**EVALUATION OF GUAR GUM AS A NOVEL ADSORBENT**

THESIS

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AFIT-ENV-MS-19-M-174

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# EVALUATION OF GUAR GUM AS A NOVEL ADSORBENT

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## Abstract

Guar gum (GG) is a promising product increasingly used in a variety of industries. It is nontoxic, inexpensive, and biodegradable. This research evaluated novel approaches using GG as an adsorbent for aromatic organic water contaminants. The application of GG demonstrated some effectiveness against all contaminants tested. Two brands of GG were tested using 5 different GG treatment strategies. Various experiments demonstrated nearly complete removal of Allura Red dye, Brilliant Blue dye, Erythrosine B dye, Methylene Blue dye, Tartrazine dye, and 2,4-dinitrotoluene; additionally, 78% adsorption was observed for Fast Green dye. GG typically removed less than 10% of toluene, which rapidly volatilizes. The application of pre-hydrated GG significantly outperformed other GG treatment techniques evaluated, and in some instances demonstrated faster adsorption than an equivalent amount of granular activated carbon. Comparatively, the use of dry GG powder required over 1 week to demonstrate appreciable results; methods of GG cleaning, crosslinking, and salification were possible, but did not appear to be substantially better than the results of using the unmodified gum. When dissolved in water, GG has unique spectrum characteristics at wavelengths below 300 nm, likely due to electronic transitions, which vary based on the quantity, age, and brand of GG used. Furthermore, adsorption performance may be correlated with pH; GG usage results in solution pH decrease over time, possibly caused by the production of a member of the carboxylic acid family. Based on these results, GG has proven to be a viable novel adsorbent product for stable non-volatile organic compounds.

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# EVALUATION OF GUAR GUM AS A NOVEL ADSORBENT

## I. Introduction

### General Issue

Within the United States, nearly 3 million people obtain drinking water from Department of Defense (DoD) water systems annually [1]. These systems must comply with drinking water standards established by the Environmental Protection Agency (EPA), and state-specific regulations enforced under the Safe Drinking Water Act. In addition to enforcing the current standards, the EPA also has the responsibility to identify unregulated contaminants and establish regulations for those that present health concerns. The DoD also has a process of identifying emerging contaminants, defined as: materials which may present an unacceptable risk to human health or the environment, materials which have a pathway to enter the environment, and materials which are either not regulated or regulatory standards are evolving due to new science, detection capabilities, or pathways [1].

The DoD's list of emerging contaminants is comprised of 49 compounds, including heavy metals, solvents, organic, and inorganic compounds [1]. Within that list, 10 contaminants have become regulated by the EPA, and 11 are currently unregulated, but are associated with an EPA health advisory [1]. This list encompasses antimony, beryllium, cadmium, dioxins, ethylbenzene, hexavalent chromium, lead, methylene chloride, phthalate esters, trichloroethylene (TCE), 1,4-dioxane, cyclotrimethylenetrinitramine (RDX), 2,4-dinitrotoluene (DNT), manganese, naphthalene, nickel, n-Nitrosodimethylamine (NDMA), perchlorate, perfluorinated

compounds (PFC), and strontium [1]. Emerging contaminants drive requirements for new treatment, sampling, and monitoring initiatives. Environmental restoration and water treatment technologies may be limited by cost, performance factors, and reuse or disposal challenges. For example, the newest additions to the DoD emerging contaminant list were 2 specific perfluorinated compounds. As of 2016, the DoD had identified 391installations potentially impacted by PFCs, had spent $142 million on environmental investigations for 263 of those sites, and $57 million on mitigation initiatives at 19 of the 391 locations [1].

This reality demonstrates the importance and necessity to develop new technologies and treatment methods which are practical, effective, and inexpensive. One potential product evaluated was guar gum (GG); it is a relatively inexpensive, biodegradable, natural polysaccharide which has demonstrated effective adsorption capabilities for various water contaminants. This research project endeavors to determine an effective novel treatment approach for several different contaminants using guar gum.

**Problem Statement**

Emerging contaminants and changing regulatory limits require that new and innovative water treatment technologies be developed. With this in mind, does guar gum use as a novel treatment provide a cost-effective, biodegradable, and viable approach against a variety of contaminants?

**Research Objectives/Questions/Hypotheses**

The objective of this research was to determine whether guar gum can be utilized as an adsorbent and its effectiveness as a treatment approach to remove water

contaminants. Various treatment methods and parameters utilizing guar gum were tested and their performance against several challenge agents was evaluated.

Objective 1 – Study GG characteristics when mixed with water

Hypothesis: Dissolving GG in water can be detected with a UV-visible spectrophotometer, and the product produces an overall UV-Vis baseline shift compared to water.

Subtask 1.1 – Determine effect of increasing quantities of GG.

Subtask 1.2 – Evaluate if GG solution spectrograph changes over time.

Subtask 1.3 – Compare baseline of different GG or sorbent applications (i.e. crosslinking, mixing, sonicating, etc.).

Subtask 1.4 – Evaluate methods to remove GG from water.

Objective 2– Evaluate color removal using GG as an adsorbent for various dyes

Hypothesis: 1 gram of unmodified GG in bottle tests will demonstrate at least 50% dye adsorption of 0.005-0.01mM solutions.

Subtask 2.1 – Compare different matrices or use/application of GG for efficient dye removal.

Subtask 2.2 – Compare GG effectiveness to carbon and other carbohydrate gums.

Subtask 2.3 – Evaluate GG reaction time for dye removal.

Subtask 2.4 – Compare effectiveness of stationary and slow movement in batch bottle tests.

Subtask 2.5 – Assess impact of temperature and pH on adsorption effectiveness.

Objective 3 – Evaluate GG effectiveness as an adsorbent for various contaminants such as dinitrotoluene (DNT), toluene, or others as available.

Hypothesis: GG will demonstrate at least 50% adsorption for 10 ppm concentration of contaminant(s) of interest.

Subtask 3.1 – Use selected GG application method (from previous objectives) to test contaminant presence using UV-Vis Spectrophotometer if applicable.

Subtask 3.2 – Use selected GG application method to test contaminant presence using Gas Chromatograph or High-Performance Liquid Chromatograph (HPLC) if possible.

Subtask 3.3 – Use selected GG application method to test contaminant presence using outside analytical laboratory if necessary.

**Research Focus**

This research focused on using GG powder as an adsorbent for different water contaminants, including 6 dyes and 2 organic compounds.

**Investigative Questions**

1. Does guar gum effectively adsorb contaminants from water?
2. What is the best method to ensure guar gum used in treatment does not impact finished water?
3. Do other water chemistry parameters, such as pH, and temperature contribute to GG adsorption of contaminants?
4. Is there a difference in effectiveness across GG brands, or do brands of GG perform similarly?
5. Is crosslinking GG with borate ions more effective than unmodified gum?
6. Do dry GG and hydrated GG perform differently?

## Methodology

Analysis was predominantly conducted using an Agilent Technologies Cary 60 Ultraviolet-Visible Spectrophotometer (UV-Vis). Twenty-seven batch tests employed a variety of guar gum matrices and treatment applications, including unmodified dry GG, hydrated GG, cleaned or dried GG, crosslinked GG, and GG with salting-out solution. It was determined that best practices included using a syringe filter or centrifuging samples prior to analysis, and utilizing a method of control subtraction for spectrogram analysis.

## Assumptions/Limitations

Guar gum proved to be challenging to work with, and its usage presented several complicating factors during analysis. When dissolved in water, GG creates a general UV-Visible baseline shift. Additionally, wide variability occurred based on the location of sample collection in a container, and different UV-Vis readings could be collected from the same sample due to suspended solids. A multitude of control samples were required, and subtraction of control absorbance values was used; this added requirements for time, supplies, and could overstate the true impact of GG adsorption. Filtration and centrifuging helped to decrease this variability and to remove the spectrum shift at higher wavelengths; however, it was discovered that lower wavelength peaks and spectrum anomalies are not completely removed by these methods.

The UV-Vis was predominantly used during this assessment, and limited the types of contaminants which could be tested. As a gum, its usage demonstrated high viscosity and resulted in decreasing sensitivity and potential obstructions within more sensitive analytical equipment such as the gas chromatograph. Based on the challenges

associated with ensuring complete GG removal prior to injection into sensitive equipment, research was limited to contaminants which could be tested on the UV-Vis, at concentrations which could produce a characteristic peak.

One of the main limitations within this research was the length of time initially demonstrated for GG adsorption. Samples were tested for several weeks and, as such, were impacted by evolving methodologies, as well as supply or equipment issues. Furthermore, the wide number of variables and contaminants evaluated resulted in many singular experiments. Direct comparisons are challenging due to changes in methodologies, and varied concentrations of GG and contaminants throughout this research. Ideally, the most promising experiments should be repeated to strengthen the initial conclusions of this research.

**Implications**

Guar gum is inexpensive, nontoxic and highly susceptible to microbial degradation. Bottle adsorption tests showed nearly complete removal of Allura Red dye, Brilliant Blue dye, Erythrosine B dye, Methylene Blue dye, Tartrazine dye, and 2,4-dinitrotoluene. Approximately 80% removal was observed for Fast Green dye and less than 10% removal was noted for toluene. Tests spanned a few hours to several weeks in length, with the fastest results occurring when testing solutions with a weight-by-volume (w/v) basis of 50% pre-hydrated GG and 50% of the contaminant of interest. In several instances, the hydrated GG performed better than activated carbon. Adsorption effectiveness may also be linked to the pH of the solution and the anionic or cationic nature of the contaminant tested. Although future research should focus on determining

the optimum GG usage parameters, secondary impacts, and life-cycle costs, overall, this research has shown that GG may be effective in removing a variety of nonvolatile, aromatic organic water contaminants.

# II. Literature Review

## Chapter Overview

This chapter will identify relevant background information regarding water treatment technologies, GG usage, and contaminants of interest as it pertains to this research initiative. There are numerous water treatment approaches available, and this research focused on the ability of a single potential adsorbent. This chapter also summarizes relevant research publications based on the usage of GG and details the technologies used, including the techniques of crosslinking, grafting, depolymerization, copolymerization, the salting-out effect, and hydrogel development. Background information is also included for the contaminants used throughout this research, their characteristics, sources, and potential toxic effects.

## Water Treatment Overview

There are a number of water treatment technologies currently available. Which treatment is implemented often depends upon the type or concentration of the contaminant(s) needing to be removed. Methods may be based on physical removal, as well as chemical treatments. Water purification may involve the following: disinfection, adsorption, filtration, reverse osmosis, oxidation, distillation, coagulation, flocculation, membrane technologies, ion exchange resins, ultraviolet irradiation, ozonation, biological

treatment, or a combination of methods [2], [3]. These technologies have different implementation and sustainment expenses; they may also present secondary challenges or consequences when used. Within the wide field of water treatment technologies, this research focuses on the ability of a single potential adsorbent, guar gum.

Adsorption is the term used to describe the adhesion of molecules to a surface. Alternatively, desorption occurs when the foreign substance is released from the adsorbent. On their surface, called the interface zone, adsorbents have active sites which allow other substances to adhere/bind. These reactions can be driven by several intermolecular forces including Van der Waals forces, electrostatic interaction, hydrogen bonding, the hydrophobic effect, and ion exchange [2]. Adsorption may also be affected by other conditions such as pH, temperature, particle diameter, pore size and surface area of adsorbent material [2],[4].

**Guar Gum, Chemical Properties**

Guar gum (GG), also known as Gavar, Guwar, Guyan bean, Guaran, Glucotard, Cuarina, Cyamopsis, and Cluster bean, is the powdered endosperm of the seeds of the *Cyamopsis tetragonolobus* legume [5]–[7]. Nearly 90% of GG used globally is cultivated in India and Pakistan [8] . Chemically, GG is a complex natural non-ionic polysaccharide, composed of galactose and mannose sugars [9], [10]. The GG molecule is comprised of 66 atoms with a linear linked mannose backbone and galactose side branches typically within a ratio of 1.8 to 1, and an average molecular weight within $10^6$ to $2x10^6$ [8], [10], [11]. GG from different sources may vary in molecular weight and the ratio or distribution of mannose-to-galactose [12]. The molecule is also surrounded by

hydroxyl (OH) groups, which form hydrogen bonds in water [6]. In addition to hydrogen bonds, when mixed with water, inter-molecular chain entanglement occurs and produces thick, viscous solutions [6].

When mixed with water, GG forms colloidal solutions, and although the molecule is hydrophilic, it is not hygroscopic and does not have a tendency to absorb moisture from the air [6]. Additionally, it attains its full viscosity potential in cold water, unique for a polysaccharide, and has an inverse relationship with temperature; when the temperature of GG solutions is increased, a decrease in viscosity occurs [6]. The rate of gum swelling and hydration is also impacted by temperature, pH, the solute present, GG concentration, and the presence of salts [8]. GG has been proven to be stable over a wide temperature range and a large pH range, spanning 1.0 to 10.5 due to its non-ionic and uncharged characteristics [8]. GG and other galactomannan polysaccharides are not soluble in organic solvents such as hydrocarbons, alcohols, or ketones, with an exception for formamide [6].

GG has a number of beneficial characteristics including its usage as a thickener, gelling agent, emulsifier, moisturizer, softener, film forming agent and even as a means of wound-healing [6]. It is used in a number of industries, including application within foods and beverages, hydraulic drilling, textile printing, personal care and cosmetics, construction, paints and coating, explosives, agriculture, pharmaceutical, and bioremediation applications [6], [8]. In animal tests, ingestion of GG exhibited beneficial effects at lower concentrations of about 0.5 to1.0 percent on weight bases; negative effects noted at higher concentrations (10 to 15 percent based on weight) were attributed to higher viscosity, resulting in decreased protein efficacy and lipid utilization of the

product [8]. Additionally, the European Food Safety Authority Panel on Food Additives classified GG as not carcinogenic, and concluded GG presented no safety concern for the general population as a food additive [13]. However, commercial food grade GG within Europe and that approved by the United States Food and Drug Administration must comply with established limits for gum content, protein, fiber, ash, metals, and microbes [13].

Wide applicability across a number of industries has created variability in GG manufacturing and labelling practices. Specification of typical GG includes: CAS number 9000-30-0; EC Number 232-536-8; HS-Code 130-232-30, and E number E 412 [6], [7]. Most manufacturers differentiate industrial and food grade gums. However, other companies sell laboratory, reagent and pharmaceutical grades of GG. Many manufacturers differentiate their guar products based on viscosity or mesh size. The normal mesh sizes commercially available are 100, 200, and 300. These values relate to the particle size, and correlate to the number and size of openings in the mesh screen through which the GG is sieved. Higher mesh sizes correlate to smaller particles, and smaller particles provide faster hydration rates [8]. Guar is also available in different forms such as dehusked or undehusked seed splits, guar meal, guar protein, powder, fast hydrating mixtures, polymer mixtures, high or low viscosity, and pre-hydrated products. GG may further differ based on where it is sourced, and could demonstrate differences in the molecular weight, as well as the ratio and distribution of galactose residues [12]. This highlights the wide variability of products available and the potential challenges in standardization of GG use in new applications.

Perhaps most importantly, GG is biodegradable, which presents both opportunities and limitations of its use. It is susceptible to microbial attack, and when ingested, GG is significantly fermented by enteric bacteria [13]. It can also be degraded by oxidants and by microbial enzymes [13]. This presents storage and shelf-life concerns, and may require additional modification such as polymerization, grafting or crosslinking to inhibit degradation and add desired characteristics [6], [14]. These modifications may then create secondary hazards or waste streams. Within the bioremediation and drug delivery fields, the ability for rapid degradation may be desirable. Degradation studies have shown unmodified GG degrading within 2 weeks while modified GG degradation occurred after a 50 day period [15]. Multiple factors may also drive degradation of GG and its modified products, including temperature, pH, oxygen content, available nutrients in surrounding environment, and even humidity [15], [16], [17].

**Relevant Research**

Within the bioremediation field, research has demonstrated that GG is an effective adsorbent for water contaminated with heavy metals, oils, and dyes. Table 1 summarizes 31 relevant studies investigating methods to modify GG and its effectiveness as an adsorbent for a variety of contaminants. Much of the available research has investigated the effectiveness of methods modifying GG via techniques such as crosslinking, grafting, depolymerization, copolymerization, the salting-out effect, or hydrogel development. S. Muthulakshmi conducted UV-Vis analysis of several polymers dissolved in water and determined the maximum absorption peak of 0.1mM GG occurred at the wavelength of 340 nanometers (nm) [18]. This peak was attributed to electronic transitions of the

carboxyl groups, where an electron from a lower energy level was elevated due to the absorption of UV light; this study theorized that the n orbital transitioned to the $\pi^*$ orbital [18], [19].

Similar to other polymers, GG can be crosslinked in the presence of other chemical agents. One of the most common crosslinking agents utilizes borate ions, commonly sourced from borax, which produce weak bonds with polymer hydroxyl (OH) groups and can link polymer chains together [7]. Crosslinking can change the characteristics of a polymer and can be very effective in forming gels due to enhanced water holding and absorption capacity. In addition to borate ions, GG can also be crosslinked using sodium periodate, hexamine, epichlorohydrin, glutaraldehyde, derivatives of methylene-bis-acrylamide, derivatives of ethylene-glycol-di(meth)acrylate, and di-vinyl-benzene [6]. Interestingly, GG crosslinked with borate ions demonstrated a shrinking of the gel when in the presence of excess salts (electrolytes). This is due to the salting-out effect, also called salification, which causes a decrease in polymer solubility and results in dehydration and collapse of the polymer network [20].

Grafting, or graft copolymerization is another technology used to modify GG. Various methodologies are used to chemically bind different compounds or functional groups, such as other polymers and composites to GG [6], [8]. Grafting can also enable the blending of synthetic and non-synthetic materials, and may include the following types of graft copolymerization: conventional radical, macromonomer radical, high-energy-initiated, microwave-assisted, gamma-radiation-initiated, ultraviolet radiation-initiated, electron beam-initiated, click chemistry, and atom transfer radical grafting [21]. Additionally, several studies modified native GG to a derivative form for further

modification and testing. Derivatization incorporates chemical modification of native GG using esterification, or etherification and can enhance GG behavior [6], [22]. For example, derivatization may change GG solubility, reaction time, clarity, rate of hydration, viscosity, or susceptibility to microbial contamination [6].

A majority of the tests summarized in Table 1 were based on batch studies or flocculation tests. Determination of adsorption effectiveness relied heavily on the use of the UV-Vis or FTIR for analysis. Research has investigated several dyes, metal ions, oil-based products, and the impact of microbial agents. Furthermore, when evaluating reaction kinetics, there was a nearly even split of the studies that concluded Langmuir compared to Freundlich isotherm interactions; however, a large majority of all the kinetic studies reviewed identified pseudo-second order models as the best fit. Additionally, solution pH appeared to have a prominent impact on the performance of the GG-based products; however, the ideal pH parameter varied based on the type of GG modification, the contaminants tested, and the range of pH's tested. While many of these studies were not directly comparable due to differences in methodology, taken together, they present a compelling picture of the flexibility and applicability of GG usage across industries and promising potential for use as an adsorbent.

