Removal of 1,4-Dioxane from Water by Adsorption to Resins

Major Qualifying Project completed in partial fulfillment

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Submitted by:

Christopher Martineau
Harsha Prasad
Patrick Roll

Professor John Bergendahl, faculty advisor
Professor Isa Bar-On, faculty co-advisor

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Abstract

The purpose of this project was to evaluate resins as adsorbents for removing 1,4-dioxane from water. The objective of this study was to find new type of remediation technology for 1,4-dioxane. A range of resins with various properties and characteristics were tested to determine if adsorption is a viable option for removing this water-soluble contaminant.

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Executive Summary

1,4-dioxane is a widely-used solvent and can be found in oils, waxes, dyes, cellulose acetate, as well as other organic and inorganic compounds. There are many occurrences of 1,4-dioxane contamination in the environment; the most common case is seepage of 1,4-dioxane from decomposed manufactured products in landfills to the soil and groundwater around it. The products decompose and the contamination then moves into groundwater sources, which in turn affects drinking water (EPA 123-91-1, Jan. 2000). When 1,4-dioxane contaminates the groundwater it becomes a direct threat to human and ecological health. Short-term effects resulting from human exposure to high concentrations of 1,4-dioxane include drowsiness, headache, irritation to skin, and irritation to the lungs (EPA 123-91-1, Jan. 2000). 1,4-dioxane exposure has also been proven to be fatal in some circumstances. Due to its widespread occurrence in the environment, effective remediation techniques for removal of this contaminant are needed. The purpose of this project was to evaluate adsorptive resins to determine their potential for removal of 1,4-dioxane from water.

Four resins were evaluated in this project. The resins used included Dowex L-493, Amberlite XAD4, Dowex Marathon C, and Amberlite XAD7HP. These resins were evaluated at different doses. In the experiments, the resin dose was varied from trial to trial; however, the amount of 1,4-dioxane in each batch adsorption test remained constant. For example, 0.5 g of a resin would be mixed for 24 hours with 40 mL of water and 100 microliters of 1,4-dioxane. It was then prepared for testing by adding 50 microliters of 10 mg/L of chlorobenzene and 4 g of NaCl. The 1,4-dioxane concentration was quantified using gas chromatography with solid phase microextraction (SPME-GC). Results ranged based on the concentration and specific resin type. SPME-GC was utilized to conduct experiments with the aim of determining if the resins changed the concentration of 1,4-dioxane in the sample. Experiments were carried out with initial concentrations of each resin mixed with water, NaCl, and a fixed amount of 1,4-dioxane.

Using gas chromatography testing, the early stages of our experimentation yielded resins XAD4 and L-493 as the most effective for removal of 1,4-dioxane per mass of resin. Based on background research, the two resins were a viable option for adsorption because both have properties that enabled them to adsorb oil and gas compounds in solution. Since both of these resins showed promise through early experimentation, they were further tested at various concentrations to try to create an isotherm as well as reproducible data and methods for 1-4-dioxane removal.

1.0 Introduction

The objective of the project was to identify and create a reproducible experiment or procedure in which 1,4-dioxane can be removed from freshwater. Based on current research in water and wastewater treatment, remediation for removal of this particular contaminant has been found to be difficult. The process used in our groups experiments was adsorption. For adsorption to occur, it is necessary that the sorbent (resin) has an affinity for the contaminants that are to be removed; therefore, due to the differing properties of the different resins tested, each resin produced a different result depending on the respective concentrations of solution and contaminant.

1.1 Chemical Contaminant

1,4-dioxane is a colorless, flammable liquid with a slightly sweet odor and is classified as an ether. 1,4-dioxane is used as a solvent for cellulose acetate, ethyl cellulose, benzyl cellulose, resins, oils, waxes, some dyes, and other organic as well as inorganic compounds (Mohr, 2010). Its primary use in the United States is as a stabilizer for methyl chloroform (Mohr, 2010). In the 1950s and 1960s there was a large demand for 1,4-dioxane for this purpose and approximately 90% of the 1,4-dioxane produced annually in the mid-1980s was also used for this purpose (Mohr, 2010).

Bond	**Bond Length (Å)**	**Bond Angle Components**	**Bond Angle (°)**	**Structure**
C-H	1.112			
C-O	1.423	C-C-O	109.2	Chair
C-C	1.523	C-O-C	112.45	

Table 1: Structural Properties of the 1,4-Dioxane Molecule

(Table 1 Source: Mohr, 2010)

Property	**Value**	**Notes**
Molecular Weight	88.106 Da	Da = Daltons
Density	1.028 g/cm^3	grams per centimeters cubed
Composition	C 54.53%; H 9.15%; O 36.32%	Carbon, Hydrogen, Oxygen
Boiling Point	101.2°C	C = Celsius
Heat of Vaporization	98.6 cal/g	calories per gram
Freezing Point	11.85°C	
Heat of Fusion	33.8 cal/g	
Specific Heat	36.01 cal/(mol*K)	calories divided by moles multiplied by Kelvin

Table 2: Properties of 1,4-Dioxane

(Table 2 Source: Mohr, 2010)

1.1.1 Direct Uses of 1,4-Dioxane

The leading U.S. producer of 1,4-dioxane, Ferro Corporation, lists the following uses of 1,4-dioxane on its web site (Ferro Corporation, 2006):

- Wetting and dispersing agent in textile processing
- Dye baths and stain and printing compositions
- Some cleaning and detergent preparations, adhesives, cosmetics, deodorants, fumigants,
- emulsions, and polishing agents
- Some lacquers, paints, varnishes, and paint and varnish removers
- Solvent for fats, oils, waxes, and natural and synthetic resins
- Purification of drugs

- Reaction media in various organic synthesis reactions
- Stabilizer for chlorinated solvents

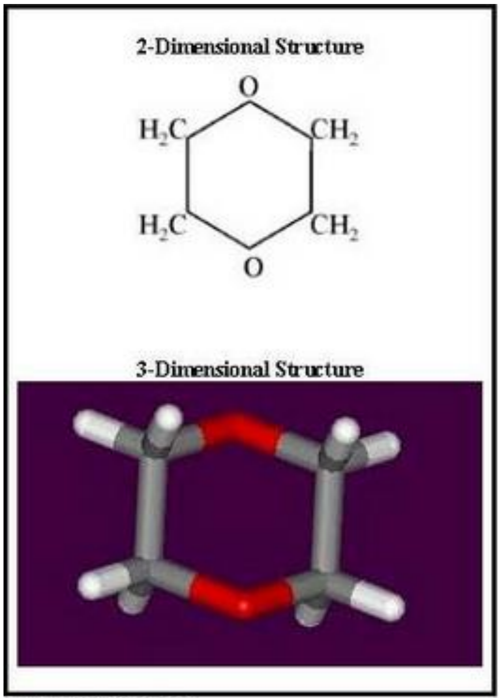
Through these uses, Ferro Corporation was expected to comply with the Environmental Protection Agency policies.

1.2 EPA Classification

The EPA has classified 1,4-dioxane as a Class B2 (probable) human carcinogen (ESEPA, 2000). The EPA has also established a drinking water health advisory with a lifetime cancer risk of 1 in 10,000 for a drinking water concentration of 0.3 mg/L. There are many occurrences of 1,4-dioxane in the environment. Due to its widespread use it is often found in wastewater streams (USEPA, 2000). 1,4-dioxane is also found in a variety of consumer products where manufacturing waste will often be treated; however, the 1,4-dioxane cannot be removed in typical wastewater treatment plants. 1,4-dioxane's chemical structure gives it an extremely high aqueous solubility making it difficult to biodegrade. These properties are a factor in it its potential hazard to surface water and groundwater. The chemical attributes also make it difficult to remove 1,4-dioxane from water and wastewater (USEPA, 2000). The 1,4-dioxane, used in commercial products, such as cosmetics, has been known to penetrate groundwater more than one mile away from the landfill that it was dumped in 1,4-dioxane can be found in air, water, and soil and can be in the form of a vapor and a liquid (USEPA, 2000).

1.3 Exposure

1,4-dioxane can enter a human being's system very easily and by several different methods. For people who work with 1,4-dioxane the exposure rate can be high and those individuals must take proper safety precautions. In the presence of 1,4-dioxane vapor, a person can become ill from the inhalation of the vapor (USEPA, 2000). Consuming foods that have been exposed to 1,4-dioxane is another way the contaminate can enter into one's system. Another simple way of absorbing 1,4-dioxane is when an individual bathes in contaminated water causing the 1,4-dioxane to come into contact with the skin (USEPA, 2000). The most common way 1,4-dioxane contaminates humans is by ingesting the 1,4-dioxane. Since the 1,4-dioxane does not readily bind to soil, it easily contaminates the groundwater. Therefore, the exposure rate is much higher than many other contaminants (USEPA, 2010).



Source: USDHHS 2003

Figure 1: Molecular Structure of 1,4-Dioxane

(Figure 1 Source: Mohr, 2010) – [*red = oxygen, gray = carbon, white = hydrogen*]

When a person drinks water contaminated by 1,4-dioxane the consumption of contaminated water puts the 1,4-dioxane directly into the human system and as a result typically causes severe health issues. Health issues vary in type and severity depending on the level of exposure (Mohr, 2010). As discussed in the Executive Summary acute (short-term) inhalation to high levels of 1,4-dioxane can result in vertigo, drowsiness, headache, anorexia, and irritation of the eyes, nose, throat, and lungs (USEPA 2000). Chronic (long-term) exposure in drinking water increases the risk of cancer has also been observed to cause damage to the liver and kidneys (USEPA 2000).

2.0 Effect on Environment

When released into the environment 1,4-dioxane causes a negative effect on the surrounding environment. The greater the quantity of 1,4-dioxane corresponds to a more serious environmental impact. Aqueous contamination by 1,4-dioxane impacts the quality of the water, which poses a threat to both human health and ecological health. National Pollution Discharge Elimination System Regulations (NPDES) cover regulations for point-source discharge of industrial wastewater, storm water; and other water streams that have contamination (Mohr, 2010). "The goal of the NPDES is to restrict or eliminate environmental impacts to aquatic life in surface water from both direct discharges into streams or indirect discharges into publicly owned treatment works (POTWs), including discharges with high biochemical oxygen demand, toxic metals and organic compounds, high temperatures, foaming agents, and other potential impacts" (Mohr, 2010). The impact on the environment from the release of 1,4-dioxane varies by the location and conditions of release into the environment. Although 1,4-dioxane is not highly toxic to aquatic organisms, it becomes a threat to aquatic organisms if the concentration reaches levels of hundreds to tens of thousands of milligrams per liter (mg/L) (Mohr, 2010).

1,4-dioxane poses the same level of threat to wildlife as it does to humans. Wildlife can be exposed to 1,4-dioxane in the same manner as humans can be exposed. Methods of exposure include ingestion, inhalation, and contact with skin. Exposure to terrestrial wildlife via the food chain is not as significant when looking at the typical concentrations of 1,4-dioxane in soil (Mohr, 2010). Chronic 1,4-dioxane exposure can cause serious harm to wildlife's internal organs; liver, heart, and kidney damage was observed in laboratory trials of rats ingesting 1,4-dioxane contaminated water over a long period of time (USEPA 2000).

3.0 Occurrences/Case Studies

Due to the large number of items that contain petroleum based products, there are various avenues in which 1,4-dioxane can enter the environment. 1,4-dioxane has been found in many international sites as well common domestic sources in the United State. Some of the methods in which 1,4-dioxane contaminates water are: through Superfund sites, point source or non-point source pollution from old buildings or development, and private/public companies that require manufacturing. Case studies have provided benchmarks for the success or failure and cost of techniques selected to treat water contaminated with 1,4-dioxane. The experiences of the water utilities and the drinking water regulators in places where 1,4-dioxane has contaminated the drinking water has been helpful to other utilities that have unfortunately discovered 1,4-dioxane in their drinking water supplies. The following are a few examples of 1,4-dioxane instances throughout the United States and the world.

