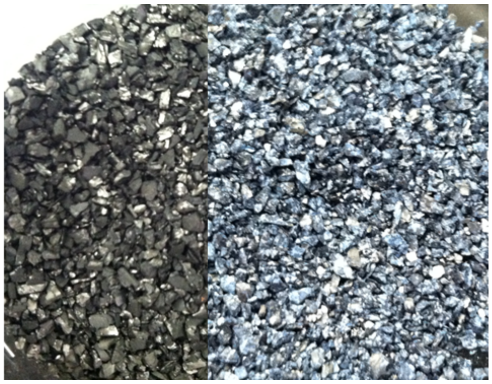

Figure 19: Omnipure 12x40 Prior to TiO_2 Embedding (left), After TiO_2 Embedding (right)

Other GAC types, like Genesis did not embed as well. It had spotty TiO_2 areas of attachment and some carbons did not have any TiO_2 at all, as seen in Figure 20 below.

Although the TiO_2 did embed to the carbon material, Genesis was not as effective as Omnipure 12x40.

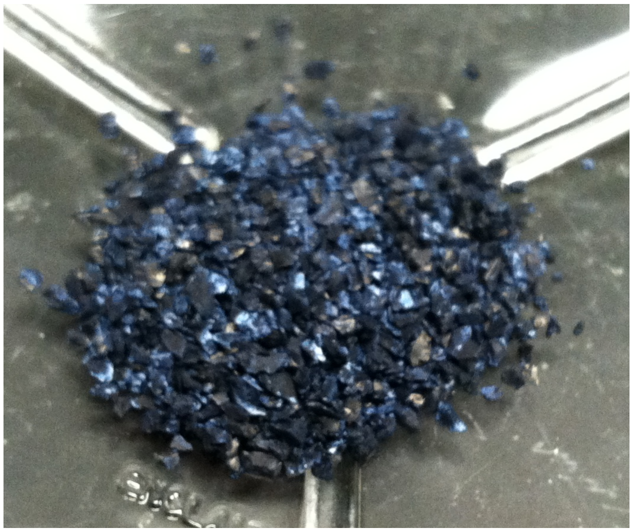

Figure 20: Genesis TiO_2 Embedded GAC

4.4 – Omnipure 12x40 Isotherm Study

Due to receptiveness to embedding with TiO_2, Omnipure 12x40 was the chosen GAC for further study. The GAC was then put through a series of 24-hour equilibrium testing to determine a mass needed to remove just above 50% of 1,4-dioxane contamination from water. From the 24-hour equilibrium testing an isotherm was constructed was constructed to display the adsorption efficiency of the GAC. To determine which isotherm, Freundlich or Langmuir, was best fit for this analysis first the linearized forms of the isotherms were constructed, shown below in Figures 21 and 22.

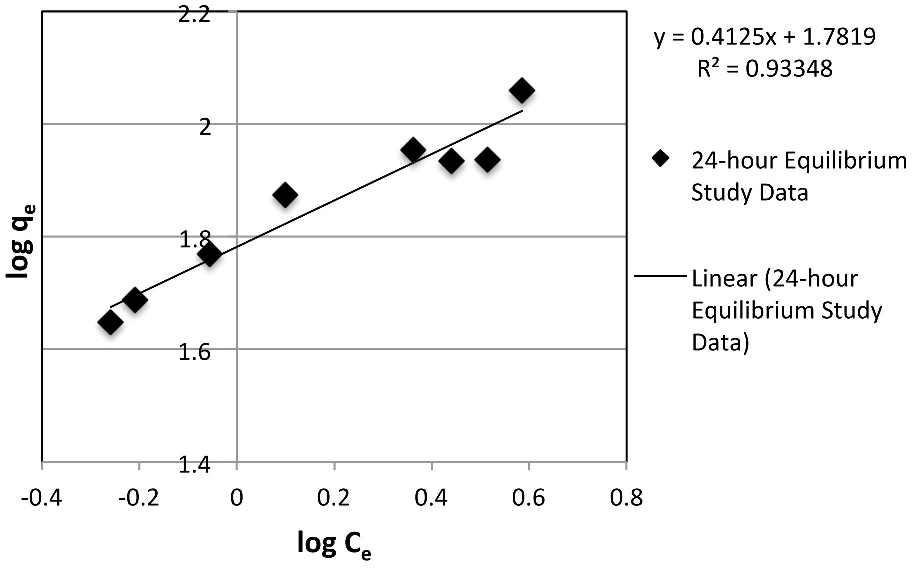

Figure 21: Plot of Linearized Freundlich Isotherm

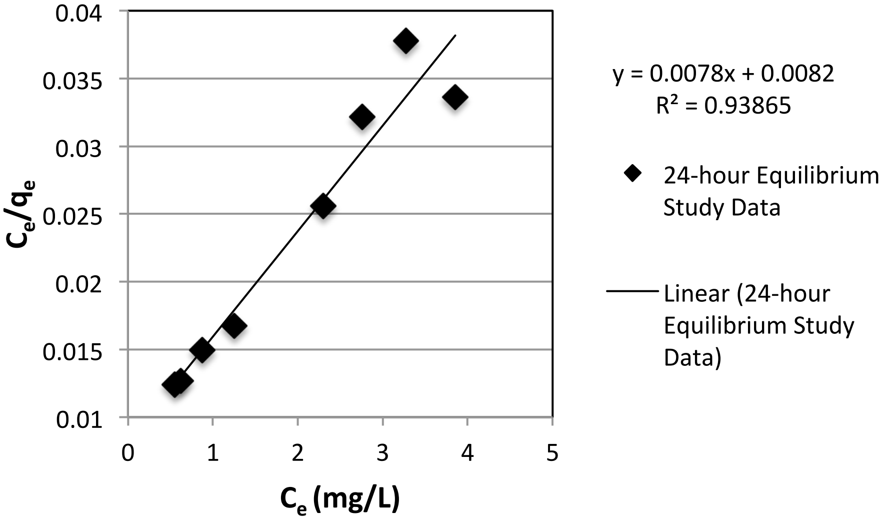

Figure 22: Plot of Linearized Langmuir Isotherm

As done previously with the equilibrium testing preformed with the TIGG GAC the R^2 values were evaluated. Both linear forms of the isotherm have a R^2 value approximately of 0.93, meaning that either isotherm would be appropriate in analyzing the adsorption of 1,4-dioxane with Omnipure 12x40 GAC. The Freundlich isotherm was chosen to represent the 24-hour equilibrium testing results to determine the GAC mass for optimal removal. This isotherm is shown below in Figure 23.