**Table 1. Summary of Published Guar Gum Research Studies**

| Author | Contaminant Removed | Research Topic | Summary of Key Findings | Ref. |
|---|---|---|---|---|
| Ahmad & Haseeb, 2016 | Lead $^{2+}$, Copper $^{2+}$ Nickel $^{2+}$ | Batch test using groundnut husk modified with GG | ~Adsorption was fast in the beginning then slowed down; the reaction best fit a pseudo second order model and Freundlich Isotherm.<br>~Maximum adsorption was determined to be 9.76 mg/g, 9.26 mg/g and 6.74 mg/g for $Pb^{2+}$, $Cu^{2+}$ and $Ni^{2+}$; equilibrium was attained in 120 minutes.<br>~Optimized parameters included: pH of 5.0, and temperature of 298K.<br>~XRD spectra indicate semi-crystalline structure. | [9] |
| Berlangieri et al., 2018 | Surface particulate matter | Surface cleaning (patina removal) using gels comprised of GG, borax and glycerol | ~The addition of borax did not significantly change the mesh size of the GG dispersion, however borax increased the solution entanglement density nearly 2 orders of magnitude.<br>~At concentrations below 1%, glycerol behaved a structuring agent, while above 1%, it acted like a plasticizer.<br>~Demonstrated potential usage for selective surface cleaning application. | [23] |
| Chandrika et al., 2016 | N/A | Development of superabsorbent hydrogels via free radical grafting polymerization of GG, using N,N-methylene bis acrylamide as a crosslinker | ~Chemical modification such as grafting inhibits fast microbial degradation and also improves the swelling and flocculation properties of GG.<br>~Maximum swelling occurred at pH of 9 and 50 ◦C; this is attributed to amide ionization and presence of −COOH groups to COO− groups<br>~ Salt solutions resulted in reduced swelling capacity.<br>~Grafting resulted in improved shelf life and bioefficacy against fungal and bacterial microbes. | [14] |
| Chauhan, Chauhan, & Ahn, 2009 | Copper $^{2+}$ | Adsorption using hydrogel created by GG depolymerization via acid hydrolysis, oxidation with nitrogen oxides, and crosslinked with ammonium persulfate and N,N-methylene bis acrylamide | ~Highest adsorption occurred at 2 hours, 40 °C, 20 ppm of Copper $^{2+}$.<br>~Maximum sorption capacity of 125.893 mg/g.<br>~Both Langmuir and Freundlich isotherms presented a good match, and fit a pseudo second order kinetic model.<br>~Increasing temperature above 55 °C resulted in desorption.<br>~The higher pH (tested at 2.5, 4.0, 6.0 and 7.0) demonstrated highest adsorption due to matrix expansion. | [24] |
| Dai, Wang, et al., 2017 | Oil-water separation: cyclohexane, canola oil, crude oil and silicone oil | Gravity filtration/separation using GG hydrogel crosslinked with metaborate, and coated onto 100µm stainless steel mesh. | ~Separation efficiency: 99.70%, 97.45%, 98.75% and 99.60%, for cyclohexane, canola oil, crude oil and silicone oil, respectively.<br>~The mesh demonstrated re-usability/recyclability (6 cycles of rinsing tested). | [25] |

| Author | Contaminant Removed | Research Topic | Summary of Key Findings | Ref. |
|---|---|---|---|---|
| Dai, Zhang, et al., 2017 | Copper $^{2+}$ | Self-assembling hydrogel using one-flask method based on formation of cyclic acetals and regioselective oxidation of GG using sodium periodate. | ~Adsorption equilibrium occurred after 5 hours; crosslinking was obtained without the addition of any crosslinking agents.<br>~The amount of adsorbed Copper$^{2+}$ was 944 mg/g GG when an initial concentration of 25 mg/mL CuSO4 and a hydrogel with 100mg GG was used.<br>~A 0.5 wt% GG solution was not able to produce hydrogel; however, 1.0 wt% was sufficient and took 10 minutes.<br>~Hydrogel demonstrated self-healing and thermoresponsive properties.<br>~Adsorption capacity increased with an additional Copper$^{2+}$ concentration.<br>~Best fit using Freundlich isotherm. | [26] |
| Gupta, Pathania, Singh, Kumar, & Rathore, 2014 | Cationic, methylene blue dye | Batch tests of GG–cerium (IV) tungstate nanocomposite cationic exchanger, synthesized using sol gel method | ~Optimum parameters: dye concentration of 0.32 mg/L, adsorbent dose of 0.4 g/50 mL, 120 minute contact time, and temperature of 30 ◦C; resulted in nearly 96% dye removal.<br>~Good fit of monolayer Langmuir isotherm, with pseudo second order kinetic model.<br>~Dye adsorption removal was increased by modifying pH from 2 to 9.<br>~Dye adsorption and ion exchange ability decreased with temperature increase.<br>~Adsorbent acted as a strong cation exchanger; selectivity for different metal ions included: Pb ($K_d$ = 223) Zn ($K_d$ = 189) > Th ($K_d$ = 90) > Cu ($K_d$ = 65.7) > Ni ($K_d$ = 61.0) > Cd ($K_d$ = 59.17) > Mg ($K_d$ = 41.5). | [27] |
| Jain et al., 2017 | Iron ore slimes (tailing ponds) | Density functional theory, modelling and preliminary test of GG as a selective flocculant | ~Modelling shows GG will be selective toward the iron hematite surface as compared to other minerals (goethite, gibbsite and kaolinite).<br>~Recommended parameters: 5 min settling time and 300 g per ton GG dosage for 1% pulp density, and 30 min settling time and 1500 g per ton GG dosage for 15% pulp density.<br>~Optimum pH for flocculation was 10.5, based on previous studies. | [10] |
| Kaith, Sharma, & Kalia, 2015 | N/A | Development of biodegradable, electrically-conductive interpenetrating network structures created via 2-step aqueous polymerization using ammonium persulfate initiator and hexamine crosslinker | ~Optimum conditions for maximum gel swelling: 60 minutes, 450mmHg vacuum pressure, 60 ◦C, and pH of 7.0; resulting in 7470% swelling.<br>~GG hydrogels were strongly active against S. aureus and also demonstrated significant reduction in E. coli bacterial growth.<br>~Hydrogels demonstrated improved water holding capacity of various soil types.<br>~GG degraded by 14 days, while GG-graft polymerization products degraded completely in a period of 50–70 days.<br>~Multiple factors influence degradation of gels, including: pH, oxygen content, temperature, available nutrients, and humidity. | [28] |
| Khouryieh, Herald, Aramouni, & Alavi, n.d. | N/A | Investigation of GG, and xanthan gum mixture properties | ~GG molecular weight was $1.45 \cdot 10^6$, much smaller than the native xanthan molecular weight of $2.65 \cdot 10^6$.<br>~Synergistic intermolecular interactions resulting in enhanced viscosity/gelation were observed for xanthan–guar mixtures in water with 2 mM Sodium Chloride, but not in 40 mM Sodium Chloride. | [29] |

| Author | Contaminant Removed | Research Topic | Summary of Key Findings | Ref. |
|---|---|---|---|---|
| Kono, Hara, Hashimoto, & Shimizu, 2015 | N/A | Nonionic gels created using hydroxypropyl GG (a derivative of native GG), and crosslinked with ethylene glycol diglycidyl ether | ~Increasing crosslinking agent resulted in larger degrees of crosslinking; various viscoelastic parameters depended on the degree of crosslinking.<br>~Hydroxypropyl GG gels absorbed buffers, aqueous saline, water, and demonstrated ability to gel in presence of organic solvents.<br>~Absorption was not affected by the ionic strength/pH of the solution. | [30] |
| Maity & Kumar Ray, 2016 | Chromium (VI) | Batch tests using composite hydrogels crafted by incorporating GG and nano-sized bentonite clay in an acrylic network, using acrylic acid, N,N- methylene bis acrylamide, and hydroxyethyl methacrylate. | ~Hydrogel showed 97.8% removal for initial concentration of 5 mg/L, and 91.4% removal for 200 mg/L concentration.<br>~Copolymer network increased gel swelling and compressive strength.<br>~Adsorption was strongly influenced by pH: the ideal pH determined was 2.<br>~Above 1 g/L of hydrogel, there was no significant increase in percent contaminant removed.<br>~First order kinetics a better fit for low concentration range, while second order kinetics a better fit for high concentration range; this indicated chemical sorption as the rate-limiting step.<br>~5 cycles of sorption/desorption, and the adsorption capacity of these gels remained 97 to 98.5%. | [31] |
| S. Pal, Ghorai, Dash, Ghosh, & Udayabhanu, 2011 | Cationic, methylene blue dye | Flocculation using grafted carboxymethyl GG (a derivative to native GG), synthesized by redox grafting and microwave assisted grafting methods | ~82% grafting efficiency occurred using conventional grafting, and 96% grafting efficiency occurred using microwave assisted method.<br>~ All grafted products demonstrated higher molecular weights, radius of gyration, viscosities, and better color removal than Carboxymethyl GG.<br>~Microwave assisted product resulted in best flocculation, percent Chemical Oxygen Demand removal, and color removal.<br>~Ideal flocculant concentration for color removal was 8 ppm; however destabilization occurred when optimal dosage was exceeded. | [32] |
| A. Pal, Nasim, Giri, & Bandyopadhyay, 2014 | Lead (II) | Evaluate hydrodynamic size and zeta potential GG grafted using surfactant mediated free radical polymerization technique | ~Use of 1000 ppm GG removed 56.72% of initial Lead (II) concentration of 100 ppm within 150 minutes.<br>~Ideal parameters: 4.5 pH and 303 K.<br>~Best fit to Langmuir isotherm, pseudo second order model.<br>~Ideal concentration: 1000 ppm GG (absorption efficiency decreases slightly at 5000 ppm).<br>~Zeta potentials of GG molecules do not vary, indicating molecular size controls adsorption efficiency.<br>~A minimum contact time of 20 min adsorbed nearly 30%, and 150 minutes at zero agitation speed demonstrated nearly 27% adsorption.<br>~Adsorption efficiency was found to increase with increasing agitation speed. | [33] |

| Author | Contaminant Removed | Research Topic | Summary of Key Findings | Ref. |
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| A. Pal, Giri, & Bandyopadhyay, 2016 | Lead (II) | Employ a surfactant mediated free radical polymerization technique used to create Papolyelectrolyte poly(acrylic acid) grafted GG | ~The initial concentration of Lead (II) was 350 ppm; a maximum adsorption of 89.62% was achieved at a pH of 4.5 after 150 minutes; the effectiveness was raised to 95.32% using pH manipulation.<br>~Unmodified GG demonstrated 57.8% adsorption.<br>~ pH 1.0 - 2.0: adsorption efficiency <5%.<br>~pH 2.0 - 3.0: improved efficiency to 80%.<br>~pH 3.0 - 5.5: increasing slowly to 95.32% at pH of 5.5.<br>~pH 5.5 - 6.5: efficiency dropped slightly.<br>~pH >6.5: efficiency increased to 100% (precipitation of LeadII).<br>~Adsorption was found to be independent of shaking speed.<br>~Best fit to Langmuir isotherm, pseudo-second order model.<br>~Nearly 86.5% of Lead (II) was adsorbed within 15 minutes; after that, it took nearly 60 additional minutes to reach maximum adsorption. | [34] |
| S. Pal et al., 2015 | Anionic, toxic reactive blue and congo red dyes | Batch tests using graft copolymerized GG-silica nanocomposite generated by microwave assisted sol-gel method. | ~Ideal parameters for Blue adsorption (94.96% removal): pH of 2, 40 minutes 313 K, dosage of 30 mg/25 mL, and initial dye concentration of 200 ppm.<br>~Ideal parameters for Red adsorption (95.98% removal): pH of 3, 30 minutes, 318 K, dosage of 40 mg/25 mL, and initial dye concentration of 150 ppm.<br>~Maximum desorption occurred in basic solution, pH 10; resulted in 10, 94.96% of Blue desorbed and 95.98% of Red desorbed.<br>~4 cycles of desorption resulted in both dyes recovering >82%<br>~Minimum desorption observed at pH2; 46.45% for Blue and 49.08% for Red.<br>~Best fit to Langmuir isotherm, pseudo-second order model. | [35] |
| Pandey, Kumar Verma, Yadav, & Behari, 2014 | Lead $^{2+}$, Nickel $^{2+}$ Zinc $^{2+}$ | Adsorption and flocculation using graft copolymerization of N,N'-dimethylacrylamide onto GG, using potassium peroxymonosulphate/glycolic acid redox pair | ~Sample with 0.02 g of highest grafting performed best with percent uptake of 11.23% for Lead$^{2+}$, 10.66% for Nickel$^{2+}$, and 9.34% for Zinc$^{2+}$.<br>~0.02 g of unmodified GG demonstrated percent uptake of 3.1% for Lead$^{2+}$, 5.1% for Nickel$^{2+}$, and 4.3% for Zinc$^{2+}$.<br>~Grafted copolymer demonstrated better flocculation efficiency than unmodified GG. | [36] |

| Author | Contaminant Removed | Research Topic | Summary of Key Findings | Ref. |
|---|---|---|---|---|
| Patra et al., 2017 | Cationic, malachite green dye, safranin dye, Lead$^{2+}$, Cadmium$^{2+}$ | Batch tests using anionically-functionalized GG embedded with silica nanoparticles, created via sol-gel technique | ~Able to selectively remove cationic dye when in solution with anionic dye tropaeolin.<br>~Ideal parameters for Green dye (98.75% removal): pH 7, 50 minutes, 400 ppm dye concentration, 303 K, 25 mg/25 m adsorbent dose.<br>~Ideal parameters for Safrin dye (98.86% removal): pH 8, 40 minutes, 100 ppm dye concentration, 298 K, 25 mg/30 mL adsorbent dose.<br>~Ideal parameters for Lead $^{2+}$ ions (93.5% removal): pH: 7, 40 minutes, 800 ppm ion concentration, 303 K, 20 mg/20 mL adsorbent dose.<br>~Ideal parameters for Cadmium $^{2+}$ ions (95.5% removal): pH 7 30 minutes, 600 ppm ion concentration, 303 K, 20 mg/20 mL adsorbent dose.<br>~Nanocomposite was able to selectively remove cationic dye when in solution with the anionic dye, tropaeolin.<br>~Maximum desorption occurred at lower pH: pH 2, resulted in desorption percentages of 84.25% for green dye, 85.42% for safrin dye, 89.7% for Lead$^{2+}$,and 89.5% for Cadmium$^{2+}$).<br>~Minimum desorption occurred at higher pH: pH 10, resulted in desorption percentages of 45.68% for green dye 48.30% for safrin dye, 54.52% for Lead$^{2+}$, and 49.65% for Cadmium$^{2+}$.<br>~Best fit to Langmuir isotherm, pseudo-second order model. | [37] |
| R. Sharma et al., 2015 | Cationic, methylene blue dye | Adsorption using interpenetrating network structures created via 2-step free-radical aqueous polymerization using ammonium persulfate and hexamine | ~Ideal parameters for hydrogel formation: 150 minutes, 80 °C, and pH 7.0.<br>~Unmodified GG was inactive against both Staphylococcus aureus and Escherichia coli bacteria, while synthesized product demonstrated antibacterial activity for both agents.<br>~An adsorption time of 4 hours resulted in 52.981-61.839% dye removal based on sample method.<br>~Dye removal increased with higher pH and higher temperature profiles. | [38] |
| S. Sharma et al., 2013 | N/A | Development of pH-responsive GG microspheres using bi-functional glutaraldehyde grafting and water-in-oil emulsion polymerization for pharmaceutical use | ~Researchers were able to develop particulate structures at the micrometer scale.<br>~Maximum drug loading/encapsulation: 94 mg/g.<br>~Product swells minimally under acidic environments and extensively in the basic conditions (i.e. the intestine).<br>~Drug release may extend beyond 72 hours; maximum drug release of 60%-70% in basic environments. | [39] |

| Author | Contaminant Removed | Research Topic | Summary of Key Findings | Ref. |
|---|---|---|---|---|
| Shi, Wang, & Wang, 2011 | N/A | Absorbent hydrogel developed by simultaneous free-radical graft copolymerization of GG, using acrylic acid, styrene and attapulgite, N,N-methylene bis acrylamide, and ammonium persulfate | ~Swelling capacity improves using anionic and non-ionic surfactants, while cationic surfactants result in less swelling capacity.<br>~The equilibrium swelling capacity increased as pH increased within the range of 4 to 9, and rapidly increased when the pH exceeded 9.<br>~Hydrogel demonstrated pH-dependent swelling reversibility attributes.<br>~Saline solution impacts swelling capacity and is dependent on the types and concentration of the cations; swelling capacity demonstrated NaCl > $CaCl_2$ >$AlCl_3$. | [40] |
| Shobha, Vishukumar, Tharanathan, Koka, & Gaonkar, 2005 | N/A | Utilization of pectinase to depolymerize GG for use in food industry | ~Enzymatic catalysis with pectinase caused debranching/depolymerization of GG.<br>~ Ideal parameters: pH of 5.0, and 50 °C.<br>~After 60 minute reaction, the GG molecular weight dropped from 240 kDa to 70 kDa, and the galactose:mannose ratio changed from 1:1.6 to 1:2.8.<br>~Modified GG demonstrated better gelling property with xanthan gum, and showed a 98% solubility compared to 60% from the unmodified GG. | [41] |
| Singh, Kumari, Pandey, & Narayan, 2008 | Chromium (VI) | Batch tests using GG purified through copper complexing and graft copolymerization using persulfate/ascorbic acid and poly-methylacrylate | ~Initial Chromium (VI) concentration of 100 mg/L decreased 72.67% and concentration of 50mg/L decreased 88.8% using 4g/L sorbent, over 8 hours.<br>~pH 1was ideal.<br>~Agitation speeds had 30–50% increase in sorption compared to stationary system.<br>~Freundlich isotherm, pseudo-second- order kinetics.<br>~Material successfully reused for 5 cycles; NaOH was the best desorption agent. | [42] |
| Singh, Tiwari, Tripathi, & Sanghi, 2004 | N/A | Develop graft co-polymerization of GG with acrylamide via microwave assisted method | ~Maximum grafting efficiency using microwave assistance: 66.66% in 0.22 minutes, compared to conventional redox method producing 49.12% efficiency in 90 minutes. | [43] |
| Thakur, Kumari, Dogra, & Chauhan, 2014 | Mercury (II) | Batch tests using GG crosslinked with epichlorohydrin, oxidized to polydialdehyde form, and converted to a Schiff-base | ~15.27mg/g of Mercury (II) was adsorbed from an initial concentration of 25 ppm in 2 hours.<br>~41.33 mg/g was adsorbed from initial 50 ppm concentration.<br>~74.67 mg/g was adsorbed from initial 100 ppm concentration.<br>~Higher adsorption capacity occurred at higher pH.<br>~Freundlich isotherm, pseudo-second order model.<br>~Reusable up to 5 cycles.<br>~GG crosslinked with epichlorohydrin is water insoluble. | [44] |

| Author | Contaminant Removed | Research Topic | Summary of Key Findings | Ref. |
|---|---|---|---|---|
| Thombare, Jha, Mishra, & Siddiqui, 2017 | Anionic, aniline blue dye | Flocculation using GG hydrogels synthesized by crosslinking with borax | ~100 mg of 15-25%Borax crosslinked hydrogels resulted in 94.30% dye adsorption from 50 ppm, 100mL solution.<br>~Ideal crosslinking percentage of borax for hydrogels: 20%.<br>~Ideal percentage of borax for flocculation: 10%; 1ppm dose outperformed commercial coagulant, alum.<br>~All crosslinked hydrogels showed improved flocculation compared to unmodified GG.<br>~Swelling index increased with increasing pH.<br>~Flocculation efficiency improved at lower pH. | [45] |
| Thombare et al., 2018 | N/A | Development of grafted GG using acrylic acid and crosslinking with ethylene glycol di methacrylic acid for agricultural use | ~Water holding capacity of soil with modified product increased 54%; porosity increased up to 9%.<br>~Swelling index increased with increasing pH.<br>~77 day biodegradation half-life estimated for buried decomposition of hydrogel. | [17] |
| M.V.G, Paixão, & R.d.C. Balaban, 2018 | Brine clarification, oil and grease solutions | Salting-out effected used to collapse of polymer network comprised of GG crosslinked with borate ions | ~Removal percentage over 90% for oil and grease concentrations above 100 ppm.<br>~Salting-out effect does not depend on multivalence ions (NaCl and $CaCl_2$ both effective).<br>~Ideal concentration of GG based on turbidity of final solution:4.8 g/L. | [20] |
| G. Wang, Wei, Tanaka, & Kataura, 2018 | Carbon nanotubes | Preparation of a chromatography gel column using GG crosslinked with glutaraldehyde, and filter aids | ~GG gel can only adsorb small diameter, <1.3 nm single-wall carbon nanotubes.<br>~Crosslinked gel was produced in 24 hours. | [46] |
| Q. Wang, Ellis, & Ross-Murphy, 2000 | N/A | Evaluation of GG stability in acidic conditions | ~0.07% GG solutions were relatively stable under mild acidic conditions.<br>~Viscosity of hydrated GG at acidic pH was slightly lower than at neutral pH.<br>~GG degradation reaction conformed to first order kinetics<br>~High temperature and low pH, both accelerate GG degradation (separately, and synergistically).<br>~Lowest pH's that GG remained stable were: 2.0 at 25°C, 3.0 at 37 °C, and 3.5 at 50 °C. | [16] |
| Yan, Chang, Zheng, & Ma, 2011 | Neutral red and cationic methylene blue dyes | Batch tests using magnetic, GG-grafted onto multiwall carbon nanotubes and iron oxides | ~Large amount of dyes were adsorbed in 10 minutes, then rate of sorption gradually slowed; equilibrium values were 120 minutes for the blue dye and 20 minutes for the red dye.<br>~At equilibrium, 1g of adsorbent in a 1 L solution removed 37.17 mg blue dye (initial concentration of 37.4 mg/L) and 28.36mg red dye (initial concentration 28.9mg/L).<br>~Langmuir isotherm, pseudo second-order model.<br>~Adsorbent could be separated from solution in a magnetic field. | [47] |

**Water Contaminants of Interest**

The majority of this research focused on the use of dyes as the source of contamination tests for adsorption using GG. These dyes may be discharged within the waste streams of a number of industries including those that produce textile, food and agricultural, personal care, pharmaceutical, and cleaning products [48]. They also prove to be a valuable surrogate for other organic and synthetic-organic compounds, especially for compounds with aromatic rings or heterocyclic structures. Additionally, preliminary tests were conducted using two organic compounds, 2,4-dinitrotoluene (DNT) and toluene. Table 2 below summarizes the compounds tested, their chemical formula, and molecular weight [49].

**Table 2. Contaminants Evaluated**

| Contaminant Name | Formula | Molecular Weight |
|---|---|---|
| Allura Red (AR) | $C_{18}H_{14}N_2Na_2O_8S_2$ | 496.42 g/mol |
| Brilliant Blue (BB) | $C_{37}H_{36}N_2O_9S_3$ 2Na | 792.86 g/mol |
| Erythrosine B (EB) | $C_{20}H_6I_4Na_2O_5$ | 879.86 g/mol |
| Fast Green (FG) | $C_{37}H_{34}N_2Na_2O_{10}S_3$ | 808.85 g/mol |
| Tartrazine (TR) | $C_{16}H_9N_4Na_3O_9S_2$ | 534.36 g/mol |
| Methylene Blue (MB) | $C_{16}H_{18}ClN_3S*3H_2O$ | 373.89 g/mol |
| 2,4-dinitrotoluene (DNT) | $C_7H_6N_2O_4$ | 182 g/mol |
| Toluene | $C_6H_5CH_3$ or $C_7H_8$ | 92 g/mol |

The dyes in total represent a wide range of molecular sizes and structures. Allura Red and Tartrazine are considered Azo dyes, which are structured with double bonded nitrogen atoms to other organic functional groups [48], [49]. Erythrosine B and Fast Green are considered Triarylmethane dyes, which have a triphenyl methane backbone comprised of $(C_6H_5)_3CH$ [48], [49]. Brilliant Blue has structural components of both Azo and Triarylmethane types [48], [49]. Erythrosine B is also considered an organoiodine

compound, due to the presence of carbon-iodine bonds [48]. These 4 dyes are anionic. Methylene Blue, however, is cationic; it is a thiazine dye which is structured with a ring of 4 carbons, 1 nitrogen, and 1 sulfur atom [48]. Although these 6 artificial dyes are considered safe for consumption in low quantities, increasing use of these compounds in personal products has generated concerns about unnecessary toxicity, and unknown impact of combining multiple long-term exposures of these agents. Many of these dyes have been linked with allergic and hypersensitivity reactions [48]. Some have also been associated with digestive and skin irritation, migraines, or sleep disturbances, and several animal studies have shown high doses can result in tumors and carcinogenicity [48].