3.1 Japan

Due to the multitude of manufactured products that contain trace levels of 1,4-dioxane the contaminate has been found in numerous international sites. As a result of a nationwide survey in Japan in 1995–1996, the level of 1,4-dioxane was reported to range from undetectable to 16 μg/L in nineteen surface water samples from ten sites taken out of six rivers. The range was from 0.3 to 0.9 μg/L for three coastal seawater samples taken from three different sites, and the range of 1,4-dioxane from undetectable to 79 μg/L for twenty-five groundwater samples from twenty five different sites (Abe, 1997). The concentration of 1,4-dioxane in raw water from the water supply ranged from undetectable to 9.1 μg/L (Abe, 1997). There was a high correlation between the concentrations of 1,4-dioxane and 1,1,1-trichloroethance (Abe, 1999). No serious health problems have been reported as a result of the nationwide survey.

3.2 Colorado

Another example of 1,4-dioxane trace levels was a case in Murphy Creek, CO. The presence of 1,4-dioxane was detected in Murphy Creek (near Denver, CO) at locations where contaminated groundwater is thought to enter the creek. Concentrations measured in Murphy Creek ranged from undetectable to as high as 79 ug/L within the Denver Arapahoe Disposal Site (DADS) property, north of the Lowry Landfill. North of the DADS property, the concentrations ranged from non-detectable up to 10 ug/L. The state of Colorado has established a 1,4-dioxane standard of 6.1 μg/L for surface water. Again, no health problems were reported near Murphy Creek that could be linked to 1,4-dioxane exposure.

3.3 Indiana

In Jackson County, Indiana from 1970 to early 1980, the Seymour Recycling Corporation (SRC) processed, stored, and incinerated chemical wastes at its site. About one hundred homes as well as land used for agriculture were contaminated as a result of the SRC activities and practices. Hazardous and toxic wastes including solvents and metal finishing wastes accumulated on the site property over several years. The waste was stored in 55-gallon drums, bulk tanks, and other containers. The waste products leaked and spilled from their containers creating both fire and odor problems. The landfills received vapor degreasing still bottoms, solvent wastes, paint filters, scintillation and other laboratory wastes (USEPA, 1987). Ink sludge, pesticide containers, household products (with methyl chloroform as an ingredient), and industrial sludge's from textile production, resin production, and cellulose acetate membrane production have shown a higher likelihood of 1,4-dioxane presence in leachate, gas, and affected groundwater. The foremost risk at the SRC site included offsite migration of highly mobile organic contaminants. The contaminants could travel to the nearest private well, one-quarter mile northwest of the site. The concentrations were so high that exposure caused a risk higher than of the levels equivalent to the 1 in 1,000,000 excess lifetime cancer risk. 1,4-dioxane was specifically identified as having the potential to exceed the recommended risk levels at the nearest private well in less than five years (USEPA,1987).

3.4 California (San Jose)

In Silicon Valley, Solvent Service Inc. (SSI) opened a facility in 1973 to reclaim spent solvents and other wastes from printed circuit board manufacturers, wafer fabs (semiconductor manufacturers), and other electronics in industrial manufacturing facilities. SSI treated solvents using a treatment, storage, and disposal facility (TSDF) permit at a facility located on a three acre parcel in an industrial area of San Jose, California. Leaking tanks in 1983 prompted testing and the discovery of subsurface contamination was revealed. (Cal EPA, 2000). Solvents were refined through the use of distillation and gravity phase separation. Distillation of vapor-degreaser still bottoms further concentrated the stabilizer compounds, including 1,4-

dioxane. Volatile organic compounds were first detected in shallow groundwater beneath underground solvent-storage tanks, wash-down sumps, a drum-storage area, and an unloading area for solvent tank trucks (Cameron-Cole, 2001). The volatile organic chemicals detected included methyl ethyl ketone, acetone, xylene isomers, perchloroethylene, trichloroethylene, methyl chloroform, 1,1-dichloroethane, cis-1,2-dichloroethylene, and others. The toxic industrial chemicals at the SSI site included 1,4-dioxane, tetrahydrofuran (THF), and 1,3-dioxolane, as well as a number of others. 1,4-dioxane and THF were detected frequently and at elevated concentrations (up to 56,000 and 850 μg/L, respectively) (McCraven, 2006).

Prior to the discovery and characterization of 1,4-dioxane at the SSI site in 1998, it was believed that the extent of groundwater contamination had been identified. Discovery of 1,4-dioxane and THF led to an investigation to characterize their downgradient extent, which was much greater than that of the chlorinated solvent. The additional characterization effort defined a 1,4-dioxane plume extending beyond the effective range of the existing remediation systems. The findings were met with regulatory actions designed to expand the monitoring network by installing additional monitoring wells and expanding the groundwater extraction system. The operational schedule of the existing remedial systems was increased to 24 hours/day, 7 days/week (24/7) for on-site soil vapor extraction. An additional 87-foot-long off-site groundwater extraction trench was installed to address 1,4-dioxane presence beyond the capture zone of the existing system (Cameron-Cole, 2006). Although the presence of fine-grained deposits limited the volatile organic compound migration, 1,4-dioxane and THF were estimated to migrate up to 41 and 35 ft/year, respectively (Cameron-Cole, 2006).

Since the sources of 1,4-dioxane contamination were being cut off by extraction trenches, the consultants have recently submitted findings indicating that concentrations should continue to decline, noting that perimeter wells are not expected to produce samples with detectable concentrations of 1,4-dioxane. Declining concentrations of 1,4-dioxane in monitoring wells between the off-site extraction trench and the perimeter monitoring wells support this assertion. In 1998 a laboratory consultant decided it would be appropriate to reanalyze the full complement of forty-eight (48) groundwater samples. 1,4-dioxane was detected in all of samples except one monitoring well. Subsequent sampling revealed a maximum 1,4-dioxane concentration of 340,000 μg/L (Cameron-Cole, 2006). As of 2006 there have been no lawsuits filed by citizens affected by the 1,4-dioxane contamination, but there have been reports of an above-average cancer rate in the affected area (Cameron-Cole, 2006).

3.5 Michigan

Gelman Sciences Inc., acquired by Pall Life Sciences in 1997 (P/GSI) and located in Ann Arbor, Michigan, produced cellulose triacetate filters used in medical and other applications. 1,4-Dioxane was used for producing microporous cellulose filters for scientific and medical applications; P/GSI began using 1,4-dioxane to create a stronger solvent system in 1986 (Fotouhi et al., 2006). In 1996, the company discontinued the use of 1,4-dioxane and phased out the line of filters that required its use in production. The line was eventually replaced by an improved filter product. At the time that P/GSI stopped using 1,4-dioxane, it was discovered that thirty (30) private wells in the Scio Township area were contaminated with 1,4-dioxane. Approximately 850,000 pounds of 1,4-dioxane was used to form triacetate filters during the twenty years before contamination was discovered (Fotouhi et al., 2006). The P/GSI site is the oldest and largest 1,4-dioxane contamination case in the United States.

The Michigan Department of Natural Resources recommended discharge of wastewater into infiltration lagoons and the removal of natural geologic barriers between the pond bottom and the water table 15 to 40 feet below the surface in order to facilitate slow infiltration into groundwater (Kellogg, 2005). The state of Michigan issued P/GSI a permit in 1964 to install a three-million-gallon wastewater lagoon to hold and infiltrate process wastes, which may have contained 1,4-dioxane in concentrations as high as 25 mg/L (City of Ann Arbor, 2006; SRSW, 2006). In order to further increase its wastewater capacity P/GSI installed two additional lagoons in 1966-67 as well as drilled an injection well at a cost of approximately $1,000,000 in 1981. Despite the multiple attempts to protect the surrounding environment from 1,4-dioxane, in 1984 a University of Michigan graduate student discovered 1,4-dioxane in Third Sister Lake near the P/GSI property in a section of Saginaw forest owned by the university. The following year, 1,4-dioxane contamination was also discovered in nearby private wells during an investigation conducted by the Washtenaw County Health Board. Between 1987 and 1994, after learning of the discovery of 1,4-dioxane contamination in late 1985, P/GSI used a water supply well to remove more than 25,000 pounds of 1,4-dioxane from groundwater near the plant. The contaminated water was not treated; instead, it was discharged into the injection well under a USEPA permit. The permitted practice of treating 1,4-dioxane laden wastewater in unlined lagoons and spray irrigating wastewater on lawns and fields clearly contributed to the widespread contamination of groundwater with 1,4-dioxane (Kellogg, 2005).

Beginning in 1986, investigations by the company identified soil contamination on the P/GSI property and groundwater contamination extending off the property. Groundwater concentrations of 1,4-dioxane were as high as 221,000 μg/L. The plumes collectively encompassed an area of approximately 0.6 square miles, as defined by the Michigan drinking water action level of 85 μg/L (Brode et al., 2005). Citizen groups define the plume to a 1 μg/L contour and describe the plume of deeper 1,4-dioxane contamination as “18 million square feet and growing, three miles long and one mile wide" (Kellogg, 2005). 1,4-dioxane method detection levels have ranged from 1 to 100 µg/L during the course of the project (Fotouhi et al., 2006). Deeper contamination was discovered during an investigation in the Spring of 2001, following the detection of 1,4-dioxane at 2 µg/L in the City of Ann Arbor's Northwest Supply well. The city turned off the well immediately following the detection, and investigations of deep aquifer contamination began. After an intensive effort to characterize deep contamination, concentrations as high as approximately 5000 µg/L were found deep in the Unit E aquifer.

P/GSI embarked on a series of treatability studies in the decades following the discovery of 1,4-dioxane contamination in private wells. Early treatability studies focused on separation methods using gas-phase separation, such as air stripping and steam stripping, and on solid-phase separation using GAC. P/GSI's treatability studies also tested destructive treatment methods including chemical destruction using hydrogen peroxide, ozone, and chlorine; physical destruction using UV light; and combinations of physical and chemical destruction methods. Biological treatability studies included microbial methods such as activated sludge and bio activated carbon, enzymes, and inoculation with engineered organisms (Fotouhi et al., 2006). Site remediation began with contaminated soil removal; the most highly contaminated soils were removed in 1979 and 1987 (MDEQ, 2000). After almost ten years with little to no action in off-site remediation, full-scale groundwater treatment resumed in 1997. The selected remedy for full-scale groundwater treatment was UV light + hydrogen peroxide (H_2O_2). P/GSI operated a full-scale UV + H_2O_2 system at its facility to remediate groundwater containing high concentrations of 1,4-dioxane. As of 2004, more than 60,000 pounds of 1,4-dioxane had been extracted from the groundwater and destroyed by UV + H_2O_2 since treatment began in 1997. (Brode et al., 2005) Altogether, P/GSI has pumped about four billion gallons of water and removed about 100,000 pounds of 1,4-dioxane. (Fotouhi et al., 2006) Since 1997, the company has been spending $5.5 million/year to clean up 1,4-dioxane pollution. (Kellogg, 2005) The value of the affected groundwater resources supplying residents of Ann Arbor, Scio Township, and Ann Arbor Township has not been identified and there have been no civil lawsuits brought about as of 2005 (Kellogg, 2005).