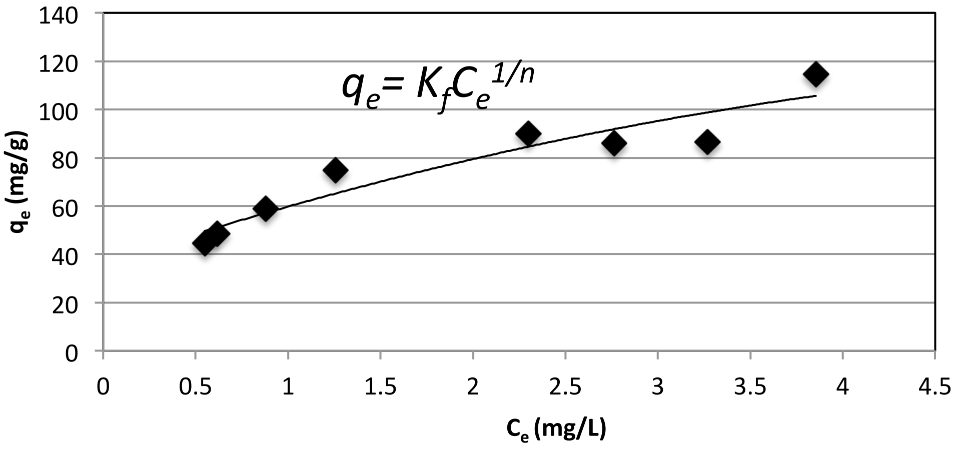

Figure 23: Isotherm of Omnipure 12x40 GAC

This figure shows that the mass capable of removing 50% of contaminant from water to be 0.03 g, as shown in Table 8.

Table 8: Masses of GAC needed for Final Concentrations of Contaminant

C_e (mg/L)	Mass of GAC (g)
1	0.07
1.5	0.05
2	0.04
2.5	0.03
3	0.02

4.5 - Preliminary Tests

Before we could accurately run our experiments we had to determine: 1) what the general 1,4-dioxane loss in the system was without GAC or UV light; and 2) what the 1,4-dioxane loss in the system was without active carbon but with UV light.

Table 9: Reactor Preliminary Test

	Time (hr)	Start Peak Area	Finish Peak Area	Peak Area Loss
No GAC No UV	3	625.12	177.91	72%
No GAC No UV	3	426	320	25%
No GAC No UV	3	1419	930.6	35%
No GAC No UV	3	607.3	547.4	10%
No GAC Yes UV	3	674	445	34%

Table 8 shows the preliminary tests in order of completion. Although the data was somewhat variable, the goal was to see a small loss in the system. The first run showed a dramatic loss of 1,4 whereas the subsequent runs improved greatly. The only factor that was manipulated with our system during these preliminary runs was the diameter of the tubing used. The tubing was reduced in diameter to reduce the atmosphere present in the system. Only after completing these preliminary runs were we able to continue with running our samples.

4.6 – Photocatalytic Reactor

The UV reactor system was used to determine the 1,4 adsorption effectiveness on GAC with regeneration by photocatalytic reactions. Figure 24 shows the reduction in concentration of 1,4 – dioxane concentration over time. This was a six-hour test with three samples analyzed prior to UV exposure and two with UV exposure. As can be seen, a majority of the 1,4 concentration reduction takes place before any UV exposure, which was the time when the system was progressing towards equilibrium. Once the UV light is turned on the concentration began to slowly drop within the hour; however, after the first hour the concentration was dramatically reduced.

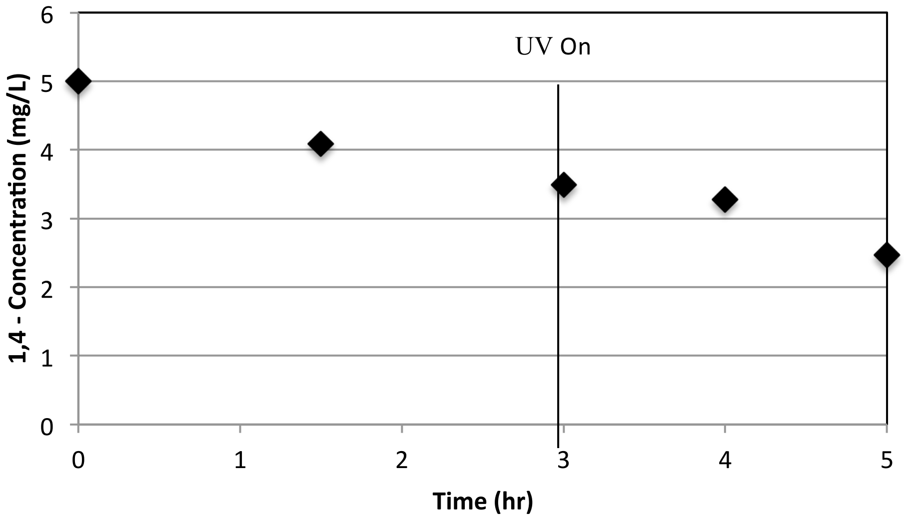

Figure 24: UV Reactor Run

After analyzing the equilibrium and UV runs the graph in Figure 25 below can be seen. This shows the equilibrium having a negative slope of 0.50 whereas the UV reactor has a negative slope of 0.51. Although this is not a significantly greater increase in negative slope it does still reveal that the UV reactor had a greater reduction in concentration over time. Also, simply observing the points at hour 4 & 5 show a significant negative slope compared to those of the equilibrium samples.

