Removal of Sulfamethoxazole from Water by Ion-Exchange Adsorption

Major Qualifying Project completed in partial fulfillment
Of the Bachelor of Science Degree at
Worcester Polytechnic Institute, Worcester, MA

Submitted by:

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April 29, 2013

Abstract

This project studies and compares the removal effectiveness of three ion-exchange resins and granular activated carbon (GAC) on aqueous solutions of sulfamethoxazole (SMX) at pH 5, 7, and 9. After treatment by adsorption, the final concentration of SMX was measured with a UV spectrophotometer. Evaluation of adsorbent effectiveness included the analysis of kinetics and equilibrium data. Results yielded that Filtrasorb 200, Marathon and Optipore worked most successfully due to chemical structuring and specific adsorption characteristics. Experiments also indicated that pH level did not significantly affect the adsorbent effectiveness.

Acknowledgements

We would like to thank our project advisor, Professor John Bergendahl, for his guidance and support throughout the year. We would also like to thank David Messier and Don Pellegrino for their help in the laboratory.

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Chapter 1: Introduction

Over the past decade, the demand for pharmaceuticals and personal care products (PPCPs) has nearly paralleled the escalating population. The pharmaceutical industry has expanded to accommodate for this need, producing hundreds of tons of synthetic chemicals per year (Pontius, 2002) and growing by nearly $500 billion in the world market between 2003 and 2011 (IMS, 2012). The prolonged use of PPCPs has led to evident emergence in the environment, creating the potential for adverse consequences to ecosystems and human health. The rise in both contamination and consumption of natural resources spurs the need to protect what we have for future generations.

PPCPs, despite years of persistent usage, have become a contemporary concern because of their widespread occurrence in the environment and their correlation to ecological disturbance. PPCPs encompass a diversity of chemicals found in veterinary medicine, agricultural practice, human health and cosmetic care. Traces of these chemicals in both aquatic and terrestrial domains, found in low concentrations ranging from nanograms to micrograms per liter (ng/L – µg/L), have only been confirmed within the past decade due to recent improvements in chemical analysis. New technology and methodologies have allowed for the execution of necessary studies, such as those involving the transport of PPCPs in the environment. The origin and fate of PPCPs varies widely, depending on discharge locality, present treatment, and chemical reactivity. However, the chemical transport of PPCPs is still chiefly unknown. On the other hand, it is known that there are multiple pathways to the environment, especially into water bodies.

In particular, antimicrobials and their metabolites are appearing in significant amounts in water supplies. Although no evidence exists that human health is affected by minute doses of antibiotics over long periods of time, changes have been observed in ecosystem functions. Studies have determined a rising level of antimicrobial-resistant organisms in the environment. In addition to antimicrobial resistance, the bacteria being studied displayed a delay in cell growth, limited denitrification, and shifts in community composition (USGS, 2012). Antimicrobials, like most PPCPs, enter ecosystems by improper disposal, excretion, and wastewater effluent discharges. The majority of these frequently-used compounds and their metabolites are not completely removed by treatment systems, with removal efficiencies reported between zero and 90% (Bhandari et al., 2008). Because of increased usage rate, lack of efficient removal technology, and environmental risks associated with PPCP occurrence, there is reason to develop new materials and processes in treatment systems in order to eliminate antibiotics from entering the environment.

A class of antimicrobial drugs commonly found in wastewater effluent is sulfanilamides. These compounds are a subset of chemicals containing the sulfonamide functional group, to which numerous prescription drugs belong. Sulfonamide drugs consist of anti-diabetic agents, anticonvulsants, diuretics, protease inhibitors, and beta-blockers. These compounds are of concern due to their expansive use and inability to readily biodegrade in the environment, despite the fact that many sulfonamides are photodegradable in surface waters (Niu et al., 2012). Sulfanilamide antimicrobials interfere with microbiological mechanisms by mimicking essential bacterial enzymes, making the compounds possibly detrimental to secondary wastewater treatment processes.

Sulfamethoxazole (SMX), a broad-spectrum biostatic sulfanilamide, has become a point of interest because of its prevalence in contaminated wastewaters at concentrations correlated to bacterial resistance and genetic mutations in organisms (Niu et al., 2012). Figure 1 shows the chemical structure of SMX. Although therapeutically active by itself, SMX is often paired with trimethoprim (TMP), creating a synthetic antibacterial combination drug that affects the biosynthesis of nucleic acids and proteins in bacteria. The SMX-TMP drug is one of the most highly prescribed antibiotics for treating bladder, lung, and ear infections. Sulfa allergies and liver toxicity pose as common side effects in consumers of this antibiotic. The human body does not fully metabolize the compound, causing about 30% to be excreted in its original pharmaceutically active form.

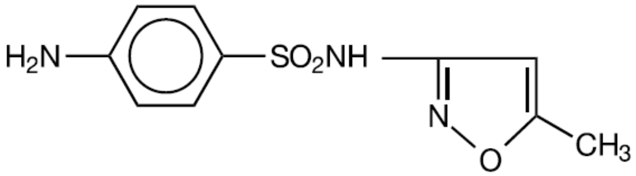

Figure 1: Molecular Structure of Sulfamethoxazole (Source: US FDA, 2012)

Taking into account the widespread use of sulfonamides and their potential environmental effects, there is importance in developing new technologies for removing SMX and similar compounds from points of discharge. Current water and wastewater treatment processes, such as advanced oxidation, photolysis, and adsorption by granular activated carbon (GAC), have shown some success in the removal of SMX. UV-light treatment has exhibited promising results because the aforementioned photosensitivity. In addition, research has been conducted on the effectiveness of high-silica zeolite adsorbents and GAC at various pH levels. Despite research with a variety of current technologies, the compound is still not entirely degraded or removed, having been found at alarming concentrations in surface water, groundwater, and soils (Bhandari et al., 2008). However, there are up-and-coming adsorbents, particularly ion-exchange resins, which have not been fully researched in SMX removal.

This project aims to analyze the removal effectiveness of ion-exchange resins on aqueous solutions of SMX in water at pH levels of 5, 7, and 9. In order to carry out this analysis, the team determined specific resins to be studied based on adsorbent properties, commercial availability and professional recommendations. The chemical properties and current removal technologies for SMX were researched to find adsorbents best suited for potentially removing the compound. Methods pertaining to adsorption as treatment were also researched in order to help tailor the experimental procedures to the resins studied in this project. Moreover, the removal efficiency of the ion-exchange resins was compared to that of Filtrasorb 200®, a brand of GAC, in order to close gaps encountered in previous research.

Chapter 2: Background

This chapter will provide an overview of research concerning the environmental presence, risks, and current treatments for SMX. In order to establish a perspective on the potential consequences of SMX in the environment, the chapter opens with a summation of PPCPs and the effects of their occurrence. The next section introduces the chemical structure, pharmacological properties, and the usage of SMX. Following the synopsis of its properties is a review of its occurrence along with a discussion focusing on associated environmental risks, including bacterial resistance and genetic mutations. A brief background of advanced oxidative processes is provided to acknowledge successful treatments in the removal of SMX. The last section details the adsorption treatment process, which is employed as a means of removing SMX in this project.

2.1 Pharmaceutical and Personal Care Products in the Environment

The development of PPCPs and pharmaceutically active compounds (PhACs) over the past century has drastically changed healthcare and world industries. This diverse group of chemicals is typically used in agriculture, veterinary medicine, human health, and cosmetic care (Daughton, 2004). However, decades of manufacturing, consumption, and disposal of these compounds have caused eminent damage in ecosystems and human health. Alongside the environmental issues pertaining to synthetic chemicals, the increasing population has triggered a corresponding trend in the consumption and pollution of water supplies, necessitating the implementation of new treatment technologies and environmental laws.

Research over the past 30 years has indicated ecological effects related to the emergence of PPCPs. Antibiotics, steroids, detergents, antidepressants, and pesticides consist of a few of the chemicals initially linked to environmental pollution. These chemicals have been found to both directly and indirectly interact with hormone receptors in organisms (Daughton, 2004). Those substances, defined as endocrine disrupting compounds (EDCs) by the United States Environmental Protection Agency (EPA), alter the balance of hormones responsible for developmental processes and homeostasis. Issues with synthetic chemicals were noticed before major research on EDCs began. A well-known case of these observations was documented with the 1962 publishing of Rachel Carson's *Silent Spring*, which described the decline in bird population in an area sprayed with DDT. Since then, studies have shown connections between

PPCP prevalence and aquatic toxicity, irregularity in ecological communities, and antibiotic resistance (USGS, 2012). These substances tend to be detected at low concentrations (ng/L – µg/L) and occur in a variety of climatic, hydrological, and land-use settings for long periods of time (Boxall et al., 2012). Despite the outcomes of these studies, the fate and transport of PPCPs is still unknown due lack of long-term investigation and appropriate chemical analyses. Furthermore, there is little evidence confirming the effects on human health from continual exposure to trace concentrations of these substances. The potential for harm to health still exists, since the combination of therapeutic doses of pharmaceuticals can generate adverse interactions (Boxall et al., 2012).

Although the exact fate and transport of PhACs is unclear, research provides an understanding of their pathways into the environment. Awareness of these pathways aids in the development of source and pollution control. Both PPCPs and PhACs enter aquatic and terrestrial domains by multiple entries, as illustrated in Figure 2.

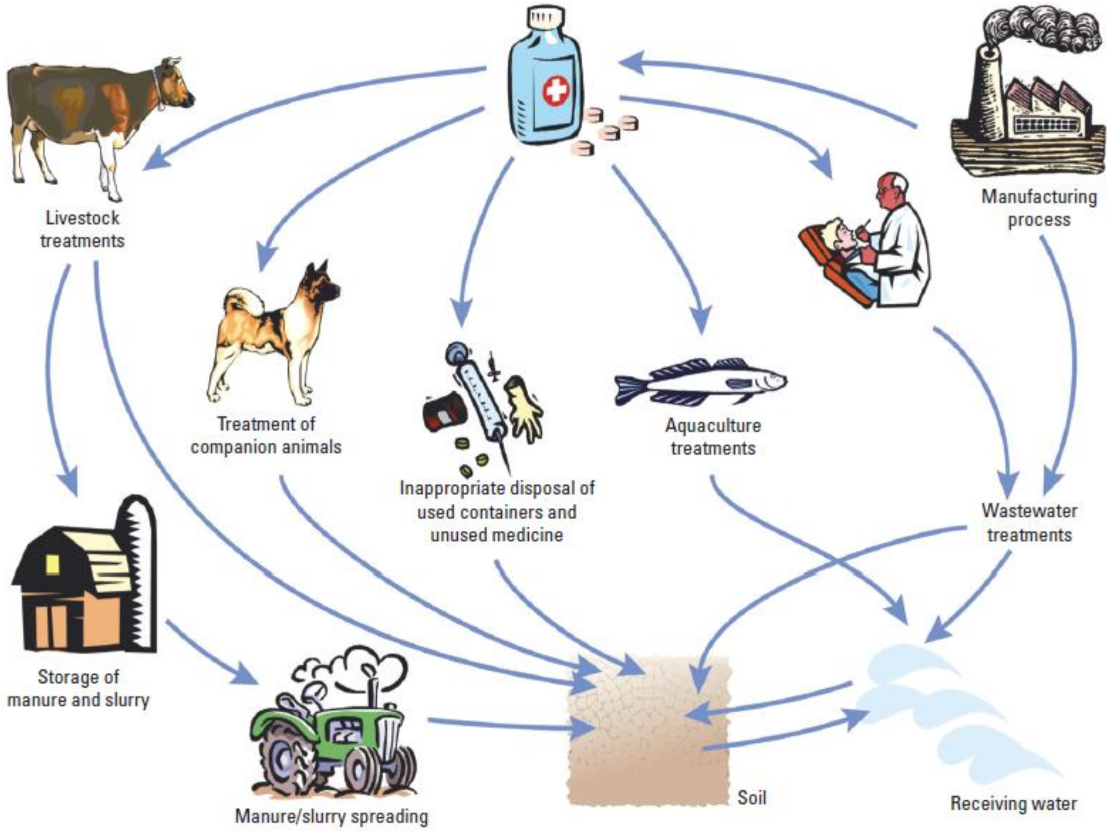

Figure 2: Pathways of PPCPs into environment. (Source: Boxall et al., 2012)

While hospitals and manufacturing facilities are significant sources of PhACs, municipal wastewater treatment plants (WWTPs) contribute the greatest amount of such into groundwater and surface waters (Bhandari et al., 2008). Major sources of substances to wastewater influent include improper disposal of medicines and excretion of metabolized drugs. Reports show some removal of PhACs during WWTP processes, but removal efficiencies range from zero to 90% and do not indicate either the exact removal or the chemical transformation of the parent compound (Bhandari et al., 2008). Considering the occurrence of pharmaceuticals and their known effects, there are risks associated with the incomplete removal of these compounds.

In particular, there are concerns about the presence of antibiotics in WWTPs and the degradation processes in septic systems. Like many PhACs, a number of antibiotics are not readily degradable in the environment and have a direct effect on microbial and ecological functions. Antimicrobials have been shown to cause bacterial resistance, which may affect the sorption of PPCPs to activated sludge treatment (Boxall et al., 2012). In turn, antimicrobials may be transformed into toxic oxidation products. Groundwater is most vulnerable to the persistence of antibiotics because of the absence of sunlight to photodegrade the contaminants (Underwood et al., 2011). The natural attenuation of antimicrobials in groundwater establishes the potential to cause adverse impacts on aquifer bacteria and associated ecosystem functions. Taking into account the known outcomes of antimicrobial occurrence, developments of new technologies are crucial in reversing the possible detrimental effects in water supplies.

2.1.1 Sulfonamides

One class of PhACs that is a growing environmental concern is sulfonamides, more commonly known as “sulfa” drugs (Bhandari et al., 2008). These particular pharmaceuticals have a molecular structure that contains a central sulfur atom belonging to a sulfonyl group and adjoins characteristic amine groups. Sulfonamides cover a wide spectrum of therapeutic substances: anti-diabetic agents, anticonvulsants, diuretics, protease inhibitors, and beta-blockers. Other applications include agricultural antibiotics (Sedlak et al., 2005). Sulfanilamides, a subcategory of sulfonamides, encompass a family of antimicrobials containing the sulfonamide functional group attached to a characteristic aniline unit (PubChem, 2005). This project focuses on the removal of one such sulfanilamide, sulfamethoxazole (SMX), by ion-exchange resins and adsorbents.

2.2 Sulfamethoxazole

SMX belongs to the sulfanilamide drug class as a wide-spectrum bacteriostatic antimicrobial. This polar, UV-light-sensitive chemical is typically combined with trimethoprim (TMP) to form a more effective antibiotic commonly known by brand names such as Bactrim®, Septra®, and Gantanol®. The SMX-TMP combination drug inhibits two crucial steps in the biosynthesis of folic acid in bacteria, limiting bacterial reproduction. The antimicrobial, one of the most frequently prescribed in the world for bladder and lung infections, works against gram-negative and gram-positive aerobic bacteria, including *Escherichia coli*, *Streptococcus*, and *Staphylococcus aurea*. In spite of its high dispense rate, SMX frequently causes severe reactions, such as anaphylaxis, rash, and Stevens - Johnson syndrome (US FDA, 2008).