DNT and toluene are both aromatic compounds, much smaller than the dyes assessed. Toluene is associated with petroleum refining, chemical manufacturing, textile, plastic, and paint industries [50]. It is used as a solvent and additive, and volatilizes readily. Although toluene is currently "not classifiable as a human carcinogen" due to inadequate information, the EPA has established a toluene Maximum Contaminant Level of 1 part per million (ppm) or 1mg/L in drinking water [50]. The primary exposure route from toluene is via inhalation; ingestion of toluene from contaminated water and food is less likely due to lower frequency of presence of toluene in these matrices [50]. Ingestion of toluene may cause neurological effects and depression of the nervous system resulting in dizziness, lethargy and possibly death [50].

Alternatively, DNT is characterized by low volatility and moderate water solubility, thus it does not readily volatilize and is likely to remain in the environment for long periods of time [51]. It is used as a precursor to toluene diisocyanate and trinitrotoluene (TNT) as well as an additive to plasticizers and propellants [51]. DNT is

also often present in the environment of hazardous waste sites containing buried ammunition [51]. Two isomers of DNT have been classified as a probable human carcinogens, and the EPA has issued health advisories for 2,4- and 2,6-DNT [51]. Exposure may adversely affect the central nervous system, heart and circulatory system, liver, and kidneys [51]. There is also evidence that exposure can increase incidences of mortality from heart disease and cancer [51]. The health advisory lifetime drinking water equivalent exposure level for 2,4- DNT is 0.1 mg/L and 0.04 mg/L for 2,6-DNT; additionally, the EPA has established an ambient water quality criteria for 2,4-DNT of 0.11 μg/L for ingestion of water and aquatic organisms [51]. Water and environmental remediation initiatives have utilized the following technologies to remove DNT contaminants: adsorption, chlorination, ozonation, UV radiation, alkaline hydrolysis and bioremediation [51].

These contaminants can be detected and analyzed using a number of analytical devices, however, this research focused on using an Ultraviolet-Visible Spectrophotometer (UV-Vis). This instrument works on the principle of light absorption; it measures the intensity of reflected (i.e. transmitted) light across the 200-800 nm wavelength spectrum. This phenomenon correlates to how the human eye perceives colors; light is absorbed when striking an object, but the perception of color is based on the wavelength of light that is reflected off the object. Using the measurement of transmittance, the UV-Vis can then determine the amount of light absorbed by a substance. Absorbance has a logarithmic relationship with the transmittance, according to the following equation [52],[19]:

$$\boldsymbol{A = -logT = -\log\left(\frac{I}{I_0}\right) = \log\left(\frac{I_0}{I}\right)} \quad \textbf{Equation 1}$$

The Absorbance (A) is the light absorbed by a sample, and the Transmittance (T) is the light reflected by a sample [19]. The initial intensity ($I_0$) is the intensity measured from the blank sample and correlates to the maximum intensity, or lowest absorbance, that will strike the detector [19]. The intensity (I), is the intensity measured with a sample, it will be less than $I_0$ because more light will be absorbed by the sample compared to the blank [19]. Absorbance is also linearly related to concentration, which enables qualitative analysis of samples. The higher the concentration of a sample correlates to higher light absorbance. The Beer-Lambert Law equation listed below, summarizes the relationship between absorbance, the molar absorptivity (ε), the path length (b), and the concentration (c) [52], [19].

$$\boldsymbol{A = \varepsilon bc} \quad \textbf{Equation 2}$$

While concentration can be calculated using the Beer-Lambert Law equation, it can also be calculated by comparing to the absorbance of solutions with known concentrations, and through generating calibration curves.

**Summary**

This chapter explored common water treatment technologies and the process of adsorption. It also summarized past research utilizing GG as a nontoxic, biodegradable product, which can be modified via techniques such as crosslinking, grafting, depolymerization, copolymerization, the salting-out effect, or hydrogel development. Finally, background information was presented regarding the contaminants evaluated in

this study such as their origins, toxicities, any published health advisory limits, and detection using the UV-Vis.

# III. Methodology

## Chapter Overview

The purpose of this chapter is to describe the various methods used during this research, the associated materials and equipment, as well as the data analysis theory implemented to understand GG applicability as an adsorbent. Two brands of GG were tested using 5 different GG treatment strategies: using GG powder in an unmodified form, pre-hydrating GG in solution, cleaning with hexane or drying GG prior to use, crosslinking GG with borate ions, and using a salt-out solution to cause a gel matrix collapse. A UV-Vis was the predominant analytical detection equipment implemented. The UV-Vis measures the absorbance of light across UV spectrum wavelengths and can be used to determine the effectiveness of each of these techniques to adsorb contaminants.

## Materials and Equipment Used

Several different methodologies and applications of GG were utilized during this research. Two brands of GG were evaluated, one produced by Fisher Scientific and one produced by TIC Gums. TIC Gums manufactures food-grade gums, and a sample of their GuarNT USA 8/22 product was utilized in this research; the Certificate of Analysis (COA) is included in Appendix A. A GG/Xanthan gum mix, a Konjac/Xanthan gum mix,

and Gellan Gum, from TIC were also used as a comparison to GG in one test. The Fisher GG is used primarily for science education purposes and a COA was not available.

The dyes used throughout this research were manufactured by Fisher Scientific, TCI America, or Crescent Chemical. Stock solutions of each dye were created, and the concentrations required for the various experiments were determined using the molarity equation:

$$\boldsymbol{M_1V_1 = M_2V_2} \qquad \textbf{Equation 3}$$

This capitalizes on the direct relationship between the Concentration/Molarity (M) in moles per liter, and Volume (V) in liters, of a solution. Anionic dyes were predominantly used and included Allura Red, Brilliant Blue, Tartrazine, Erythrosine B and Fast Green. One cationic dye, Methylene Blue was also utilized. The 2, 4-DNT and toluene were supplied by Sigma Aldrich. Several tests used borate ions for crosslinking which originated from Sigma-Aldrich sodium tetra borate decahydrate or Fisher Chemical boric acid. Sodium chloride, from Fisher Scientific, was used during salt-out experiments. Also, pre-mixed stock solutions of 0.25M sodium hydroxide or hydrochloric acid were used for pH modification. Tests which compared GG adsorption to carbon utilized Calgon Carbon Filtrasorb 600.

Miscellaneous supplies also included filter bags, centrifuge tubes, glass or plastic bottles, miscellaneous laboratory glassware, and pipettes and tips. Syringe filters, as shown in Figure 1, proved to be valuable during several experiments; 0.2µm cellulose acetate and mixed cellulose ester (MCE) hydrophilic filters manufactured by Fisher Scientific and Sartorius were used. However, it should be noted that certain

contaminants could also be removed by these filters, and some high viscosity solutions were incapable of being passed through the filters. This required additional control samples and various methodologies to be employed throughout the research.

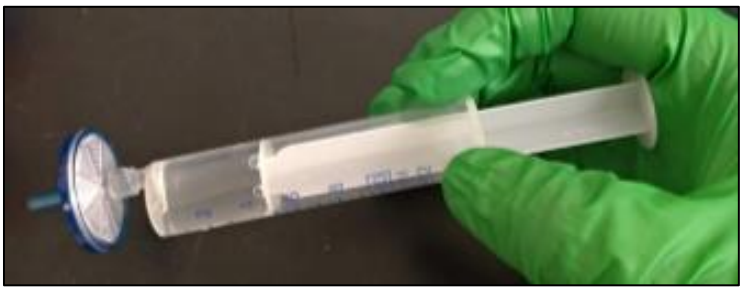


**Figure 1. Syringe Filter**

In order to increase mixing of multiple samples or stock solutions simultaneously, stir bars, a bottle tumbler and tube rotator were used. As shown in Figure 2, the tumbler could accommodate large containers, 250 to 1000mL in volume and the rotator was used for smaller 10mL sample tubes. A QSonica sonication probe, captured in Figure 3, was also used during some tests to disperse materials in a solution. Additionally, samples in 10mL test tubes may have also been mixed using a Southwest Science test tube vortex mixer for 10 seconds, shown in Figure 3. Samples needing to be dried were placed in a furnace oven, vacuum oven, or dried in ambient conditions in a fume hood.

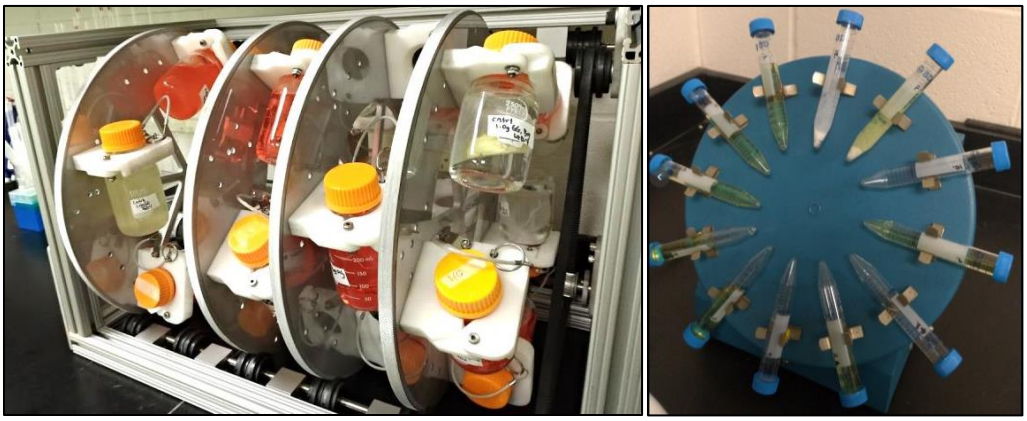


**Figure 2. Bottle Tumbler and Tube Rotator**

**Figure 3. Sonication Probe and Test Tube Vortex Mixer**

Analysis of samples was conducted primarily using an Agilent Technologies Cary 60 ultraviolet-visible spectrophotometer which measures the amount of light absorbed in a sample across a range of wavelengths. Samples were placed in a 1 centimeter semi-micro or micro quartz cuvette which was triple-rinsed with deionized water. Limited use of a gas chromatograph was employed, using an Agilent Technologies GC/MS Triple Quad 7000C model; before injection into the GCMS, 2 mL samples were filtered through a 0.2µm syringe filter. Additionally, a scanning electron microscope (SEM) was used to observe surface morphology of the GG products and crosslinked GG powders. The SEM was operated under the following conditions: high pass mode, 30µm aperture, 10.75 kV electron source hit tension beam accelerating voltage, 16pA probe current, 2.255 A beam current, 8.5mm working distance, 0° take-off angle, and first filament. Supplementary equipment used during this research also included a MettlerToledo SevenMulti pH Probe, a Mettler AT261 DeltaRange scale, an Across International StableTemp furnace oven, an

Isotemp 280A vacuum oven, and an Eppendorf Centrifuge programmed at 4000 rpm for 10 minutes.

**Types of Guar Gum Application**

GG was tested using several different application methodologies. Many of the tests were conducted as batch or bottle tests on the tumbler shown in Figure 2. Twenty-seven experimental studies were conducted using varying sample types, quantities of GG, and concentrations of contaminants. The percentage of GG (% GG) dispersed in a sample was based on a weight-by-volume (w/v) basis. 1mL of water weighs approximately 1 gram, thus 1 gram of GG dispersed in a 200mL (200g) water solution, results in a 0.5 % GG solution. This relationship can also be demonstrated using the following equation:

$$\boldsymbol{Weight\ percent}\ (\%\ \boldsymbol{GG}) = \frac{\boldsymbol{Weight\ of\ solute\ (g)}}{\boldsymbol{Volume\ of\ solution\ (mL)}} * \mathbf{100} \qquad \textbf{Equation 4}$$

The percent of GG used during testing is summarized with other experiment specifics included in Table 4. The following sections detail the various applications of GG and include using the gums as an unmodified dry powder, a pre-hydrated solution, a cleaned or dried GG product, crosslinked with borate ions, and an application capitalizing on the salting-out effect. Table 3 below, provides a broad summary of the method tested for each contaminant included in this report.

**Table 3. Overview of GG Application Method and Contaminant Studied**

| | Allura Red | Brilliant Blue | Erythrosine B | Fast Green | Tartrazine | Methylene Blue | 2,4-DNT | Toluene |
|---|---|---|---|---|---|---|---|---|
| **Unmodified, Dry GG** | X | X | X | X | X | | X | X |
| **Cleaned/Dried GG** | X | X | | | | X | | |
| **Hydrated GG** | X | X | | | | X | X | X |
| **Crosslinked GG** | X | | X | | X | | | |
| **GG with Salting-Out** | X | X | | | X | | | |

**Unmodified, Dry Guar Gum**

Both brands of GG, shown in Figure 4, were used in their unmodified form. The dry GG was initially dispersed in solution; however, it was determined that the use of a cotton filter bag or 25µm nylon filter bag to contain the GG powder provided the same benefits of GG and were able to decrease the turbidity and some of the challenges using the UV-Vis with colloid solutions. Once the dry GG powder was weighted and added to a solution, it was shaken, stirred, sonicated, or placed on the tumbler or tube rotator. The percentages of GG and sample volumes used in various tests are summarized in Table 4.

**Figure 4. Unmodified Fisher brand GG (left) and unmodified TIC brand GG (right)**

**Cleaned or Dried Guar Gum**

In order to determine if another substance or water was sorbed onto the starting GG material and causing slower adsorption, samples of dried and cleaned GG were tested. Pre-weighed GG powder was dehydrated in the furnace and vacuum ovens for 24 hours at approximately 45 °C (113 °F). Additionally, a sample was completely baked/burnt for analysis by placing in the furnace for 3 hours at 204 °C (400 °F), and the burnt product is demonstrated in Figure 5. Dried samples were then added to solutions in the same manner as the unmodified GG powders. Once added, the cleaned/dried GG powder was stirred, sonicated, vortexed, or placed on the tumbler or tube rotator.

**Figure 5. GG powder before baking, after baking for 3 hours at 204 degrees Celsius, and dissolved in water**

Additionally, samples of dry GG and pre-hydrated GG were mixed with hexane (manufactured by Sigma-Aldrich) in a separatory funnel, as shown in Figure 6 before further use. As shown on the left image in Figure 6, approximately 4 grams of dry fisher GG was mixed with 150mL hexane. GG is insoluble in hexane; it settled and stratified quickly, but the solution was allowed to fully settle for 4 days. The bottom layer of GG was removed and dried in ambient conditions within a fume hood. Dried samples were then weighed and added to solutions in the same manner as the unmodified GG powders.

Shown on the right side of Figure 6, 50mL of hexane was mixed with 25mL of 1% pre-hydrated TIC GG. After hand-shaking the mixture, it was also allowed to settle for 4 days. Prior to testing, the desired amount was measured using a graduated cylinder and its performance was compared to the same volume of an unmodified GG hydrate.

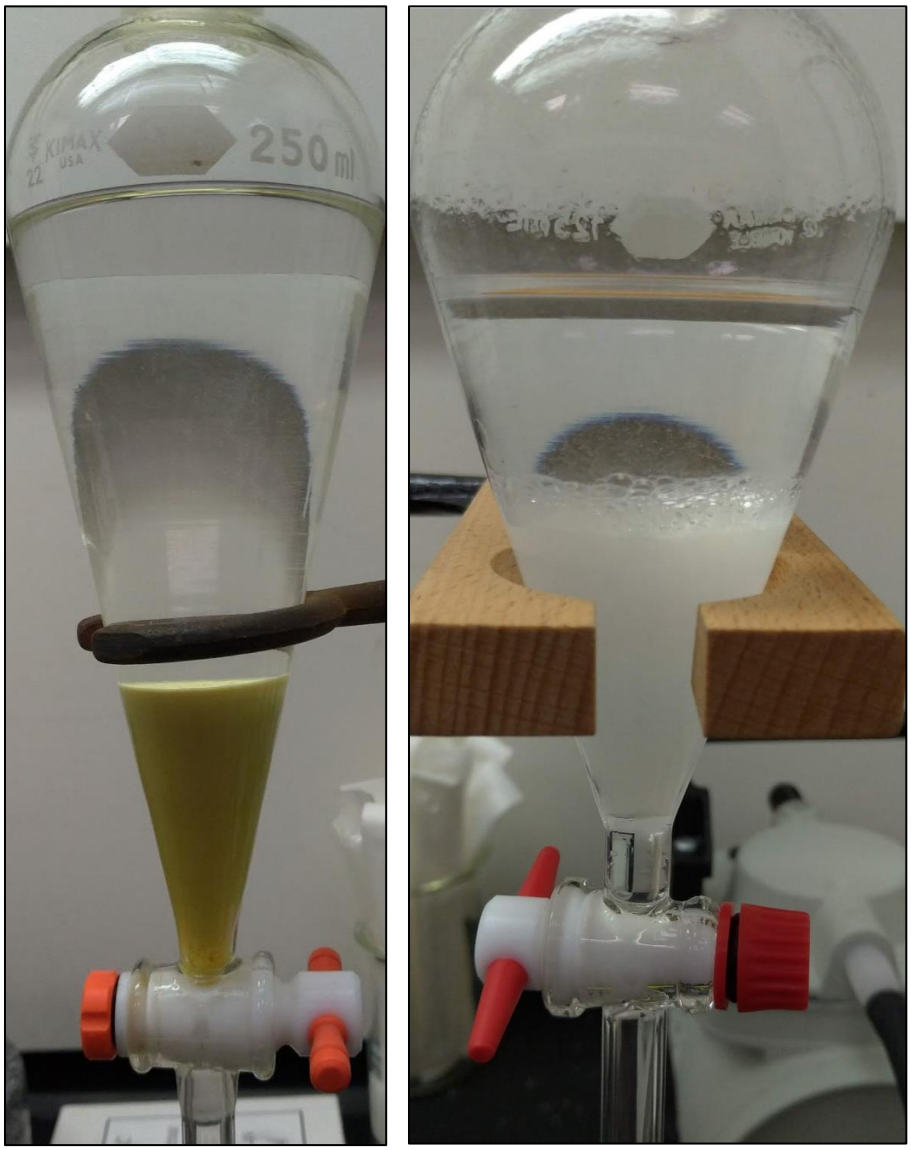



**Figure 6. Separatory Funnel set-up used to clean dry Fisher GG powder, and pre-hydrated TIC GG solution**

**Hydrated Guar Gum**

GG previously dissolved in water or pre-agglomerated was also used for several tests. Solutions were given varying times to hydrate, from a few hours to several days, and were mixed on either a stir plate or the tumbler. Generally, solutions using more than 1 percent of GG were too viscous after a 24-hour hydration time to be effectively used, however, additional time resulted in diminished gelling and viscosity. Also, different from the dry GG powder tests, adsorption tests with pre-hydrated GG used a higher ratio of GG; the sample was comprised of 50% of a concentrated contaminant and 50% of the GG pre-hydrate. For example, mixing 100mL of 20 ppm 2,4-DNT solution with 100mL of 1% GG solution would result in a 200mL sample that was ultimately 10 ppm of 2,4-DNT with 0.5% GG. The desired amount of hydrated GG was measured using either a pipette for quantities less than 10mL or a graduated cylinder. Specific contaminants using this technique and the final mixture concentrations tested are summarized in Table 4.

**Crosslinked Guar Gum**

Crosslinking GG using sodium tetra borate decahydrate (i.e. borax) was accomplished using several different methods and included the following techniques: using crosslinked gels, soaking filters or glass beads in GG and spraying with borax as described by Dai, et al., hydrating GG with borax instead of water, and creating dry crosslinked powders as described by Thombare, et al [25], [45]. Figure 7 demonstrates a sample of hydrated GG with and without the addition of borax.

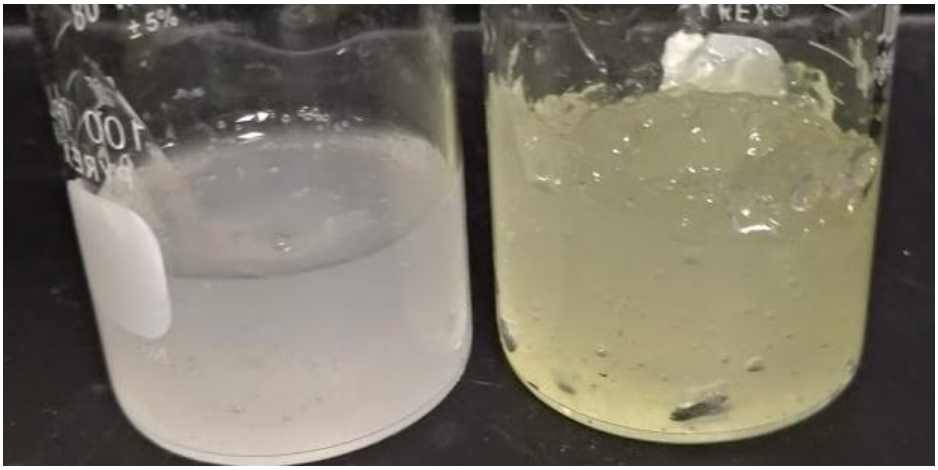


**Figure 7. Comparison of GG dissolved in water (left), and GG solution with borax (right)**

Dry crosslinked powder was made by creating and mixing a 1% GG solution for at least 2 hours, then stirring with 10-20% borax, for 30 minutes, and allowing at least 3 hours for the crosslinking reaction to occur. Next, the gels were gently rinsed to remove any unreacted borax, crushed, and soaked in acetone for dehydration. The gels were further crushed or pumped through a vacuum funnel/sieve for a more consistent gel size. Next, the gel was placed in the furnace oven at 25 °C (77 °F) to dry to a constant weight. Figure 8 demonstrates 2 batches of dried crosslinked powder, and a crosslinked hydrogel.