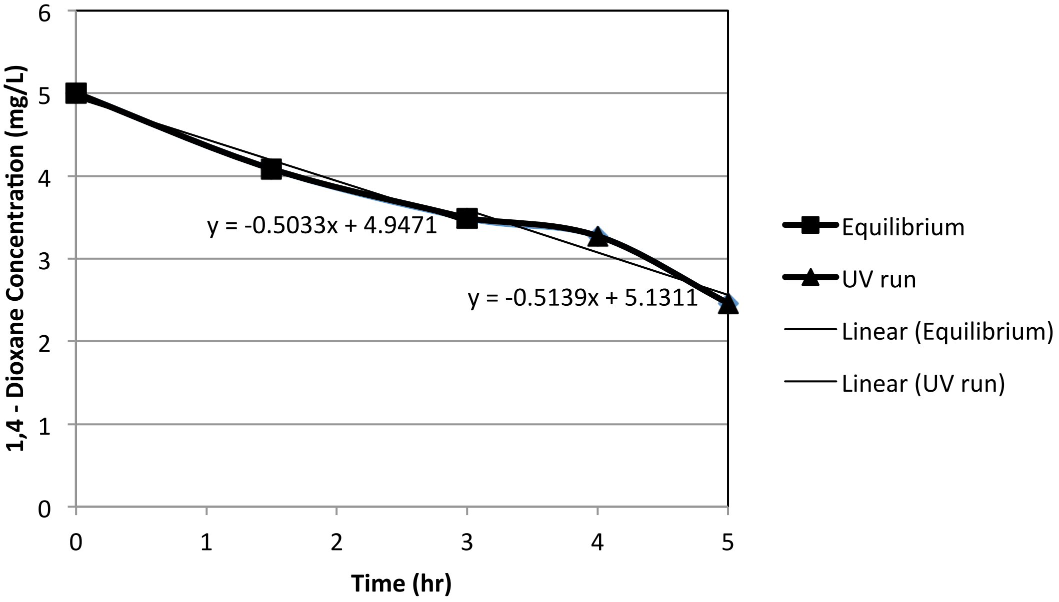

Figure 25: UV Reactor Run with Equilibrium and UV Run Slopes

The increase in negative slope can represent the photocatalytic regeneration reaction occurring from the TiO_2. To confirm the photocatalytic adsorption properties the graph would ideally show a gradual decrease in concentration prior to the UV light. Over a period of time it would begin to level off as it would reach equilibrium and there would be a very small decrease in concentration over time. Then after the UV light is turned on the 1,4 – dioxane concentration would begin to decrease again as the regeneration photocatalytic reactions occur. The graph above does show the trend of decreasing initially to equilibrium and then after the UV light is turned on the concentration begins to decrease again. Thus, GAC regeneration through this photocatalytic process shows great potential.

5.0 – Full-Scale Design System

This chapter details a possible full-scale version of the reactor system detailed throughout this report. The proposed product allows for a better visualization of our design by evaluating it in a practical application rather than on a laboratory bench.

5.1 - System Design Parameters

The design parameters for this full-scale design consists of a maximum flow rate of 12,000 gallons/month of contaminated water with a 1,4 – dioxane concentration of 600 μg/L. Figure 26 below shows the flow schematic for this system.

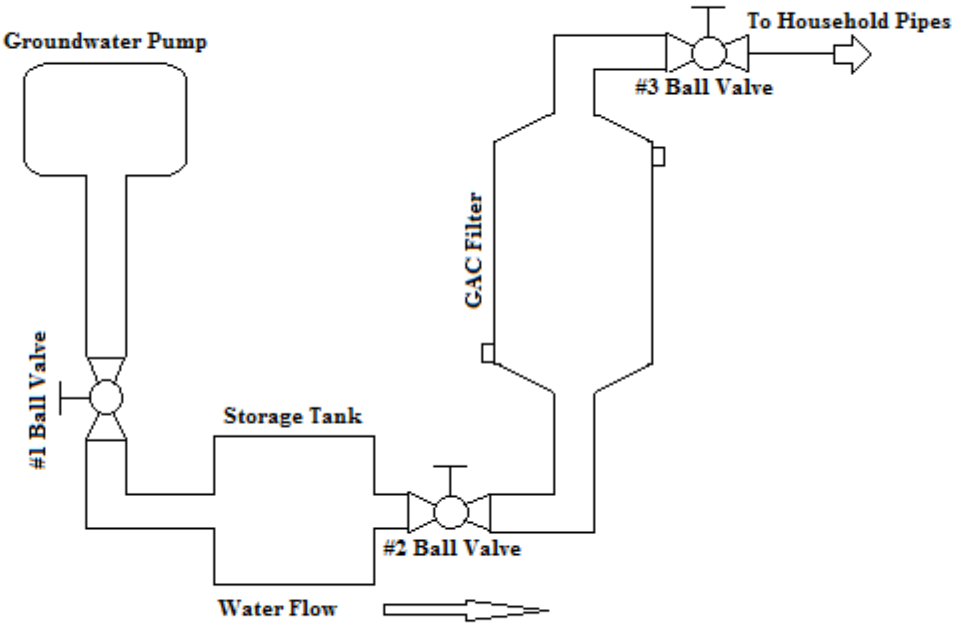

Figure 26: Proposed Flow Schematic

The system is designed to reduce the 1,4-dioxane concentration to 0 μg/L for the entirety of the twenty-four month lifespan of the filter. The mass of activated carbon is 20% above the calculated required amount as a factor of safety to ensure that the life of the bed will last the full 6 months. The materials used for the system are normal household ¾” copper piping, Polyvinyl Chloride (PVC) 50 gallon storage tank, and a

PVC GAC filter. PVC was chosen to avoid the complications that arise with steel tanks such as corrosion, which would reduce the tanks lifespan. Also, ball valves were used for simplicity and durability for the system.

5.2 - Calculations

The general calculations performed to determine the optimal dimensions for this GAC filter follow below. This household system was designed for a family of 4 which results in an average flow rate of about 12,000 gal/month (USEPA, 2014). Thus, for a system designed to have an average bed life of 50years, assuming 1,4 – dioxane is the only contaminant present in the water, the total volume of water would be 7.2 x 10^6 gallons.

$$600\text{ months} = \frac{\mathrm{V}}{12{,}000\,\frac{\mathrm{gal}}{\mathrm{month}}}$$

$$\mathbf{V = 7.2 * 10^6\ gal}$$

This system is being designed to exhaustion which results in the final concentration being 0 μg/L. The calculations to determine the mass required of GAC per volume are found below. The q_e value is determined by analyzing the Omnipure 12x40 Freundlich graphs linear trendline of slope and y-constant.

$$\frac{V_{\mathrm{fluid}}}{V_{\mathrm{GAC}}} = \frac{q_e \rho_{\mathrm{GAC}}}{C_0}$$

$$\frac{V_{\mathrm{GAC}} \rho_{\mathrm{GAC}}}{V_{\mathrm{fluid}}} = \frac{C_0}{q_e}$$

$$\frac{M_{\mathrm{GAC}}}{V_{\mathrm{fluid}}} = \frac{C_0}{q_e}$$

$$\frac{M_{\mathrm{GAC}}}{V_{\mathrm{fluid}}} = \frac{0.600\,\frac{\mathrm{mg}}{\mathrm{L}}}{60.52 * (0.600^{0.4125})}$$

$$\frac{\mathbf{M_{GAC}}}{\mathbf{V_{fluid}}} = \mathbf{0.012\frac{mg}{L}}$$

After converting to mg/gal the resulting mass per volume will be 0.012 mg/gal. Which to determine the mass over a 50-year lifespan the required mass would be 8.64 x 10^4 mg of GAC. This filter will also have a velocity of 0.4 m/min with an average GAC density of 2 x 10^9 mg/m^3 (TIGG, 2014). This previous information was then used to calculate the dimensions of the filter.