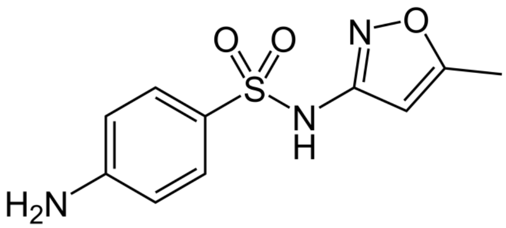

Figure 3: Molecular Structure of Sulfamethoxazole (Source: US FDA http://www.fda.gov)

Figure 3 shows the basic molecular arrangement of SMX ($C_{10}H_{11}N_3O_3S$). The molecule is structured with a sulfonyl group, connected to an amine group to the right and an aniline group to the left. The compound acts as an analog to para-aminobenzoic acid (PABA) in the bacterial production of folic acid. In the combination SMX-TMP antibiotic, SMX blocks the first step in the synthesis by competing with PABA, hindering the production of dihydrofolic acid. TMP affects the second step by binding to dihydrofolate reductase, an enzyme essential to the production of tetrahydrofolic acid (US FDA, 2008). After absorption in the human body, SMX is excreted in its original form (approximately 30%) as well as two metabolites, N_4-acetyl-SMX and SMX-N_1-glucuronide (Radke et al., 2009).

At standard temperature and pressure, SMX exists in solid form as yellow-white powder or crystals with a molecular weight of 253.28 grams per mole. In neutral form, it has a melting point of 166 °C and is poorly soluble in water. SMX exhibits acid/base characteristics, appearing in ionic and neutral forms corresponding to pKa values of 1.7 ± 0.1 and 5.64 ± 0.07 (Knappe et al., 2007). Figure 4 illustrates the acid-base speciation of SMX.

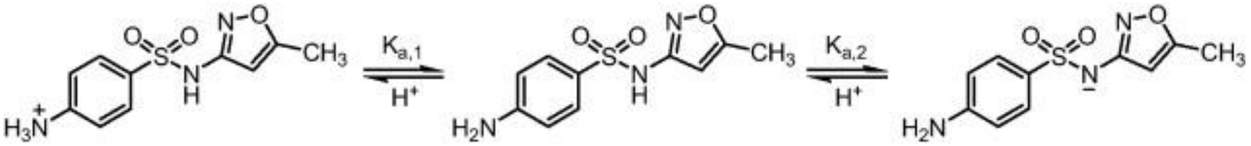

Figure 4: Acid-Base Dissociation Equilibrium of SMX (Source: Xekoukoulotakis, 2011)

SMX predominantly occurs in its neutral form, appearing in relatively acidic solutions where its pKa value (5.64 ± 0.07) corresponds to the average pH level of surface water. Since the pH in surface water falls between 5 and 9, the negatively-charged form of SMX also appears often (USGS, 2012). The aniline group on the molecule has a negative charge on the nitrogen atom, which acts as an ionic binding site. SMX rarely exists in its protonated form, which requires an extremely acidic setting. The variance in pH throughout WWTP processes and the environment causes the charge on SMX to change, which may allow for successful removal by ion-exchange sorption.

2.3 Sulfamethoxazole in the Environment

The expanding production and consumption of antimicrobials are correlated to their frequent occurrence in water supplies. Antimicrobials enter water bodies via several pathways, with the main routes of release being improper disposal and human excretion (Bandari et al., 2008). The widely-used antibiotic SMX recurs in water supplies and WWTP effluent for these reasons. Corresponding to its demand and environmental prevalence are emerging issues with bacterial resistance and toxicity in aquatic organisms.

2.3.1 Prevalence in Aquatic Systems

Research indicates that SMX is among the most ubiquitous antimicrobial contaminants in the aquatic domain. Surface waters, groundwater, drinking water, and wastewater effluents all have been found to contain traces of SMX. Recent technological improvements in chemical analysis and detection methods have allowed for the detection of low SMX concentrations and, in turn, for these studies to take place.

A study by Bhandari et al. (2008) evaluated the occurrence of several widely prescribed antibiotics, including SMX, in municipal WWTPs. Effluent samples were taken over the course of a year from four facilities, all of which utilized activated sludge systems, in the Midwestern

United States. The treatment capacities among the sampled facilities ranged from 3 million to 80 million liters per day. From two of the smaller facilities, influent and effluent SMX concentrations averaged 18.3 ± 10.6 μg/L and 3.25 ± 5.49 μg/L, respectively. Other WWTP effluents reported outside the Bhandari study have detected concentrations between 0.21 and 7.9 μg/L. The Bhandari study observed a seasonal variability in SMX concentrations. According to the analysis, SMX effluent concentrations are much lower in the summer than in the winter, but the opposite holds true for contaminated influent.

Another study revealed the prevalence of SMX in groundwater (Underwood et al., 2011). In a nationwide groundwater survey conducted by the United States Geological Survey (USGS), SMX appeared in 23% of the samples at an average concentration of 1.11 μg/L. The study also mentions the presence of SMX in contaminated waters globally, reporting concentrations between 0.25μg/L and 68μg/L. This publication also states that there are high occurrence rates of SMX in groundwater from a sandy drinking-water aquifer on Cape Cod, MA. The variance in SMX concentrations suggests that, while there is natural attenuation of SMX in surface waters and evidence of reduction in WWTPs, the persistent low concentrations of SMX may inhibit ecosystem health in groundwater.

The 2005 publication “Occurrence Survey of Pharmaceutically Active Compounds” reported a wide range of SMX concentrations from various sources (Sedlak et al., 2005). In the survey, an evaluation of PhAC concentrations was conducted on engineered treatment wetlands, effluents from conventional and advanced WWTPs, and the Sweetwater soil aquifer treatment system. SMX was found in over 50% of samples collected from wastewater effluent and surface water (Table 1.8: “Summary of occurrence data for antibiotics”, p. 23). The highest concentrations detected in conventional WWTPs were a result of SMX presence, ranging from 60 to 2000 ng/L (0.06 to 2 μg/L). High concentrations of SMX also appeared in samples from the Mt. View engineered treatment wetland and in shallow well samples from the Sweetwater soil aquifer treatment system.

2.3.2 Risks to Environment and Human Health

As an antibiotic, SMX is often associated with antibacterial resistance, but its risks to ecological systems and human health extend beyond this typical issue. Examples of these issues are alterations to the balance of naturally-occurring microorganisms, the nitrogen cycle, genetic mutations, and aquatic toxicity. The following studies validate the current and potential risks correlated to the environmental occurrence of SMX.

The previously mentioned 2011 publication on a nationwide groundwater survey describes the effects of SMX on bacterial enrichment (Underwood et al., 2011). In the experimental portion of the survey, an enrichment culture prepared with groundwater samples taken from a Cape Cod drinking-water aquifer were exposed to environmentally relevant concentrations of SMX. Experimental findings concluded that SMX delayed cell growth, decreased nitrate reduction rate potentials, and caused genetic interference in *Pseudomonas* soil bacteria. These findings suggest that ecological exposure to SMX directly affects the nitrogen cycle by decreasing bacterial metabolic ability of nitrogen, which, in turn, increases NO_3 concentrations. This is a concern because NO_3 contamination in drinking water is related to serious health disorders such as methemoglobinemia.

Antimicrobial resistance is one of the prominent environmental concerns correlated to SMX. The concentrations found in WWTP effluent and surface waters are equivalent to the minimum inhibitory concentrations (MICs) of bacteria. MICs estimate the susceptibility of bacteria to antimicrobials. According to the 2012 US FDA data sheet for Bactrim®, MICs for susceptibility of *Enterobacteriaceae* family of pathogens are less than 20 µg/L (US FDA, 2012). Long-term bacterial exposure to this concentration allows for genetic mutations contributing to bacterial resistance (Pruden et al., 2006). In addition to bacterial mutations, SMX has exhibited biotoxicity for fish and algae growth, having caused genetic mutations and chronic effects (Niu et al., 2012).

2.4 Treatment Technologies

2.4.1 Advanced Oxidation Treatments

Oxidation

In the process of ozonation, ozone (O_3) gas is generated by running a current through O_2 gas. The O_3 is then bubbled through liquid containing the compound to be removed. Because O_3 is unstable, it decomposes into O_2 and an oxygen radical. In ozone treatments on SMX, this free radical is attracted to available hydrogen on the organic structure of SMX.

The use of ozonation in water treatment constitutes advantages and disadvantages. As an advantage, the resulting by-products of ozonation are smaller and easier to be biodegraded. This is especially desirable when there is a high concentration of complex organic carbons in the water. On the other hand, molecular ozone also oxidizes naturally-occurring bromine atoms. The resulting bromate is difficult to remove from water and is strongly suspected of being a carcinogen. As a result, bromate concentration in water is regulated and must be kept below 10 μg/L (Viessman et al, 2009).

UV Photolysis

UV Photolysis is an advanced oxidation process (AOP) in which energy from ultraviolet light ($100 < \lambda < 400$ nm) strikes a molecule and breaks bonds. Most times, this occurs in the presence of a catalyst. The extent of dissociation depends on the contact time and the intensity of the UV rays. The reaction can be enhanced using H_2H_2. However, like ozonation, UV photolysis may result in disinfection by-products, which can have variable toxicity.

Chlorination

Chlorine disinfection is the most common disinfection method in water and wastewater treatment in the United States. It is used for both primary and secondary disinfection as free and combined chlorine. Free chlorine in particular has been shown to be effective in the treatment of SMX, reacting with the neutral and anionic forms of SMX (García-Galán et al., 2008). However, this results in the formation of byproducts. Those byproducts may not show up in a measurement of UV absorbance because of a change in structural characteristics (Radjenovic et al., 2009). Additionally, the treatment reactions must take place in excess of free chlorine in order to maintain treatment. One of the chlorination products, N-chlorinated SMX, was found to yield the parent SMX in the absence of reducing agents, or when there is no significant excess of free chlorine, within hours (Dodd and Huang, 2004). Because of this, chlorination treatment of SMX requires excessive disinfectant and is not as effective overall.

2.4.2 Adsorption and Ion Exchange

This project focuses on the use of adsorption, a key stage found in water treatment processes, to remove a polar compound from water. Adsorption is the accumulation of molecules on the interface of phases, commonly being either gas-solid or liquid-solid. Adsorbents have an adhesive energy greater than the cohesive energy of the adsorbate. Activated carbon, silica gel, activated alumina, and aluminosilicates are among the most common adsorbents. The adsorbents used in this study were chosen based on potential removal effectiveness for the adsorbate, SMX.

In general, the polarity, molecular size, characteristics of the solvent, and the functionality of adsorbate determine the proper adsorbents to use.

The mechanisms behind adsorption involve weak and reversible molecular bonds, allowing for adsorbent regeneration and adsorbate extraction. Van der Waals forces, steric interaction, hydrogen bonds, hydrophobicity and polarity are some of the mechanisms associated with adsorption, which can be categorized by two basic types: physical adsorption and chemisorption (Chiou, 2002). Physical adsorption, the type that entails van der Waals forces, does not require functional sites on a surface and generates multilayer accumulation. Chemisorption, which generates single-layer accumulation, involves chemical bond forces and requires functional sites within the adsorbent in order for bonds to form. Often times, there is a combination of the two types, since adsorption energies vary among different substances being adsorbed and the materials to which they adhere (Chiou, 2002). In addition to the types of bonding, the adsorption process involves thermodynamics such that there is a reduction in freedom of molecular motion that causes a loss in system entropy.

Ion exchange, although not formally recognized as adsorption, is a sorption process in which ions in solution are transferred to a solid matrix containing ions of similar polarity (Armenante, 1999). This process differs from adsorption because it requires an interchange of materials for the purpose of maintaining electroneutrality. No chemical alterations take place to either the adsorbent or the contaminant, but regeneration is required to replace the ions adsorbed. This process works well on organic compounds and ionized substances that are small in molecular size, as size affects the charge density of the molecule and the ion exchange rate (Armenante, 1999). When removing organic compounds, ion exchangers tend to act more as conventional adsorbents. As a process overall, ion exchange is practical because of its handling capacity and its ability to recover expensive materials, concentrate pollutants, and be regenerated.

Factors Affecting Adsorption

The rate of adsorption changes according to adsorbent and adsorbate characteristics, such as surface area, particle size, solubility, and pH (Armenante, 1999). The surface area of the adsorbent plays a role in adsorption capacity, with larger sizes implying greater capacity. Smaller adsorbent particle size increases adsorption capacity since it reduces limitations on internal diffusional and mass transfer. The solute, or adsorbate, also affects this process, depending on its solubility in liquid, affinity for the adsorbent, ionization, and molecular size compared to the adsorbent pore size. In addition to the structural and physical aspects of the materials involved, this process is contingent on other factors such as contact time and pH. Temperature has one of the greater impacts on the extent of adsorption (McCabe et al., 2005).

Several of the aforementioned attributes posed as critical parameters in determining potential adsorbents for SMX. These parameters included pore size, specific surface area, and loading capacity. Other attributes covered adsorbent functional groups, structure, and compatibility with neutral and anionic forms of SMX.

Granular Activated Carbon

The granular activated carbon (GAC) evaluated in this project was Filtrasorb® 200 (FS-200), manufactured by Calgon Carbon Corporation. The product data sheet is shown in Appendix D. GAC falls under the larger of two sizes in activated carbons, which are the most commonly used adsorbents in wastewater treatment (Armenante, 1999). The smaller size, powdered activated carbon (PAC), is produced for direct addition to small amounts of wastewater and is characteristically small in particle size (<200 mesh). GAC, often used in adsorption columns, is comprised of reagglomerated coal-based activated carbon and has a high specific surface area with a particle size range of 0.4 to 2.5 mm. Activated carbons have a complex pore structure ranging in diameters from 10 to 10,000 Å, enabling a diversity of molecules to adsorb to the surface. Micropores, or pores having a diameter smaller than 1000 Å, are the key adsorption locations in activated carbon (Armenante, 1999).

Ion Exchange and Polymeric Resins

An application that has not been significantly studied for SMX removal is ion exchange with resins. Ion-exchange resins are small porous plastic beads with polystyrenic matrix structures that contain permanently attached, or fixed, ions (De Dardel, 2010). Free-moving counterions are integrated into the resin to neutralize the fixed ions. Fixed ions contain the functional groups that attract the solute, which in turn are exchanged for the mobile counterions. Figure 5 shows the basic structure of cation and anion resin beads. Functional groups can be seen attached to the skeleton, whereas the counterions fill the available spaces in the resin.

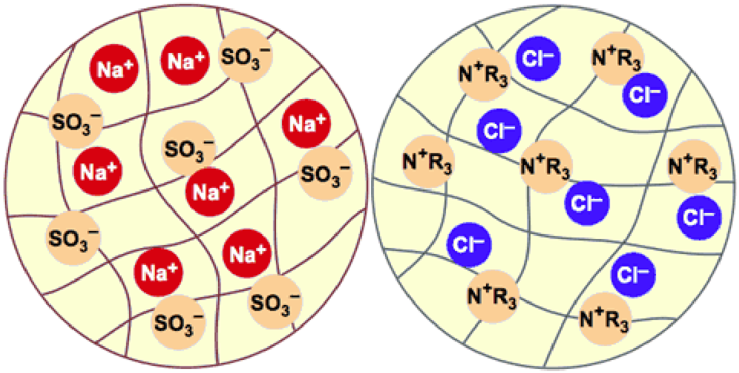

Figure 5: Schematic cation and anion resin beads (Source: http://dardel.info)

The polystyrenic matrix of a resin is composed of styrene monomers in cross-linked chains. Resins are activated for different types of ion exchange reaction, which generally falls under one of the following: strongly acidic cation, weakly acidic cation, strongly basic anion, and weakly basic anion. Some resins are not classified as ion-exchange, but they act similarly due to the chemical nature of their unique structures (De Dardel, 2010). Strongly acidic cation exchange resins are activated via sulphonation, producing hydrogen as the exchange ion. Weakly acidic cations involve the hydrolization of carboxylic acid groups in acrylic polymers. Both strongly and weakly basic anion exchange resins are formed from a two-step process, which requires chloromethylation followed by animation, or the replacement of a covalent chloride by an amine (De Dardel, 2010). Other polymeric resins act as chelates, which surround adsorbates in a claw-like formation.