3.6 California (Orange County)

The Orange County Water District (OCWD) in Orange County, CA, was formed in 1933 to manage water supply and groundwater in a 360 square-mile area in the lower Santa Ana River watershed, covering much of Orange County on the southern California coast. OCWD is the water provider to about 2.3 million people in more than twenty cities, including Newport Beach, Huntington Beach, and Seal Beach on the coast; Cypress and Fullerton on the northern end; Anaheim and Yorba Linda to the east; and Santa Ana and Irvine to the south. The groundwater basin is a 3000-ft-thick slab of alluvium on top of bedrock formations. The water supply wells extend as deep as 1000 ft. Under normal operating conditions, groundwater is the resource for about 70% of the water provided by OCWD. (Deshmukh, 2007) In December 2001, 1,4-Dioxane was discovered in Water Factory 21 at concentrations ranging from 1 to 75 μg/L, as well as two detections at 150 and 200 μg/L. Since the Talbert Gap injection barrier had been receiving highly treated water from Water Factory 21 for decades, in January 2002 the OCWD staff decided to sample nineteen water supply wells that drew water from the affected aquifers. 1,4-dioxane was detected in nine of these supply wells at concentrations ranging from 4 to 20 μg/L, which is above California's 3 μg/L action level, but below the threshold for shutting down said water supply wells (Mehta, 2002).

Table 3 below shows all of the known major producers of 1,4-dioxane circa 1985. This illustrates how 1,4-dioxane is manufactured and used globally.

Company	**Location**
Ferro Corporation/Grant Chemical Division	Baton Rouge, Louisiana, USA
Union Carbide	South Charleston, West Virginia, USA
CPS Chemical Company	Old Bridge, New Jersey, USA
Dow Chemical Company	Freeport, Texas, USA
Ugine-Kuhlmann	Frankfurt, Germany
BASF Aktiengesellschaft	Ludwigshafen, Germany
Dow Chemical Company	Terneuzen, Netherlands
Osaka Organic Chemical Industry, Ltd.	Osaka, Japan
Sanraku-Ocean Company	Tokyo, Japan
Toho Chemical Industry Company	Tokyo, Japan

Table 3: Producers of 1,4-Dioxane (circa 1985)

(Table 3 Source: Mohr, 2010).

4.0 Risk and Regulation

As a result of the pollution problems that occur in the environment, the Clean Water Act, also known as the Federal Water Pollution Control Act, developed standards to preserve the uses of a specific body of water by devising a list of criteria to protect the habitat from degradation by unknown hazards. The purpose of these guidelines was designed to preserve the flora, fauna, and environment.

4.0.1 Federal

There is currently no federal MC or MCL Goal for 1,4-dioxane in drinking water. However according to the Environmental Protection Agency (EPA) website dating as far back as 2008 there are currently twenty-two (22) states that have standards for the allowable concentration of 1,4-dioxane in micrograms per liter (µg/L). The state standards are illustrated in Table 4 and Figure 2 below. Two states, Michigan and South Carolina, have a much higher concentration standard when compared to the other states. The heightened standards are due to the number of occurrences of 1,4-dioxane in those states being much greater than the rest of the states. It is simply not feasible, nor is it safe for the citizens of those states, to have lower standards for Michigan and South Carolina.

State	**1,4-Dioxane Standard**
Arizona	6.1 µg/L
Arkansas	6.1 µg/L
California	3 µg/L
Colorado	6.1 µg/L
Delaware	6 µg/L
Florida	3.2 µg/L
Louisiana	6.1 µg/L
Maine	3.2 µg/L
Maryland	6.1 µg/L
Massachusetts	3 µg/L
Michigan	85 µg/L
Missouri	3 µg/L
Nevada	6.1 µg/L
New Hampshire	3 µg/L
New Mexico	6.1 µg/L
North Carolina	7 µg/L
Oklahoma	6.1 µg/L
Pennsylvania	5.6 µg/L
South Carolina	70 µg/L
Texas	8.3 µg/L
Virgina	6.1 µg/L
West Virginia	6.1 µg/L

Table 4: 1,4-Dioxane Standards by State

(Table 4 Source: Rayle, *Spatial Synthesis*, Oct. 2008)

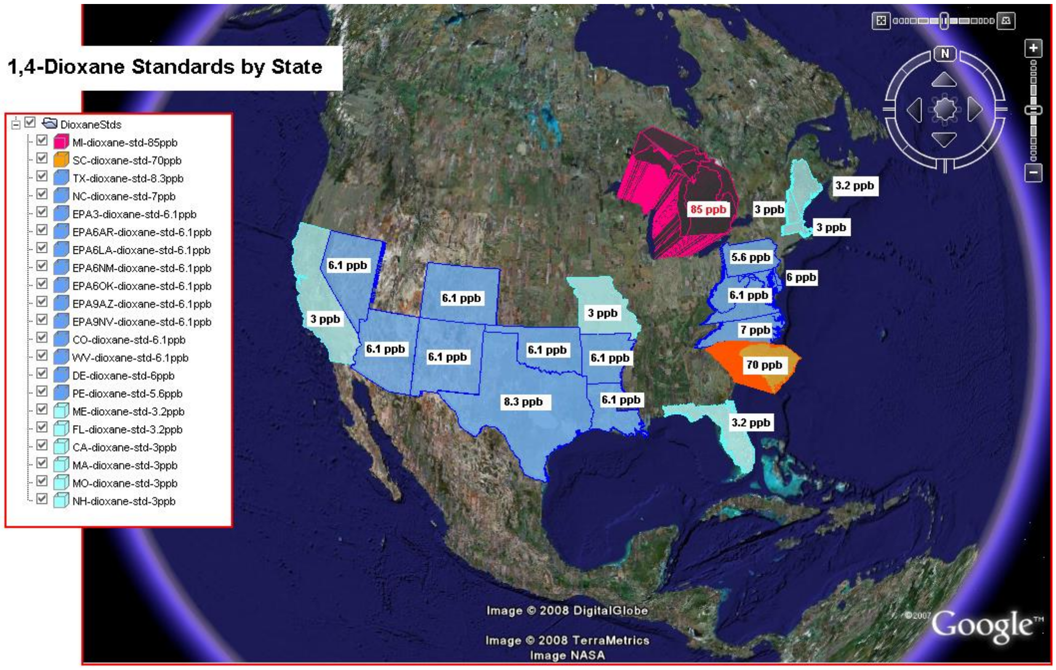


Figure 2: 1,4-Dioxane Standard by State

(Figure 2 Source: Rayle, *Spatial Synthesis*, Oct. 2008)

4.0.2 Massachusetts

Given that Worcester Polytechnic Institute is located in the state of Massachusetts our project group researched any guidelines and regulations relating to 1,4-dioxane in Massachusetts state laws. The guidelines below provide a good example and are similar to regulations found in the rest of the 21 states that have state laws relating to 1,4-dioxane.

Guidelines

- Drinking water: 3 µg/L (Mohr, 2010).
- Groundwater (guidance value—issued in 2007)

- 3 μg/L Groundwater (shallow aquifer with vapor-intrusion potential) (Mohr, 2010)
- 6000 μg/L Groundwater (ecological risk) (Mohr, 2010)
- 50,000 μg/L Soil (direct contact and leaching) or 0.005 mg/kg (Mohr, 2010).

4.1 Policy Implications

An important aspect of clean drinking water is prevention. Prevention is the only means to preserve the national environment for future generations. In order to apply this precautionary principle individuals must "be open, informed, and democratic and must include parties potentially affected by the environmental consequence at issue" (Global Development Research Center [GDRC], 1998). The purpose of this section is to highlight some important policy implications that can arise when trying to find the best methods for contamination remediation. The following five precautionary principles are listed below as a means for being proactive in monitoring waste in the environment.

1. Acknowledge and respond to ignorance, as well as uncertainty and risk, in technology.
2. Provide adequate long-term environmental and health monitoring and research into early detection of environmental threats.

> During the initial manufacturing of early solvent stabilizers certain consequences of adding toxic and persistent compounds to chlorinated solvents prevailed. This toxic aspect of the process was overlooked as the health issues to employees and eventual smog occurred in the 1960's. Although there were such drastic changes, there was little motivation to promote water quality protection with solvents treated as hazardous waste. This protection came only with the adoption of the Resource Conservation and Recovery

Act (RCRA) in 1976. Creation of the RCRA helped individuals realize the potential risk, particularly in relation to occupational exposure. Eventually there were discoveries identifying the risk to workers, but not delving into the environmental effects. The widespread use of these chemicals was not regulated thus making it difficult to address the uncertainty of health effects and risks. The identification of risks to workers was tied to the precautionary concept for occupational health and exposure. In early manufacturing there was little information related to the direct health consequences of exposure. In time the frequency of 1,4-dioxane use increased because it was employed as a solvent stabilizer. (Barber, 1934) With the increase in production, eventually toxicology research warranted both health monitoring and further research into the potentially toxic effects of exposure.

3. Identify and work to reduce “blind spots” and gaps in scientific knowledge.

    Since 1,4-dioxane is known to be used as a solvent stabilizer, there has been oversight prior to its introduction into manufacturing. A key aspect of this rule, is the role of 1,4-dioxane in the potential harm from chemicals during the time period. Certain processes, such as vapor degreasing, yielded much higher quantities of 1,4-dioxane than the solvent stabilizer itself. In addition, both industry and Government personnel overlooked the possibility that direct dumping of hazardous wastes into sewers or the sending of drummed solvent wastes to unlined landfills would cause significant groundwater contamination.

4. Identify and reduce interdisciplinary obstacles to learning.

For industrial chemists, in addition to professionals in the field, the impact of disposal methods was not analyzed therefore the dangerous impacts were unable to be prevented. A major factor behind the lack of preventive contamination planning was the absence of motivation or the presence of a mandate requiring the assessment of health risks from their own chemical inventions in the environment.

5. Avoid "paralysis by analysis" by acting to reduce potential harm when there are reasons.

    The "paralysis by analysis" refers to the long timeframe required to investigate the potential presence of a chemical in the environment before it is considered for regulation. The phrase is used because residents have been consuming contaminated water for an extended length of time. In scenarios where the information is available on the environmental consequences of emerging contaminants, there has been an absence of "political will" to take action to reduce hazards in the face of conflicting costs and benefits. (EEA, 2000)

5.0 Current Remediation Techniques

1,4-dioxane is a contaminant that is difficult to extract from water due to its high solubility. Soil contaminated with 1,4-dioxane is rare to find since 1,4-dioxane is known to bypass soil and directly dissolve into groundwater. In a document on 1,4-dioxane, the EPA describes the contaminant by claiming "1,4-dioxane's physical property indicates that it is theoretically volatile enough to be removed in situ using soil vapor extraction or ex situ with thermal desorption even though its vapor pressure is lower than many volatile organic compounds" (EPA-542-R-06-009).

1,4-dioxane contamination is most commonly seen in groundwater. T reatments that have proven successful in extracting 1,4-dioxane from groundwater involve advanced oxidation involving hydrogen peroxide and UV light. Another form proven slightly less successful, but has had some success, is chlorination. The concern with chlorination is the byproduct tends to be more toxic than the 1,4-dioxane itself. This raises the question of whether it is worth using chlorination. It is difficult to remove 1,4-dioxane from the environment because it is so highly volatile.

One method of extracting the groundwater for testing is through water pump testing. Water Pump Testing is conducted to determine if the groundwater is contaminated. Water Pump Testing is also used to control contaminated water to prevent further pollution. The Water Pump Testing process works by pumping out the groundwater. The groundwater undergoes ex-situ treatment and is released. Water Pump Testing remediation is a good temporary fix for a small local problem but for long term solutions this process will cost far too much for the temporary reward it offers.

In a document on 1,4-dioxane, the EPA described the contaminant by stating “1,4-Dioxane’s physical property indicates that it is theoretically volatile enough to be removed *in situ* using soil vapor extraction or *ex situ* with thermal desorption even though its vapor pressure is lower than many volatile organic compounds” (EPA-542-R-06-009, December 2006).