**Figure 8. Comparison of 2 different batches of crosslinked powder and a hydrogel, each comprised of 1 gram of GG**

Preliminary tests were conducted using a variety of crosslinking techniques. Crosslinking was attempted on the surfaces of glass pellets, and filters which were coated in a hydrated solution of 1% GG and dipped or sprayed with a 0.2M borax solution. Other tests pre-hydrated GG in borax rather than water, placed the dry GG in filter bags to pre-hydrate in water and dip in borax, or placed the dry GG in filter bags to pre-hydrate in borax. Additionally, a 1% GG solution was mixed with red dye prior to crosslinking as described above. The dyed crosslinked gel and powder were added to clear water solutions to further evaluate the behavior of crosslinked products.

**Guar Gum with Salting-Out Solution**

Using the methodology as described by Paixão and Balaban, a gel collapse was used to test the effectiveness of a salting-out solution treatment with dyes [20]. Solutions comprised of 4.8g/L of GG were pre-solubilized, and mixed with 20g/L sodium chloride (i.e. salt) for several hours to several days. To initiate the gel collapse, borate ions were provided from either 3g/L boric acid powder, 3g/L sodium tetra borate decahydrate powder, or 3mL/L 0.02M of pre-hydrated sodium tetra borate decahydrate. Samples with the boric acid also underwent a pH modification step, with the addition of sodium hydroxide until a pH of 12 was reached. Several tests based on the salification effect were conducted for Allura Red, Brilliant Blue, and Tartrazine dyes using different percentages of GG. Allura Red dye was mixed with 0.1% GG and 0.5% GG solutions for 10 days before a gel collapse was initiated. Brilliant Blue was mixed in a 0.5% GG solution for 2 hours before the collapse occurred. Tartrazine samples were mixed with 0.025% GG and 0.5% GG for 4 days prior to initiating gel collapse.

Additionally, collapsed hydrogel “pucks” were tested as an adsorbent using both the wet and dried forms shown in Figure 9. These pucks were made in deionized water using the process described above. After the collapse had occurred, these structures were then placed in a dye solution.

**Figure 9. Wet and dried “pucks” produced by collapsed GG polymer network initiated by salting-out effect**

**Table 4. Summary of Individual Experiments and Test Parameters**

| GG Application (Methodology) | Contaminant Evaluated | Concentration of Contaminant | %, Ratio of GG Used (w/v) | Sample Size | UV-Vis Characteristic Wavelength | Type of mixing | Pre-treatment prior to analytical testing |
|---|---|---|---|---|---|---|---|
| Unmodified, Dry GG<br>Crosslinked GG | Allura Red | 5 ppm; 0.01mM | 0.2% GG,<br>2020 ppm | 500mL | 505nm | Stationary | Varied - periodic syringe filter |
| Unmodified, Dry GG<br>Crosslinked GG | Allura Red | 5 ppm; 0.01mM | 0.2%-0.4%GG,<br>4000 ppm | 250mL | 505nm | Tumbler | Varied - some in filter bags, periodic syringe filter |
| Unmodified, Dry GG<br>Cleaned/Dried GG | Allura Red | 5 ppm; 0.01mM | 0.2%GG,<br>2000 ppm | 500mL | 505nm | Stationary | Varied - periodic syringe filter |
| Unmodified, Dry GG | Allura Red | 5 ppm; 0.01mM | 0.2%GG,<br>2000 ppm | 50mL | 505nm | Stationary | Varied - periodic syringe filter |
| GG with Salting-Out | Allura Red | 1.986 ppm; 0.004mM | 0.1%GG,<br>2400 ppm | 100mL | 505nm | Stirred | Varied - periodic syringe filter |
| GG with Salting-Out | Allura Red | 1.986 ppm; 0.004mM | 0.5%GG,<br>5000 ppm | 100mL | 505nm | Tumbler | Varied - periodic syringe filter |
| Unmodified, Dry GG | Allura Red<br>Brilliant Blue | AR: 5 ppm; 0.01mM<br>BB: 7.9 ppm; 0.01mM | 0.05-0.5%GG,<br>500-5000 ppm | 10mL | AR: 505nm<br>BB:630nm | Stationary | Centrifuge |
| Crosslinked GG<br>GG with Salting-Out | Allura Red | 2.5 ppm; 0.005mM | 0.3%GG,<br>3000 ppm | 200mL | 505nm | Stirred | Varied - periodic syringe filter and centrifuge |
| Unmodified, Dry GG | Allura Red<br>Erythrosine B<br>Brilliant Blue<br>Fast Green | AR: 4.96 ppm; 0.01mM<br>ER: 8.8 ppm; 0.01mM<br>BB:3.96 ppm; 0.005mM<br>FG: 4.04 ppm; 0.005mM | 0.4%GG,<br>4000 ppm | 250 mL | AR: 505nm<br>ER: 527nm<br>BB: 635nm<br>FG: 624nm | Tumbler | Varied - some in filter bags, periodic syringe filter |
| Hydrated GG | Allura Red<br>Methylene Blue<br>Brilliant Blue<br>2,4-DNT<br>Toluene | AR: 4.96 ppm; 0.01mM<br>MB:1.87 ppm; 0.005mM<br>BB: 3.96 ppm; 0.005mM<br>DNT:10 ppm; 0.05mM<br>Toluene:10 ppm; 0.1mM | 0.5%GG,<br>5000 ppm | 6mL | AR: 505nm<br>MB: 665nm<br>BB: 630 nm<br>DNT: 250nm<br>Toluene: 261nm | Stationary | Centrifuge |

| GG Application (Methodology) | Contaminant Evaluated | Concentration of Contaminant | %, Ratio of GG Used (w/v) | Sample Size | UV-Vis Characteristic Wavelength | Type of mixing | Pre-treatment prior to analytical testing |
|---|---|---|---|---|---|---|---|
| Hydrated GG | Allura Red<br>Methylene Blue<br>Brilliant Blue<br>2,4-DNT<br>Toluene | AR: 4.96 ppm; 0.01mM<br>MB:1.87 ppm; 0.005mM<br>BB: 3.96 ppm; 0.005mM<br>DNT:10 ppm; 0.05mM<br>Toluene:50 ppm; 0.5mM | 0.5%GG,<br>5000 ppm | 6mL | AR: 505nm<br>MB: 665nm<br>BB: 630 nm<br>DNT: 250nm<br>Toluene: 261nm | Stationary | Centrifuge |
| Unmodified, Dry GG<br>Cleaned/Dried GG | Brilliant Blue | 3.96 ppm; 0.005mM | 0.2%,<br>2000 ppm | 500mL | 630nm | Stationary | Syringe filter |
| Cleaned or Dried GG<br>Hydrated GG | Brilliant Blue | 2 ppm; 0.0025mM | 0.5%,<br>5000 ppm | 6mL | 630nm | | Centrifuge |
| GG with Salting-Out | Brilliant Blue | 3.96 ppm; 0.005mM | 0.5%GG,<br>4800 ppm | 250mL | 630nm | Stationary | None |
| Hydrated GG<br>Cleaned/Dried GG | Brilliant Blue<br>Methylene Blue | BB:3.96 ppm; 0.005mM<br>MB:1.87 ppm; 0.005mM | 0.5%GG,<br>5000 ppm | 100mL | BB: 630nm<br>MB: 665nm | Tumbler | Centrifuge |
| Unmodified, Dry GG | 2,4-DNT | 10 ppm; 0.05mM | 0.5-0.75%GG,<br>4000-7600 ppm | 250mL | 250nm | Tumbler | Filter bags |
| Unmodified, Dry GG | 2,4-DNT | 10 ppm; 0.05mM | 0.01%GG,<br>126 ppm | 50ml | 250 nm | Stirred and Stationary | Varied - periodic centrifuge |
| Unmodified, Dry GG | 2,4-DNT | 10 ppm; 0.05mM | 0.5-0.75%GG,<br>5000-7600 ppm | 250mL | 250 nm | Tumbler | Varied -filter bags, periodic centrifuge |
| Crosslinked GG | Erythrosine B | 8.3 ppm; 0.01mM | 0.0004-<br>0.0264%GG,<br>3.77-264.15 ppm | 265mL | 527nm | Stationary | None |
| Crosslinked GG | Erythrosine B | 5.5 ppm; 0.006mM | 0.0002-<br>0.25%GG,<br>2.5-2500 ppm | 400mL | 527nm | Stationary | None |

| GG Application (Methodology) | Contaminant Evaluated | Concentration of Contaminant | %, Ratio of GG Used (w/v) | Sample Size | UV-Vis Characteristic Wavelength | Type of mixing | Pre-treatment prior to analytical testing |
|---|---|---|---|---|---|---|---|
| Unmodified, Dry GG | pH buffer solution | unknown | 0.8%GG, 8000 ppm | 50mL | pH4: 505nm pH7: 427nm pH10: 588nm | Stirred and Stationary | Varied - periodic syringe filter and centrifuge |
| Unmodified, Dry GG Crosslinked GG | Tartrazine | 5.3 ppm; 0.01mM | 0.4%GG, 4000 ppm | 250mL | 427nm, and 258nm | Stationary | Varied - some in filter bags, periodic syringe filter |
| Unmodified, Dry GG | Tartrazine | 5.3 ppm; 0.01mM | 0.5-3%GG, 5000-30000 ppm | 250mL | 427nm, and 258nm | Tumbler | Filter bags, syringe filter |
| Unmodified, Dry G GG with Salting-Out | Tartrazine | 5.3 ppm; 0.01mM | 0.025%GG, 254.5 ppm | 10mL | 427nm, and 258nm | Tube rotator | Varied - periodic centrifuge |
| Unmodified, Dry GG GG with Salting-Out | Tartrazine | 5.3 ppm; 0.01mM | 0.5%GG, 5000 ppm | 10mL | 427nm, and 258nm | Tube rotator | Varied - periodic centrifuge |
| Unmodified, Dry GG | Toluene | 10 ppm; 0.1mM | 0.05%GG, 502.5 ppm | 60mL | 261nm | Stirred | Varied - periodic centrifuge |
| Hydrated GG | Toluene | 10 ppm; 0.1mM | 0.5%GG, 5000 ppm | 100mL | 261nm | Stirred | Varied - periodic centrifuge |

**Analysis Methodology**

Dissolving GG in a solution creates a general baseline shift compared to water across the entire UV-Vis spectrum. The use of syringe filters or centrifuging samples can decrease the impact at higher wavelengths, those above 400nm. However, spectrum correction was required for a majority of the research conducted. This is related to the principle of additivity; according to Beer-Lambert's law, absorbance of a mixture at any wavelength is equal to the sum of the absorbance's for each substrate at that wavelength [19], [52]. Using a spectrum correction, called control subtraction, the baseline GG interference from control samples was subtracted from the total absorbance values at the reference wavelength for the contaminant of interest. An example of this correction is demonstrated in Figure 10.

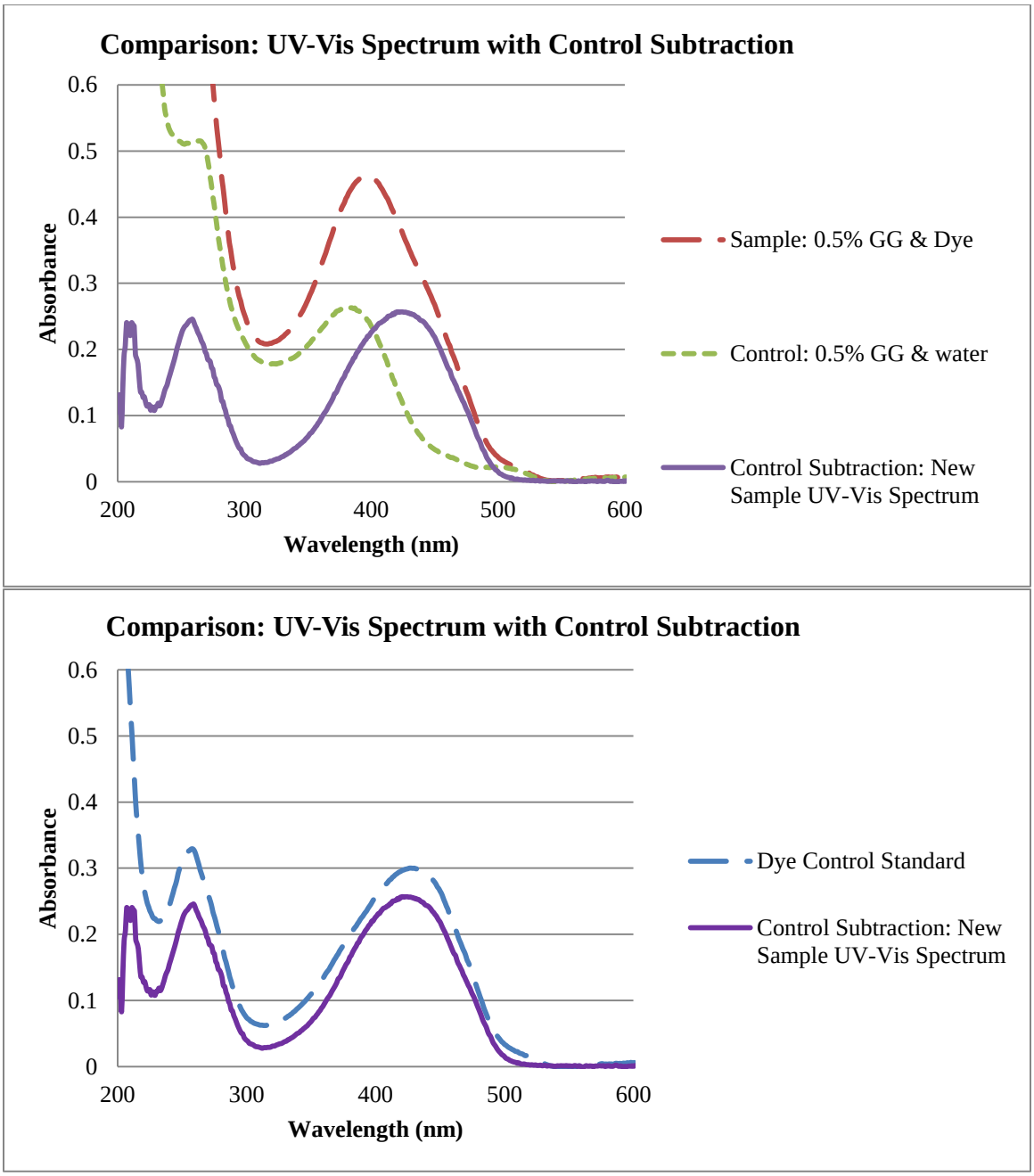



**Figure 10. Example of Spectrum Control Subtraction**

Additionally, 4- or 5-point calibration curves were developed using calibration standards for the contaminants tested. Due to differences in concentrations used and contaminants evaluated, calibration curves were standardized to percent of contaminant remaining. Standards were diluted to known values and UV-Vis absorbance measured at

100%, 50%, 25%, 10%, and blank levels. Long term tests required additional calibration curves be conducted to validate the standard was stable over a longer period of time. In the few instances a calibration curve was not appropriate or not available (such as if samples were potentially diluted by adding additional solvents like NaOH), the percent of contaminant remaining was calculated using the removal efficiency equation. The percent removal efficiency (RE) was calculated using the initial UV-Vis absorbance ($C_0$), the sample absorbance ($C_t$) and the following equation:

$$\mathbf{RE}(\%) = \frac{\mathbf{C_0 - C_t}}{\mathbf{C_0}} \times \mathbf{100} \quad \textbf{Equation 5}$$

Alternatively, the percent of contaminant remaining can be calculated by subtracting the RE from 100, or using the following consolidated equation:

$$\%\mathbf{Remaining} = [\mathbf{1} - \frac{\mathbf{C_0 - C_t}}{\mathbf{C_0}}] \times \mathbf{100} \quad \textbf{Equation 6}$$

**Summary**

This section described the materials, supplies and equipment employed during this research. It also detailed the various applications of GG, including: using the gum in its unmodified dry powder state, as a pre-hydrated solution, undergoing a pre- cleaning or drying process, crosslinking methods, and use of the salt-out effect. Table 4 summarizes the individual tests conducted throughout this research; it specifies the contaminant concentration and predominant UV-Vis wavelength, as well as the amount of GG used, and the general GG usage methodology.

# IV. Analysis and Results

## Chapter Overview

This chapter specifies the results of a diverse set of experiments utilizing 8 different contaminants and 5 methods of employing GG. It is organized based on characteristics of GG assessed, followed by an analysis of the effectiveness of GG as an adsorbent with each contaminant evaluated. Sub-sections are organized by what contaminant was tested and which GG treatment method was utilized. A majority of the data used the control subtraction method to estimate the percent of a contaminant remaining; any sample results that demonstrated a lower value than the associated control sample are listed as "< 0."

While varying levels of contaminants and GG were used throughout this research, some general trends can be determined. GG treatment demonstrated removal effectiveness with all contaminants; however, GG was least effective with toluene, which rapidly volatilizes. Overall, the use of pre-hydrated GG significantly outperformed other treatment techniques. GG can change the pH of a solution over time, and the associated age and pH of a solution can also have a significant impact on adsorption. Based on this characteristic, several samples of hydrated gum and anionic contaminants demonstrated higher adsorption than using a similar quantity of granular activated carbon. Comparing Fisher GG and TIC GG brands tested, TIC GG tended to be more effective with anionic products, and Fisher GG with cationic. While the precise factor behind this occurrence is unknown, it may be related to different GG particle sizes, ages, source material, or the manufacturing and bleaching processes for the different brands. Although hydrated GG

demonstrated the ability to remove contaminants in a matter of hours, the use of dry GG powder required over 1 week to demonstrate appreciable results. Additionally, cleaning or drying the GG product did not appear to result in substantial adsorption enhancement, and in several cases decreased the amount of contaminant removed. While crosslinking and gel salification collapse were possible, these did not demonstrate substantially better performance than the results of using the unmodified gum.

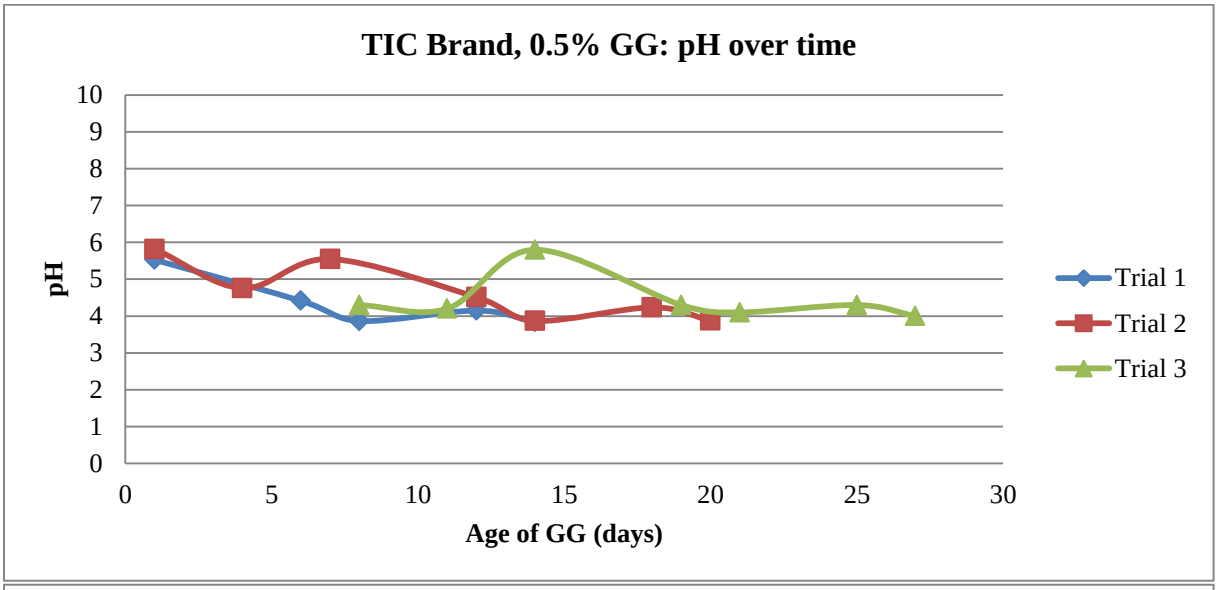
**Role of pH**

The effectiveness of GG as an adsorbent may be correlated to the pH of a solution. Additionally, it was determined that the pH of GG mixtures decrease over time. Older GG solutions, associated with lower pH values, were most effective against anionic substances; while younger GG mixtures, with higher pH values, were more effective against cationic contaminants. The observed change in pH is likely indicative of a deprotonation process. Samples also demonstrated a release of gas and pungent odor as they aged. A possible explanation for these observations is that a member of the carboxylic acid family was being formed in solution from the carboxyl groups present on the GG structure. This theory is also supported by some published research which indicates the degradation of monosaccharides forms carboxylic acids [53].

The pH of a series of 0.5% GG solutions was monitored over time, and results are summarized in Table 5 and Figure 11. While both brands of GG ultimately reached a pH near 4, the Fisher Brand demonstrated an initial increase in pH, followed by a drop.