One polymeric resin identified as potentially effective was Amberlite® XAD4 (AMB), an industrial grade cross-linked polymeric adsorbent manufactured by Dow Chemical Company. This adsorbent comes in the form of white insoluble beads and tends to remove organic substances with low molecular weight. Although non-ionic, its macroreticular aromatic structure enables the adsorption of hydrophobic molecules from polar solvents. Its structure, shown in Figure 6, contains a continuous polymer and pore phase, yielding a high surface area and broad micropore distribution. The engineering data sheet for AMB is shown in Appendix D.

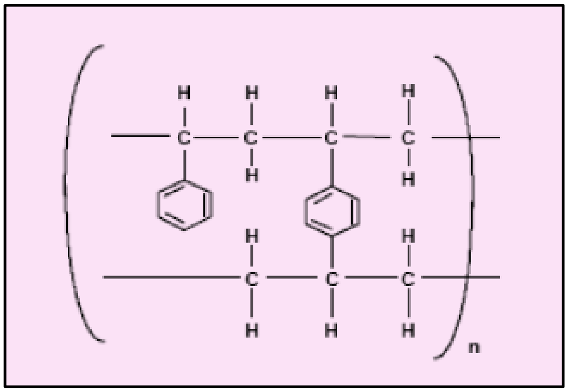

Figure 6: Amberlite XAD4 molecular structure

Another resin that was analyzed in this study is DOWEX Marathon® C (MAR), a uniform particle size, high capacity cation exchange resin used in demineralization and softening applications. Its small and uniform particle size enables efficient regeneration, kinetics, and higher operating capacity. MAR is produced as amber translucent spherical beads that contain styrene-DVB matrices, with sulfonic acid as the functional group. Because of its high acidity, the resin requires a rinse before application. Appendix D contains the product data sheet for MAR.

Lastly, Optipore® L493 (OPT) was studied. OPT is a highly cross-linked polymeric resin that has a hydrophobic surface and contains no functional group. This resin has a high surface area and a broad pore size distribution of 20 to 50 mesh, which concentrates organic compounds. OPT regeneration includes several methods, such as steam and water rinse, and depends on the nature of the adsorbate. The OPT product information sheets are found in Appendix D.

Isotherms

Adsorption effectiveness can be changed by numerous factors, such as temperature, contaminant polarity, and pH. By studying adsorption at equilibrium conditions, a relationship can be developed between the remaining concentration of the contaminant and the amount of contaminant adsorbed. Adsorption isotherms express this graphically by plotting equilibrium concentration against the mass of the contaminant removed per mass adsorbent.

Different types of isotherms portray different efficiencies of an adsorbent at removing a given contaminant. Two typical adsorption isotherm models are the Freundlich and Langmuir isotherm equations, which model different behaviors of data and their appropriate applications. A linear isotherm goes through the origin of the graph and occurs when the amount of contaminant removed is directly proportional to the concentration left in solution (McCabe et al., 2005). Favorable isotherms are shown graphically as being convex up, and unfavorable isotherms are concave up (McCabe et al., 2005). Irreversible isotherms describe adsorption in which the concentration has no impact on the amount of substance adsorbed and in which desorption must be performed at significantly higher temperatures than other isotherms.

Freundlich Model

The Freundlich isotherm is described using an empirically derived equation that portrays strongly favorable adsorption. Developed by Herbert Freundlich in 1926, this equation often better fits data from liquid-solid adsorption (McCabe et al., 2005). Equation (1) displays the Freundlich equation.

$$q_e = K_f C_e^{\left(\frac{1}{n}\right)} \tag{1}$$

In the Freundlich equation, q_e is the ending loading rate, C_e is the ending concentration in solution, and K_f and n are constants. K_f is an equilibrium constant based on the y-intercept of the data trendline on a log-log graph, and n the reciprocal of the slope of the trendline.

Langmuir Model

In contrast to the Freundlich isotherm, the Langmuir isotherm was theoretically developed by Irving Langmuir in 1916 and portrays favorable adsorption. Because the Langmuir equation was developed assuming adsorption only occurs on a single layer of the sorbent, it often best fits gas adsorption data rather than liquid adsorption (Davis and Masten, 2009). However, an extension to the Langmuir isotherm model, the BET isotherm, was developed by Brunauer, Emmett, and Teller in 1938 to account for multi-layer adsorption on sorbents (Droste, 1997). The appropriate isotherm model to use must be found by comparing the behavior of each to adsorption data and selecting the best-fitting equation. Using that isotherm, the expected removal can be found for any ending concentration. The Langmuir equation is shown in Equation (2).

$$q_e = q_{max} \frac{KC_e}{1+KC_e} \tag{2}$$

In the Langmuir equation, q_e is the ending loading rate, and q_{max} is the maximum possible loading rate, which is typically equal to q_e for single-layer adsorption. C_e is the ending concentration, and K is the linearized equilibrium constant.

2.5 Summary

As one of the most prescribed antibiotics in the world, SMX occurs frequently in wastewater and, by extension, water supplies and sediments. Studies show that its extensive use has triggered bacterial resistance, genetic mutations, and ecological disruption in naturally-occurring organisms. Current treatment technologies, including AOPs, photolysis, and GAC adsorption, show evidence of some removal of SMX. However, the antimicrobial is not completely removed by WWTPs, causing further environmental occurrence and risk.

Chapter 3: Methodology

This section will serve to outline all general laboratory procedures pertaining to the analysis of GAC and ion-exchange resins in the removal of SMX. Amberlite XAD4, Marathon C, Optipore L493, and pure SMX were purchased from Sigma-Aldrich Co. LLC. Available Filtrasorb 200 was received from Calgon Carbon Corporation. Tests were performed at pH levels of 5, 7, and 9 in order to simulate typical water and wastewater treatment processes.

3.1 Sample Preparation

Solutions of known initial concentrations of Fluka® Brand SMX in Barnstead E-Pure water (ROpure ST Reverse Osmosis/tank system, Thermo Scientific) were prepared for each treatment procedure. Fixed amounts of SMX were weighed using a Mettler Toledo (AB104-S) scale and added to E-Pure water. Solutions were protected from light and continuously stirred with a magnetic stirrer for at least 24 hours prior to experimental use. Separate solutions for each pH level of 5, 7, and 9 were adjusted by the drop-wise addition of NaOH or HCl and measured with an Accumet Basic AB 15 (Fisher Scientific) pH meter.

3.2 Measuring Sample Absorbance

In order to measure the amount of SMX removed during adsorption, the initial and final concentrations of SMX were determined before and after each trial. A Varian-Cary 50 UV-visible spectrophotometer operated at a wavelength of 257 nm was used with Fisherbrand® Suprasil quartz 3-mL (10x10x45mm) cuvettes to measure sample absorbance.

3.3 Sulfamethoxazole Concentration Standard Curves with Detection Limit

Standard concentration curves at pH 5, 7, and 9 were created with samples of known aqueous SMX concentrations in order to determine unknown concentrations of treated samples. Aqueous solutions of SMX at each pH and five known concentrations, ranging from 0.125 mg/L to 50 mg/L, were measured for absorbance by the Varian-Cary 50 Scan UV-visible spectrophotometer. Standard concentration curves for each pH level were then developed using the relationship between known sample concentration and the absorbance readings. Detection limits were established using the Student's t-test statistical calculations in Microsoft Excel for the purpose of finding the point at which no statistical difference exists between a blank sample and SMX.

3.4 Adsorption Treatment

Adsorption treatment experiments were executed for analyzing the removal efficiency of specific adsorbent types on SMX. Adsorbents included one GAC, Filtrasorb 200, and three ion-exchange resins, Amberlite XAD4, Marathon C, and Optipore L493. Prior to experiments, Marathon C required a rinse with E-Pure so that impurities in the resin could be removed and an appropriate pH could be maintained. In order to effectively analyze removal efficiency, adsorption was tested in a series of equilibrium and kinetics trials. Equilibrium trials measured the ending concentration at which the accumulation of SMX on resin surfaces ends and the rate of adsorption equals the rate of desorption. The rates of adsorption for each resin were assessed with kinetics trials.

For each treatment experiment, fixed amounts of adsorbent were weighed and added to 42 mL amber glass vials. 10-mL volumes of solution were added to each vial, capped and placed into a rotisserie mixer for the purpose of continuous, uniform mixing and motion. Following treatments, each sample was removed from the rotisserie and centrifuged in an Eppendorf Centrifuge 5804 for 20 to 30 minutes at 2680 rpm, the highest velocity at which no damage could occur to the vials. Supernatant liquid was then decanted with a pipette into glass vials for analysis.

3.4.1 Adsorption Equilibrium Trials

For maximum adsorption of SMX, equilibrium trials were performed over a 48-hour contact period. Equilibrium trials were conducted in pH series, all of which had a range of initial concentrations and a fixed amount of adsorbent. Initial concentrations of aqueous SMX were 10, 20, 30, 40 and 50 mg/L. Solutions were added to vials containing approximately 0.2 g of adsorbent. After treatment and decantation, the pH was measured and corrected to the initial pH. Adjusted samples were then pipetted into cuvettes and measured for absorbance in the UV-visible spectrophotometer. The final concentration of the sample was then calculated using the final absorbance value and calibration curves to the corresponding pH.

3.4.2 Adsorption Kinetics Trials

The adsorption kinetics was assessed with series of time trials at intervals of 6, 12, 24, and 48 hours for each pH level (5, 7, 9). Solutions with initial concentrations of 10, 20, 30, 40 and 50 mg/L were added to vials containing 0.2 g of adsorbent. Following treatment, samples were centrifuged and decanted into glass vials. The pH was measured and corrected to the initial pH. Samples were then analyzed by the spectrophotometer for absorbance and the corresponding final concentration.

Chapter 4: Results and Discussion

The aim of this study was to evaluate the removal of SMX from water at pH 5, 7, and 9 by adsorption to GAC and by ion exchange sorption to polymeric resins. The data obtained from experimental tests were analyzed for the purpose of comparing the removal effectiveness of ion exchange resins and activated carbon on SMX. In addition, the parameters calculated from the data helped to determine a potential removal system for a small pharmaceutical manufacturer. All raw experimental data is presented in Appendix B.

4.1 Calibration Curves

In order to determine the final concentration of SMX after treatment, calibration curves were constructed for each pH tested. Known concentrations of SMX were analyzed for absorbance using the UV spectrometer, which was set at a wavelength of 257 nm, the wavelength at which SMX displayed the highest peak in absorption spectra. The three calibration curves are presented in Figure 7.

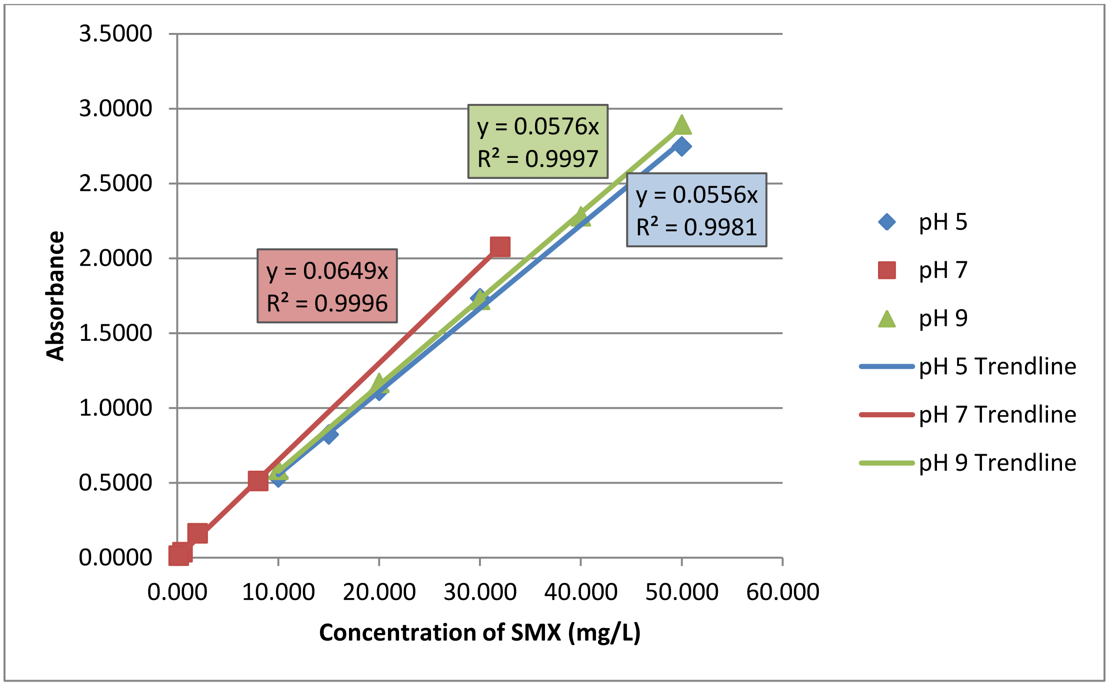

Figure 7: Calibration Curves for SMX at pH 5, 7, and 9

All curves displayed fractions of variance (R^2) above 0.998, indicating accurate detections below concentrations of 50 mg/L. Although similar in slope, the curves differed slightly as a result of the change in molecular charge when pKa values were reached. At pH 5, the neutral form of SMX is dominant. At pH levels higher than 5.6, the molecule becomes deprotonated on its amine group. As the pH increases, a higher fraction of anionic SMX species exists compared to that of its neutral form.

4.2 Adsorption Isotherms

Isotherms were established in order to model and assess the adsorption behavior at equilibrium. Final concentration readings from equilibrium trials were calculated using the calibration curves. The ending concentrations were then used to generate isotherm curves for each resin. Values were compared and contrasted to Langmuir and Freundlich models to find the best fit. Between the two adsorption isotherm models, the Freundlich model best fit the data for each resin. As shown in all equilibrium data, AMB was not successful in removing SMX, likely due to lack of proper rinsing before application.