Since the most widespread presence of the contaminant 1,4-dioxane is in groundwater more specific ways of extracting it have been attempted . Six remedial technologies have been studied to remove 1,4-Dioxane from contaminated groundwater. The six processes (Mohr, 2010) consist of:

1. Vapor-phase transfer (air stripping)

2. Sorption

3. Natural attenuation

4. Phytoremediation

5. Bioremediation

6. Chemical oxidation.

Vapor-Phase Transfer (air Stripping) removes 1,4-dioxane from groundwater by converting the 1,4-dioxane contaminant from its liquid phase into its vapor phase. Once the contaminant is in the vapor phase it is filtered so when the vapor is released back into the atmosphere it is non-toxic. “Air Stripping is a common method of removing volatile organic compounds from groundwater because the relationship between solubility and volatility is optimal in this group of contaminants” (Mohr, 2010). One of the most powerful air stripping processes is the Accelerated Remediation Technologies, LLC (ART). ART is “a more focused and comprehensive mass-transfer approach-combining air stripping, air sparing, soil-vapor extraction, enhanced bioremediation, and underground circulation. It has been proven to be effective for 1,4-dioxane removal under specific circumstances” (Mohr 2010). The figure below is the ART method. This method has been proven to reduce 1,4-dioxane levels; however, the process for removal is still undetermined.

Sorption is another remediation technique studied to remove 1,4-dioxane from groundwater. Sorption was the area of concentration our group chose to research and our experiments were focused around the process of sorption in extracting 1,4-dioxane from ground water. Different materials can be used in the process of sorption depending on how the process is performed. Activated carbon, clays, and synthetic resins are all materials that possess adsorptive qualities (Mohr, 2010). This specific project focused on sorption via resins to achieve clean water. The specific resins are as follows.

5.1 Resin Types

In the current market there are numerous resins that are available each with their own properties for adsorption. The resins with high hydrogen content are primarily used for solutes and solvents with highly polar attractions in addition to the removal of by products during the manufacturing process for different industries. The first step was to conduct an experiment using one resin per experiment. The goal was to determine if any of these existing resins would remove 1,4-dioxane from water. The resins evaluated were Dowex Optipore L-493, Amberlite XAD4, Dowex Marathon C, and Amberlite XAD7HP. Four independent experiments were conducted using these resins.

According to The Dow Chemical Company, Dowex Optipore L-493 is a polymer adsorbent with a high surface area of 1100 m^2/g and a pore volume of 1.16 cc/g. Its primary purpose is to extract aromatic molecules from water. It is used in removing BTEX from oil field produced water, chlorinated solvents from water, and VOC from water. This product was manufactured to have a high organic loading, good regeneration efficiency, and being physically stable (Products L-493, 2014).

Amberlite XAD4 was another resin is described according to The Dow Chemical Company: “Amberlite XAD4 is a polymeric adsorbent based on highly cross linked, macro reticular polystyrene, aliphatic, or phenol-formaldehyde condensate polymers” (Products XAD4, 2014). This resin can be used to extract pollutants from ground water and vapor streams. It is also used to remove chlorinated solvents, herbicides, and pesticides from aqueous streams

(Products XAD4, 2014). “Dowex Marathon C resin is a high capacity, gel strong acidation exchange resin of uniform bead size distribution.” It is designed to “give high throughput and economical operation in both water and non-water applications.” The small size of the resin and its respective core strength causes the resin to partake in rapid exchange kinetics reactions during operation and regeneration (Products Marathon C, 2014). The uniform beads of Dowex Marathon C resin make the resin more efficient than others. It reduces the waste and decreases the cost (Products Marathon C, 2014).

“Amberlite XAD7HP is a polymeric adsorbent, supplied as white insoluble beads. It is a non-ionic all phatic acrylic polymer which derives its adsorptive properties from its patented macro reticular structure” (Products Amberlite, 2014). The structure allows the resin to be more stable physically and thermally. This resin can be used to remove polar compounds from aqueous solvents, removal of non-aromatic compounds from polar solvents, recovery of plant extracts, recovery of antibiotics, and removal of organic pollutants from aqueous waste, groundwater, and vapor streams. It is used in food processing, bioprocessing, and pharmaceutical processin (Products Amberlite, 2014).

Natural Attenuation has specific regulations asserted by the EPA. The EPA states that the natural attenuation processes “acts without human intervention to reduce the mass, toxicity, volume, or concentrations of contaminants in soil or groundwater” (USEPA 2000). Natural attenuation is not usually used as a remediation for 1,4-dioxane but if it were to be used it would require significant adherence to the EPA’s evaluation elements.

Phytoremediation is the process of removing contaminants from groundwater or soil by the use of plants. The largest phytoremediation process is transpiration. “Transpiration involves the transfer of soluble groundwater contaminants through the plant's root, stem, and leaf systems to the atmosphere" (USEPA 2000). The process for removing 1,4-dioxane from groundwater through the use of phytoremediation has been proven successful in numerous experiments. The primary removal mechanisms include uptake into the plant and transpiration of the 1,4-dioxane out of the leaves and into the atmosphere. Since 1,4-dioxane dissipates quickly in the atmosphere, the transpiration process could definitely be considered an effective long-term method for the removal and destruction of 1,4-dioxane (USEPA 2000).

6.0 Methodology

The purpose of this study was to identify possible resins that could adsorb 1,4-dioxane from water. Due to the nature of 1,4-dioxane, very few filtration techniques remove it from solution. To test the solubility of the compound and dissolution properties, resins were used to try and remove the contaminant from water.

For the first resin L-493 and the additional three resins a scale was used to measure the respective quantities of resin which varied throughout the experiment. After the resins were weighed out and transferred into their respective 40 mL VOA Vials, water and 1,4-dioxane concentrate were added to solution. During the course of the experiment two variations were used to mix the 1,4-dioxane with the resin. The first method involved pipetting 100 uL of a 2000 mg/L 1,4-dioxane concentrate, and the other method involved using a prepared batch of 5 mg/L solution at pH 7 of 1,4-dioxane solution.

After the 1,4-dioxane solution was added to the resins in the vials, they were mixed for twenty-four (24) hours. Throughout the tests from week to week there was always a "control" vial with 1,4-dioxane in solution that mixed with the other samples. After the twenty-four (24) hours the samples were either stored in a refrigerator or run that same day.

To test each sample using the BTEX method on the gas chromatographer, 4 grams of NaCl was added to each GC vial. The next step required transferring 10ml of each sample out of each VOA vial into a respective GC test vial. This procedure was repeated for all of the samples using a different pipette tip to prevent contamination.

Table 5 illustrates examples of the concentrations that were used in our planned procedure for testing the 1,4-dioxane. The test matrix represents a subset of the actual experiments conducted in the laboratory.

Type Of Resin	**Dowex Optipore L-493**		
Trial	1	2	3
Amount Resin (g)	.5 g	1 g	1.5 g
Amount of Chemical (uL)	100uL	100uL	100uL
Concentration of Chemical (mg/L)	5 mg/L	5 mg/L	5 mg/L
Type Of Resin	**Amberlite XAD4**		
Trial	1	2	3
Amount Resin (g)	.5 g	1 g	1.5 g
Amount of Chemical (uL)	100uL	100uL	100uL
Concentration of Chemical (mg/L)	5 mg/L	5 mg/L	5 mg/L

Table 5: Resin Concentration's (Testing Examples)

7.0 Results

The following data represents the isotherms of the XAD4, L-493, and the non-ideal resins XAD7HP and Dowex Marathon C. In the section below, the logarithmic Q_e vs C_e tables, Isotherms, and equations representing the ideal conditions for the resins can be seen with their respective C_e removal.

The purpose of manipulating the data into a logarithmic scatter plot was to identify a linear trend in the data. We used the Q_e vs C_e table as a means to identify the concentration of the 1,4-dioxane to the surface of the adsorbent to the concentration of the 1,4 in solution at equilibrium for the Freundlich Isotherm. The resulting relationship dictates the proper Q_e value that can be the most efficient for contaminant removal.

Freundlich Equation:

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

where:

$K_F \equiv$ Freundlich adsorption coefficient (capacity of adsorption)

$1/n \equiv$ intensity of adsorption

The slope of the trend line is equivalent to the 1/n value and 10^x, with 'x' referring to the y-intercept as K. The values for the slope and y-intercept are taken from the logarithmic calculations Q_e vs C_e values.

The Langmuir Isotherm also requires the similar relationship but with regards of adsorption of molecules to the relative gas pressure or concentration of a medium at a fixed temperature.

Langmuir Equation:

$$q_e = \frac{abC_e}{1 + bC_e}$$

where:

a ≡ empirical constant

b ≡ saturation coefficient [m^3/g]

The Langmuir Isotherm required calculation for both constants. The empirical constant and Saturation Coefficient for L-493 and XAD4 are 5.05, 1100 m^3/g, and 3.15, 750 m^3 /g respectively. For all of the Q_e vs C_e tables the concentration of C_e is in mg/L and the units for Q_e g/gal (grams per gallon).

Figure 3 below identifies the Freundlich Isotherm for the L-493 data points. This figure identifies the linear trend in the data with a very poor regression value. Since this isotherm does not identify a clear correlation of Q_e vs C_e the Langmuir Isotherm can be used as an alternative.

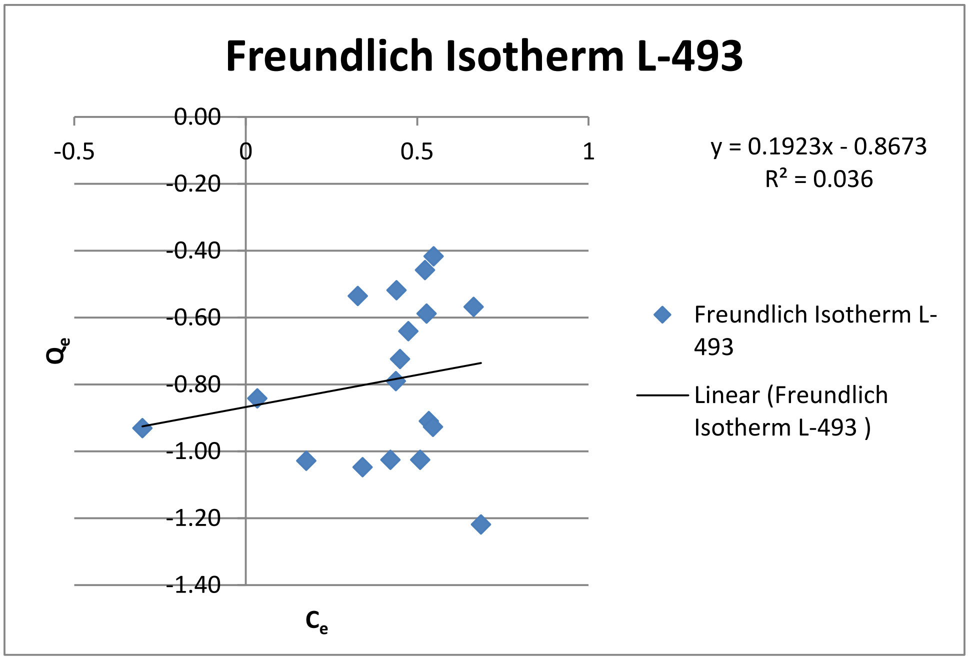


Figure 3: Freundlich Isotherm for all L-493 Data

Figure 4 below shows the calculated Langmuir isotherm. The regression value for this isotherm is significantly better making it the better isotherm to use for 1,4-dioxane removal calculations.