$$Q = vA$$

$$0.0011\frac{m^3}{min} = \left(0.4\frac{m}{min}\right) * A$$

$$\mathbf{A = 0.0028\ m^2}$$

From this cross-sectional area, it was found that the required diameter of the contactor is 0.06 m or about 2.37 inches. The next required dimension is the height of the reactor, which was designed to be roughly 0.07 m or about 2.8 inches with a 20% factor of safety. The required mass of GAC to fill the filter is 3.92 x 10^5 mg, accounting for the 20% factor of safety.

$$\rho = \frac{m}{V}$$

$$\rho = \frac{m}{A * h}$$

$$2x10^9\ \frac{mg}{m^3} = \frac{3.28 *\ 10^5\ mg}{0.0028\ m^2 * h}$$

$$h = \frac{3.28 *\ 10^5\ mg}{0.0028\ m^2 * 2 * 10^9\ \frac{mg}{m^3}}$$

$$h = 0.059\ m$$

With 20% factor of safety:

$$\mathbf{h = 0.07\ m}$$

With these dimensions and flow results an inflow filter schematic image is shown in Figure 27.

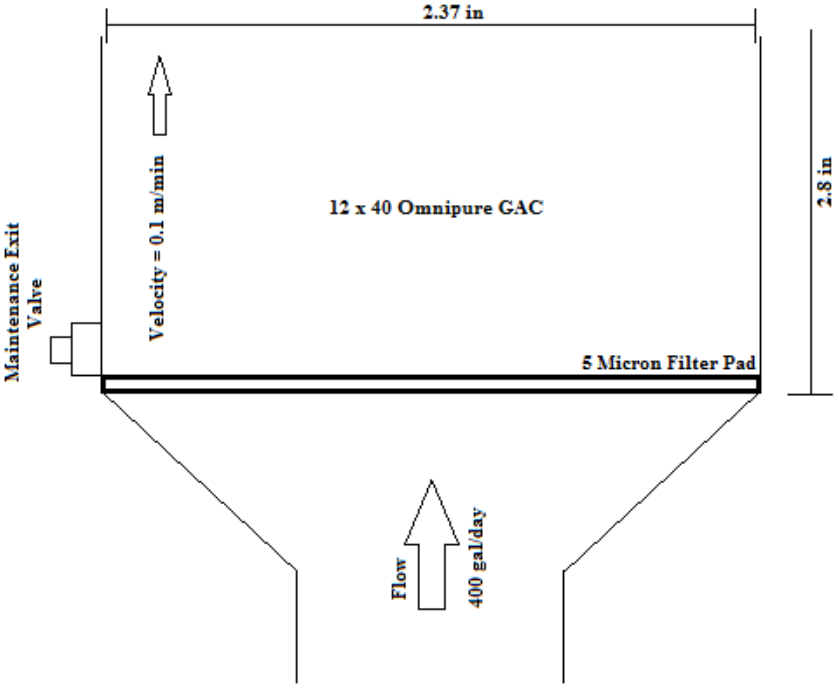

Figure 27: Proposed Filter Schematic

The 5-micron filter pad is placed in the filter at the bottom (inflow) and top (outflow) to allow the passage of the water but secure the GAC in the filter and not allow it to be released in the outflow. Two 0.5 inches maintenance screw caps are located on the bottom and top of the filter to allow the system to be flushed of saturated GAC and stocked with virgin GAC.

6.0 – Recommendations

We recommend that further research and experimentation be done to improve the process to embed the TiO_2 on GAC, and to further develop our understanding of the photocatalytic adsorption characteristics with 1,4 – dioxane. This further research will be able to clarify certain unknowns in this process and gather more data to support the photocatalytic GAC regeneration hypothesis.

The attachment of TiO_2 to GAC could be better quantified and researched further to explore the attachment efficiency within the macro and micro pores of the particles. Throughout our experiments, the results of TiO_2 embedding were analyzed through only qualitative observations of the particles. Being able to quantify the attachment efficiency would allow improvement of the embedding process, and decrease excess raw materials. Also, quantifying the process would allow for attachment methods to be further explored, optimizing the efficiency of adsorption and strength of the embedded TiO_2.

The photocatalytic reactor should be further explored as well. First, further testing should be completed with the shown reactor design. Eventually, however, an improved reactor design in regards to system and flow process is also essential in continued studies. It is suggested to decrease the headspace in the system, which will limit the loss of 1,4 – dioxane. A zero loss system would be ideal, however, a system allowing minimal loss is a more reasonable goal. Limiting the atmospheric loss will strengthen the hypothesis of GAC regeneration with TiO_2 and UV light. Other factors that should be researched are the optimal time of exposure for the photocatalytic regeneration and more frequent sampling of the reactor. More frequent sampling will allow for more complete data collection.

Completing this study is an achievable goal now that base knowledge has been gathered and fabricated promising results. The primary requirement to complete the study is ample amounts of testing of the reactor designed and improvements in system efficiency.

7.0 – Conclusion

From the work completed in this study and those previously performed, it is apparent that the treatment of 1,4 – dioxane with GAC embedded with TiO_2 and exposed to ultraviolet light, is feasible to reduce the concentration of the contaminant in water through adsorption with regeneration processes. The graph represents the ideal slopes and line curves that exist in common adsorption and regeneration plots. Also, it was determined that GAC particles can effectively be embedded with TiO_2 in a heat treatment coating process. The specific GAC types will vary in adsorption efficiency of 1,4 – dioxane and TiO_2 embedding due to the particles characteristics.

From our testing of various GAC types, we were able to determine that treatment of 1,4 – dioxane is feasible with activated carbon. We also found that Omnipure 12x40 was most effective in the removal of 1,4 – dioxane. Out of the seven different GAC types tested it adsorbed 3.22 mg/L from a 5 mg/L solution, 1.83 mg/L more than the lowest removal and 0.07 mg/L more than the second highest GAC. This is thought be due to the GAC being derived from a coconut source, which is known to perform well in the treatment of 1,4 – dioxane, as well as its physical characteristics.

The Omnipure 12x40 was also the GAC type that most efficiently embedded with TiO_2 nanoparticles. It visually showed the most efficient coverage on each GAC particle and also had a large quantity of particles with TiO_2 embedded.

Lastly, after a series of reactor tests with the photocatalytic compound it was found that the system began to reach saturation after 3 hours and also was successful in regenerating the GAC to adsorb a higher mass of 1,4 – dioxane. This method of treatment shows great promise and it is concluded that further research should be pursued to fully analyze the treatment capability of this method.