4.2.1 Equilibrium at pH 5

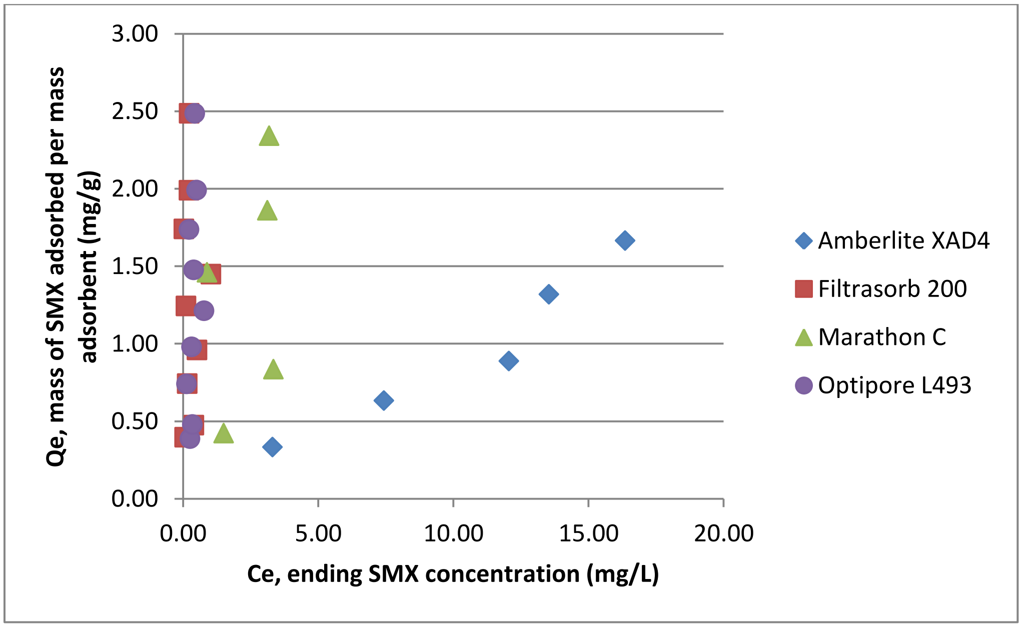

Figure 8: Equilibrium data for all adsorbents, pH 5

Figure 8 displays the equilibrium data for all adsorbents at pH 5. OPT and FS-200 had the highest adsorption capacity at this pH, followed by that of MAR and AMB. At this pH, the majority of SMX is in neutral form, enabling maximum adsorption to activated carbon and non-ionic polymeric resins. The high acidity of MAR may have attributed to its poor adsorption of

SMX at this pH, since the concentration of H^+ competes with the functional groups of MAR. Additionally, the neutral form of SMX has no ions to exchange with MAR. The following Freundlich isotherm equations model the equilibrium relationships of each adsorbent at pH 5:

$$\text{FS-200:} \qquad Q_e = 1.1426{C_e}^{0.0304} \qquad (3)$$

$$\text{AMB:} \qquad Q_e = 0.0988{C_e}^{0.9642} \qquad (4)$$

$$\text{MAR:} \qquad Q_e = 0.9171{C_e}^{0.3302} \qquad (5)$$

$$\text{OPT:} \qquad Q_e = 1.8400{C_e}^{0.4801} \qquad (6)$$

4.2.2 Equilibrium at pH 7

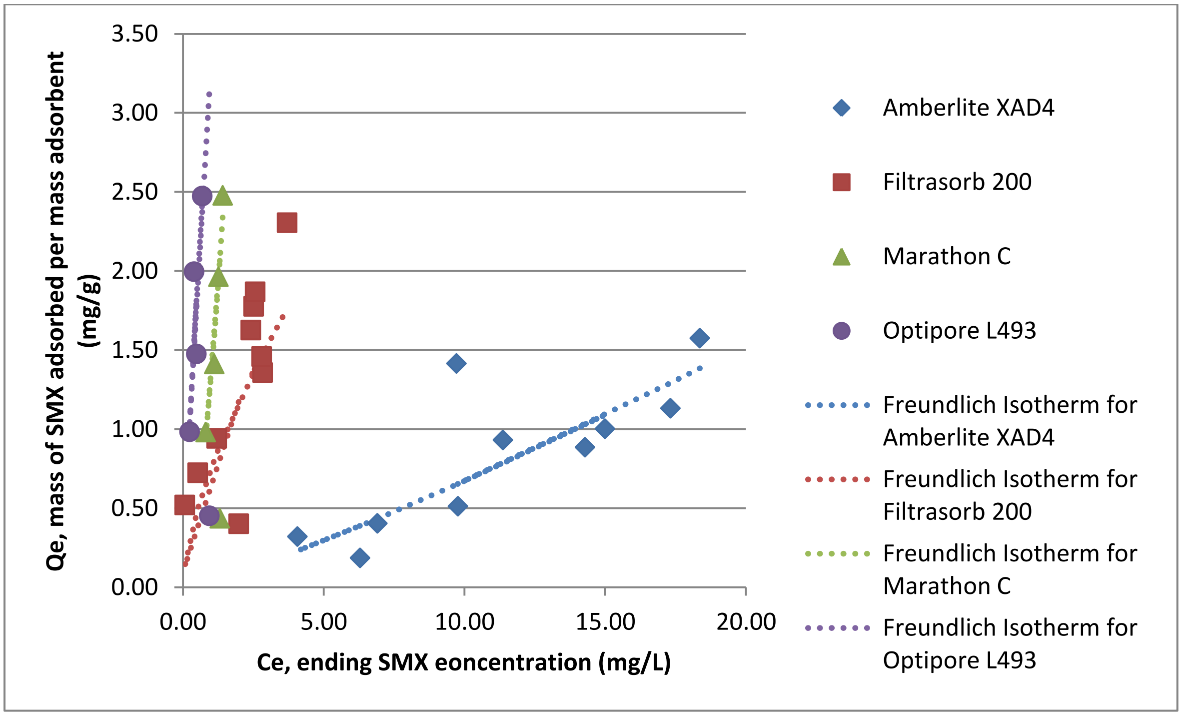

Figure 9: Isotherms for all adsorbents, pH 7

Equilibrium tests at pH yielded the most efficient adsorption capacities among all the adsorbents. Out of all, OPT and MAR had the highest adsorption rates, which may be a result of the higher number of anionic SMX species present. The isotherms for all adsorbents at this pH are shown in Figure 9. When the pH level is about 7, the SMX molecule exists as both neutral and anionic, with the anionic species being dominant. The anionic form of SMX was more likely to be attracted to the hydrophobic surface of OPT. This adsorption was amplified by the extensive pore surface area of OPT. Again, the Freundlich isotherm model closely fit the equilibrium data for pH 7. The following equations were generated:

FS-200: $$Q_e = 0.7520 {C_e}^{0.6497} \tag{7}$$

AMB: $$Q_e = 0.0437 {C_e}^{1.1869} \tag{8}$$

MAR: $$Q_e = 1.3279 {C_e}^{1.6350} \tag{9}$$

OPT: $$Q_e = 3.277 {C_e}^{0.7988} \tag{10}$$

4.2.3 Equilibrium at pH 9

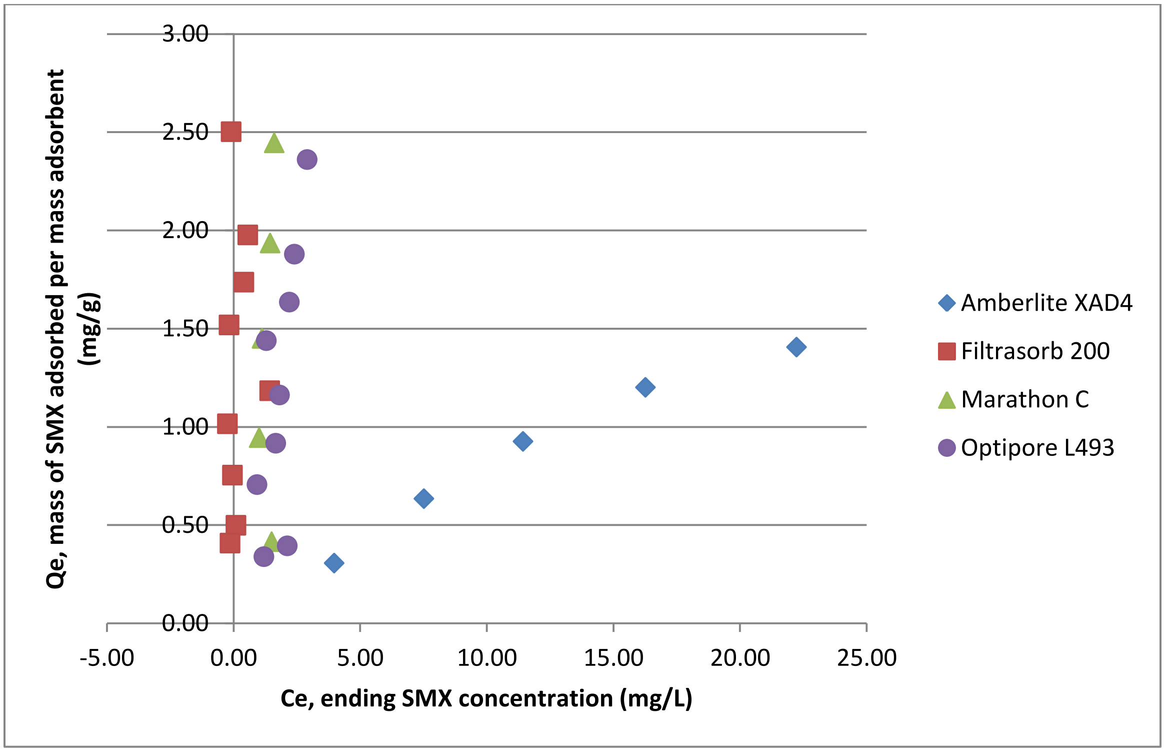

Figure 10: Equilibrium data for all adsorbents, pH 9

Similar to tests performed at pH 7, tests at pH 9 yielded a higher a higher adsorption capacity with OPT and MAR. However, FS-200 appears to have worked the best at this pH. This was shown by the higher affinity of the anionic molecule to adsorb to MAR and OPT in addition to FS-200. The isotherms generated for all adsorbents at pH 9 are displayed in Figure 10. Equations 11 through 14 show the Freundlich isotherms for each adsorbent at pH 9.

FS-200: $$Q_e = 1.1958{C_e}^{0.2103} \tag{11}$$

AMB: $$Q_e = 0.0971{C_e}^{0.8928} \tag{12}$$

MAR: $$Q_e = 1.0176{C_e}^{1.8513} \tag{13}$$

OPT: $$Q_e = 0.7615{C_e}^{0.6932} \tag{14}$$

4.3 Adsorption Kinetics

Kinetics tests were necessary for further evaluating the reactions over time. The kinetics trials showed that the most adsorption occurred within the first six hours of testing, regardless of pH. Equilibrium was reached between 12 and 24 hours, as shown in Figures 11, 12, and 13. This validated the use of 48-hour trials as equilibrium trials because all adsorption had reached equilibrium by that time. In addition, the following graphs illustrate that pH levels between 5 and 9 do not significantly affect the rate of adsorption.

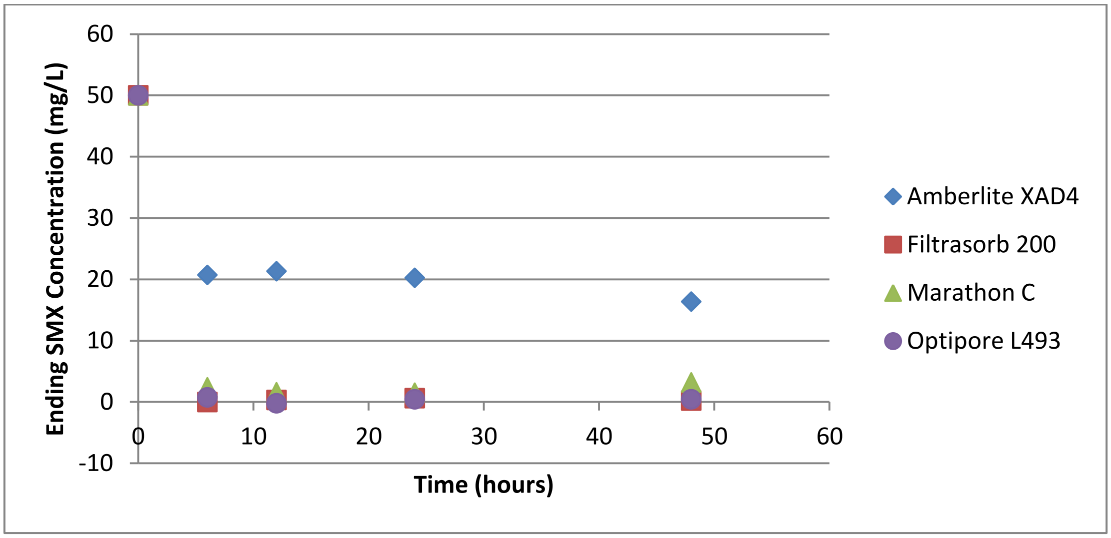

Figure 111: Adsorption Kinetics at pH 5

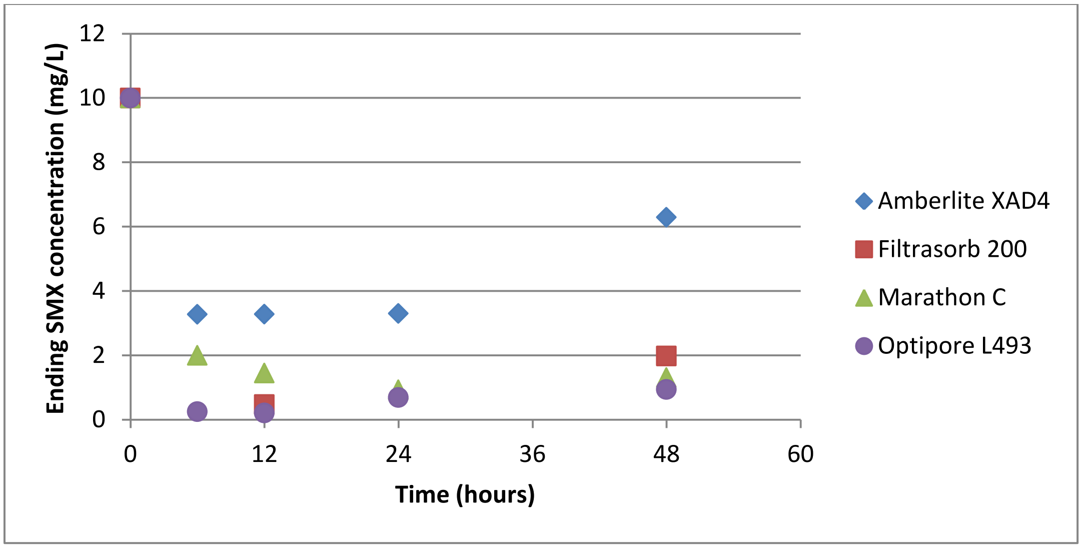

Figure 12: Adsorption Kinetics at pH 7

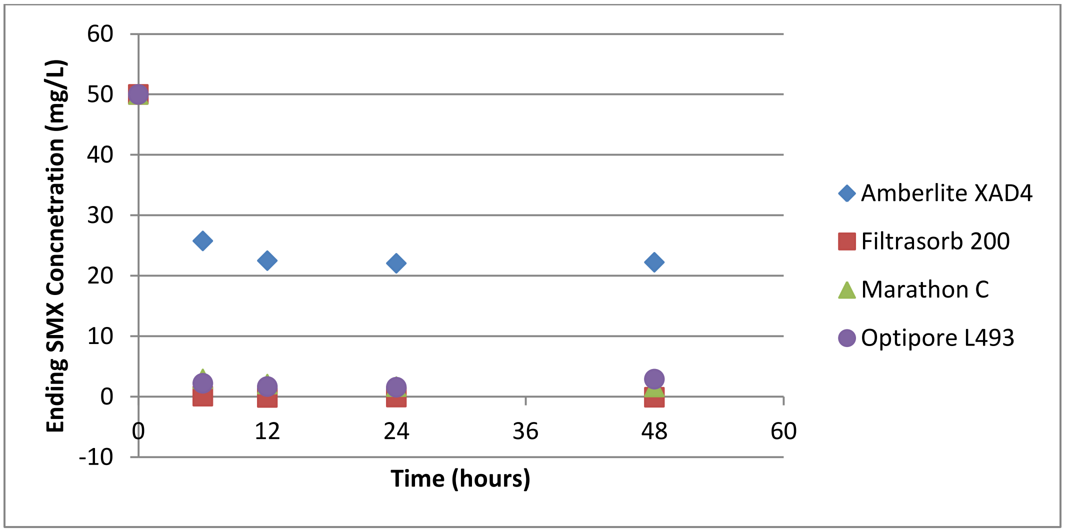

Figure 13: Adsorption Kinetics at pH 9

In comparison to FS-200, OPT was the most effective adsorbent, closely followed by MAR. However, while AMB did not yield results as favorable as the other two resins, it was discovered later on that AMB resin beads should be washed before use so as to maintain an appropriate pH. If the resin had been washed, the beads might have adsorbed more of the contaminant. Regardless, the unwashed results showed AMB to be effective. According to the data, the most effective removal method proved to involve OPT or MAR used in a neutral to acidic setting for 6 to 12 hours.