**Table 5. pH of Guar Gum Solutions, over Time**

| | Age of GG (days) | 27 | 25 | 21 | 20 | 19 | 18 | 14 | 12 | 11 | 8 | 7 | 6 | 4 | 1 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **pH: TIC Brand** | Trial 1 | | | | | | | 3.8 | 4.1 | | 3.9 | | 4.4 | | 5.5 |
| | Trial 2 | | | | 3.9 | | 4.2 | 3.9 | 4.5 | | | 5.5 | | 4.8 | 5.8 |
| | Trial 3 | 4 | 4.3 | 4.1 | | 4.3 | | 5.8 | | 4.2 | 4.3 | | | | |
| **pH: Fisher Brand** | Trial 1 | | | | | | | 4.2 | 4.2 | | 4.4 | | 4.7 | | 9.4 |
| | Trial 2 | | | | 4.3 | | 4.2 | 4.4 | 4.6 | | | 4.8 | | 6.3 | 9.2 |
| | Trial 3 | 4.7 | 5.4 | 4.6 | | 4.4 | | 4.5 | | 4.2 | 4.2 | | | | |



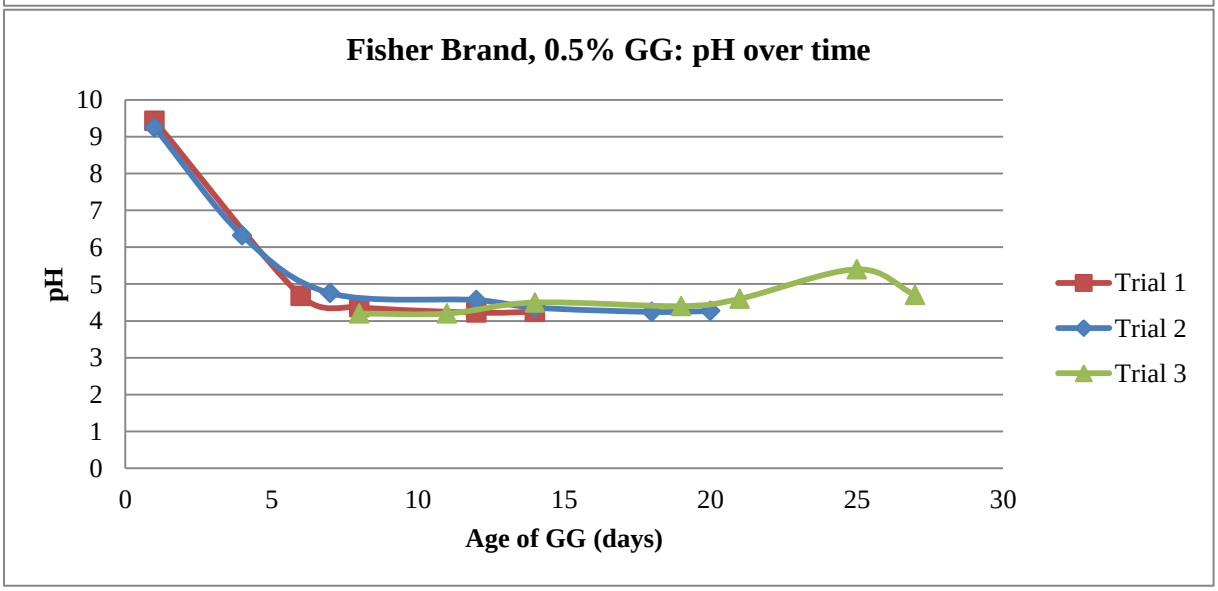




**Figure 11. Comparison of Fisher and TIC GG pH Over Time**

Another sample, using a higher quantity of GG was monitored over 3 months, and is shown in Figure 12. After 50 days, the pH began rising which could be in response to the reduction, degradation, or volatilization of the carboxyl products.

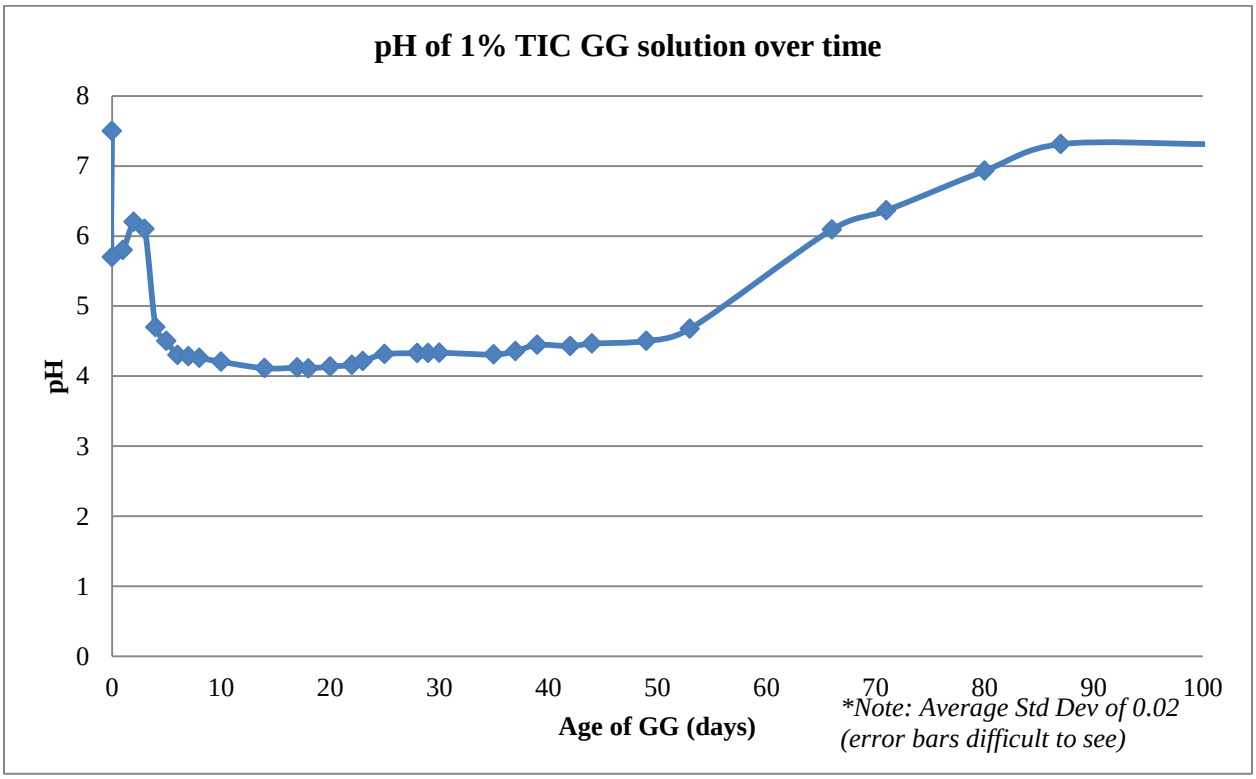


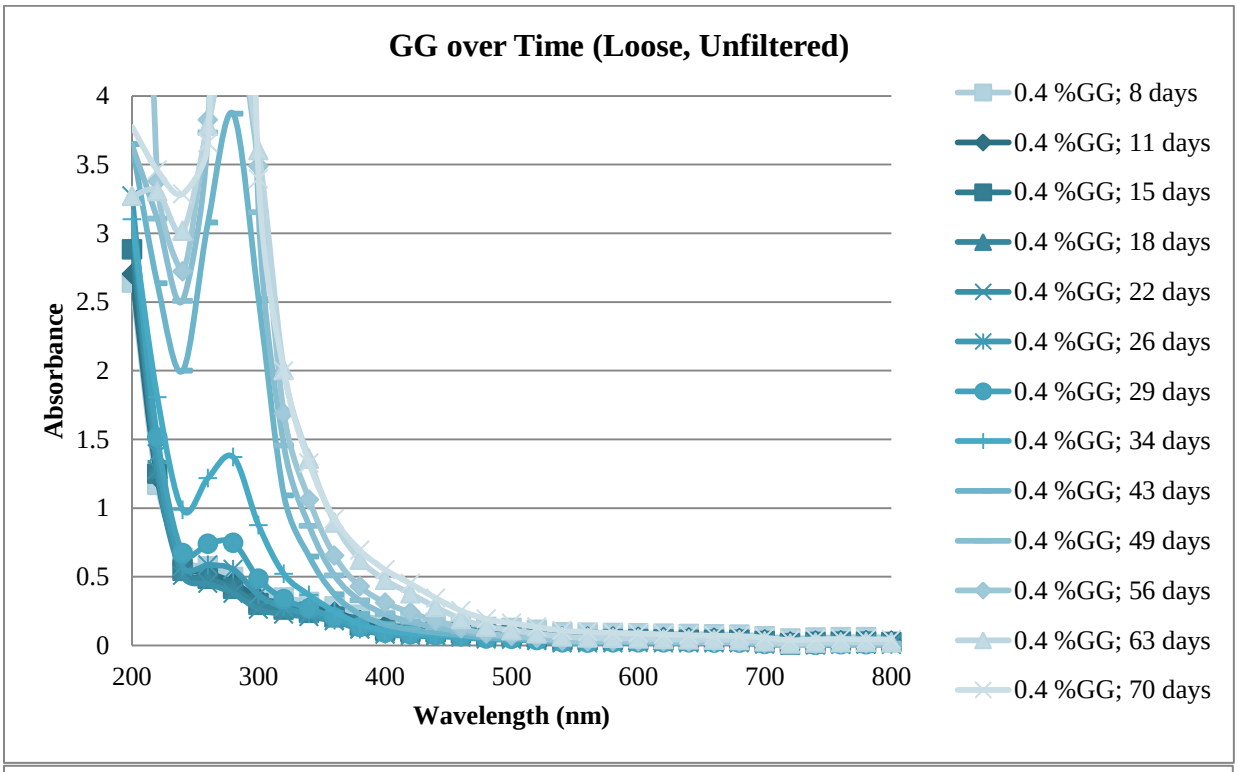

**Figure 12. GG Long Term pH Observation**

**UV-Vis Spectrum**

When dissolving GG in water, a general shift from the water baseline occurs over the 200-800nm range. The spectrum changes based on the amount of time elapsed and the amount of GG used. Additionally, the use of filter bags, 0.2µm syringe filters, or centrifuging samples controls the GG dispersion and decreases the spectrum interference caused by the dissolved solids. Figure 13 and Figure 14 demonstrate the changing GG spectrum over time, as well as the positive impact of filter bags and syringe filtration.

Increasing concentrations of GG also result in higher UV-Vis absorbance spectrums as shown in Figure 15, Figure 16 and Figure 17.

Although filter bags, syringe filters, and centrifuging removes much of the baseline shift, GG does appear to have some unique spectrum characteristics, which often present non-uniform peaks and rises at wavelengths below 300 nm. These artifacts are most likely due to electronic transitions caused by the absorption of UV light. Additionally, the spectrum of GG samples hydrating for 24 hours or less, demonstrate a peak near 400nm, which appears to shift to a shorter wavelength over time. This is considered a hypsochromic shift and could be caused by a number of factors such as increasing solution polarity, pH, or unpaired electrons impacted by GG introduced carboxyl groups. This transition could also be related to the hydration or saturation process, as molecules with unsaturated centers typically require less energy for electronic transitions (i.e. lower wavelengths).



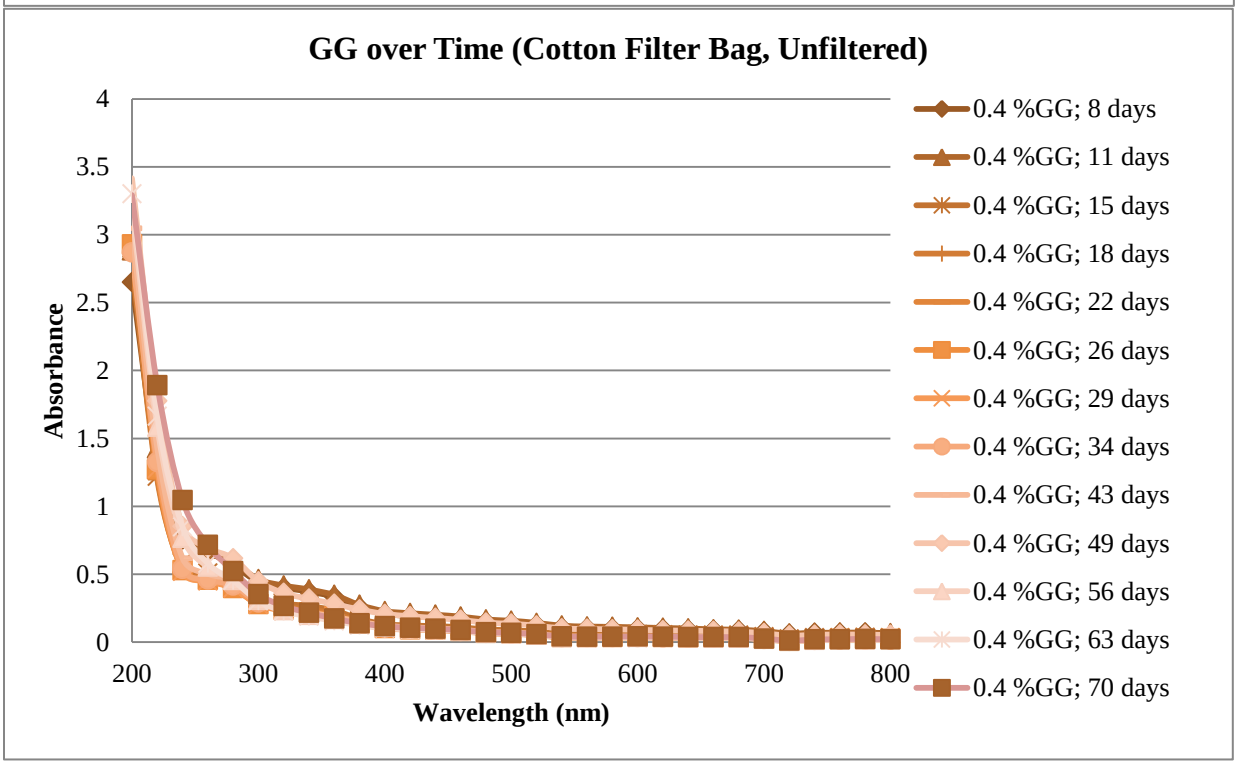




**Figure 13. Comparison: Spectrogram of Freely Dispersed GG and GG Contained in Filter Bag**

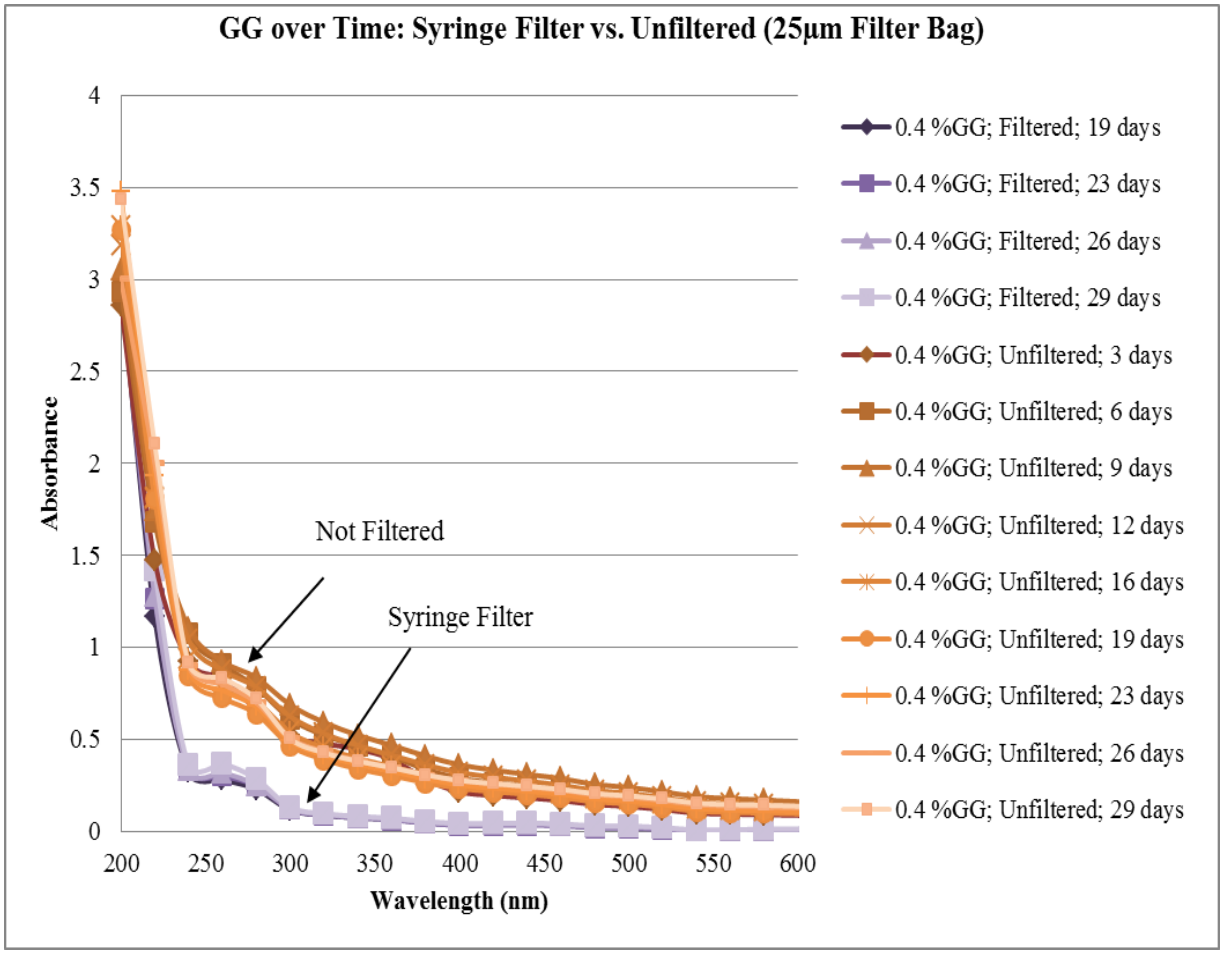
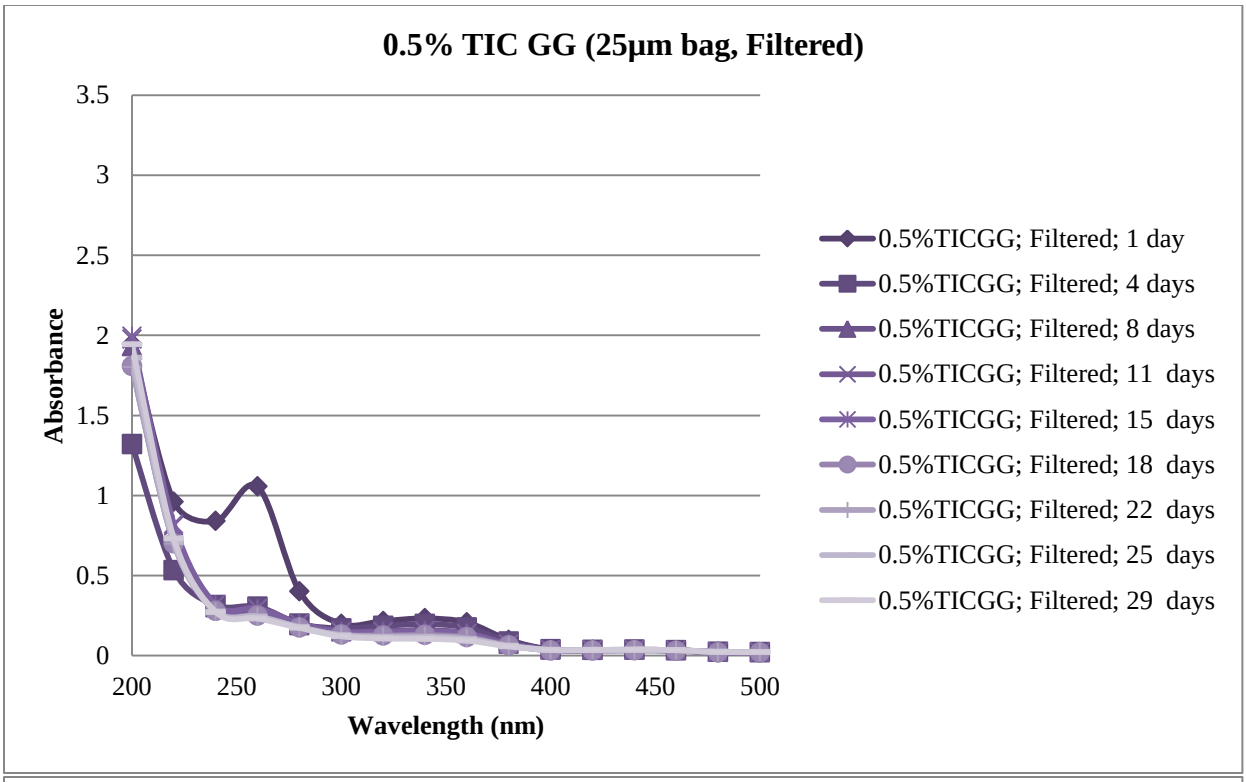