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Appendices

Appendix A – Levels of Significant Exposure to 1,4 – Dioxane – Oral

(ASTDR, 2007)

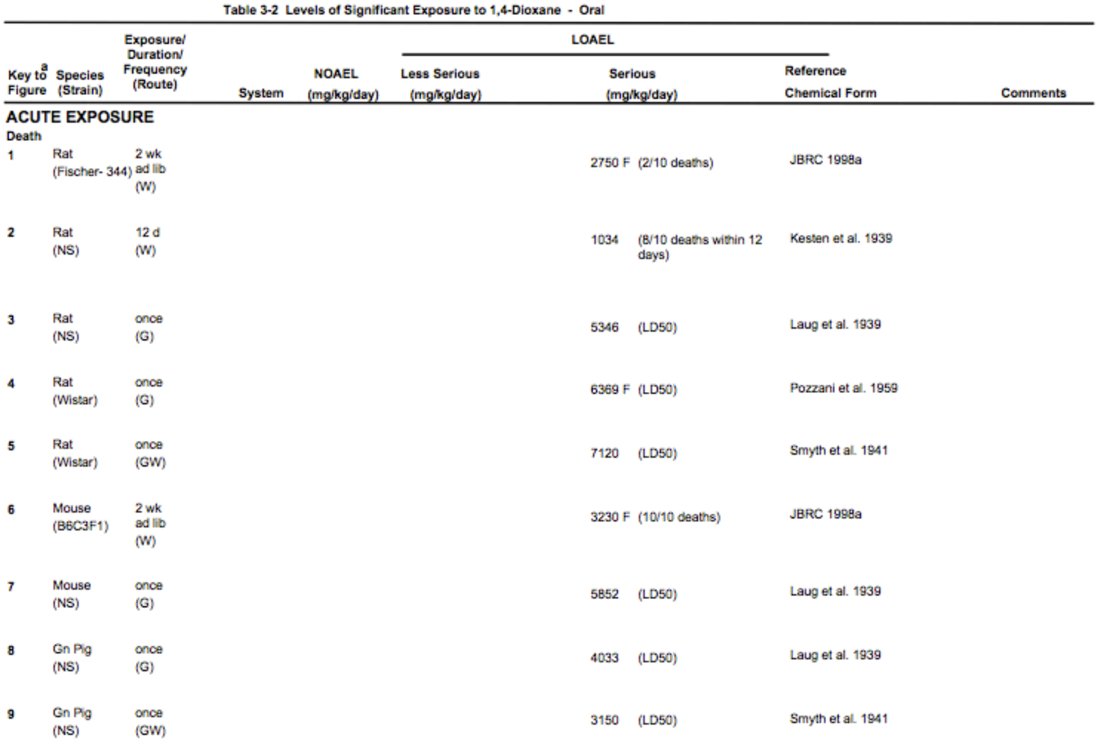

Table 3-2 Levels of Significant Exposure to 1,4-Dioxane - Oral

					LOAEL			
Key to[a] Figure	Species (Strain)	Exposure/ Duration/ Frequency (Route)	System	NOAEL (mg/kg/day)	Less Serious (mg/kg/day)	Serious (mg/kg/day)	Reference Chemical Form	Comments
ACUTE EXPOSURE								
Death								
1	Rat (Fischer- 344)	2 wk ad lib (W)				2750 F (2/10 deaths)	JBRC 1998a	
2	Rat (NS)	12 d (W)				1034 (8/10 deaths within 12 days)	Kesten et al. 1939	
3	Rat (NS)	once (G)				5346 (LD50)	Laug et al. 1939	
4	Rat (Wistar)	once (G)				6369 F (LD50)	Pozzani et al. 1959	
5	Rat (Wistar)	once (GW)				7120 (LD50)	Smyth et al. 1941	
6	Mouse (B6C3F1)	2 wk ad lib (W)				3230 F (10/10 deaths)	JBRC 1998a	
7	Mouse (NS)	once (G)				5852 (LD50)	Laug et al. 1939	
8	Gn Pig (NS)	once (G)				4033 (LD50)	Laug et al. 1939	
9	Gn Pig (NS)	once (GW)				3150 (LD50)	Smyth et al. 1941	

Table 3-2 Levels of Significant Exposure to 1,4-Dioxane - Oral (continued)

Key to[a] Figure	Species (Strain)	Exposure/ Duration/ Frequency (Route)	System	NOAEL (mg/kg/day)	LOAEL		Reference Chemical Form	Comments
					Less Serious (mg/kg/day)	Serious (mg/kg/day)		
10	Rabbit (NS)	once (GW)				2068 (5/5 deaths in 2-6 days)	De Navasquez 1935	
Systemic								
11	Rat (Fischer- 344)	2 wk ad lib (W)	Resp	370 M	1010 M (nuclear enlargement of olfactory epithelium)		JBRC 1998a	
			Hepatic	1040 F	2750 F (hepatocyte swelling and vacuolation)			
			Renal	1040 F	2750 F (hydropic change in proximal tubule)			
			Bd Wt	1040 F		2750 F (24% reduced body weight gain)		
12	Rat (NS)	12 d (W)	Hepatic		1034 (unspecified liver abnormalities)		Kesten et al. 1939	
			Renal			1034 (kidney degeneration)		
13	Rat (Sprague-Dawley)	once (GW)	Hepatic	1000 M			Stott et al. 1981	No histopathological alterations in the liver.
14	Mouse (B6C3F1)	2 wk ad lib (W)	Hepatic	1380 M	2550 M (swelling of central area)		JBRC 1998a	
			Bd Wt	1380 M	2550 M (swelling of central area)			

Table 3-2 Levels of Significant Exposure to 1,4-Dioxane - Oral (continued)

Key to[a] Figure	Species (Strain)	Exposure/ Duration/ Frequency (Route)	System	NOAEL (mg/kg/day)	LOAEL		Reference Chemical Form	Comments
					Less Serious (mg/kg/day)	Serious (mg/kg/day)		
Neurological								
15	Rat (Fischer- 344)	2 wk ad lib (W)		1040 F		2750 F (vacuolar changes in the brain)	JBRC 1998a	
16	Rabbit (NS)	once (GW)		207		1034 (narcolepsy, slow gate, ataxia)	De Navasquez 1935	
17	Rabbit (NS)	once (G)		1760		4400 (staggering)	Knoefel 1935	
Developmental								
18	Rat (Sprague-Dawley)	9 d Gd 6-15 (GW)		516[b]	1033 (decreased fetal weight; reduced sternum ossification)		Giavini et al. 1985	
INTERMEDIATE EXPOSURE								
Death								
19	Rat (NS)	34 d ad lib (W)				1000 (5/6 deaths before the 35th day)	Fairley et al. 1934	
20	Rat (Sherman)	2-4 mo ad lib (W)				1015 M (significant early mortality beginning at 2 months in the study)	Kociba et al. 1974	