Chapter 5: Conclusions and Recommendations

In this project, ion exchange was proven to be an effective method for the removal of SMX from water. However, not all adsorbents were equally effective, as dictated by differences in chemical structures. The most efficient resins of the four tested were OPT and FS-200. Should future testing be performed, these experiments can be expanded by considering other methods of treatment or more extensive testing on these adsorbents. For example, proper pretreatment and regeneration of the adsorbents should be examined, and filtration of the tested samples should be considered for all adsorption results. By investigating these additional parameters, a larger-scale operation or the use of columns could be utilized and more properly evaluated.

5.1 Removal System Design

The experimental procedures used in this project employed laboratory bench-scale contact vials to determine equilibrium loading rates. The resulting data were used to develop a small-scale industrial design for a batch reactor intended to remove SMX from wastewater. Specifically, a half-sized system was designed for an arbitrary manufacturing plant that produces SMX to treat wastewater effluent for the antibiotic. In a manufacturing plant, products are susceptible to occurring in wastewater due to equipment washing and general waste discharge. A design such as this would prevent excessive SMX from being discharged into the environment. This design can also be repurposed for other applications, such as a small-scale package wastewater treatment plant. The proposed sequencing batch reactors (SBRs) closely model the experimental procedures utilized in this project, since SBRs maximize contact between adsorbent and contaminated water. The equilibrium loading rates determined in Chapter 4 were used to find the optimum volume of adsorbent for target removal of SMX from waste effluent.

A few notes bear mention to accompany this design. This proposed system was designed to be half the size of a typical system for real applications. This is because experimental results did not yield enough information to determine other parameters for full-scale operation. Additionally, other conditions may change when expanding the system size. For example, the theoretical amount of adsorbent may not be equal to the necessary mass of adsorbent.

The design itself is based on factory operations spanning an eight-hour workday and on an effluent wastewater discharge rate of 5,000 gallons per day. The initial concentration of SMX in the water was taken to be 0.05 mg/L, and the target effluent concentration was 0.00001 mg/L, a value corresponding to the MIC of a common soil bacteria family, *Pseudomonas* (Qin 2012). The adsorbent that would be used is OPT, since it was successful in the removal of SMX and has characteristics that correlate to optimal adsorption. These characteristics include high surface area, an applicable range of pore sizes, and a high loading rate capacity. To achieve this removal, the total mass of OPT needed was 54,000 kg. This design incorporated four main operating tanks with one offline back-up tank, all holding a maximum volume of 400 gallons. A schematic of the reactors in parallel is shown in Figure 14.

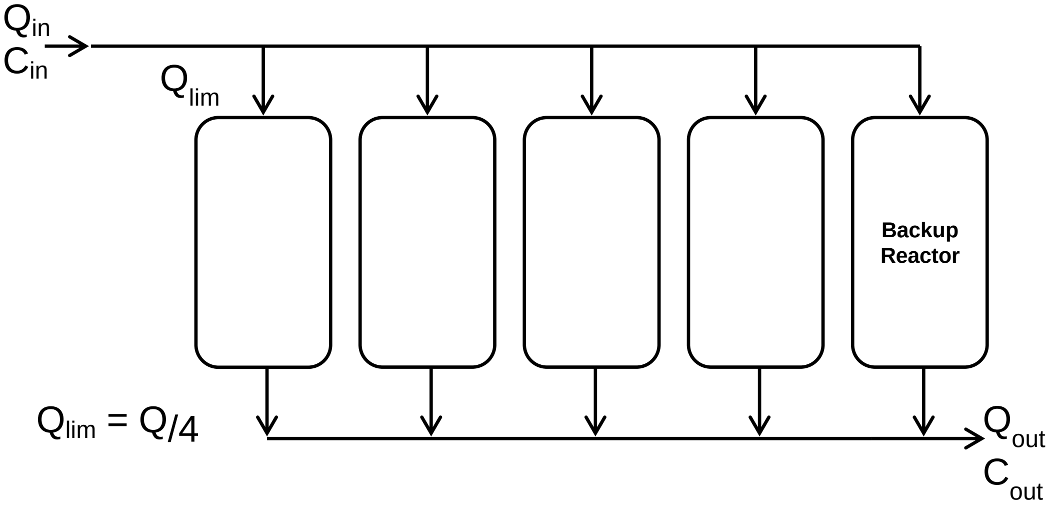

Figure 14: Schematic of SBRs

5.1.1 Process

The proposed system calls for five sequencing batch reactors operating in parallel. Four are designed to operate simultaneously with one offline as needed. Each tank ensures full contact between 313.5 gallons of contaminated water and 10,400 kg of adsorbent over the span of six hours. Vessels would be constructed from A36 steel, a type of carbon steel alloy. To minimize the cost of materials, a height-diameter aspect ratio of 2:1 was chosen for the tanks. The pH of the water being treated would be monitored and maintained with a separate system containing a pH probe and applicators for acid and base injection. A schematic of one batch reactor from the prospective design is shown in detail in Figure 15.

At the beginning of operation, freshly regenerated adsorbent is fed into the bottom of the tank. The feed at the top of the reactor delivers contaminated water, which the tank mixes for six hours. The high crushing capacity of OPT allows it to be mixed at a moderate speed without risking damage to the resin. The solution is then allowed to settle before the water is decanted by an outlet pipe located above the settled adsorbent bed. After the water has exited the tank, a water wash stream is fed into the tank to ensure that all adsorbent beads are removed. The adsorbent beads are removed through the outlet at the bottom of the tank and piped to a steam regeneration tank. Meanwhile, the reactor is refilled with previously regenerated adsorbent and the process begins once more. This occurs simultaneously in each tank in order to treat all effluent flow throughout the day.

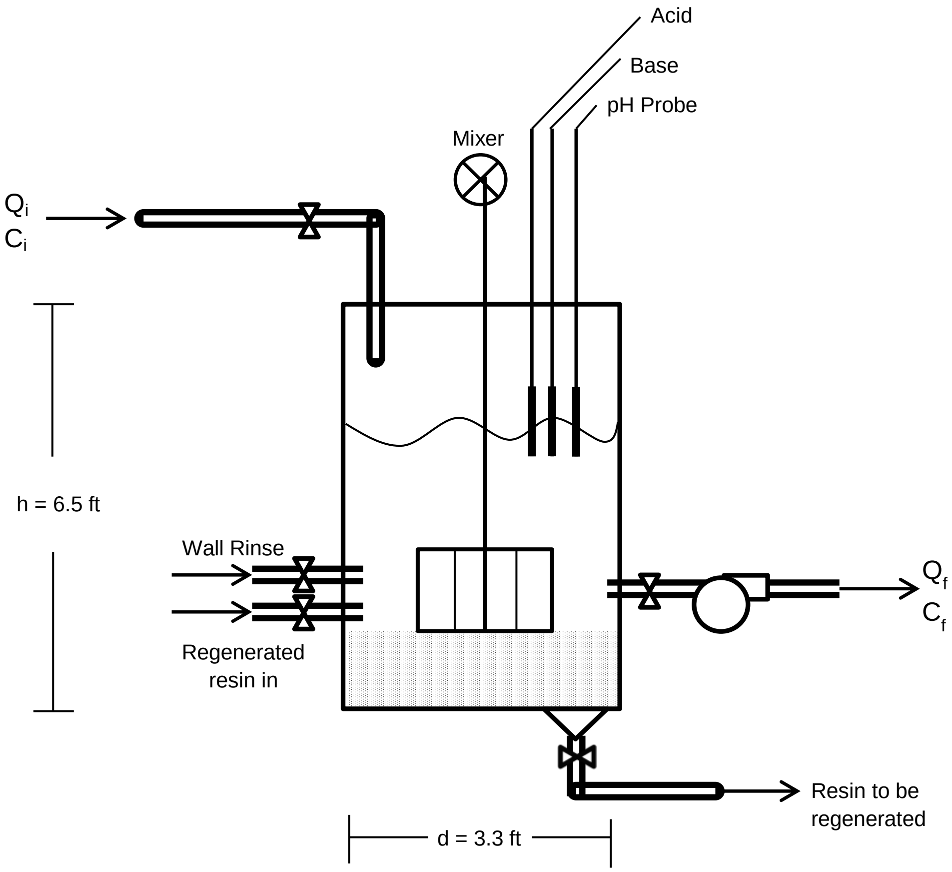

Figure 15: Schematic of one SBR in parallel

5.2 Future Recommendations

The tests performed over the course of this project did not comprehensively evaluate all treatment and regeneration options. Methods of adsorbent regeneration and recycled adsorbent efficiency were not investigated. This should be studied in greater detail to determine the best regeneration process for a particular adsorbent. Additionally, it would be prudent to further study the use of these adsorbents on other polar organic contaminants (POCs). This would compare the removal of SMX to that of other organics and would aid plants such that they could remove multiple contaminants with one process.

When developing the design portion of this report, it was noted that the use of columns may dramatically improve process efficiency. The amount of necessary adsorbent would be reduced due to the occurrence of equilibrium adsorption in a moving zone across the column (Droste, 1997). Contaminated water can be recycled through the column multiple times. While column studies were not performed during experimentation, they are highly suggested for future testing. It is also recommended that further experiments study lower concentrations of contaminants in water. The use of an HPLC would allow for accurate measurements at such low concentrations. With improvements in technology and a better understanding of the behavior of POCs and their removal, there can be healthier ecosystems and water supplies in the future.

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Appendix A: List of Abbreviations

AMB – Amberlite® XAD4
AOP – Advanced Oxidation Process
EDC – Endocrine Disrupting Compound
FS-200 – Filtrasorb® 200
GAC – Granular Activated Carbon
MAR – DOWEX® Marathon® C
MIC – Minimum Inhibitory Concentration
OPT – Optipore® L493
PAC – Powdered Activated Carbon
PhAC – Pharmaceutically Active Compound
POC – Polar Organic Compound or Polar Organic Contaminant
PPCP – Pharmaceutical and Personal Care Products
SBR – Sequencing Batch Reactor
SMX – Sulfamethoxazole
STP – Standard Temperature and Pressure
TMP – Trimethoprim
US EPA – United States Environmental Protection Agency
US FDA – United States Food and Drug Administration
WTP – Water Treatment Plant
WWTP – Wastewater Treatment Plant

Appendix B: Experimental Data

Calibration Curves

Table 1: Calibration Curves of SMX at pH 5, 7, and 9

Measured Concentration of SMX (mg/L)	pH	Absorbance
pH 5 Series		
50.000	5.05	2.7470
30.000	5.02	1.7325
20.000	5.04	1.1137
15.000	4.97	0.8223
10.000	4.94	0.5348
pH 7 Series		
32.000	6.87	2.0760
8.000	6.98	0.5117
2.000	7.10	0.1621
0.500	6.94	0.0359
0.125	6.93	0.0127
pH 9 Series		
50.000	8.96	2.8939
40.000	8.94	2.2804
30.000	9.03	1.7222
20.000	8.94	1.1672
10.000	8.95	0.5865

Example T-test Calculation

SMX Concentration (mg/L)	Zero (blank)	10	5	1	0.5	0.1	0.05
Absorbance	-0.0014	0.4741	0.2509	0.0491	0.0230	0.0030	-0.0003
	-0.0019	0.4758	0.2524	0.0491	0.0235	0.0020	0.0001
	-0.0015	0.4762	0.2553	0.0505	0.0239	0.0019	-0.0006
	-0.0009	0.4759	0.2551	0.0495	0.0239	0.0020	-0.0013
	-0.0018	0.4766	0.2556	0.0498	0.0250	0.0029	-0.0013

t-Test: Paired Two Sample for Means		
	Variable 1	***Variable 2***
Mean	-0.0015	-0.00068
Variance	1.55E-07	3.82E-07
Observations	5	5
Pearson Correlation	-0.472607	
Hypothesized Mean Difference	0	
df	4	
t Stat	-2.093636	
P(T<=t) one-tail	0.0522005	
t Critical one-tail	2.1318468	
P(T<=t) two-tail	0.1044009	
t Critical two-tail	2.7764451	

Adsorption Equilibrium (48-hour) Data

Amberlite XAD4

Table 2: Amberlite XAD4 Isotherm Data, pH 5

Mass of Adsorbent (g)	**Starting pH**	**Ending pH**	**Adjusted pH**	**C_i (mg/L)**	**Abs (A)**	**Ce (mg/L)**	**% Decrease**	**Qe (mg/g)**
0.2001	5.00	9.66	4.96	10	0.1856	3.31	66.9	0.33
0.1982	5.03	9.50	5.02	20	0.4144	7.43	62.9	0.63
0.2018	5.04	9.36	4.98	30	0.6712	12.1	59.8	0.89
0.2005	4.99	8.92	4.98	40	0.7535	13.5	66.2	1.32
0.2019	5.05	9.62	4.93	50	0.9100	16.4	67.3	1.67

Table 3: Amberlite XAD4 Isotherm Data, pH 7

Mass of Adsorbent (g)	**Starting pH**	**Ending pH**	**Adjusted pH**	**C_i (mg/L)**	**Abs (A)**	**Ce (mg/L)**	**% Decrease**	**Qe (mg/g)**
0.1995	6.95	9.61	7.04	10	0.4157	6.29	37.1	0.19
0.1996	6.98	9.42	7.04	20	0.6400	9.77	51.2	0.51
0.2000	6.96	9.74	7.03	30	0.7431	11.4	62.1	0.93
0.2003	6.99	9.78	7.05	40	1.1269	17.3	56.7	1.13
0.2008	6.97	9.77	7.02	50	1.1941	18.4	63.3	1.58
0.2005	6.96	9.85	6.91	10.5	0.2722	4.07	61.2	0.32
0.2001	7.03	9.49	6.97	15	0.4554	6.91	53.9	0.40
0.2000	6.96	9.79	6.91	32	0.9311	14.3	55.4	0.89
0.1995	6.96	9.80	6.99	35	0.9769	15.0	57.2	1.00
0.1998	6.98	9.85	7.01	38	0.6366	9.72	74.4	1.42

Table 4: Amberlite XAD4 Isotherm Data, pH 9

Mass of Adsorbent (g)	**Starting pH**	**Ending pH**	**Adjusted pH**	**C_i (mg/L)**	**Abs (A)**	**Ce (mg/L)**	**% Decrease**	**Qe (mg/g)**
0.1966	9.02	8.97	8.96	10	0.2393	3.97	60.3	0.31
0.1967	9.02	9.83	9.00	20	0.4423	7.52	62.4	0.63
0.2005	9.00	9.85	8.94	30	0.6665	11.4	61.9	0.93
0.1976	9.06	9.86	8.98	40	0.9435	16.3	59.3	1.20
0.1975	8.94	9.89	8.99	50	1.2853	22.2	55.5	1.41