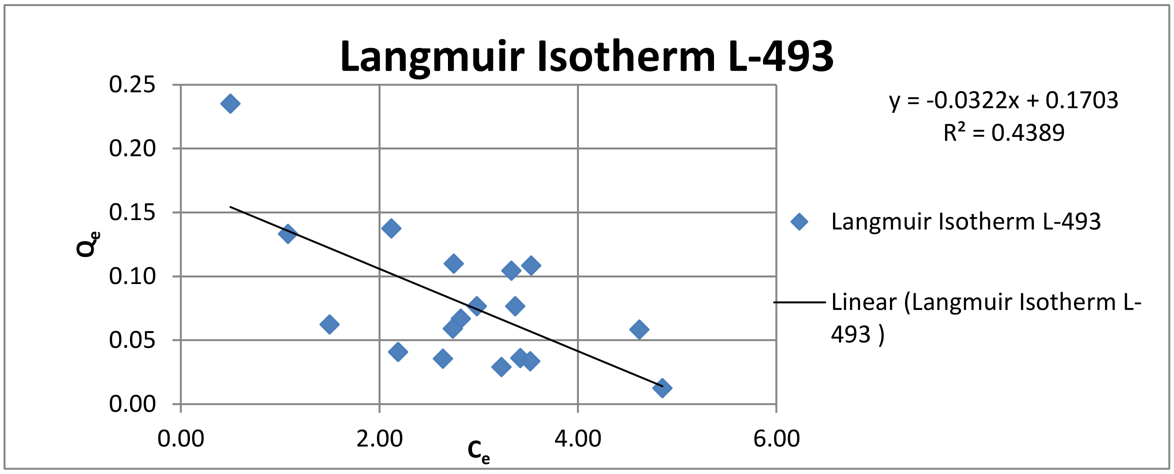


Figure 4: Langmuir Isotherm for all L-493 Data Points

It is evident that the L-493 resin has a lower accepted regression value than that of the Langmuir Isotherm. As a result, the Langmuir Isotherm for L-493 was used for reactor calculations in the next chapter of this report.

Figure 5 below depicts the Langmuir Model for L-493, the optimal resin, based on the data acquired. The linear regression identifies this resin as a high efficiency for the given parameters.

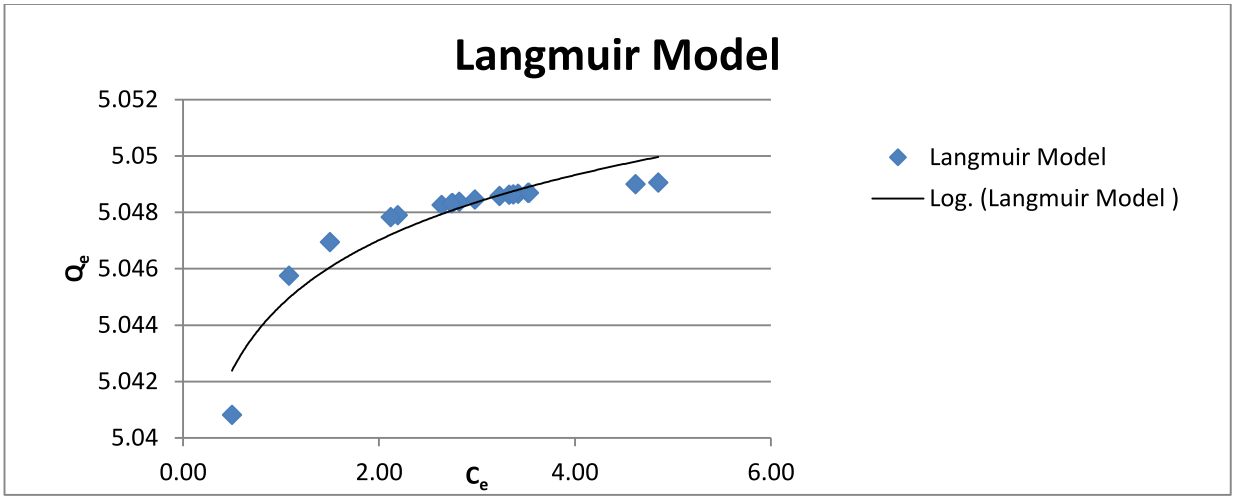


Figure 5: Langmuir Model for all L-493 Data Points

Figure 6 below depicts the Freundlich Isotherm for the resin we identified as the second most effective (XAD4) in the logarithmic scale.

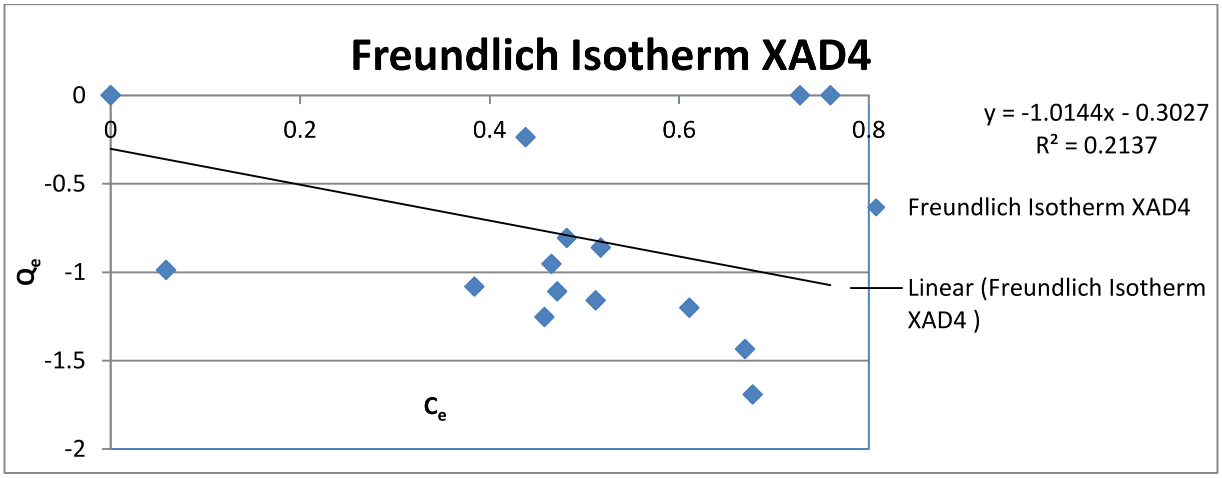


Figure 6: Freundlich Isotherm for all XAD4 Data Points

Figure 7 below is the Langmuir Isotherm for XAD4.

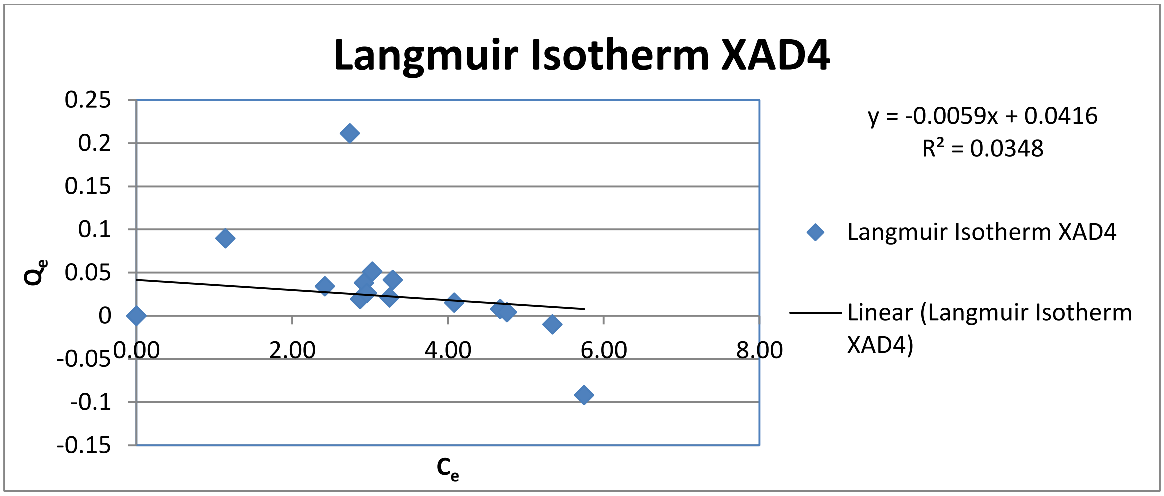


Figure 7: Langmuir Isotherm for all XAD4 Data Points

These isotherms show that both resins are viable but with significantly different regression. Although the Langmuir model was better for the L-493 resin, in this situation the Freundlich model gives a better fit for XAD4. As a result a model for the Freundlich Isotherm of XAD4 is below.

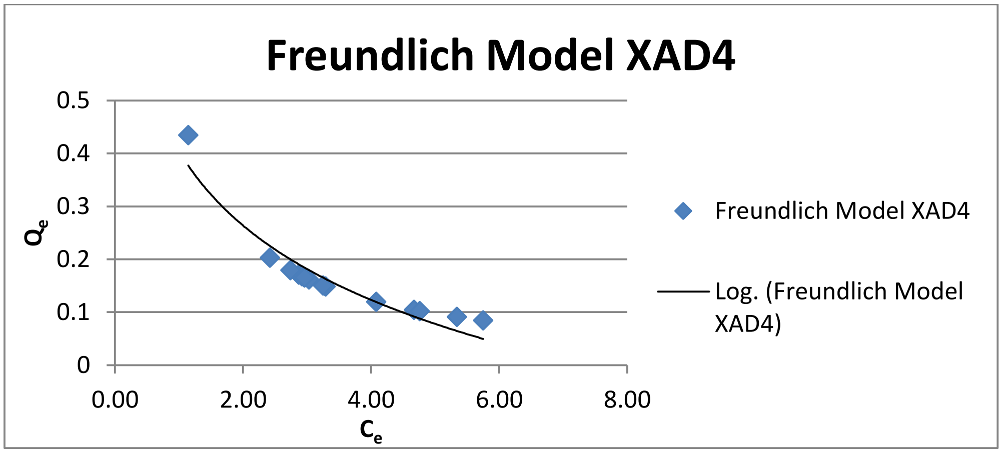


Figure 8: Freundlich Model for all XAD4 Data Points

Although the Freundlich Isotherm had the best fit line with respective regression, the model itself does not yield a possible outcome. This model doesn't show the ideal removal for a removal system; therefore L-493 is the best option. Based on these results, if a treatment system was to be able to treat contaminated water with a 1,4-dioxane concentration of 50 µg/L, 1 mg/L, and 5 mg/L, the respective calculated Q_e values from the given equation in the Langmuir Isotherm for L-493 would be 0.17, 0.138, and 0.0093 respectively. These numbers are based on the assumption that the goal of the system is 100% removal of contaminant.

Table 6 below shows the calculated concentration values for resin XAD7HP and Marathon C. Considering the starting concentration for all trials was 5 mg/L, it was evident that these trials proved inconclusive because some of the calculated values were well over 5 mg/L. Since these values were over the normal and control, they were considered outliers and were not used for the isotherm data or reactor system.

Peak Area (Pa*s)	**Dowex C C_e (mg/L)**	**Peak Area (Pa*s)**	**XAD7HP C_e (mg/L)**
395.56	1.695543	10402.21	44.58842
706.76	3.029482	10233.4	43.86482
1621.09	6.9487	14623.3	62.68185
1755.87	7.526426	9886.6	42.37829
2075.85	8.898	14819.2	63.52157

Table 6: Concentrations of Resins after Equilibrium

The control peak area for this trial was 1166.47 Pa*s. Some of the values recorded were significantly larger than the standard. Considering these results were not ideal for this application it was expected to receive outlier data. Due to the variation from the resins in Table 6, these resins were not tested further; we continued our project with the emphasis on L-493 and XAD4.