Table 3-2 Levels of Significant Exposure to 1,4-Dioxane - Oral (continued)

Key to^a Figure	Species (Strain)	Exposure/ Duration/ Frequency (Route)	System	NOAEL (mg/kg)	LOAEL		Reference Chemical Form	Comments
					Less Serious (mg/kg)	Serious (mg/kg)		
Systemic								
21	Rat (NS)	34 d ad lib (W)	Gastro		1428 (gastroenteritis)		Fairley et al. 1934	
			Hepatic			1428 (hepatocyte degeneration)		
			Renal			1428 (renal cortex degeneration)		

Table 3-2 Levels of Significant Exposure to 1,4-Dioxane - Oral (continued)

Key to^a Figure	Species (Strain)	Exposure/ Duration/ Frequency (Route)	System	NOAEL (mg/kg/day)	LOAEL		Reference Chemical Form	Comments
					Less Serious (mg/kg/day)	Serious (mg/kg/day)		
22	Rat (Fischer- 344)	13 wk ad lib (W)	Resp	52 M	126 M (nuclear enlargement of respiratory epithelium)		Kano et al. 2008	NOAELs are for histopathology of organs and tissues.
			Cardio	1614 F				
			Gastro	1614 F				
			Hemato	657 M	1554 M (increased red blood cell, hemoglobin, hematocrit, neutrophils)			
			Musc/skel	1614 F				
			Hepatic	52^c M	126 M (swelling in central area)			
			Renal	274 M 83^d F	657 M (nuclear enlargement of proximal tubule) 185^d F (increased kidney weight)			
			Endocr	1614 F				
			Dermal	1614 F				
			Ocular	1614 F				
			Bd Wt	657 M	756 F (12% reduction in weight gain)	1614 F (21% reduction in body weight gain)		
23	Rat (Sprague-Dawley)	7 wk 5 d/wk (GW)	Hepatic	100 M	1000 M (fatty vacuoles in cytoplasm of hepatocytes)		Lundberg et al. 1987	

Table 3-2 Levels of Significant Exposure to 1,4-Dioxane - Oral (continued)

Key to^a Figure	Species (Strain)	Exposure/ Duration/ Frequency (Route)	System	NOAEL (mg/kg/day)	LOAEL		Reference Chemical Form	Comments
					Less Serious (mg/kg/day)	Serious (mg/kg/day)		
24	Rat (Sprague-Dawley)	11 wk ad lib (W)	Hepatic	10 M	1000 M (minimal hepatocellular swelling)		Stott et al. 1981	
			Bd Wt	1000 M				
25	Mouse (NS)	67 d ad lib (W)	Hepatic			2916 (hepatocyte degeneration)	Fairley et al. 1934	Only one dose level was tested.
			Renal			2916 (cell degeneration in renal cortex)		

Table 3-2 Levels of Significant Exposure to 1,4-Dioxane - Oral (continued)

Key to Figure[a]	Species (Strain)	Exposure/ Duration/ Frequency (Route)	System	NOAEL (mg/kg/day)	LOAEL Less Serious (mg/kg/day)	LOAEL Serious (mg/kg/day)	Reference Chemical Form	Comments
26	Mouse (B6C3F1)	13 wk ad lib (W)	Resp	170 F	387 F (nuclear enlargement of bronchial epithelium)		Kano et al. 2008	NOAELs are for microscopic examination of organs and tissues.
			Cardio	2669 F				
			Gastro	2669 F				
			Hemato	882 M	1570 M (increase red blood cell, hemoglobin, hematocrit, corpuscular volume)			
			Musc/skel	2669 F				
			Hepatic	231 M	585 M (single cell necrosis and swelling of central area)			
			Renal	1620 F	2669 F (increased relative kidney weight)			
			Endocr	2669 F				
			Dermal	2669 F				
			Ocular	2669 F				
			Bd Wt	882[d] M 2669 F		1570 M (29% reduced body weight gain)		
Immuno/ Lymphoret								
27	Rat (Fischer- 344)	13 wk ad lib (W)		1614 F			Kano et al. 2008	No histological effects in lymph nodes, spleen, or thymus.

Table 3-2 Levels of Significant Exposure to 1,4-Dioxane - Oral (continued)

Key to Figure[a]	Species (Strain)	Exposure/ Duration/ Frequency (Route)	System	NOAEL (mg/kg/day)	LOAEL Less Serious (mg/kg/day)	LOAEL Serious (mg/kg/day)	Reference Chemical Form	Comments
28	Mouse (B6C3F1)	13 wk ad lib (W)		2669 F			Kano et al. 2008	No histological effects in lymph nodes, spleen, or thymus.
Neurological								
29	Rat (Fischer- 344)	13 wk ad lib (W)		657 M		1554 M (vacuolar changes in the brain)	Kano et al. 2008	
30	Mouse (B6C3F1)	13 wk ad libi (W)		2669 F			Kano et al. 2008	No histological effects in brain, spinal cord, or sciatic nerve.
Reproductive								
31	Rat (Fischer- 344)	13 wk ad lib (W)		1554[d] M 1614 F			Kano et al. 2008	No histological effects in reproductive organs.
32	Mouse (B6C3F1)	13 wk ad lib (W)		1570[d] M 2669 F			Kano et al. 2008	No histological effects on reproductive organs.
CHRONIC EXPOSURE								
Death								
33	Rat F344/DuCrj	2 yr ad lib (W)				274 M (increased early mortality)	Kano et al. 2009	

Table 3-2 Levels of Significant Exposure to 1,4-Dioxane - Oral (continued)

Key to Figure[a]	Species (Strain)	Exposure/ Duration/ Frequency (Route)	System	NOAEL (mg/kg/day)	LOAEL		Reference Chemical Form	Comments
					Less Serious (mg/kg/day)	Serious (mg/kg/day)		
34	Rat (Osborne-Mendel)	110 wk ad lib (W)				240 M (early mortality)	NCI 1978	
35	Mouse Crj:BDF1	2 yr ad lib (W)				278 F (increased early mortality)	Kano et al. 2009	
36	Mouse (B6C3F1)	90 wk ad lib (W)				380 F (early mortality)	NCI 1978	
Systemic								
37	Rat (Wistar)	452 d ad lib (W)	Renal			584 M (glomerulonephritis)	Argus et al. 1965	

Table 3-2 Levels of Significant Exposure to 1,4-Dioxane - Oral (continued)