Adsorption Equilibrium (48-hour) Data

Marathon C

Table 5: Marathon C Isotherm Data, pH 5

Mass of Adsorbent (g)	Starting pH	Ending pH	Adjusted pH	C_i (mg/L)	Abs (A)	Ce (mg/L)	% Decrease	Qe (mg/g)
0.1992	*5.01*	*3.48*	*4.93*	*10*	*1.4614*	*26.3*	*-162.9*	*-0.82*
0.1992	*5.00*	*3.44*	*5.01*	*20*	*1.5831*	*28.5*	*-42.4*	*-0.43*
0.2009	*5.01*	*3.49*	*4.97*	*30*	*1.6256*	*29.2*	*2.5*	*0.04*
0.2009	*5.00*	*3.41*	*5.01*	*40*	*1.6840*	*30.3*	*24.3*	*0.48*
0.1988	*5.04*	*3.46*	*4.95*	*50*	*1.6514*	*29.7*	*40.6*	*1.02*
0.2003	4.91	4.06	5.04	10	0.0853	1.50	85.0	0.42
0.1990	4.94	3.59	4.98	20	0.1875	3.34	83.3	0.84
0.1992	4.96	4.30	4.99	30	0.0510	0.88	97.1	1.46
0.1981	4.92	4.03	5.01	40	0.1750	3.12	92.2	1.86
0.1998	5.00	3.91	5.04	50	0.1787	3.18	93.6	2.34

*Data displayed in italicized font indicates unwashed resin

Table 6: Marathon C Isotherm Data, pH 7

Mass of Adsorbent (g)	Starting pH	Ending pH	Adjusted pH	C_i (mg/L)	Abs (A)	Ce (mg/L)	% Decrease	Qe (mg/g)
0.1989	*6.99*	*3.52*	*6.95*	*10*	*1.4618*	*22.51*	*-125.1*	*-0.63*
0.2000	*6.96*	*3.45*	*6.92*	*20*	*1.6474*	*25.39*	*-27.0*	*-0.27*
0.1994	*6.96*	*3.46*	*7.03*	*30*	*1.5653*	*24.12*	*19.6*	*0.3*
0.1994	*6.97*	*3.52*	*7.03*	*40*	*1.5434*	*23.78*	*40.6*	*0.81*
0.1995	*7.01*	*3.49*	*6.93*	*50*	*1.6010*	*24.67*	*50.7*	*1.27*
0.1991	6.98	2.88	6.95	10	0.0943	1.31	86.9	0.44
0.1955	6.94	4.73	6.98	20	0.0619	0.81	96.0	0.98
0.2045	6.99	4.61	6.94	30	0.0817	1.11	96.3	1.41
0.1972	6.96	4.14	6.94	40	0.0912	1.26	96.9	1.96
0.1960	6.95	4.24	6.93	50	0.1010	1.41	97.2	2.48

*Data displayed in italicized font indicates unwashed resin

Adsorption Equilibrium (48-hour) Data

Marathon C (Continued)

Table 7: Marathon C Isotherm Data, pH 9

Mass of Adsorbent (g)	Starting pH	Ending pH	Adjusted pH	C_i (mg/L)	Abs (A)	Ce (mg/L)	% Decrease	Qe (mg/g)
0.1996	*8.99*	*3.47*	*9.01*	*10*	*1.4750*	*25.55*	*-155.5*	*-0.78*
0.2000	*8.94*	*3.63*	*9.03*	*20*	*1.8516*	*32.12*	*-60.6*	*-0.61*
0.2002	*9.05*	*3.40*	*8.99*	*30*	*1.7960*	*31.15*	*-3.8*	*-0.06*
0.1997	*9.00*	*3.36*	*8.96*	*40*	*1.8639*	*32.34*	*19.2*	*0.38*
0.2000	*8.94*	*3.45*	*9.01*	*50*	*1.8338*	*31.81*	*36.4*	*0.91*
0.2044	9.05	4.67	9.03	10	0.0978	1.50	85.0	0.42
0.2009	9.01	4.24	9.01	20	0.0696	1.01	95.0	0.95
0.1991	9.00	4.19	9.02	30	0.0761	1.13	96.2	1.45
0.1992	9.03	4.00	8.95	40	0.0944	1.44	96.4	1.94
0.1979	9.01	3.93	8.95	50	0.1037	1.61	96.8	2.45

*Data displayed in italicized font indicates unwashed resin

Optipore L493

Table 8: Optipore L493 Isotherm Data, pH 5

Mass of Adsorbent (g)	Starting pH	Ending pH	Adjusted pH	C_i (mg/L)	Abs (A)	Ce (mg/L)	% Decrease	Qe (mg/g)
0.1991	4.94	4.64	4.99	8	0.0161	0.26	96.8	0.39
0.2012	5.01	4.78	5.04	10	0.0210	0.34	96.6	0.48
0.2004	5.04	4.12	4.95	15	0.0090	0.13	99.1	0.74
0.2007	5.00	4.67	5.03	20	0.0194	0.31	98.5	0.98
0.1996	5.05	5.52	5.01	25	0.0449	0.77	96.9	1.21
0.2004	5.01	4.59	4.95	30	0.0237	0.39	98.7	1.48
0.2001	5.06	4.63	5.03	35	0.0141	0.22	99.4	1.74
0.1983	5.00	4.51	4.92	40	0.0297	0.50	98.8	1.99
0.1993	5.04	4.50	4.90	50	0.0259	0.43	99.1	2.49

Adsorption Equilibrium (48-hour) Data

Optipore L493 (Continued)

Table 9: Optipore L493 Isotherm Data, pH 7

Mass of Adsorbent (g)	Starting pH	Ending pH	Adjusted pH	C_i (mg/L)	Abs (A)	Ce (mg/L)	% Decrease	Qe (mg/g)
0.2003	6.99	4.90	6.96	10	0.0704	0.94	90.6	0.45
0.2009	6.96	5.45	6.99	20	0.0251	0.24	98.8	0.98
0.1984	6.97	6.23	6.94	40	0.0354	0.40	99.0	2.00
0.2000	6.96	5.85	6.95	30	0.0406	0.48	98.4	1.48
0.1993	7.01	6.38	6.94	50	0.0541	0.69	98.6	2.47

Table 10: Optipore L493 Isotherm Data, pH 9

Mass of Adsorbent (g)	Starting pH	Ending pH	Adjusted pH	C_i (mg/L)	Abs (A)	Ce (mg/L)	% Decrease	Qe (mg/g)
0.1997	9.02	6.25	8.98	10	0.1332	2.12	78.8	0.39
0.2000	9.02	7.54	8.97	20	0.1071	1.67	91.7	0.92
0.1995	9.00	7.47	9.05	30	0.0858	1.29	95.7	1.44
0.2001	9.06	7.26	8.98	40	0.1493	2.40	94.0	1.88
0.1995	8.94	7.73	9.00	50	0.1782	2.91	94.2	2.36
0.2005	9.06	8.68	9.04	8	0.0803	1.20	85.0	0.34
0.1993	8.95	8.50	8.98	15	0.0647	0.93	93.8	0.71
0.1995	8.94	8.66	8.93	25	0.1156	1.81	92.8	1.16
0.2006	9.00	8.40	8.98	35	0.1379	2.20	93.7	1.63

Adsorption Equilibrium (48-hour) Data

Filtrasorb 200

Table 11: Filtrasorb 200 Isotherm Data, pH 5

Mass of Adsorbent (g)	Starting pH	Ending pH	Adjusted pH	C_i (mg/L)	Abs (A)	Ce (mg/L)	% Decrease	Qe (mg/g)
0.2018	5.00	6.34	5.04	10	0.0241	0.40	96.0	0.48
0.2028	5.03	5.94	5.01	20	0.0305	0.51	97.5	0.96
0.1998	5.04	7.01	4.93	30	0.0591	1.03	96.6	1.45
0.1998	4.99	6.06	4.95	40	0.0141	0.22	99.5	1.99
0.2001	5.05	7.22	4.97	50	0.0144	0.22	99.6	2.49
0.1996	4.94	6.07	4.93	8	0.0052	0.06	99.3	0.4
0.1996	5.04	6.11	4.96	15	0.0104	0.15	99.0	0.74
0.2000	5.05	6.10	5.02	25	0.0079	0.11	99.6	1.24
0.2008	5.06	6.15	5.01	35	0.0036	0.03	99.9	1.74
0.1996	4.94	6.07	4.93	8	0.0148	0.23	97.1	0.39
0.1996	5.04	6.11	4.96	15	0.0066	0.08	99.5	0.75
0.2000	5.05	6.10	5.02	25	0.0053	0.06	99.8	1.25
0.2008	5.06	6.15	5.01	35	0.0071	0.09	99.7	1.74

Table 12: Filtrasorb 200 Isotherm Data, pH 7

Mass of Adsorbent (g)	Starting pH	Ending pH	Adjusted pH	C_i (mg/L)	Abs (A)	Ce (mg/L)	% Decrease	Qe (mg/g)
0.1995	6.95	8.07	7.02	10	0.1376	1.98	80.2	0.4
0.2005	6.96	7.34	6.95	10.5	0.0056	0.07	99.3	0.52
0.1998	7.03	7.16	7.16	15	0.0437	0.53	96.5	0.72
0.1996	6.98	8.48	7.08	20	0.0872	1.20	94.0	0.94
0.2000	6.96	9.24	7.04	30	0.1924	2.83	90.6	1.36
0.2001	6.96	7.10	7.10	32	0.1902	2.80	91.3	1.46
0.2003	6.96	7.30	7.11	35	0.1654	2.41	93.1	1.63
0.1997	6.98	7.21	7.01	38	0.1719	2.51	93.4	1.78
0.2003	6.99	9.50	7.03	40	0.1754	2.57	93.6	1.87
0.2008	6.97	9.76	7.01	50	0.2486	3.70	92.6	2.31

Adsorption Equilibrium (48-hour) Data

Filtrasorb 200 (Continued)

Table 13: Filtrasorb 200 Isotherm Data, pH 9

Mass of Adsorbent (g)	Starting pH	Ending pH	Adjusted pH	Ci (mg/L)	Abs (A)	Ce (mg/L)	% Decrease	Qe (mg/g)
0.1985	8.92	7.16	8.98	10	0.0171	0.10	99.0	0.5
0.1993	9.06	6.41	9.01	8	0.0037	-0.14	101.8	0.41
0.1994	8.95	7.85	8.97	15	0.0092	-0.04	100.3	0.75
0.1993	9.04	8.47	8.95	20	-0.0022	-0.24	101.2	1.02
0.1991	8.94	3.25	8.93	25	0.0935	1.43	94.3	1.18
0.1987	8.98	8.40	8.97	30	0.0015	-0.18	100.6	1.52
0.1992	9.00	8.72	9.03	35	0.035	0.41	98.8	1.74
0.1995	8.94	8.35	8.94	40	0.0439	0.56	98.6	1.98
0.2002	8.94	8.42	8.96	50	0.0062	-0.09	100.2	2.5

Adsorption Kinetics Data

Table 14: Amberlite XAD4 Kinetics Data

pH series	Conc$_i$ (mg/L)	Time (hours)	pH$_i$	pH$_f$	Conc$_f$ (mg/L)
5	50	0	5.03	4.96	50
	50	6	5.03	4.95	20.71
	50	12	5.05	4.96	21.31
	50	24	5.00	5.05	20.24
	50	48	5.05	4.93	16.36
7	50	0	7.01	7.01	50
	50	6	7.04	6.95	20.11
	50	12	7.03	6.95	19.45
	25	24	6.99	6.96	8.56
	50	48	6.97	7.02	18.36
9	50	0	9.01	9.03	50
	50	6	9.01	9.03	25.77
	50	12	8.96	8.98	22.50
	50	24	8.95	9.02	22.07
	50	48	8.94	8.99	22.24

Table 15: Marathon C Kinetics Data

pH series	Conc$_i$ (mg/L)	Time (hours)	pH$_i$	pH$_f$	Conc$_f$ (mg/L)
5	50	0	5.04	5.03	50
	50	6	5.04	5.03	2.38
	50	12	5.02	5.00	1.57
	50	24	5.00	4.98	1.50
	50	48	5.00	5.04	3.18
7	50	0	7.01	7.08	50
	50	6	7.01	7.08	2.24
	50	12	6.95	6.97	2.08
	50	24	6.95	7.00	1.62
	50	48	6.95	6.93	1.41
9	50	0	9.00	8.98	50
	50	6	9.00	8.98	2.95
	50	12	8.97	8.97	2.09
	50	24	9.01	8.99	1.67
	50	48	9.01	8.95	1.61

Adsorption Kinetics Data

Table 16: Optipore L493 Kinetics Data

pH series	$Conc_i$ (mg/L)	Time (hours)	pH_i	pH_f	$Conc_f$ (mg/L)
5	50	0	5.04	4.98	50
	50	6	5.04	4.98	0.74
	50	12	5.01	4.94	-0.22
	50	24	4.99	4.98	0.43
	50	48	5.04	4.90	0.43
7	50	0	7.01	6.95	50
	50	6	7.01	6.95	0.11
	50	12	6.94	6.97	0.45
	50	24	7.02	7.00	1.10
	50	48	7.01	6.94	0.69
9	50	0	9.00	9.04	50
	50	6	9.00	9.04	2.22
	50	12	8.97	9.01	1.68
	50	24	8.95	8.95	1.57
	50	48	9.00	8.98	2.91

Table 17: Filtrasorb 200 Kinetics Data

pH series	$Conc_i$ (mg/L)	Time (hours)	pH_i	pH_f	$Conc_f$ (mg/L)
5	50	0	5.03	5.05	50
	50	6	5.03	5.05	-0.02
	50	12	5.05	5.02	0.32
	50	24	5.00	5.01	0.61
	50	48	5.05	4.97	0.22
7	50	0	7.04	7.01	50
	50	6	7.04	7.01	-0.09
	50	12	7.03	7.03	0.16
	25	24	6.99	6.95	0.10
	50	48	6.97	7.01	3.70
9	50	0	9.01	9.03	50
	50	6	9.01	9.03	0.09
	50	12	8.96	8.93	-0.12
	50	24	8.95	8.91	-0.06
	50	48	8.94	8.96	-0.09