**Figure 14. Comparison: Spectrogram of GG With and Without Syringe Filtration**



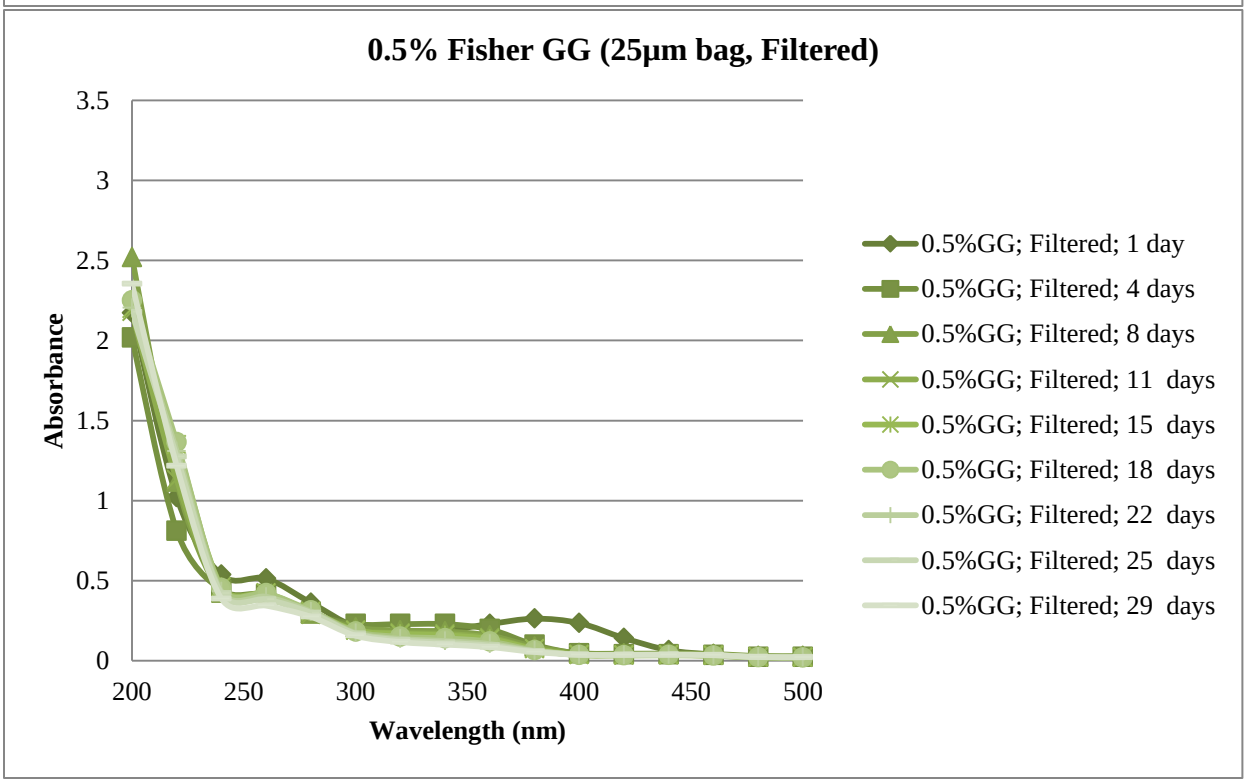
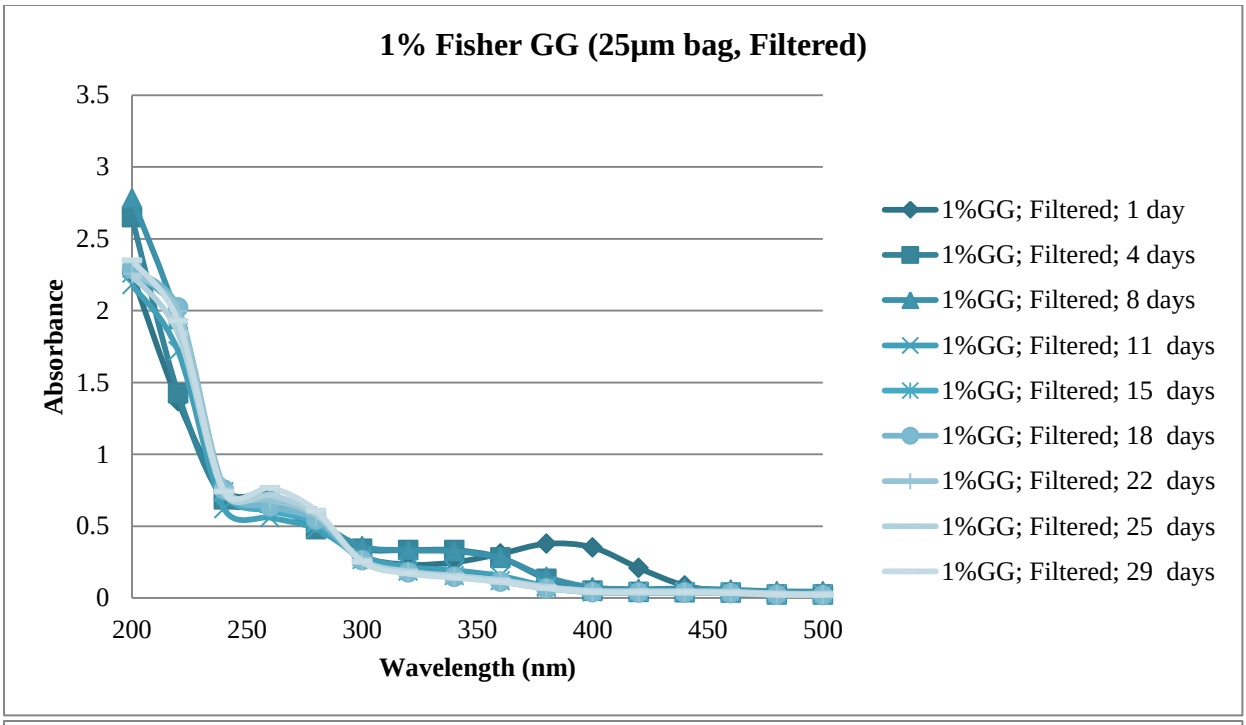




**Figure 15. Comparison: Spectrogram of TIC and Fisher GG over Time**



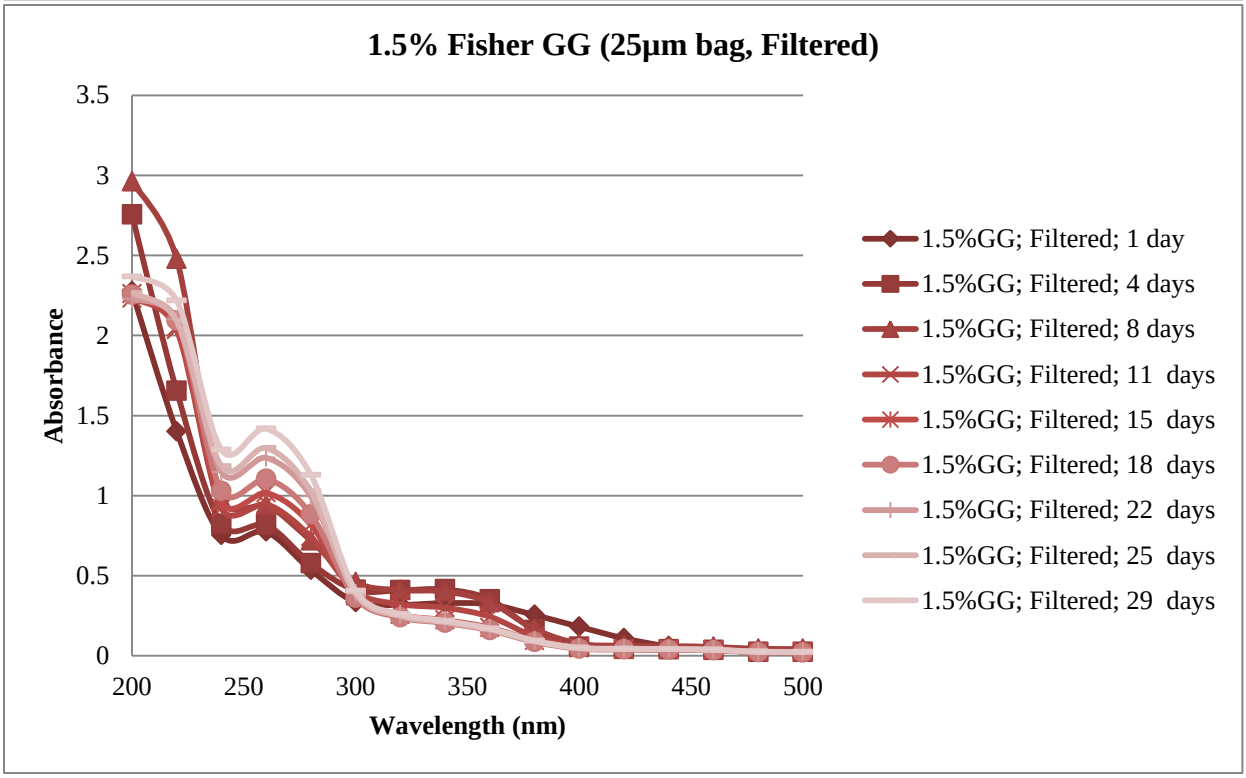
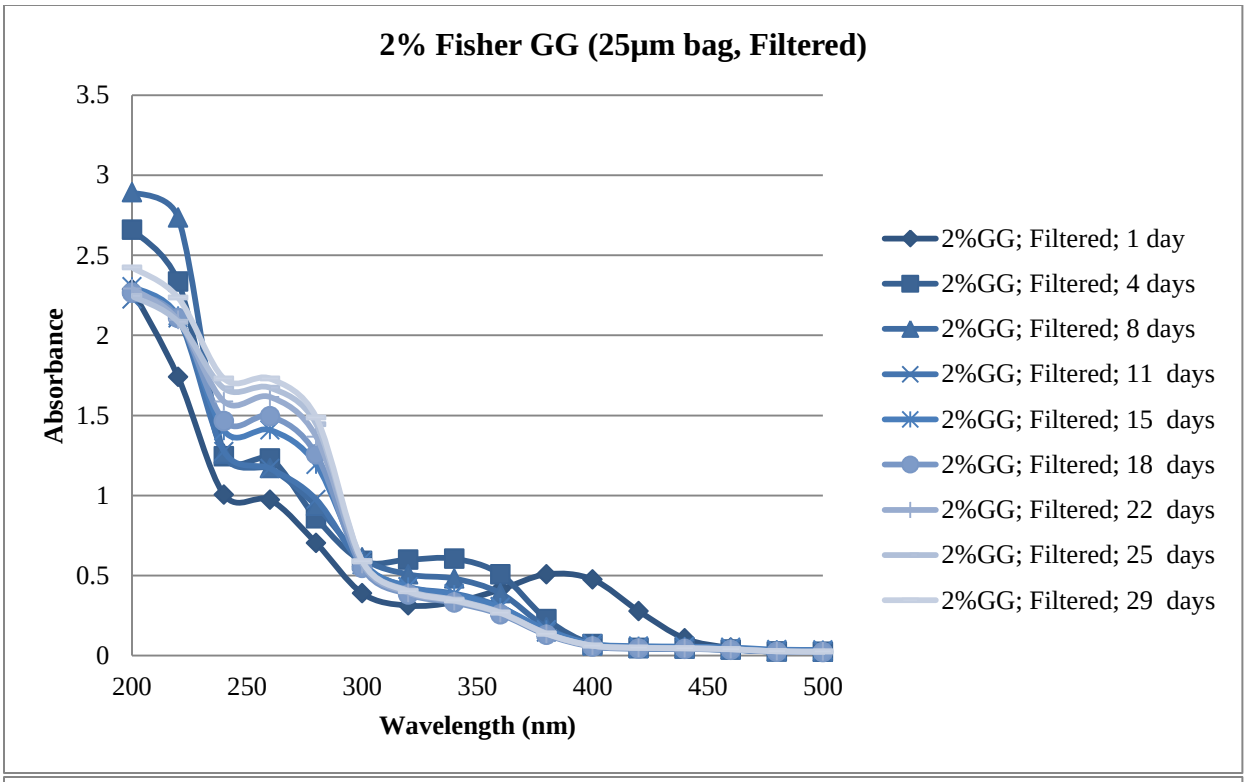




**Figure 16. Comparison: Increasing Quantities of GG, over Time (1-1.5%)**



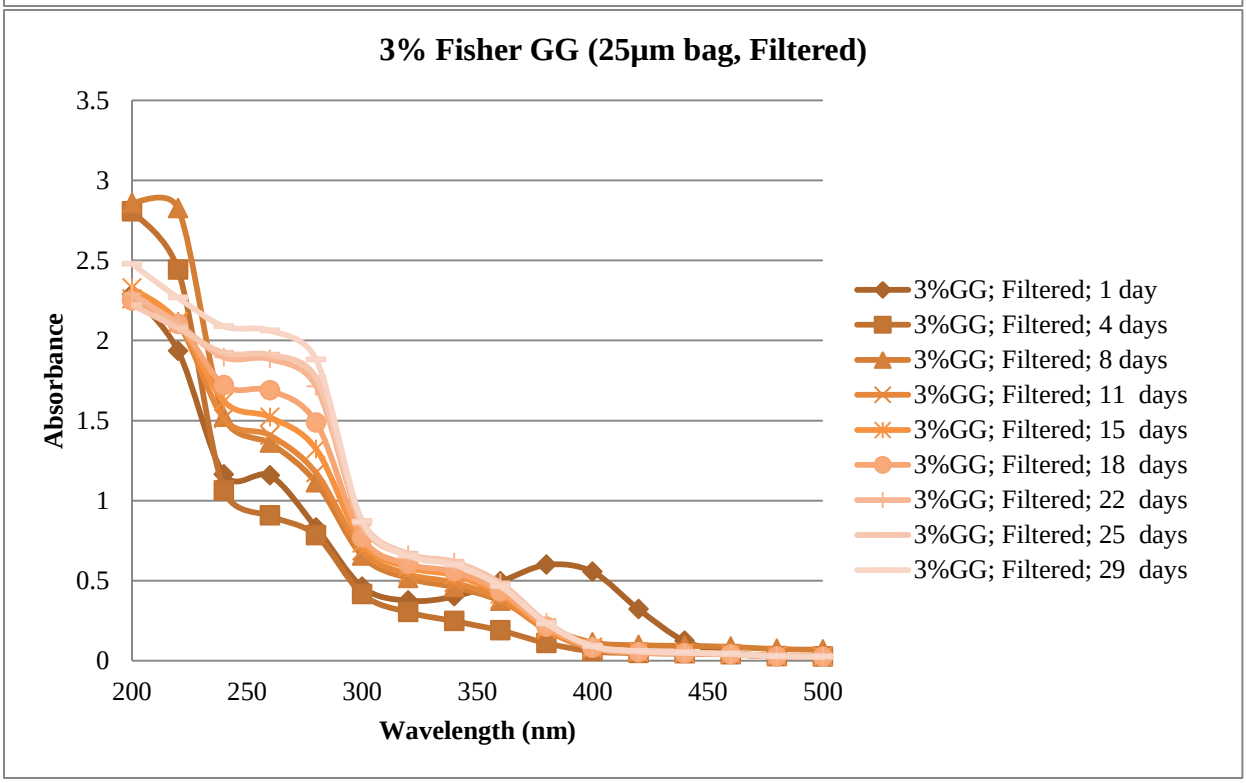




**Figure 17. Comparison: Increasing Quantities of GG, over Time (2-3%)**

## Microbial Growth

GG products demonstrate microbial growth, which becomes visible within 4 to 8 weeks. Stationary samples demonstrate bacterial growth on the surface of the liquid or gels exposed to air, and samples in filter bags tend to demonstrate growth on the outside of the bags. Samples that are constantly mixed, also demonstrate bacterial growth, however, it may take longer to become visible. Heated samples tend to develop bacterial growth at a faster rate, while refrigerated samples did not demonstrate bacterial growth. Additionally, refrigerated samples were not effective in adsorbing dye, which indicated that biodegradation may impact the effectiveness of GG. Further preliminary sampling was conducted using low levels of ethanol, bleach, and hydrogen peroxide as microbial inhibitors. Over a 4 month observation period, all samples with these microbial inhibitors demonstrated bacterial growth, with the exception of the 1% peroxide sample. Additionally, when tested against a dye, the samples performed similarly to the unmodified GG comparison. While biodegradation may play a role in the GG adsorption process, other factors are also involved. Furthermore, long term testing of GG samples, spanning up to 9 months, maintained microbial growth, but have not demonstrated any release of the original contaminant adsorbed.

## Scanning Electron Microscopy Analysis

SEM micrographs were captured for both brands of unmodified GG and the 2 batches of crosslinked powder shown previously in Figure 8. While imaging, it became apparent that higher magnification levels resulted in charging of the GG product. Charging can interfere with the image, causing artifacts or secondary electron images, and reduction in power and magnification setting were required. Figure 18 and Figure 19

demonstrate the SEM image of the TIC brand GG, Figure 20 the Fisher GG, Figure 21 the first batch of crosslinked GG and Figure 22 the second batch of crosslinked GG. The images of the GG and crosslinked product are similar to those in other published studies. The brands of GG have a similar surface morphology, which is smooth and homogeneous. The crosslinked products demonstrated a substantial change from the unmodified GG appearing to have layers, voids, cavities and jagged edges.