Key to Figure[a]	Species (Strain)	Exposure/ Duration/ Frequency (Route)	System	NOAEL (mg/kg/day)	LOAEL		Reference Chemical Form	Comments
					Less Serious (mg/kg/day)	Serious (mg/kg/day)		
38	Rat F344/DuCrj	2 yr ad lib (W)	Resp	18 F	83 F (nuclear enlargement of olfactory epithelium)		Kano et al. 2009	NOAELs are for no histopathological effects in organs and tissues.
			Cardio	429 F				
			Gastro	429 F				
			Musc/skel	429 F				
			Hepatic	11 M	55 M (mixed cell foci)			
			Renal	429 F				
			Endocr	429 F				
			Dermal	429 F				
			Ocular	429 F				
			Bd Wt	83 F		429 F (20% reduced body weight gain)		

Table 3-2 Levels of Significant Exposure to 1,4-Dioxane - Oral (continued)

Key to Figure[a]	Species (Strain)	Exposure/ Duration/ Frequency (Route)	System	NOAEL (mg/kg/day)	LOAEL		Reference Chemical Form	Comments
					Less Serious (mg/kg/day)	Serious (mg/kg/day)		
39	Rat (Sherman)	716 d ad lib (W)	Resp	1599 F			Kociba et al. 1974	NOAELs are for no histopathological effects in organs and tissues.
			Cardio	1599 F				
			Gastro	1599 F				
			Hemato	1599 F				
			Hepatic	9.6[e] M		94 M (hepatocellular degeneration and necrosis)		
			Renal	9.6 M		94 M (degeneration and necrosis of tubular epithelium)		
			Endocr	1599 F				
			Bd Wt	94 M	1015 M (>10% reduced weight gain)			

Table 3-2 Levels of Significant Exposure to 1,4-Dioxane - Oral (continued)

Key to[a] Figure	Species (Strain)	Exposure/ Duration/ Frequency (Route)	System	NOAEL (mg/kg/day)	LOAEL		Reference Chemical Form	Comments
					Less Serious (mg/kg/day)	Serious (mg/kg/day)		
40	Rat (Osborne-Mendel)	110 wk ad lib (W)	Resp		240 M (increased incidence of pneumonia)		NCI 1978	NOAELs are for no histopathological effects in organs and tissues.
			Cardio	640 F				
			Gastro		240 M (stomach ulcers)			
			Musc/skel	640 F				
			Hepatic	240 M	350 F (hepatocytomegaly)			
			Renal			240 M (cortical tubular degeneration)		
			Endocr	640 F				
			Dermal	640 F				
			Bd Wt	240 M	530 M (reduced body weight gain, unquantified)			

Table 3-2 Levels of Significant Exposure to 1,4-Dioxane - Oral (continued)

Key to[a] Figure	Species (Strain)	Exposure/ Duration/ Frequency (Route)	System	NOAEL (mg/kg/day)	LOAEL		Reference Chemical Form	Comments
					Less Serious (mg/kg/day)	Serious (mg/kg/day)		
41	Mouse Crj:BDF1	2 yr ad lib (W)	Resp	49 M	191 M (nuclear enlargement of olfactory epithelium in nasal cavity)		Kano et al. 2009	NOAELs are for no histopathological effects in organs and tissues.
			Cardio	964 F				
			Gastro	964 F				
			Musc/skel	964 F				
			Hepatic	49 M	191 M (increased relative liver weight)			
			Renal	964 F				
			Endocr	964 F				
			Dermal	964 F				
			Ocular	964 F				
			Bd Wt	191 M [d]66 F	278 F (16% reduced terminal body weight)	677 M (45% reduced terminal body weight)		

Table 3-2 Levels of Significant Exposure to 1,4-Dioxane - Oral (continued)

Key to Figure[a]	Species (Strain)	Exposure/ Duration/ Frequency (Route)	System	NOAEL (mg/kg/day)	LOAEL Less Serious (mg/kg/day)	LOAEL Serious (mg/kg/day)	Reference Chemical Form	Comments
42	Mouse (B6C3F1)	90 wk ad lib (W)	Resp		380 F (increased incidence of pneumonia)		NCI 1978	NOAELs are for no histopathological effects in organs and tissues.
			Cardio	860 F				
			Gastro	860 F				
			Musc/skel	860 F				
			Hepatic	860 F				
			Renal	860 F				
			Endocr	860 F				
			Dermal	860 F				
			Bd Wt	830 M 380[d] F	860 F (decreased body weight gain, unquantified)			
Immuno/ Lymphoret								
43	Rat F344/Du/DuCrj	2 yr ad lib (W)		429 F			Kano et al. 2009	No histopathological effects in spleen, lymph nodes, or thymus.
44	Rat (Sherman)	716 d ad lib (W)		1599 F			Kociba et al. 1974	No histopathological effects in spleen or mesenteric lymph nodes.
45	Rat (Osborne-Mendel)	110 wk ad lib (W)		640 F			NCI 1978	No histopathological effects in spleen, lymph nodes, or thymus.

Table 3-2 Levels of Significant Exposure to 1,4-Dioxane - Oral (continued)

Key to Figure[a]	Species (Strain)	Exposure/ Duration/ Frequency (Route)	System	NOAEL (mg/kg/day)	LOAEL Less Serious (mg/kg/day)	LOAEL Serious (mg/kg/day)	Reference Chemical Form	Comments
46	Mouse Crj:BDF1	2 yr ad lib (W)		964 F			Kano et al. 2009	No histopathological effects in spleen, lymph nodes, or thymus.
47	Mouse (B6C3F1)	90 wk ad lib (W)		860 F			NCI 1978	No histopathological effects in spleen, lymph nodes, or thymus.
Neurological								
48	Rat F344/DuCrj	2 yr ad lib (W)		429 F			Kano et al. 2009	No histopathological effects in brain, spinal cord, or sciatic nerve.
49	Rat (Sherman)	716 d ad lib (W)		1599 F			Kociba et al. 1974	No histopathological alterations in the brain or spinal cord.
50	Rat (Osborne-Mendel)	110 wk ad lib (W)		640 F			NCI 1978	No histopathological effects in the brain, spinal cord, or sciatic nerve.
51	Mouse Crj:BDF1	2 yr ad lib (W)		964 F			Kano et al. 2009	No histopathological effects in the brain, scpinal cord, or sciatic nerve

Table 3-2 Levels of Significant Exposure to 1,4-Dioxane - Oral (continued)

Key to^a Figure	Species (Strain)	Exposure/ Duration/ Frequency (Route)	System	NOAEL (mg/kg/day)	LOAEL		Reference Chemical Form	Comments
					Less Serious (mg/kg/day)	Serious (mg/kg/day)		
52	Mouse (B6C3F1)	90 wk ad lib (W)		860 F			NCI 1978	No histopathological alterations in the brain, spinal cord, or sciatic nerve.
Reproductive								
53	Rat F344/DuCrj	2 yr ad lib (W)		429 F			Kano et al. 2009	No histopathological effects in reproductive organs.
54	Rat (Sherman)	716 d ad lib (W)		1599 F			Kociba et al. 1974	No histopathological effects in reproductive organs.
55	Rat (Osborne-Mendel)	110 wk ad lib (W)		640 F			NCI 1978	No histopathological effects in reproductive organs.
56	Mouse Crj:BDF1	2 yr ad lib (W)		964 F			Kano et al. 2009	No histopathological effects in reproductive organs.
57	Mouse (B6C3F1)	90 wk ad lib (W)		860 F			NCI 1978	No histopathological effects in reproductive organs.