Appendix C: Design Calculations

Mass of OPT

Q_e=5.1558x10^{-6} (mg SMX/g Optipore); Q_0= 0 mg/g

C_0=0.05 mg/L SMX; C_e=0.00001 mg/L SMX

B= Mass of Optipore needed

Q=5,000 gallons/day → Q=209 gal/h=791 L/h

$$V = 791.5\frac{L}{h} \times 6h$$

$$V = 4747\ L$$

$$V(C_0 - C_e) = B(Q_e - Q_0)$$

$$(4747\ L)\left(0.04999\ \frac{mg}{L}\right) = B(5.1558 \times 10^{-6})$$

$$B = 53{,}008{,}000\ g$$

$$B = 54{,}000\ kg$$

Volume of tank

Q=5,000 gal/day = 209 gal/h; t= 6 h

$$V_{all\ tanks} = Q \times t$$

$$V_{all\ tanks} = \left(209\frac{gal}{h}\right) \times (6h)$$

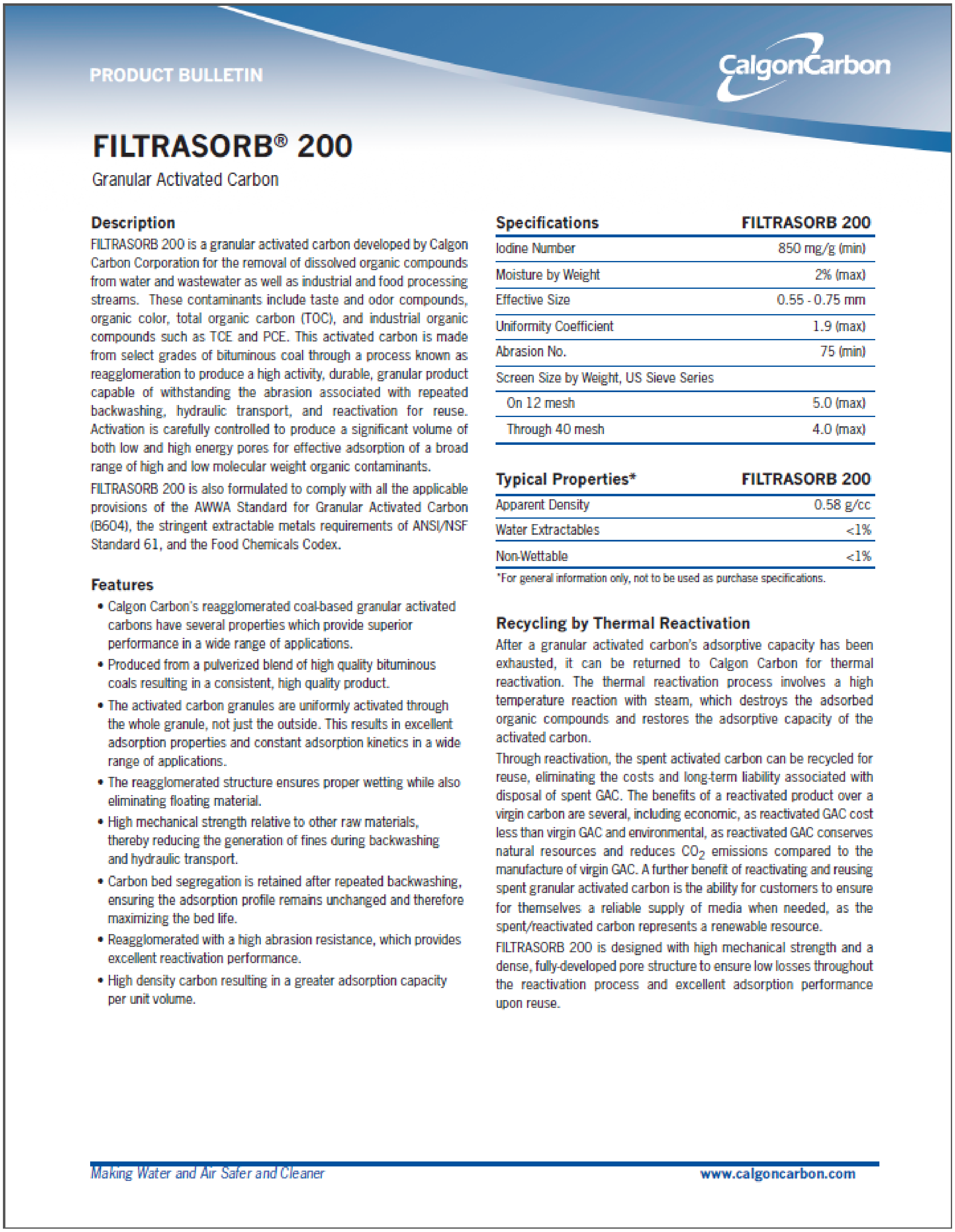
$$V_{all\ tanks} = 1254\ gal$$

$$V_{one\ tank} = 1254\ gal \div 4$$

$$V_{one\ tank} = 313.5\frac{gal}{tank}$$

Appendix D: Product Information Sheets

Filtrasorb® 200 – Calgon Carbon Corporation



PRODUCT BULLETIN

FILTRASORB® 200

Granular Activated Carbon

Description

FILTRASORB 200 is a granular activated carbon developed by Calgon Carbon Corporation for the removal of dissolved organic compounds from water and wastewater as well as industrial and food processing streams. These contaminants include taste and odor compounds, organic color, total organic carbon (TOC), and industrial organic compounds such as TCE and PCE. This activated carbon is made from select grades of bituminous coal through a process known as reagglomeration to produce a high activity, durable, granular product capable of withstanding the abrasion associated with repeated backwashing, hydraulic transport, and reactivation for reuse. Activation is carefully controlled to produce a significant volume of both low and high energy pores for effective adsorption of a broad range of high and low molecular weight organic contaminants.

FILTRASORB 200 is also formulated to comply with all the applicable provisions of the AWWA Standard for Granular Activated Carbon (B604), the stringent extractable metals requirements of ANSI/NSF Standard 61, and the Food Chemicals Codex.

Features

- Calgon Carbon's reagglomerated coal-based granular activated carbons have several properties which provide superior performance in a wide range of applications.
- Produced from a pulverized blend of high quality bituminous coals resulting in a consistent, high quality product.
- The activated carbon granules are uniformly activated through the whole granule, not just the outside. This results in excellent adsorption properties and constant adsorption kinetics in a wide range of applications.
- The reagglomerated structure ensures proper wetting while also eliminating floating material.
- High mechanical strength relative to other raw materials, thereby reducing the generation of fines during backwashing and hydraulic transport.
- Carbon bed segregation is retained after repeated backwashing, ensuring the adsorption profile remains unchanged and therefore maximizing the bed life.
- Reagglomerated with a high abrasion resistance, which provides excellent reactivation performance.
- High density carbon resulting in a greater adsorption capacity per unit volume.

Specifications	FILTRASORB 200
Iodine Number	850 mg/g (min)
Moisture by Weight	2% (max)
Effective Size	0.55 - 0.75 mm
Uniformity Coefficient	1.9 (max)
Abrasion No.	75 (min)
Screen Size by Weight, US Sieve Series	
On 12 mesh	5.0 (max)
Through 40 mesh	4.0 (max)

Typical Properties*	FILTRASORB 200
Apparent Density	0.58 g/cc
Water Extractables	<1%
Non-Wettable	<1%

*For general information only, not to be used as purchase specifications.

Recycling by Thermal Reactivation

After a granular activated carbon's adsorptive capacity has been exhausted, it can be returned to Calgon Carbon for thermal reactivation. The thermal reactivation process involves a high temperature reaction with steam, which destroys the adsorbed organic compounds and restores the adsorptive capacity of the activated carbon.

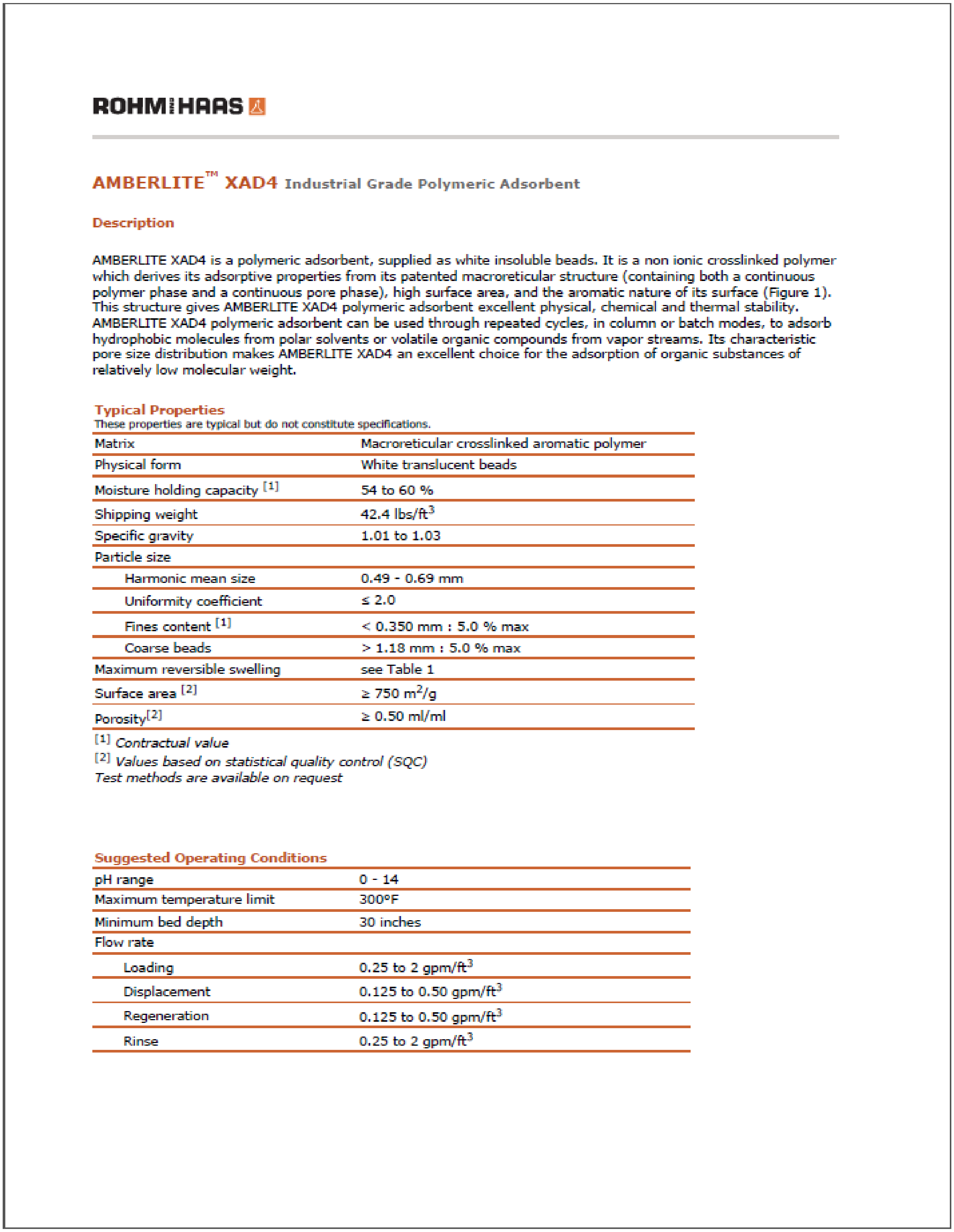
Through reactivation, the spent activated carbon can be recycled for reuse, eliminating the costs and long-term liability associated with disposal of spent GAC. The benefits of a reactivated product over a virgin carbon are several, including economic, as reactivated GAC cost less than virgin GAC and environmental, as reactivated GAC conserves natural resources and reduces CO_2 emissions compared to the manufacture of virgin GAC. A further benefit of reactivating and reusing spent granular activated carbon is the ability for customers to ensure for themselves a reliable supply of media when needed, as the spent/reactivated carbon represents a renewable resource.

FILTRASORB 200 is designed with high mechanical strength and a dense, fully-developed pore structure to ensure low losses throughout the reactivation process and excellent adsorption performance upon reuse.

Making Water and Air Safer and Cleaner **www.calgoncarbon.com**

Figure 16: FS-200 Data Sheet (Calgon Carbon Corporation, 2013)

Amberlite® XAD4 – Dow Chemical Company



ROHM HAAS

AMBERLITE™ XAD4 Industrial Grade Polymeric Adsorbent

Description

AMBERLITE XAD4 is a polymeric adsorbent, supplied as white insoluble beads. It is a non ionic crosslinked polymer which derives its adsorptive properties from its patented macroreticular structure (containing both a continuous polymer phase and a continuous pore phase), high surface area, and the aromatic nature of its surface (Figure 1). This structure gives AMBERLITE XAD4 polymeric adsorbent excellent physical, chemical and thermal stability. AMBERLITE XAD4 polymeric adsorbent can be used through repeated cycles, in column or batch modes, to adsorb hydrophobic molecules from polar solvents or volatile organic compounds from vapor streams. Its characteristic pore size distribution makes AMBERLITE XAD4 an excellent choice for the adsorption of organic substances of relatively low molecular weight.

Typical Properties

These properties are typical but do not constitute specifications.

Matrix	Macroreticular crosslinked aromatic polymer
Physical form	White translucent beads
Moisture holding capacity [1]	54 to 60 %
Shipping weight	42.4 lbs/ft^3
Specific gravity	1.01 to 1.03
Particle size	
Harmonic mean size	0.49 - 0.69 mm
Uniformity coefficient	≤ 2.0
Fines content [1]	< 0.350 mm : 5.0 % max
Coarse beads	> 1.18 mm : 5.0 % max
Maximum reversible swelling	see Table 1
Surface area [2]	≥ 750 m^2/g
Porosity[2]	≥ 0.50 ml/ml

[1] *Contractual value*

[2] *Values based on statistical quality control (SQC)*

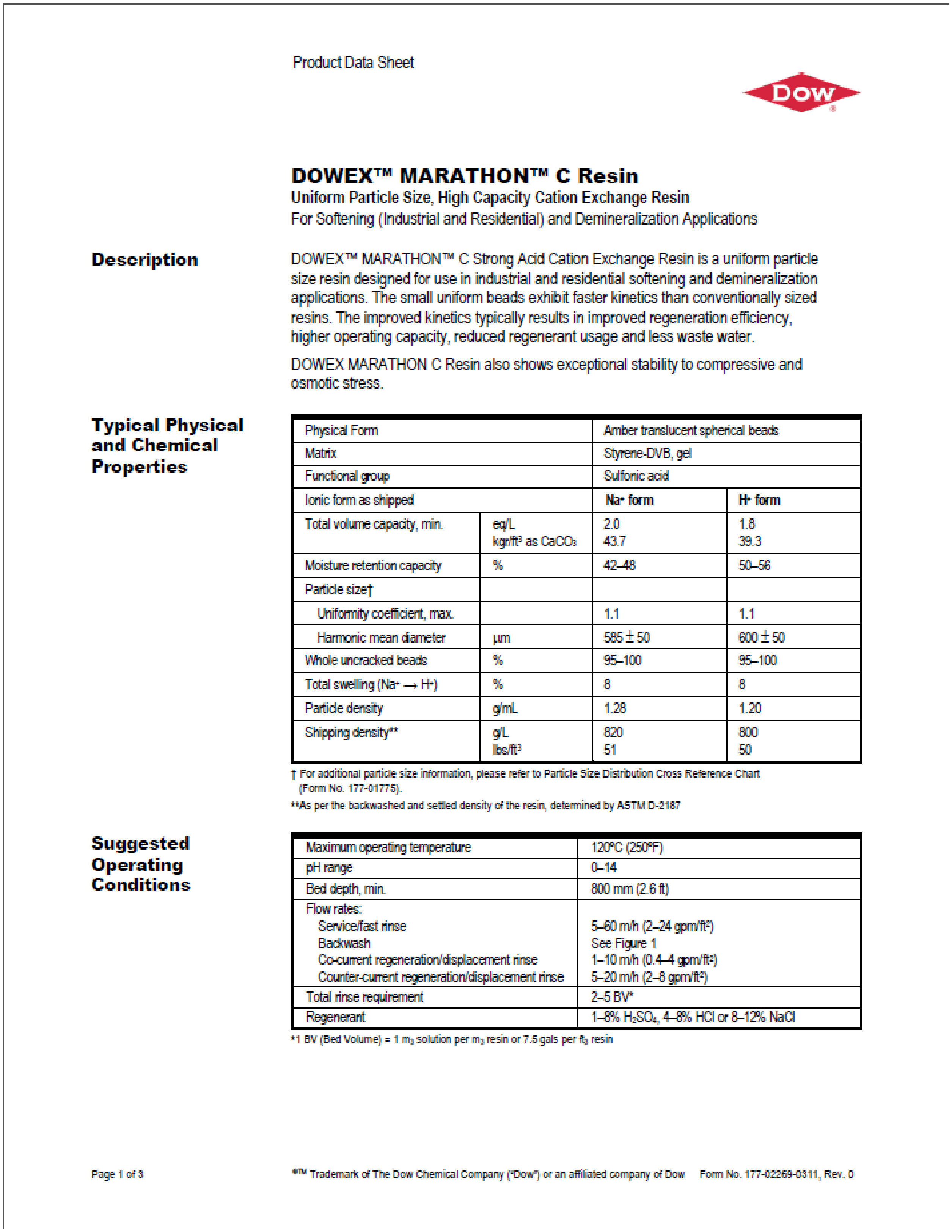
Test methods are available on request

Suggested Operating Conditions

pH range	0 - 14
Maximum temperature limit	300°F
Minimum bed depth	30 inches
Flow rate	
Loading	0.25 to 2 gpm/ft^3
Displacement	0.125 to 0.50 gpm/ft^3
Regeneration	0.125 to 0.50 gpm/ft^3
Rinse	0.25 to 2 gpm/ft^3

Figure 17: Amberlite XAD4 Product Information Sheet (Dow Chemical Company, 2013)

Marathon® C – Dow Chemical Company



Product Data Sheet

DOWEX™ MARATHON™ C Resin

Uniform Particle Size, High Capacity Cation Exchange Resin

For Softening (Industrial and Residential) and Demineralization Applications

Description

DOWEX™ MARATHON™ C Strong Acid Cation Exchange Resin is a uniform particle size resin designed for use in industrial and residential softening and demineralization applications. The small uniform beads exhibit faster kinetics than conventionally sized resins. The improved kinetics typically results in improved regeneration efficiency, higher operating capacity, reduced regenerant usage and less waste water.