8.0 Discussion and Design

As stated earlier our group determined that L-493 was the most effective resin in removing 1,4-dioxane from water. In most of the trials L-493 caused a significant decrease in the concentration of 1,4-dioxane, even with very small amounts of the resin. The next step was to choose a real world reaction system that could treat water contaminated with 1,4-dioxane through the use of synthetic resin L-493. After research we decided that we should attempt to design a system that can treat 10,000 gallons of contaminated water per day.

8.1 Reactor Systems

One type of reactor system that we researched for this project was a fixed-bed contactor system. "A fixed-bed system consists of a stationary column in which the waste flows through the bed at a constant rate" (Celenza, 2000). Fixed-bed systems are best used for the process of adsorption using the Mass Transfer Zone (MTZ) height as a characteristic for adsorption (Celenza, 2000). A multiple unit system is more practical for a fixed-bed system; it enables flexibility in the reaction process and allows for mass production and efficiency. The main purpose of the second column in the multiple unit system is to act as a safety net; this will protect against negative discharge when the first column is exhausted (Celenza, 2000). In our case the reactants and the catalysts include the contaminated water and resin. A single column can carry out a sequence of different operations without the need to break containment which is useful when dealing with toxic material such as 1,4-dioxane; however, the second column acting as a safety will allow for secondary scrubbing to ensure all the 1,4-dioxane has been extracted and the water purified (Celenza, 2000). The goal of this part of the project was to use a fixed-bed system to treat water that had been contaminated with 1,4-dioxane by the process of adsorption using resins.

The advantage of using a fixed-bed system instead of a batch reactor is that a fixed-bed system allows for secondary treatment in the second column; this allows for a more accurate and reliable system whereas a batch reactor requires one to put all the material into one tank and then treat it all at once (Celenza, 2000). The fixed-bed system would be the most beneficial in extracting 1,4-dioxane because it allowed for one to pump a fixed amount of water into the first column, add the proper amount of resin per unit volume and mix for a set period of time. Then transfer the material into the second column for secondary testing. A system schematic of a typical fixed-bed system is shown in Figure 9 below.

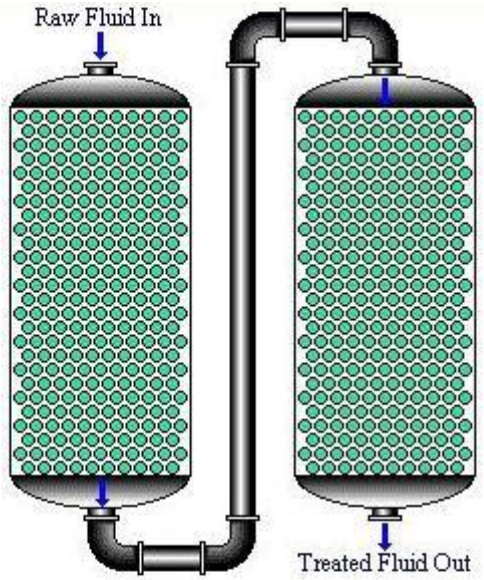


Figure 9: Fixed-Bed Reactor with Dual Columns System Schematic

(Figure 9 Source: Celenza, 2000)

8.2 Reactor Design

The first step in our design of a dual fixed-bed reactor system was to determine the size of the contactor. The contactor height, width, and bed depth is dependent on transfer units related to the influent and effluent concentration (to determine contact time) as well as the equilibrium characteristics of our L-493 and 1,4-dioxane contaminated water. The contactor diameter is based on loading limitations and maintaining a physically stable contactor bed (Celenza, 2000). Assuming a contact time of contaminated water and resin of one hour based on our experimental results we can determine the contactor must be able to hold up to 416.67 gallons at a time (converted from 10,000 gallons per day to 416.7 gallons per hour). We designed for a 500 gallon tank, which requires about 70 cubic feet to operate. We decided to size our contactor with a height of 4 feet and a radius of 2.36 feet (diameter of 5.57 feet). An example of a contactor of this size is shown below in Figure 10.

Figure 10: Fixed-Bed Reactor Example

(Figure 10 Source: Products. Alibaba.com®. Accessed 4/30/2014)

The chosen reactor design to be used will call for piping installation that will be able to withstand the anticipated amount of flow into and out of the reactor filter. Our anticipated flow rate of ten thousand gallons per day will call for a fairly small pipe size. The pipe material we chose for the chamber is Poly Vinal Chloride (PVC) piping. The way to determine what size piping is needed one must calculate the flow rater per unit time. Using PVC piping in batch reactor system requires that the piping consist of “domestically produced rigid PVC compound Type 1 Grade 1, with a Cell classification of 12454 as defined in ASTM D1784 and approved by the National Sanitation Foundation (NSF)” [Harvel Co., 2014].

With the designed contactor handling a flow of ten thousand gallons per day, our hourly flow will be 416.67 gallons. A pre-calculated chart provided by the company, FlexPVC®, allowed us to choose our PVC piping size. The chart values are found by considering the “potential damage from hydraulic hammer (shock) and noise considerations due to excessive fluid velocity” ((FlexPVC, 2014).). Since our hourly flow rate is 416.67 gallons per hour (GPH), a pipe was selected by evaluating the GPH above 416.67 GPH. If our flow is considered to be low pressure (Gravity or >20 psi), then our pipe inner diameter will be 0.5 to 0.6 inches; this allows for a flow rate of 420 GPH. If our flow exhibits average pressure (20-100 psi) then the ideal pipe inner diameter would again be 0.5 to 0.6 inches, with a maximum flow rate of 840 GPH. If there is a high pressure flow rate then the ideal pipe inner diameter will again be 0.5 to 0.6 inches, allowing a maximum flow rate of 1260 GPH (FlexPVC, 2014). Since our system is a relatively small fixed-bed reactor system of 10,000 gallons per day we assume it will be of low pressure, therefore we would require a PVC piping system using pipes with an inner diameter of 0.5 inches.

Another consideration our group had to consider was size of the stainless metal ball valves that will control flow leading into and out of the reactor. According to the FlexPVC® website for a flow rate at 416.67 GPH, a valve size of 0.5 inches would be required for this system to be functional (FlexPVC, 2014). The anticipated flow rate of 6.94 gallons per minute

(GPM) in our chamber would require the valve size to be 0.5 inches with a durability of 26 GPM (FlexPVC, 2014).

The next step is to determine the amount of L-493 resin required to operate the system. Possible water contamination levels of 50 µg/L, 1 mg/L, and 5 mg/L yield necessary Q_e values of 0.17, 0.138, and 0.0093. We will use these Q_e values in the equations below to determine the amount of resin required for each contamination level. To design the system on a larger scale the ten thousand gallon a day system was chosen as a potential option. The density of L-493 needed to be converted from 0.68 g/cm^3 to g/gal and the initial concentration needed to be converted as well. The initial concentration levels of 50 µg/L, 1 mg/L, and 5 mg/L convert to concentration levels of 0.00019 g/gal, 0.0038 g/gal, and 0.019 g/gal respectively. The following calculations illustrate the calculation of resin required to treat water contaminated with level of 50 µg/L.

Equation 1:

$$\frac{V\ Fluid}{V\ 493} = \frac{(Q_e)(Density\ Resin)}{Co}$$

Equation 2:

$$\frac{\mathrm{V\ Fluid}}{\mathrm{V\ 493}} = \frac{0.17 * 2574.1\,\frac{\mathrm{g}}{\mathrm{gal}}}{.00019\ \mathrm{g/gal}}$$

$$\frac{\mathrm{10000\ gallons\ per\ day}}{\mathrm{V\ 493}} = \frac{437.597}{.00019\ \mathrm{g/gal}}$$

V493: 0.00434189 gallons

After solving for the gallons of resin it needs to be multiplied by the density to solve for the actual amount of resin that needs to be mixed for a volume of 10,000 GPD at 50 µg/L.

$$0.00434189 * \ 2574.1\,\frac{\mathrm{g}}{\mathrm{gal}} = 11.18\ grams$$

The same calculations were repeated with the aforementioned values for contaminant concentrations of 1 mg/L and 5 mg/L. The results are shown in Table 7 below.

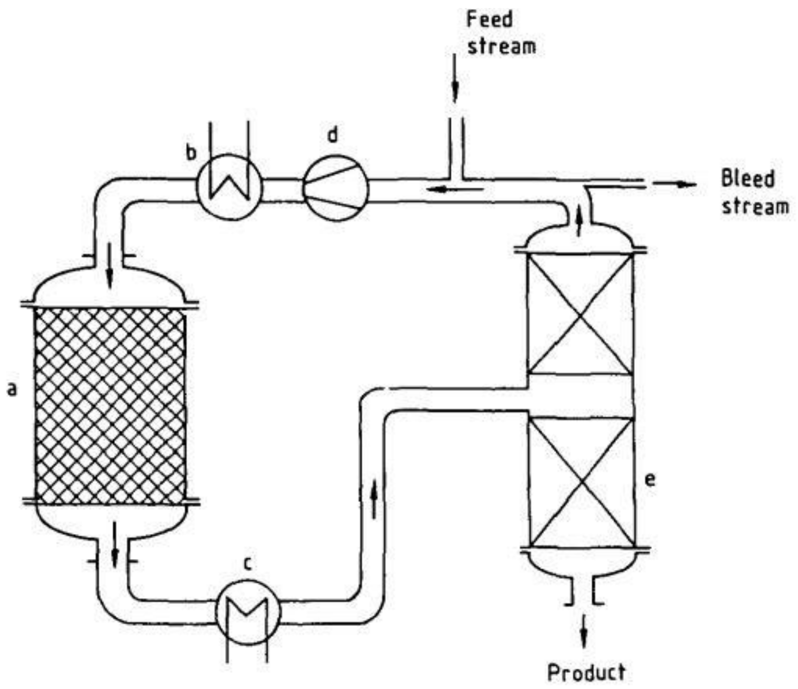
Resin Type	1,4-dioxane concentration	Q_e	Grams required for 10000 GPD
L-493	50 µg/L	0.17	11.18 grams
L-493	1 mg/L	0.138	275.36 grams
L-493	5 mg/L	0.0093	20430.11 grams

Table 7: Resin Required for Reactor System

As expected the higher the concentration of 1,4-dioxane in the contaminated water corresponds to a higher necessary mass of resin for removal. As stated in our earlier case studies occurences in the environment of 1,4-dioxane rarely exceed 1 mg/L except in extreme cases (see chapter 3.5 above) so these required resin values are reasonable for a ten thousand gallon per day system.

8.3 Cost Analysis

In order to do an effective cost analysis for the construction of a 10,000 GPD fixed-bed reactor system one must take into account the material cost, the construction cost, and the cost of L-493 resin required to operate. A 10,000 GPD system is fairly small, consisting of the contactor, a feed preheater, an exit cooler, a recirculation compressor, and a separation column. Costs also include a piping and valve system to control the flow of water in the entire system. These components are shown in Figure 11 below.