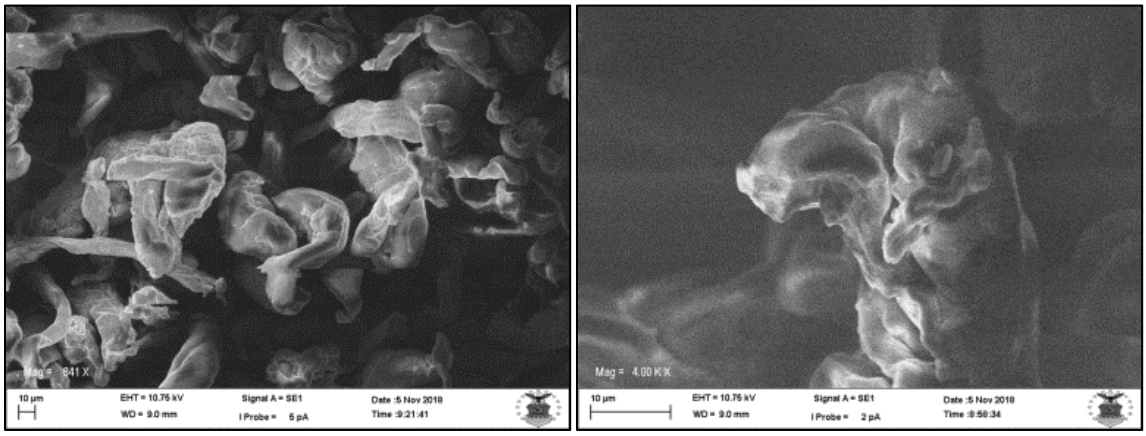



**Figure 18. SEM Micrograph of TIC GG**

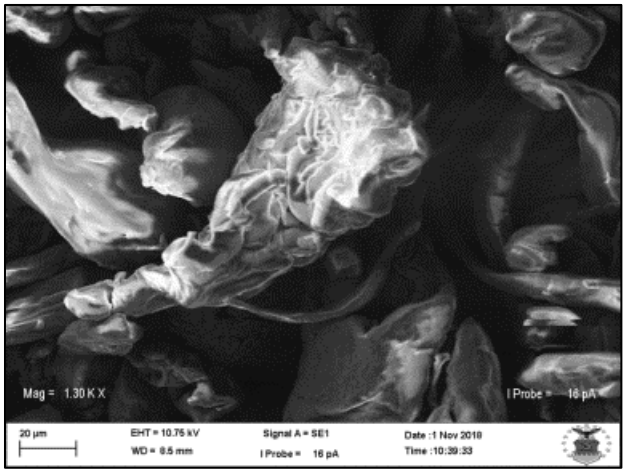



**Figure 19. SEM Micrograph Demonstrating Charging of TIC GG**

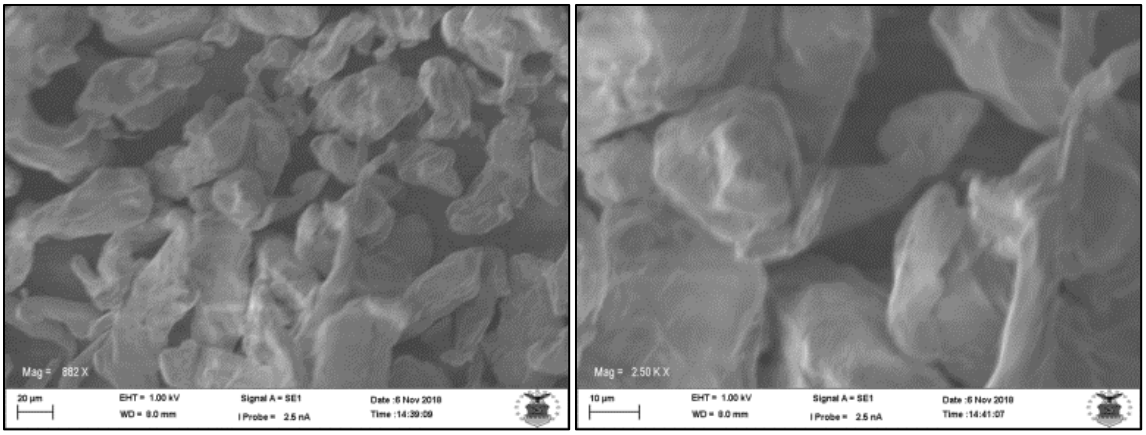



**Figure 20. SEM Micrograph of Fisher GG**

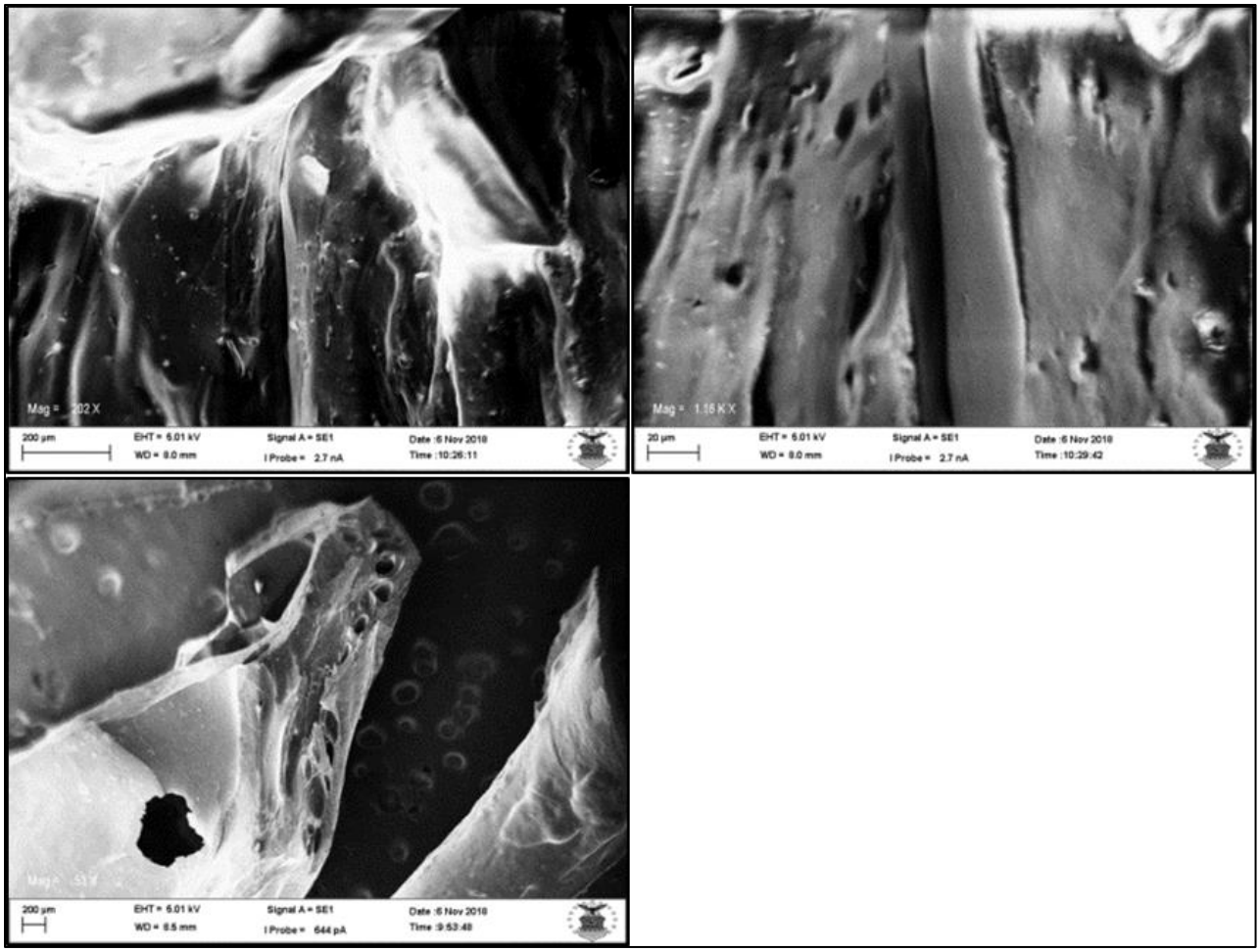



**Figure 21. SEM Micrograph of Crosslinked GG (Batch 1)**

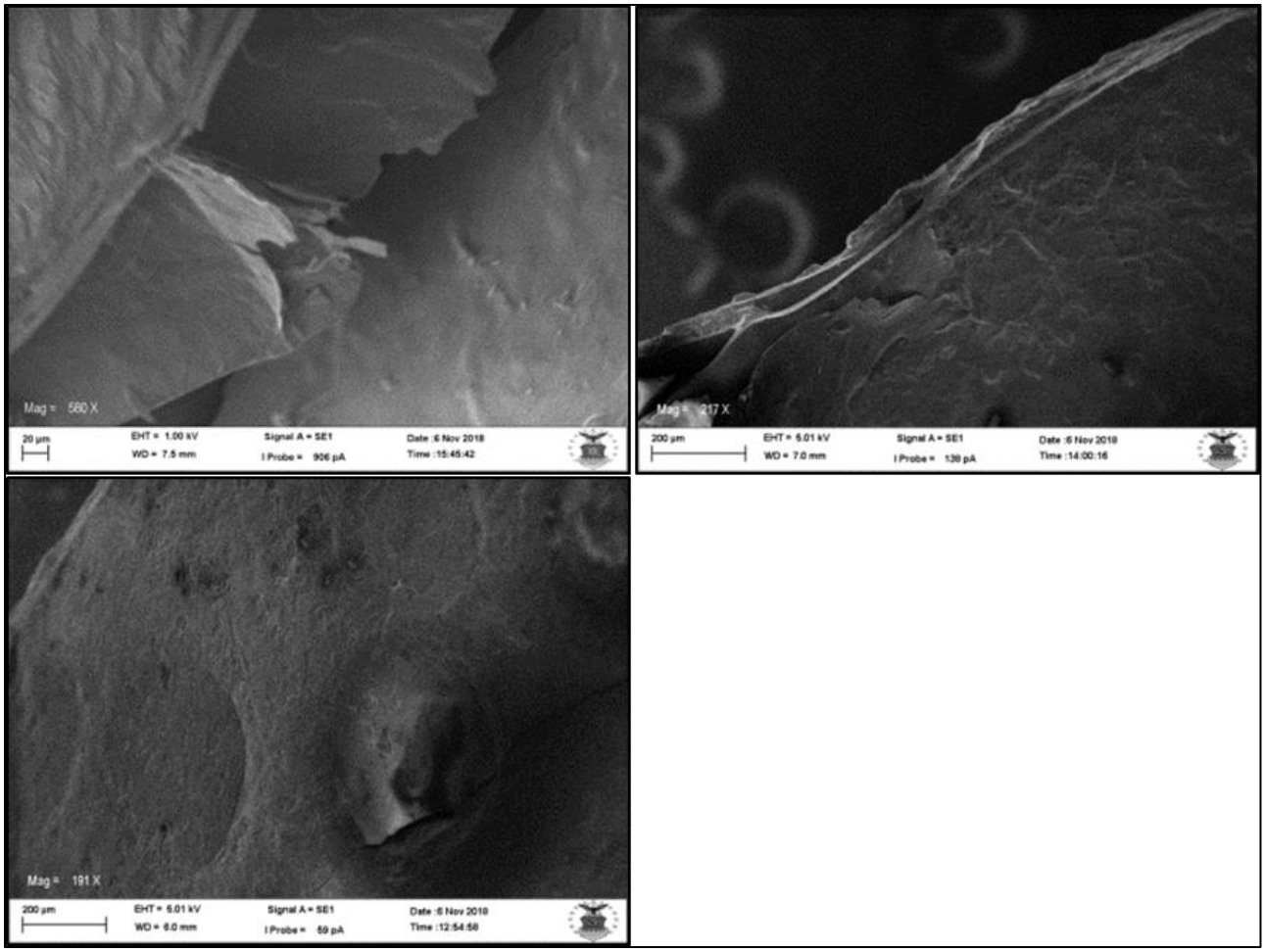



**Figure 22. SEM Micrograph of Crosslinked GG (Batch 2)**

## Allura Red Results

### Allura Red: Unmodified, Dry Guar Gum

An initial test compared the UV-Vis absorbance of 3 different percentages of GG mixed with Allura Red after 2 days and after 1 month. The highest GG quantity tested, 0.5%, resulted in complete removal after a month. This was compared to the same weight of carbon in solution, and the carbon outperformed at each concentration tested. Results of this test are summarized in Table 6.

**Table 6. Allura Red Adsorption with Unmodified GG and Carbon**

| Percent Allura Red (5 ppm) Remaining: Unmodified GG and Carbon comparison | | | | | | |
|---|---|---|---|---|---|---|
| | **Guar Gum (GG)** | | | **Carbon: Filtrasorb 600** | | |
| % Ratio (% GG, % Carbon), w/v | 0.05% | 0.10% | 0.50% | 0.05% | 0.10% | 0.50% |
| Weight used (g) | 0.005 | 0.01 | 0.05 | 0.005 | 0.01 | 0.05 |
| % dye remaining - 2 days | 93.8 | 94.8 | 102.4 | 48.3 | 40.3 | 15.4 |
| % dye remaining - 1 month | 66.3 | 22.0 | < 0 | 5.3 | < 0 | < 0 |

Subsequent samples of 0.2% GG freely dispersed in a larger stationary solution demonstrated an average 35% removal within a week, 68% within 2 weeks, 80% removal in 3 weeks, and complete removal within 4 to 5 weeks. A series of pictures demonstrating this adsorption are included in Figure 23. The same mass of carbon removed 92% within a week, 96% in 2 weeks and 99% in 3 weeks. This same concentration of GG was also tested with a refrigerated sample and a heated sample. The refrigerated sample showed less than 10% removal throughout the test duration, while the heated sample removed dye faster than the room temperature sample until both reached the same level at approximately 4 weeks. When comparing other gum products at this concentration, the Fisher brand outperformed the TIC gum for nearly 4 weeks. Both brands of GG and a GG-Xanthan mix outperformed Gellan and the Konjac gums. The TIC GG and GG-Xanthan performed similarly, which may be due to the same GG source material potentially used in both TIC brand products.

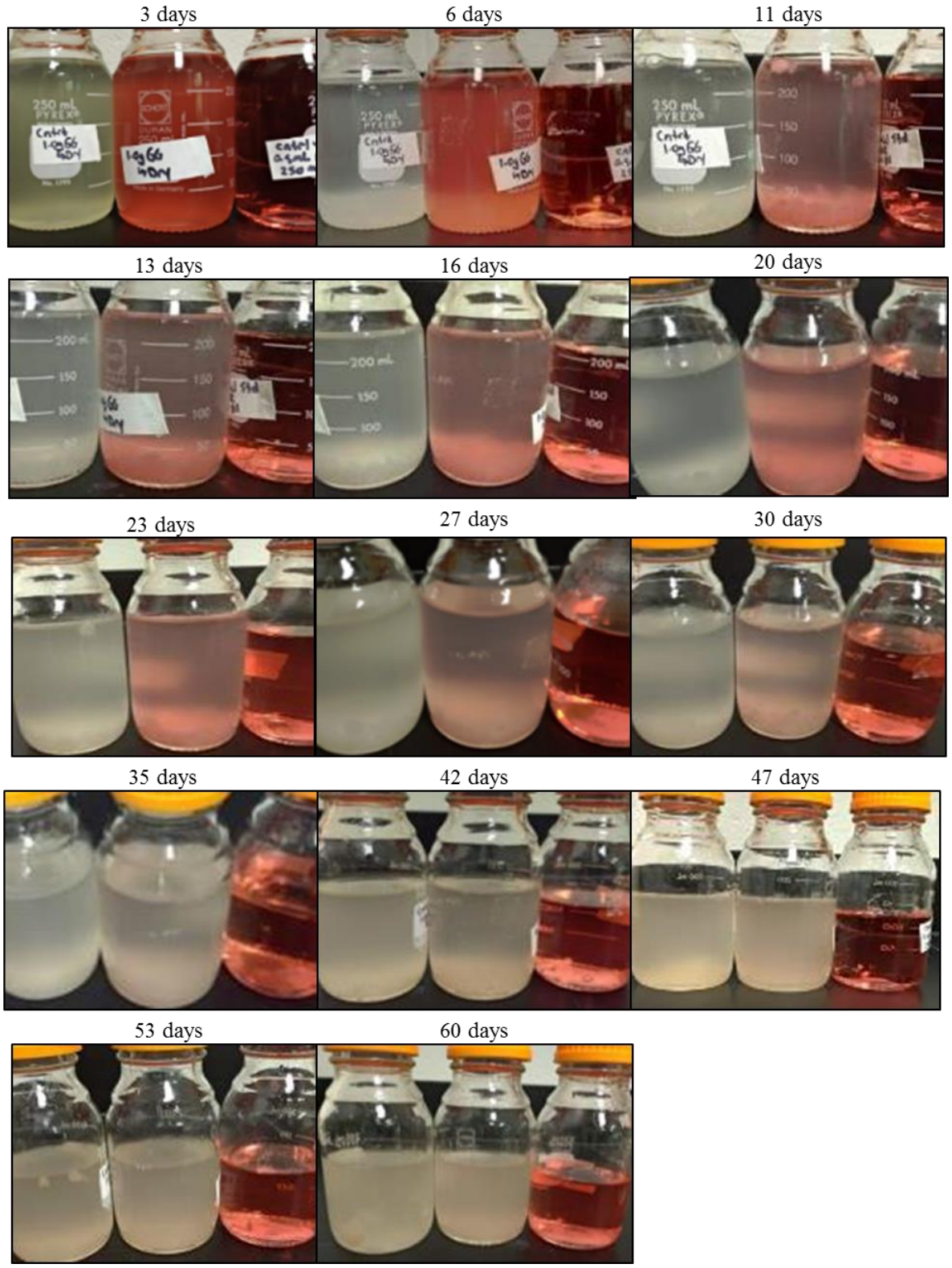



**Figure 23. Adsorption over Time; Freely Dispersed GG with Allura Red Dye**

Another test, shown in Figure 25, evaluated the effectiveness of 0.4% GG w/v (1 gram) of dry unmodified GG placed in a filter bag and mixed on the tumbler. Table 7 and Figure 24 summarize the results of this test. Based on the calibration curve, complete dye removal was obtained on day 9 (using the control subtraction method, the GG/water control sample had a higher UV-Vis absorbance than the sample with GG and dye); a filtered sample collected on day 19 indicated that 99.9% of the dye had been removed. Additionally, the percentage of dye removed by the filter and filter bag was measured; the syringe filter removed an average of 3.5%, and the bag sorbed increasing quantities throughout the test. By day 9, the filter bag potentially removed 22% of the dye. A similar test using a cotton bag demonstrated the cotton bag adsorbed less dye than the nylon (the bag increased by an average of 6% compared to the dye control standard), and that test demonstrated 0.4% of GG removed 94% of the dye by day 11.

**Table 7. Allura Red Adsorption with Unmodified GG in Filter Bag**

| **Percent Allura Red (5 ppm) Remaining: Unmodified GG in 25μm filter bag** | | | | | |
|---|---|---|---|---|---|
| **Time Elapsed (Days)** | **Control - Allura Red Dye** | **Filter Bag & 0.4% GG** | **Filter Bag & 0.4% GG (Filtered)** | **Control – Empty Bag** | **Control – Empty Bag (Filtered)** |
| 3 | 100.4 | 85.4 | | 93.7 | |
| 6 | 96.6 | 33 | | 86.2 | |
| 9 | 98.2 | < 0 | | 78.4 | |
| 12 | 97.6 | < 0 | | 69.6 | |
| 16 | 96.1 | < 0 | | 63.8 | |
| 19 | 96.4 | 17.5 | 0.1 | 53.7 | 46.5 |

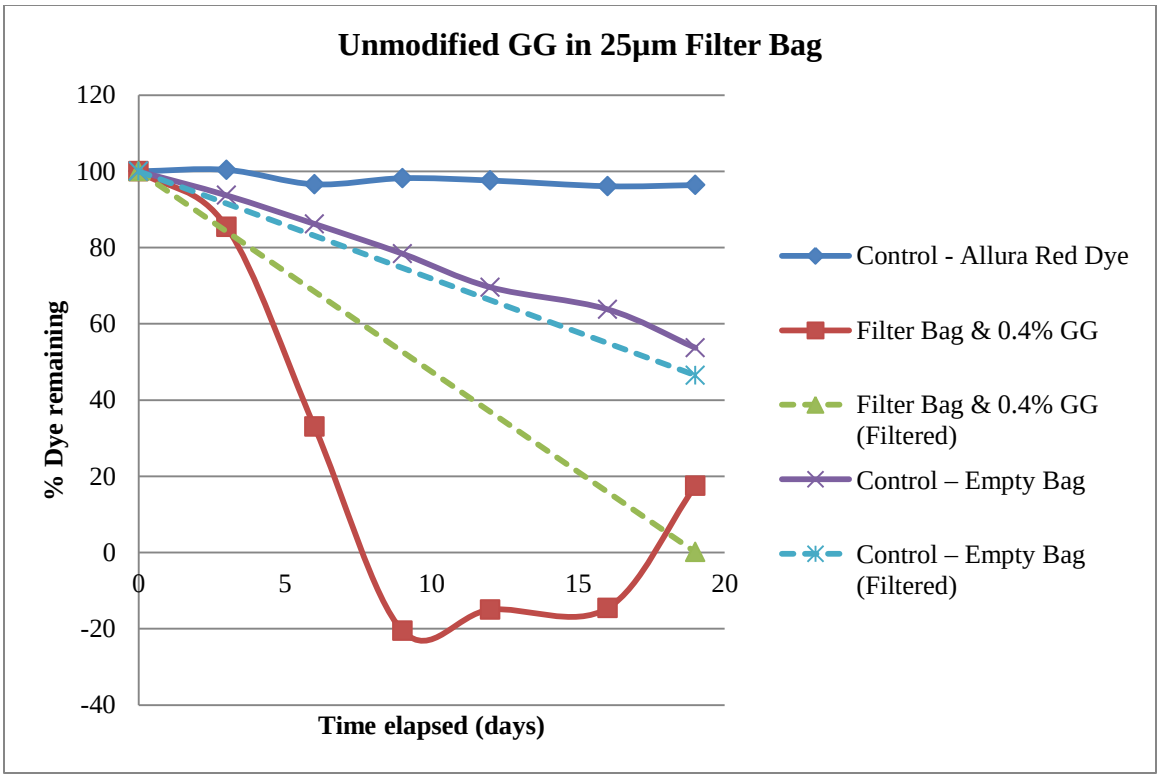



**Figure 24. Allura Red Adsorption with Unmodified GG in Filter Bag**

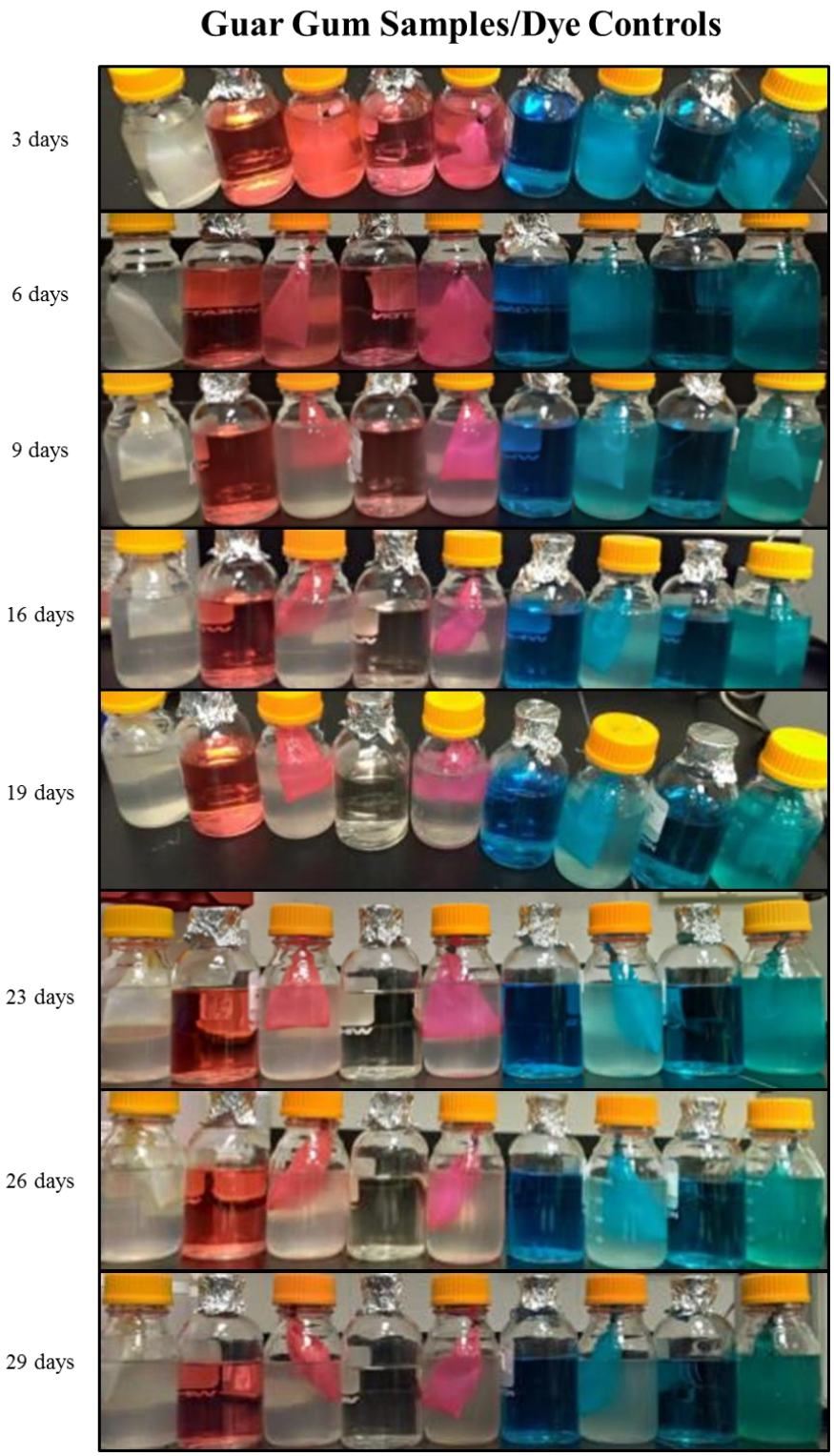



**Figure 25. Adsorption over Time; GG in Filter Bags with 4 Dyes**

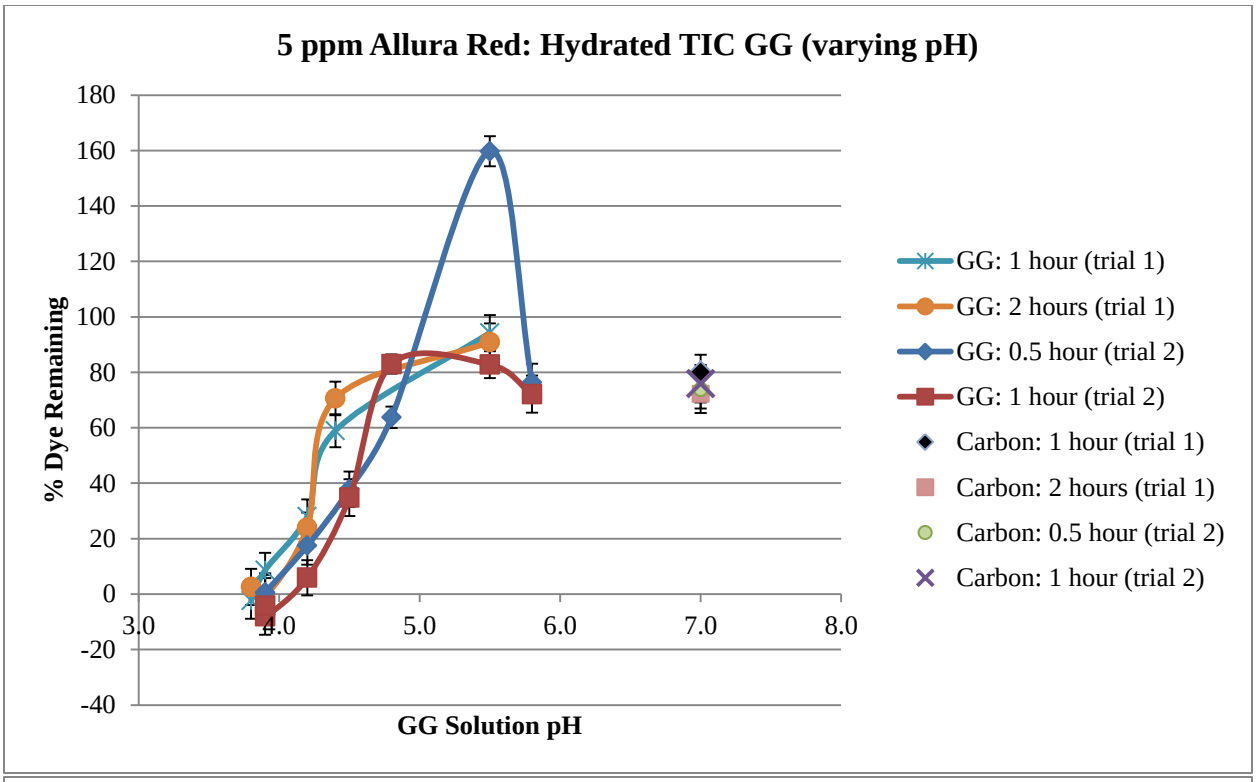
Sample order: GG/water control, Allura Red dye standard, GG/Allura Red, Erythrosine B dye standard, GG/Erythrosine B, Brilliant Blue dye standard, GG/Brilliant Blue, Fast Green dye standard, GG/Fast Green

**Allura Red: Cleaned or Dried Guar Gum**

A dehydrated sample was compared to unmodified GG. While the dehydrated GG removed dye, it did so at a slower rate than the unmodified GG, resulting in complete removal after an additional 2 weeks, compared to unmodified GG. Additionally, a sample of burnt GG, shown in Figure 5, was ineffective and removed less than 10% dye throughout the test period.