DOWEX MARATHON C Resin also shows exceptional stability to compressive and osmotic stress.

Typical Physical and Chemical Properties

Physical Form		Amber translucent spherical beads	
Matrix		Styrene-DVB, gel	
Functional group		Sulfonic acid	
Ionic form as shipped		**Na^+ form**	**H^+ form**
Total volume capacity, min.	eq/L kgr/ft³ as $CaCO_3$	2.0 43.7	1.8 39.3
Moisture retention capacity	%	42–48	50–56
Particle size†			
Uniformity coefficient, max.		1.1	1.1
Harmonic mean diameter	µm	585 ± 50	600 ± 50
Whole uncracked beads	%	95–100	95–100
Total swelling ($Na^+ \rightarrow H^+$)	%	8	8
Particle density	g/mL	1.28	1.20
Shipping density**	g/L lbs/ft³	820 51	800 50

† For additional particle size information, please refer to Particle Size Distribution Cross Reference Chart (Form No. 177-01775).

**As per the backwashed and settled density of the resin, determined by ASTM D-2187

Suggested Operating Conditions

Maximum operating temperature	120°C (250°F)
pH range	0–14
Bed depth, min.	800 mm (2.6 ft)
Flow rates:	
Service/fast rinse	5–60 m/h (2–24 gpm/ft²)
Backwash	See Figure 1
Co-current regeneration/displacement rinse	1–10 m/h (0.4–4 gpm/ft²)
Counter-current regeneration/displacement rinse	5–20 m/h (2–8 gpm/ft²)
Total rinse requirement	2–5 BV*
Regenerant	1–8% H_2SO_4, 4–8% HCl or 8–12% NaCl

*1 BV (Bed Volume) = 1 m_3 solution per m_3 resin or 7.5 gals per ft_3 resin

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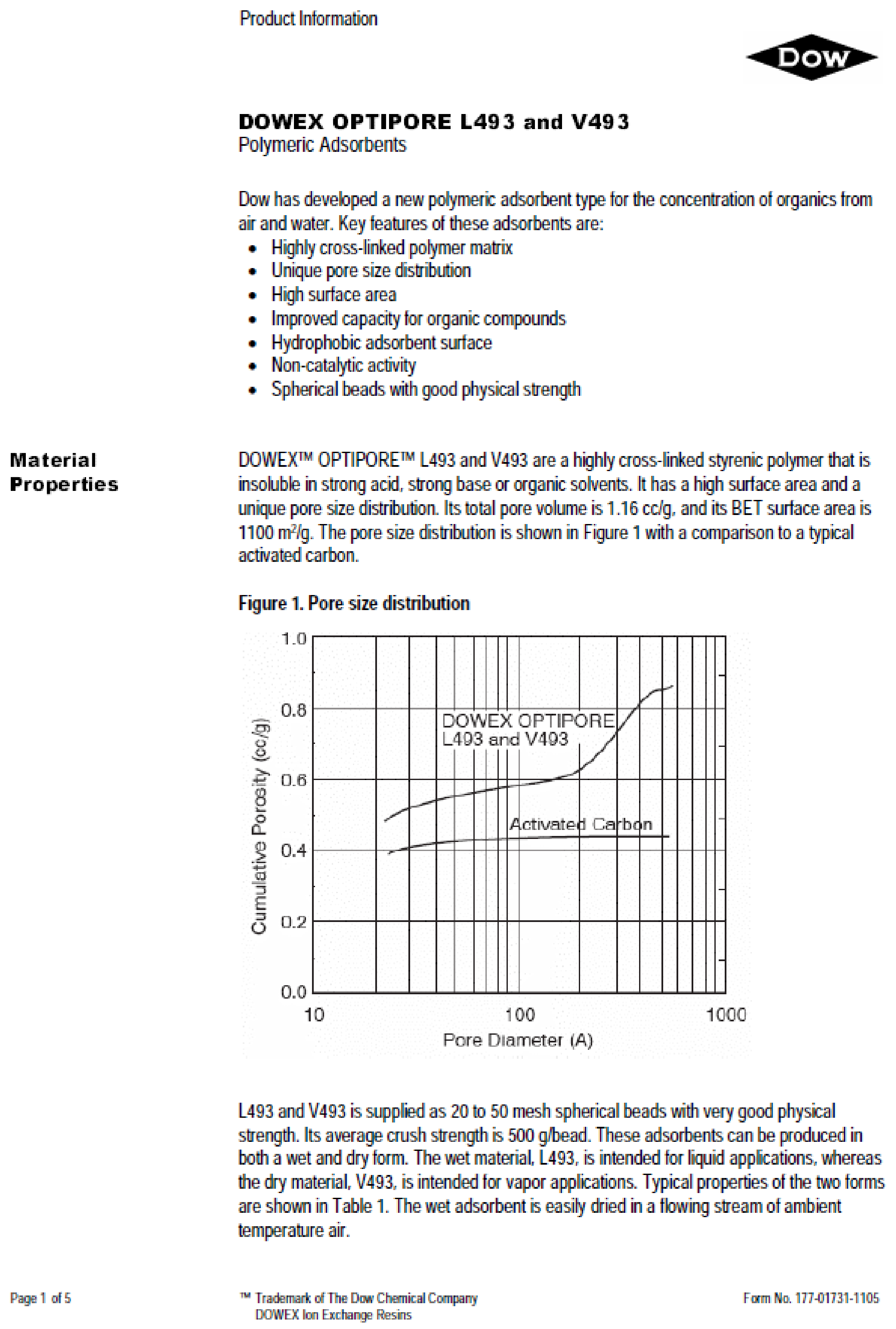
Figure 18: Marathon C Product Data Sheet (Dow Chemical Company, 2013)

Optipore® L493 – Dow Chemical Company



Product Information

DOWEX OPTIPORE L493 and V493
Polymeric Adsorbents

Dow has developed a new polymeric adsorbent type for the concentration of organics from air and water. Key features of these adsorbents are:

- Highly cross-linked polymer matrix
- Unique pore size distribution
- High surface area
- Improved capacity for organic compounds
- Hydrophobic adsorbent surface
- Non-catalytic activity
- Spherical beads with good physical strength

Material Properties

DOWEX™ OPTIPORE™ L493 and V493 are a highly cross-linked styrenic polymer that is insoluble in strong acid, strong base or organic solvents. It has a high surface area and a unique pore size distribution. Its total pore volume is 1.16 cc/g, and its BET surface area is 1100 m^2/g. The pore size distribution is shown in Figure 1 with a comparison to a typical activated carbon.

Figure 1. Pore size distribution

L493 and V493 is supplied as 20 to 50 mesh spherical beads with very good physical strength. Its average crush strength is 500 g/bead. These adsorbents can be produced in both a wet and dry form. The wet material, L493, is intended for liquid applications, whereas the dry material, V493, is intended for vapor applications. Typical properties of the two forms are shown in Table 1. The wet adsorbent is easily dried in a flowing stream of ambient temperature air.

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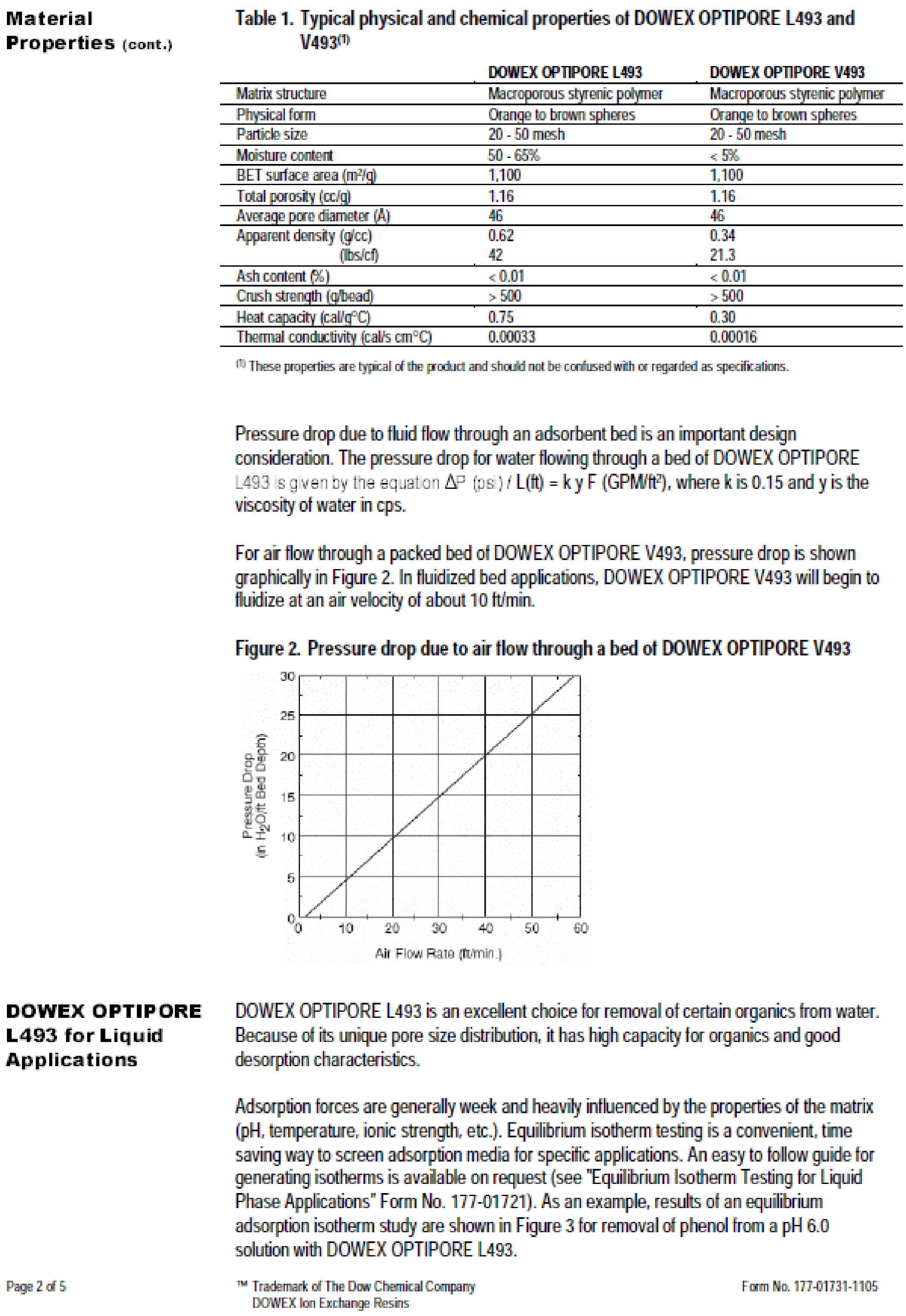
DOWEX Ion Exchange Resins

Form No. 177-01731-1105

Figure 19: Optipore L493 Product Information Sheet p. 1 (Dow Chemical Company, 2013)



Material Properties (cont.)

Table 1. Typical physical and chemical properties of DOWEX OPTIPORE L493 and V493[1]

	DOWEX OPTIPORE L493	DOWEX OPTIPORE V493
Matrix structure	Macroporous styrenic polymer	Macroporous styrenic polymer
Physical form	Orange to brown spheres	Orange to brown spheres
Particle size	20 - 50 mesh	20 - 50 mesh
Moisture content	50 - 65%	< 5%
BET surface area (m^2/g)	1,100	1,100
Total porosity (cc/g)	1.16	1.16
Average pore diameter (Å)	46	46
Apparent density (g/cc)	0.62	0.34
(lbs/cf)	42	21.3
Ash content (%)	< 0.01	< 0.01
Crush strength (g/bead)	> 500	> 500
Heat capacity (cal/g°C)	0.75	0.30
Thermal conductivity (cal/s cm°C)	0.00033	0.00016

[1] These properties are typical of the product and should not be confused with or regarded as specifications.

Pressure drop due to fluid flow through an adsorbent bed is an important design consideration. The pressure drop for water flowing through a bed of DOWEX OPTIPORE L493 is given by the equation ΔP (psi) / L(ft) = k y F (GPM/ft^2), where k is 0.15 and y is the viscosity of water in cps.

For air flow through a packed bed of DOWEX OPTIPORE V493, pressure drop is shown graphically in Figure 2. In fluidized bed applications, DOWEX OPTIPORE V493 will begin to fluidize at an air velocity of about 10 ft/min.

Figure 2. Pressure drop due to air flow through a bed of DOWEX OPTIPORE V493

DOWEX OPTIPORE L493 for Liquid Applications

DOWEX OPTIPORE L493 is an excellent choice for removal of certain organics from water. Because of its unique pore size distribution, it has high capacity for organics and good desorption characteristics.

Adsorption forces are generally week and heavily influenced by the properties of the matrix (pH, temperature, ionic strength, etc.). Equilibrium isotherm testing is a convenient, time saving way to screen adsorption media for specific applications. An easy to follow guide for generating isotherms is available on request (see "Equilibrium Isotherm Testing for Liquid Phase Applications" Form No. 177-01721). As an example, results of an equilibrium adsorption isotherm study are shown in Figure 3 for removal of phenol from a pH 6.0 solution with DOWEX OPTIPORE L493.

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Figure 20: Optipore L493 Product Information Sheet p. 2 (Dow Chemical Company, 2013)