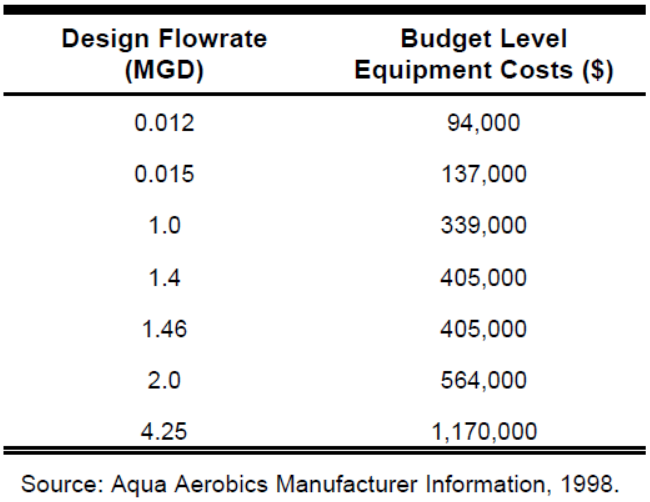


a) Fixed-bed reactor, b) Feed preheater; c) Exit cooler; d) Recirculation compressor, e) Separation column

Figure 11: Fixed-Bed Reactor Components

(Figure 11 Source: Eigenberger, 1992)

As our reactor system is fairly small, operating only at 10,000 GPD it is less expensive than systems treating water at a higher flow rate. Taking into account all of the equipment in the system allows you to estimate the cost based on the design flow rate; our estimated cost is shown below in Table 9; we used the estimated cost of a 12,000 GPD system.



Design Flowrate (MGD)	Budget Level Equipment Costs ($)
0.012	94,000
0.015	137,000
1.0	339,000
1.4	405,000
1.46	405,000
2.0	564,000
4.25	1,170,000

Source: Aqua Aerobics Manufacturer Information, 1998.

Table 8: Budget Level Costs

(Table 8 Source: EPA 832-F-99-073. Sept. 1999)

In order to operate the fixed-bed reactor system we need a sufficient amount of resin in order to treat 10000 GPD of contaminated water. The prices of 500 g of L-493 were found on the Sigma-Aldrich website and extrapolated to the amount that our system required. The total cost of L-493 resins for each contaminant concentration are illustrated in Table 10.

Resin	**Contaminant Concentration**	**Unit Cost**	**Amount of Resin Required for 10000 GPD**	**Total Cost**
L-493	50 µg/L	$113 for 500g	12	$113 (500 g order)
L-493	1 mg/L	$113 for 500g	275	$113 (500 g order)
L-493	5 mg/L	$113 for 500g	20430	$565 (2500 g order)

Table 9: Resin Cost

Total cost of construction for this fixed-bed reactor system operating at 10000 GPD treating contaminated water using resin L-493 is shown in Equation 3.

Equation 3

$$\boldsymbol{Total\ Cost = Budget\ Costs + Equipment\ Costs + Resin\ L - 493\ Costs}$$

$$\boldsymbol{Total\ Cost = \$94,000 + +\$565}$$

$$\boldsymbol{Total\ Cost = \$93,565}$$

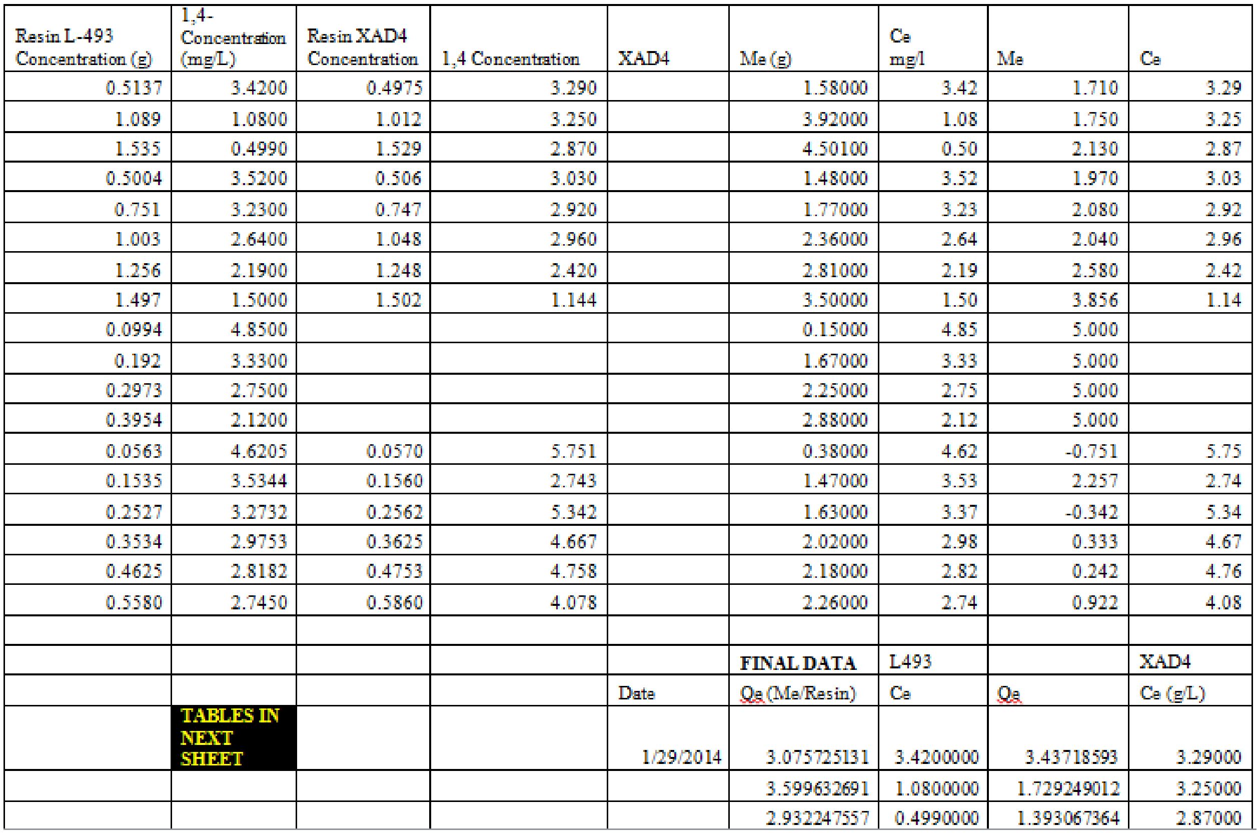
A small system such as this at a cost of under $100,000 dollars is very reasonable and could possibly be designed for use as an in-home system.

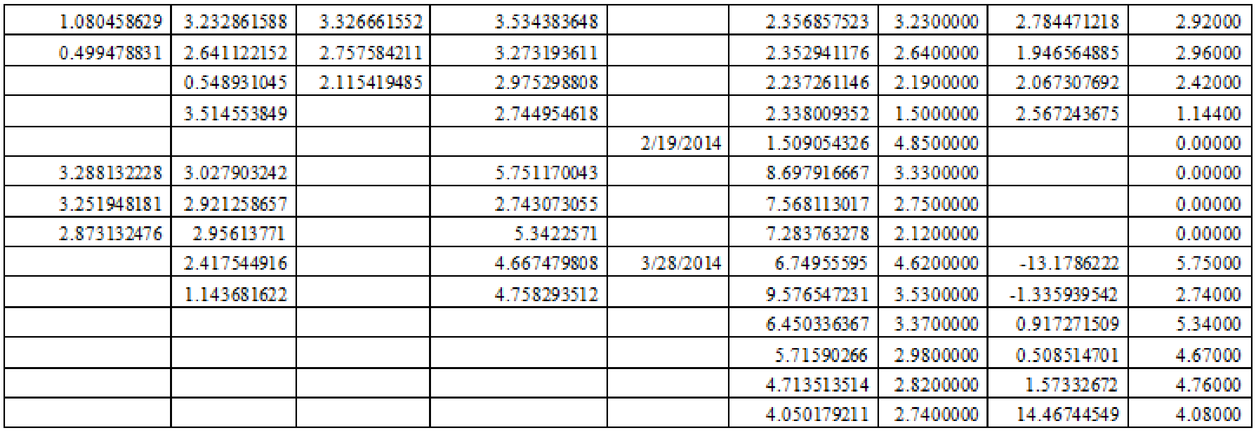
9.0 Conclusions

After the initial analysis of the four resins, our group used a process of elimination utilizing our thorough methods and identified Dowex Optipore L-493 as the best resin for 1,4-dioxane adsorption. This resin was chosen because our trials indicated that L-493 illustrated the largest removal of contaminant for least amount of resin used. The reactor system implemented is designed for a large-scale system but can easily be adjusted for a personal in-home system or a site-specific system for a landfill that is polluting groundwater resources. Creating a portable smaller system can be more effect than a larger batch reactor that would require more time and money than a two-chamber direct filtration system.

Using this method as a process for removal of 1,4-dioxane from water using a sequence batch reactor or as a two-chamber system are the primary options that we identified. In a two chamber system, two resin filled chambers would require the flow volume to be much less than 1 MGD; therefore the lifespan for a system of this design would be significantly longer in comparison to having it as a tertiary process in a sequence batch reactor. For both systems, it is important to note that although the resins can be saturated, they can be regenerated using brine. This as a result creates another filtration byproduct that requires proper hazardous disposal.