Table 3-2 Levels of Significant Exposure to 1,4-Dioxane - Oral (continued)

Key to^a Figure	Species (Strain)	Exposure/ Duration/ Frequency (Route)	System	NOAEL (mg/kg/day)	LOAEL		Reference Chemical Form	Comments
					Less Serious (mg/kg/day)	Serious (mg/kg/day)		
Cancer								
58	Rat (Wistar)	452 d ad lib (W)				584 M (CEL: liver tumors)	Argus et al. 1965	
59	Rat F344/DuCrj	2 yr ad lib (W)				274 M (CEL: hepatocellular adenoma or carcinoma; mesothelioma of the peritoneum)	Kano et al. 2009	
60	Rat (Sherman)	716 d ad lib (W)				1015 M (CEL: hepatocellular carcinomas)	Kociba et al. 1974	
61	Rat (Osborne-Mendel)	110 wk ad lib (W)				350 F (CEL: hepatocellular carcinomas)	NCI 1978	
						240 (CEL: nasal carcinomas in both sexes)		
62	Mouse Crj:BDF1	2 yr ad lib (W)				66 F (CEL: hepatocellular adenomas or carcinomas)	Kano et al. 2009	

Table 3-2 Levels of Significant Exposure to 1,4-Dioxane - Oral (continued)

Key to Figure[a]	Species (Strain)	Exposure/ Duration/ Frequency (Route)	System	NOAEL (mg/kg/day)	LOAEL		Reference Chemical Form	Comments
					Less Serious (mg/kg/day)	Serious (mg/kg/day)		
63	Mouse (B6C3F1)	90 wk ad lib (W)				380 F (CEL: increased incidence of hepatocellular carcinomas and adenomas)	NCI 1978	
64	Gn Pig (NS)	23 mo ad lib (W)				1014 M (CEL: increased incidence of hepatomas)	Hoch-Ligeti and Argus 1970	

Appendix B – Granular Activated Carbon Stock

Granular Activated Carbon EVE Lab Stock

MQP: 1,4 Dioxane Adsorption from Water

Eric Rooney & Caroline Eigenbrodt

10/17/2013

Quantity	Container Color	Company Name	Type	Size	Amount	Specifications	
1	🟥 Clear	ESV Aquarium Products	bituminous coal		enough	Iodine #: 900 min...CAS #: 7440-44-0....Don't really care about this sample since it is primairly aquarium carbon.	🟥 Not Used
2	🟥 Blue	Calgon Carbon Corporation			Plenty	CAS #: 7440-44-000...Product: WPH-650	🟩 Used
3	🟥 Blue	Calgon Carbon Corporation			Plenty	CAS #: 7440-44-000...Product: WPH-650	
4	🟥 Blue	Calgon Carbon Corporation			Plenty	CAS #: 7440-44-000...Product: WPH-1000	
5	🟥 Blue	Calgon Carbon Corporation			Plenty	CAS #: 7440-44-000...Product: WPH-1000	
6	🟩 Paint-like metal Jar	Fisher Brand		lot# V-6732	enough	Catalog #: 05-685A (107?)...Activated Carbon 6-14 mesh	
7	🟥 Paint-like metal Jar	Fisher Brand		lot# V-6732	enough	Catalog #: 05-685A (107?)...Activated Carbon 6-14 mesh	
8	🟥 Clear	Centaur-Calgon Carbon		8x30	enough	CAS #: 7440-44-0...Type Centaur 8x30	
9	🟥 Black	Norit	Coal		Plenty	Norit GAC 300...M-1887...(See Attached Picture)	
10	🟥 Black	Norit	Coal		Plenty	Norit GAC 300...M-1887...(See Attached Picture)	
11	🟩 Black	Norit	Coal		Plenty	Norit GAC 300...M-1887...(See Attached Picture)	
12	🟩 Black	Norit	Coal		Plenty	Norit Hydrodarco 4000...M-1785...(See Attached Picture)	
13	🟥 Black	Norit	Coal		Plenty	Norit Hydrodarco 4000...M-1785...(See Attached Picture)	
14	🟥 Black	Norit	Coal		Plenty	Norit Hydrodarco 4000...M-1785...(See Attached Picture)	
15	Located above GAC previously located in lab						
16	🟩 Black	TIGG	Coconut	12x30	Plenty	TIGG 5DC 1230...Iodine #: 1050 mg/g.min...(See Attached Picture)	
17	🟥 Black	TIGG	Coconut	12x30	Plenty	TIGG 5DC 1230...Iodine #: 1050 mg/g.min...(See Attached Picture)	
18	🟥 Black	TIGG	Coconut	12x30	Plenty	TIGG 5DC 1230...Iodine #: 1050 mg/g.min...(See Attached Picture)	
19	🟩 Clear Bag	Genesis Water Technologies, Inc.	Coconut	8x30	enough	GAC-COCO...1000 iodine....60 CTC	
20	🟩 Blue Jar	Calgon Carbon Corporation				Filtrasorb 300	
21	🟩 Clear Bag	Omnipure FilterCo.	Coconut	12x40	Plenty	AW(Acid Washed)	
22	🟩 Clear Bag	Omnipure FilterCo.	Coconut	20x50	Plenty	AW(Acid Washed)	
23	🟥 Clear Bag	Omnipure FilterCo.	Coconut	40x80	Plenty	AW(Acid Washed)	

Appendix C - Calculations

1,4 dioxane Dilution

$$\left(670\frac{\text{mg}}{\text{L}}\right)(0.15\text{L}) = 100.5\text{ mg}$$

$$\left(\frac{100.5\text{ mg}}{1.03\ \frac{\text{g}}{\text{mL}}}\right)\left(\frac{1\text{g}}{1000\text{ mg}}\right) = 0.098\text{ mL to }98\ \mu\text{L}$$

$$\frac{670}{5} = 134$$

$$1{:}\,134$$

$$\frac{0.098\text{ mL}}{133\text{ mL}} = \frac{\text{x}}{150\text{ mL}}$$

$$\text{x} = 0.111\text{ mL to }\mathbf{111\ \mu L}$$