Appendix A Resin Data

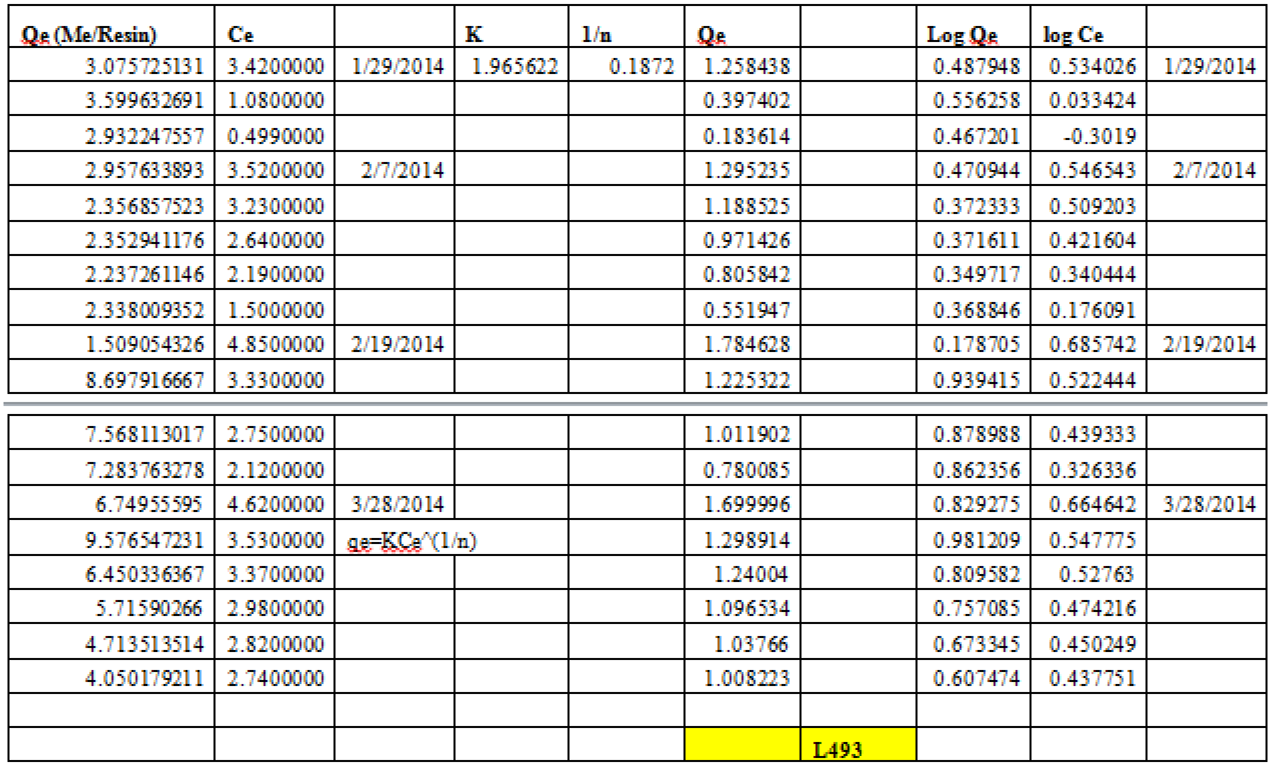




Resin L-493 Concentration (g)	1,4-Concentration (mg/L)	Resin XAD4 Concentration	1,4 Concentration	XAD4	Me (g)	Ce mg/l	Me	Ce
0.5137	3.4200	0.4975	3.290		1.58000	3.42	1.710	3.29
1.089	1.0800	1.012	3.250		3.92000	1.08	1.750	3.25
1.535	0.4990	1.529	2.870		4.50100	0.50	2.130	2.87
0.5004	3.5200	0.506	3.030		1.48000	3.52	1.970	3.03
0.751	3.2300	0.747	2.920		1.77000	3.23	2.080	2.92
1.003	2.6400	1.048	2.960		2.36000	2.64	2.040	2.96
1.256	2.1900	1.248	2.420		2.81000	2.19	2.580	2.42
1.497	1.5000	1.502	1.144		3.50000	1.50	3.856	1.14
0.0994	4.8500				0.15000	4.85	5.000	
0.192	3.3300				1.67000	3.33	5.000	
0.2973	2.7500				2.25000	2.75	5.000	
0.3954	2.1200				2.88000	2.12	5.000	
0.0563	4.6205	0.0570	5.751		0.38000	4.62	-0.751	5.75
0.1535	3.5344	0.1560	2.743		1.47000	3.53	2.257	2.74
0.2527	3.2732	0.2562	5.342		1.63000	3.37	-0.342	5.34
0.3534	2.9753	0.3625	4.667		2.02000	2.98	0.333	4.67
0.4625	2.8182	0.4753	4.758		2.18000	2.82	0.242	4.76
0.5580	2.7450	0.5860	4.078		2.26000	2.74	0.922	4.08
					FINAL DATA	L493		XAD4
				Date	Qe (Me/Resin)	Ce	Qe	Ce (g/L)
	TABLES IN NEXT SHEET			1/29/2014	3.075725131	3.4200000	3.43718593	3.29000
					3.599632691	1.0800000	1.729249012	3.25000
					2.932247557	0.4990000	1.393067364	2.87000
1.080458629	3.232861588	3.326661552	3.534383648		2.356857523	3.2300000	2.784471218	2.92000
0.499478831	2.641122152	2.757584211	3.273193611		2.352941176	2.6400000	1.946564885	2.96000
	0.548931045	2.115419485	2.975298808		2.237261146	2.1900000	2.067307692	2.42000
	3.514553849		2.744954618		2.338009352	1.5000000	2.567243675	1.14400
				2/19/2014	1.509054326	4.8500000		0.00000
3.288132228	3.027903242		5.751170043		8.697916667	3.3300000		0.00000
3.251948181	2.921258657		2.743073055		7.568113017	2.7500000		0.00000
2.873132476	2.95613771		5.3422571		7.283763278	2.1200000		0.00000
	2.417544916		4.667479808	3/28/2014	6.74955595	4.6200000	-13.1786222	5.75000
	1.143681622		4.758293512		9.576547231	3.5300000	-1.335939542	2.74000
					6.450336367	3.3700000	0.917271509	5.34000
					5.71590266	2.9800000	0.508514701	4.67000
					4.713513514	2.8200000	1.57332672	4.76000
					4.050179211	2.7400000	14.46744549	4.08000

Table 10: Multiple Trial Values

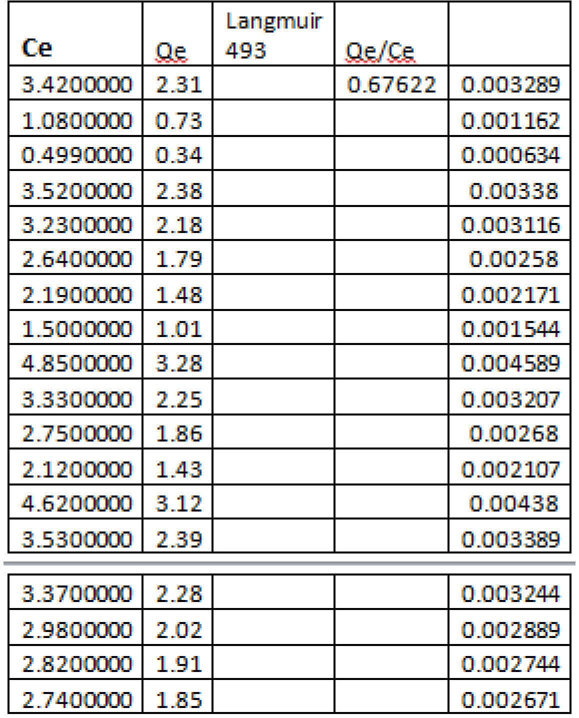
L-493 Data



Qe (Me/Resin)	Ce		K	1/n	Qe		Log Qe	log Ce	
3.075725131	3.4200000	1/29/2014	1.965622	0.1872	1.258438		0.487948	0.534026	1/29/2014
3.599632691	1.0800000				0.397402		0.556258	0.033424	
2.932247557	0.4990000				0.183614		0.467201	-0.3019	
2.957633893	3.5200000	2/7/2014			1.295235		0.470944	0.546543	2/7/2014
2.356857523	3.2300000				1.188525		0.372333	0.509203	
2.352941176	2.6400000				0.971426		0.371611	0.421604	
2.237261146	2.1900000				0.805842		0.349717	0.340444	
2.338009352	1.5000000				0.551947		0.368846	0.176091	
1.509054326	4.8500000	2/19/2014			1.784628		0.178705	0.685742	2/19/2014
8.697916667	3.3300000				1.225322		0.939415	0.522444	
7.568113017	2.7500000				1.011902		0.878988	0.439333	
7.283763278	2.1200000				0.780085		0.862356	0.326336	
6.74955595	4.6200000	3/28/2014			1.699996		0.829275	0.664642	3/28/2014
9.576547231	3.5300000	qe=KCe^(1/n)			1.298914		0.981209	0.547775	
6.450336367	3.3700000				1.24004		0.809582	0.52763	
5.71590266	2.9800000				1.096534		0.757085	0.474216	
4.713513514	2.8200000				1.03766		0.673345	0.450249	
4.050179211	2.7400000				1.008223		0.607474	0.437751	
						L493			

Table 11: L-493 Data

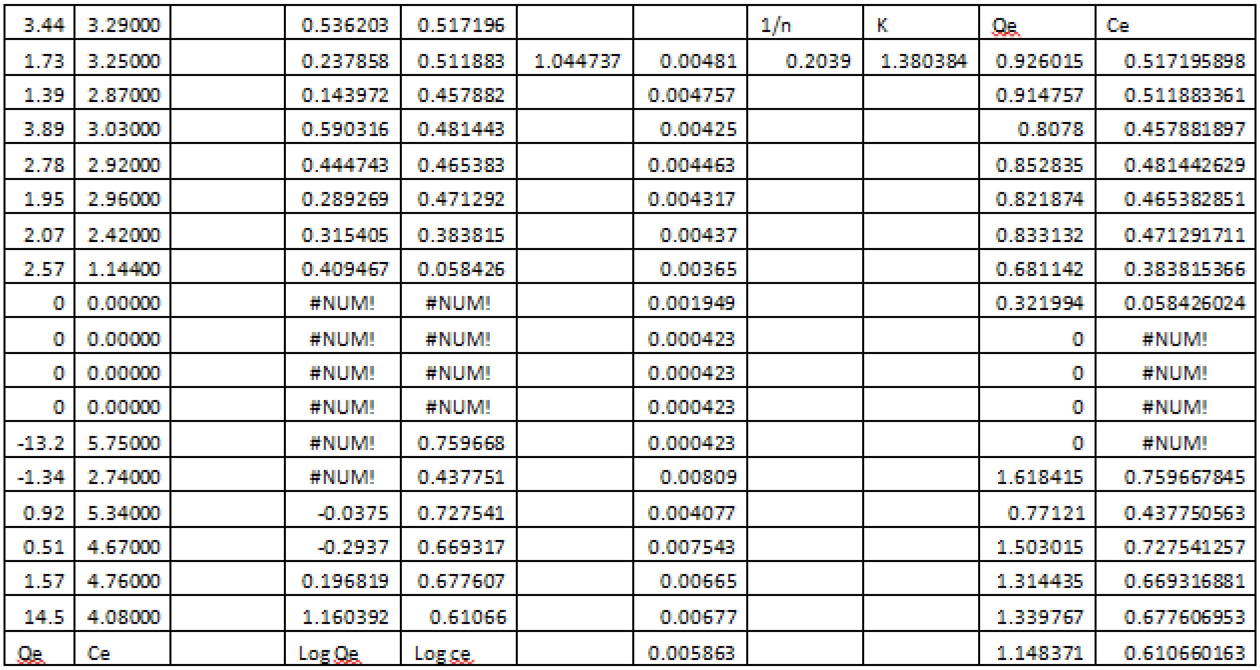
L-493 Langmuir Data



Ce	Qe	Langmuir 493	Qe/Ce	
3.4200000	2.31		0.67622	0.003289
1.0800000	0.73			0.001162
0.4990000	0.34			0.000634
3.5200000	2.38			0.00338
3.2300000	2.18			0.003116
2.6400000	1.79			0.00258
2.1900000	1.48			0.002171
1.5000000	1.01			0.001544
4.8500000	3.28			0.004589
3.3300000	2.25			0.003207
2.7500000	1.86			0.00268
2.1200000	1.43			0.002107
4.6200000	3.12			0.00438
3.5300000	2.39			0.003389
3.3700000	2.28			0.003244
2.9800000	2.02			0.002889
2.8200000	1.91			0.002744
2.7400000	1.85			0.002671

Table 12: Langmuir Data

XAD4 Data



3.44	3.29000		0.536203	0.517196			1/n	K	Qe	Ce
1.73	3.25000		0.237858	0.511883	1.044737	0.00481	0.2039	1.380384	0.926015	0.517195898
1.39	2.87000		0.143972	0.457882		0.004757			0.914757	0.511883361
3.89	3.03000		0.590316	0.481443		0.00425			0.8078	0.457881897
2.78	2.92000		0.444743	0.465383		0.004463			0.852835	0.481442629
1.95	2.96000		0.289269	0.471292		0.004317			0.821874	0.465382851
2.07	2.42000		0.315405	0.383815		0.00437			0.833132	0.471291711
2.57	1.14400		0.409467	0.058426		0.00365			0.681142	0.383815366
0	0.00000		#NUM!	#NUM!		0.001949			0.321994	0.058426024
0	0.00000		#NUM!	#NUM!		0.000423			0	#NUM!
0	0.00000		#NUM!	#NUM!		0.000423			0	#NUM!
0	0.00000		#NUM!	#NUM!		0.000423			0	#NUM!
-13.2	5.75000		#NUM!	0.759668		0.000423			0	#NUM!
-1.34	2.74000		#NUM!	0.437751		0.00809			1.618415	0.759667845
0.92	5.34000		-0.0375	0.727541		0.004077			0.77121	0.437750563
0.51	4.67000		-0.2937	0.669317		0.007543			1.503015	0.727541257
1.57	4.76000		0.196819	0.677607		0.00665			1.314435	0.669316881
14.5	4.08000		1.160392	0.61066		0.00677			1.339767	0.677606953
Qe	Ce		Log Qe	Log ce		0.005863			1.148371	0.610660163

Table 13: XAD4 Data

Appendix B: Images

Image 1: Gas Chromatography Machine

Image 2: 24 Hour Mixer

Image 3: L-493 Resin

Image 4: XAD4 Resin

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