**Allura Red: Hydrated Guar Gum**

During this research, it was observed that a sample using an older stock solution of hydrated GG adsorbed at a significantly faster rate than fresher solutions. Subsequent short term tests were conducted comparing hydrated GG of varying age and pH; results are included in Figure 26 and Figure 27. The TIC brand performed substantially better than the Fisher brand, and adsorption may be correlated to the solution pH. Averaging the 1 hour samples, the 1 day old TIC GG samples removed approximately 17% of the dye while the 2 week old sample removed 100%. The fresh Fisher GG solution removed an average 31%, and the 2 week old Fisher GG removed 37%. Both outperformed a similar weight of carbon which demonstrated an average 22% removal after 1 hour. Based on these results, GG was effective within minutes, and surpassed one of the most commonly used water treatment technologies, granular activated carbon. Further research using this method should be conducted and compared to additional carbon treatments and pH modification to identify what mechanisms are involved in this adsorption process.



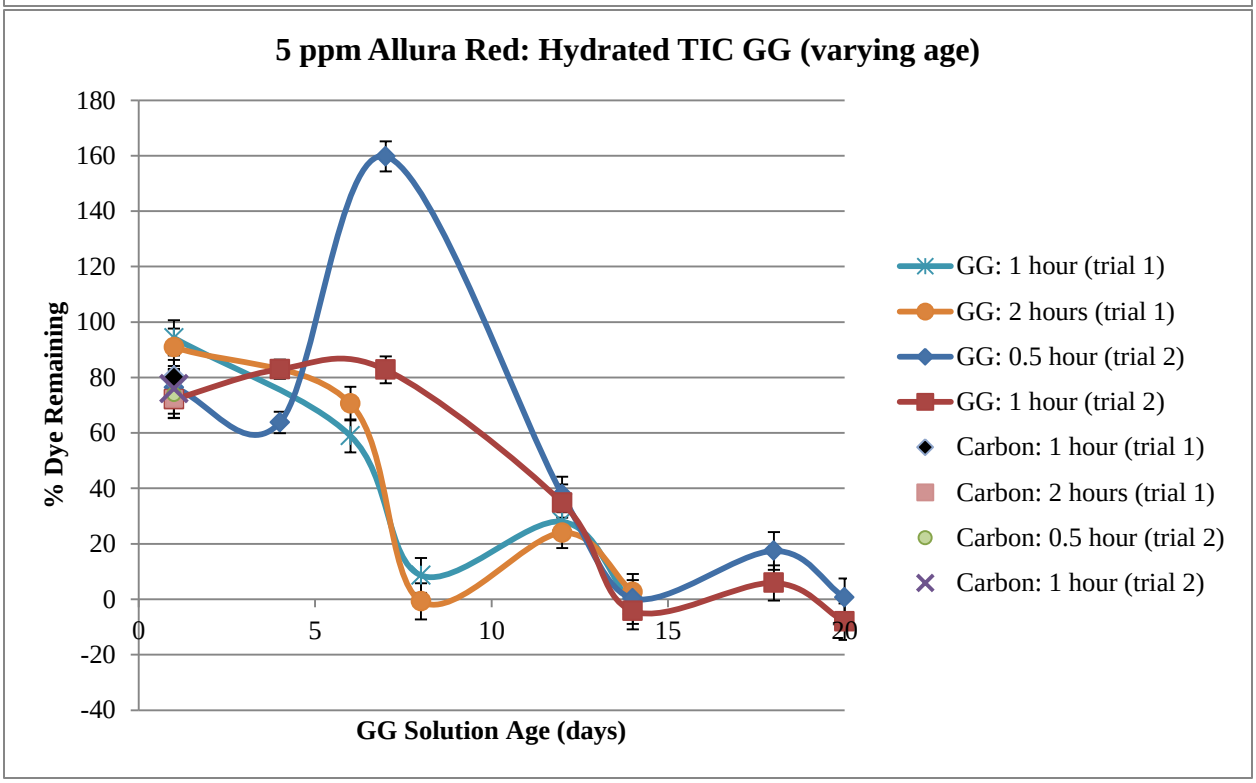




**Figure 26. TIC Adsorption of Allura Red, Comparison of GG Solution pH and Age**

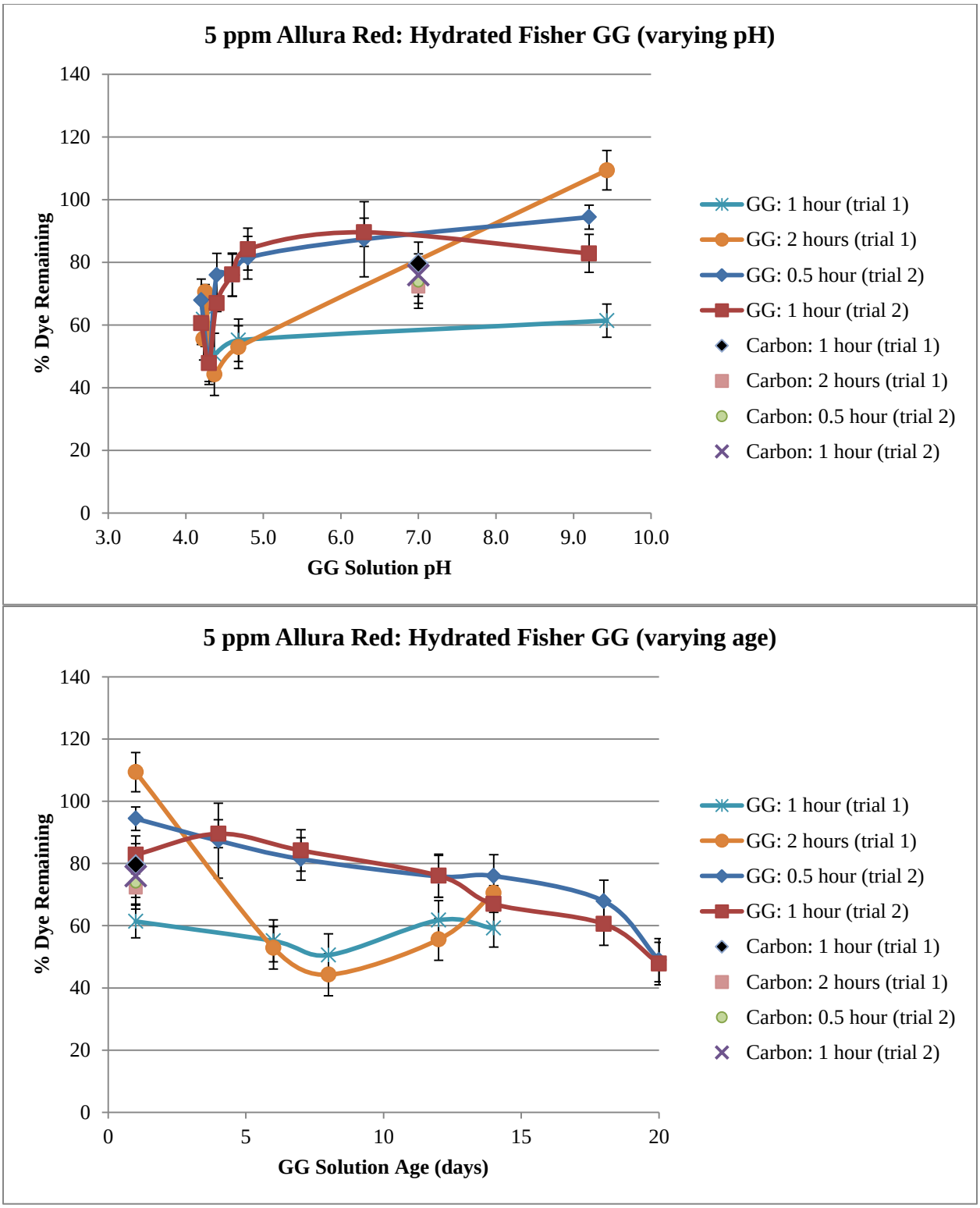



**Figure 27. Fisher Adsorption of Allura Red, Comparison of GG Solution pH and Age**

**Allura Red: Crosslinked Guar Gum**

A few experiments were conducted to evaluate the effectiveness of crosslinking. First, a filter was soaked in GG solution and then crosslinked with borax; this test was stationary bottle test, but showed less than 5% removal during a 6 week period. Another used 0.5g (approx. 0.2% w/v) of crosslinked powder which formed a sphere in solution, shown in Figure 28, and removed 21% in 5 weeks.

**Figure 28. Image of Crosslinked Powder in Solution after 6 and 20 days**

An experiment using a lower Allura Red concentration than those previously described and comparing a 0.3% GG (w/v) of the batches of crosslinked GG shown in Figure 8, demonstrated that the first batch that was darker with larger particle sizes was more effective than the second. This crosslinked powder removed 92.5% of the dye, while the other powder removed 22% after 2 weeks. These powders did not behave as a flocculant, but rather completely dispersed and dissolved in solution resulting in an incredibly viscous product, as shown in Figure 29. The difference in these batches was the type of borax powder used, and how they had dried. Additionally, the performance of a crosslinked gel using the same amount to GG was compared to these samples, and it removed 45% of the dye after 2 weeks.

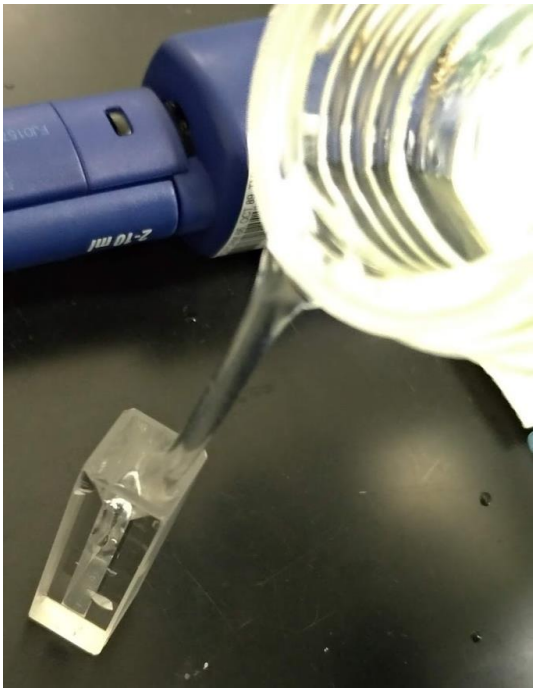


**Figure 29. Image of Crosslinked Powder in Solution (High Viscosity)**

Furthermore, it was observed that the crosslinked powders had a large UV-Vis absorbance spike initially, possibly due to hydration. The crosslinking did not appear any more effective in eliminating the large absorbance spectrum increase, which occurs with unmodified GG.

A GG crosslinked gel and powder which had been pre-mixed with dye and added to a clear water solution resulted in red dye desorbing. This can indicate that the gels may have a potential for recyclability, but also shows that the dye was not strongly bound to the gel matrix, and is likely impacted by other electrostatic reactions in solution.

**Allura Red: Guar Gum with Salting-Out Solution**

Two tests based on the salification effect were conducted for Allura Red. The first test used a lower quantity of GG and created less dense matrix products, while the subsequent test used a higher percentage of GG and demonstrated a more consolidated

polymer network as shown in Figure 30. Results comparing the performance of boric acid, concentrated borax powder, diluted 0.02M borax solution, and unmodified GG are summarized in Table 8. The set of 0.02M borax samples did not generate a collapsed network. However, the collapse initiated by boric acid and borax powder decreased the impact of GG baseline UV-Vis absorbance shift by about 40-50%.

**0.1% GG**

**0.5% GG**

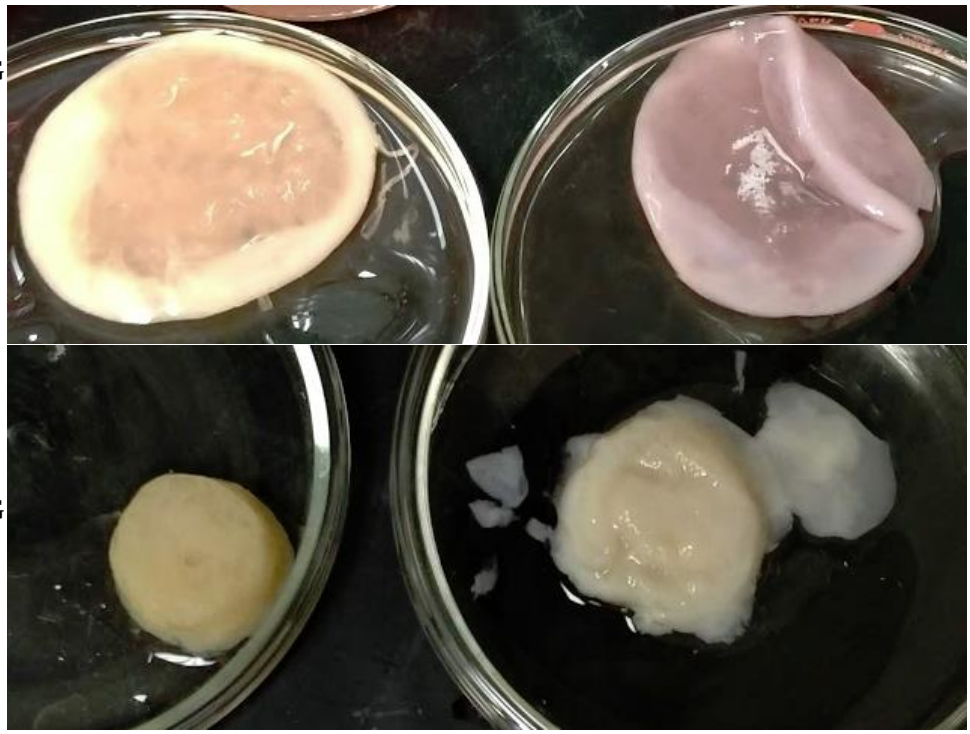


**Figure 30. Comparison of Salt-out Products Based on 0.1% and 0.5% GG.** Boric acid-initiated pucks located on the left of each image, matrix resulting from borax powder on the right side of each image above.

After the collapse, it was noted that SFCA filters were more effective than MCE filters, which may have been due to the salt in solution or creation of larger particles. The second test had additional controls, and it became apparent that the presence of salt in the dye also improved the filters' ability to remove dye; the use of syringe filters with the control sample removed nearly 40% of the dye. The presence of GG and borate ions

did further increase the color removal between 35% and 60%. One of the limiting factors of this analysis was that a lower dye concentration was used, meaning the UV-Vis peak was smaller, and interference was more pronounced, where some variability and small changes could result in large "percent remaining" shifts.

**Table 8. Comparison of Results of Salt-out based on 0.1% and 0.5% GG**

| Percent Allura Red (2 ppm) Remaining: 0.1% GG; Salt-out | | | | |
|---|---|---|---|---|
| | Before borate ions added | Minutes after borate added | SFCA syringe filter after collapse | MCE syringe filter after collapse |
| Control Allura Red Dye | 98.4 | 96.6 | 101.1 | 96.3 |
| Boric Acid, GG, Salt | 58.8 | 46.4 | 19.4 | 60.1 |
| Borax powder (concentrated), GG, Salt | 59.8 | 70.8 | 27.2 | 72.0 |
| 0.02M Borax solution (diluted), GG, Salt | 54.9 | 68.4 | 22.2 | 56.8 |

| Percent Allura (2ppm) Red Remaining: 0.5% GG; Salt-out | |
|---|---|
| | Average SFCA Filter after collapse |
| Control Allura Red Dye, & Salt | 59.8 |
| Boric Acid, GG, Salt | 25.2 |
| Borax powder (concentrated), GG, Salt | 12.6 |
| 0.02M Borax solution (diluted), GG, Salt | < 0 |
| GG, salt (no borate ions) | 9.4 |

Pre-made collapsed gel "pucks" using 0.3% GG were also tested as an adsorbent. The dried pucks were more durable than the wet matrix, but both eventually broke down. Both types performed similarly, and after 12 days, both pucks demonstrated 35% removal. However, when using the syringe filter, both samples indicated higher dye removal, potentially due to increased filter efficiency caused by the salt. Syringe filtration of the same day 12 sample showed 88% removal of the dye with the dried puck, while the wet pucks demonstrated 55% removal. This variability may be due to how the pucks dissolved or particle sizes produced as they broke down in solution.

## Brilliant Blue Results

### Brilliant Blue: Unmodified, Dry Guar Gum

An initial test compared the UV-Vis absorbance of 3 different percentages of GG mixed with Brilliant Blue after 3 days and after 1 month. The highest GG quantity tested, 0.5% GG, resulted in 13% removal within 3 days and 22% removal after a month. This was compared to the same weight of carbon in solution; the carbon outperformed at each concentration tested. Results of this test are summarized in Table 9.

**Table 9. Brilliant Blue Adsorption with Unmodified GG and Carbon**

| Percent Brilliant Blue (8 ppm) Remaining: Unmodified GG and Carbon comparison | | | | | | |
|---|---|---|---|---|---|---|
| | Guar Gum | | | Carbon: Filtrasorb 600 | | |
| % Ratio (% GG, % Carbon), w/v | 0.05% | 0.10% | 0.50% | 0.05% | 0.10% | 0.50% |
| Weight used (g) | 0.005 | 0.01 | 0.05 | 0.005 | 0.01 | 0.05 |
| % dye remaining - 3 days | 100.6 | 100.9 | 86.9 | 71.4 | 33.4 | 17.3 |
| % dye remaining - 1 month | 97.8 | 97.8 | 77.7 | 23.1 | < 0 | < 0 |

Another test evaluated the effectiveness of 0.4% GG (1 gram) of dry unmodified GG placed in a filter bag. Table 10 and Figure 31 summarize the results of this test. Based on the calibration curve, the percentage of dye remaining decreased to 9% on day 12, indicating a total of 91% dye was removed. A filtered sample collected on day 19 indicated that 96% of the dye had been removed. Additionally, the percentage of dye removed by the filter was measured. The paired sample on day 19 demonstrated the filter removed 18% of the dye; however, subsequent samples demonstrated an average removal by the filter of only 6%. This variation could be due to filter type or age, and new filters were available after the day 19 sampling occurred.

**Table 10. Brilliant Blue Adsorption with Unmodified GG in Filter Bag**

| Percent Brilliant Blue (4 ppm) Remaining: Unmodified GG in 25µm filter bag | | | | | |
|---|---|---|---|---|---|
| **Time Elapsed (Days)** | **Control - Brilliant Blue Dye** | **Filter Bag & 0.4% GG** | **Filter Bag & 0.4% GG (Filtered)** | **Control – Empty Bag** | **Control – Empty Bag (Filtered)** |
| 3 | 100 | 52 | | 99.5 | |
| 6 | 101.4 | 42.9 | | 99.1 | |
| 9 | 101.3 | 14.6 | | 98.5 | |
| 12 | 99.8 | 9 | | 97.6 | |
| 16 | 99.2 | 15.3 | | 99.3 | |
| 19 | 98.6 | 21 | 3.8 | 97.4 | 73.7 |

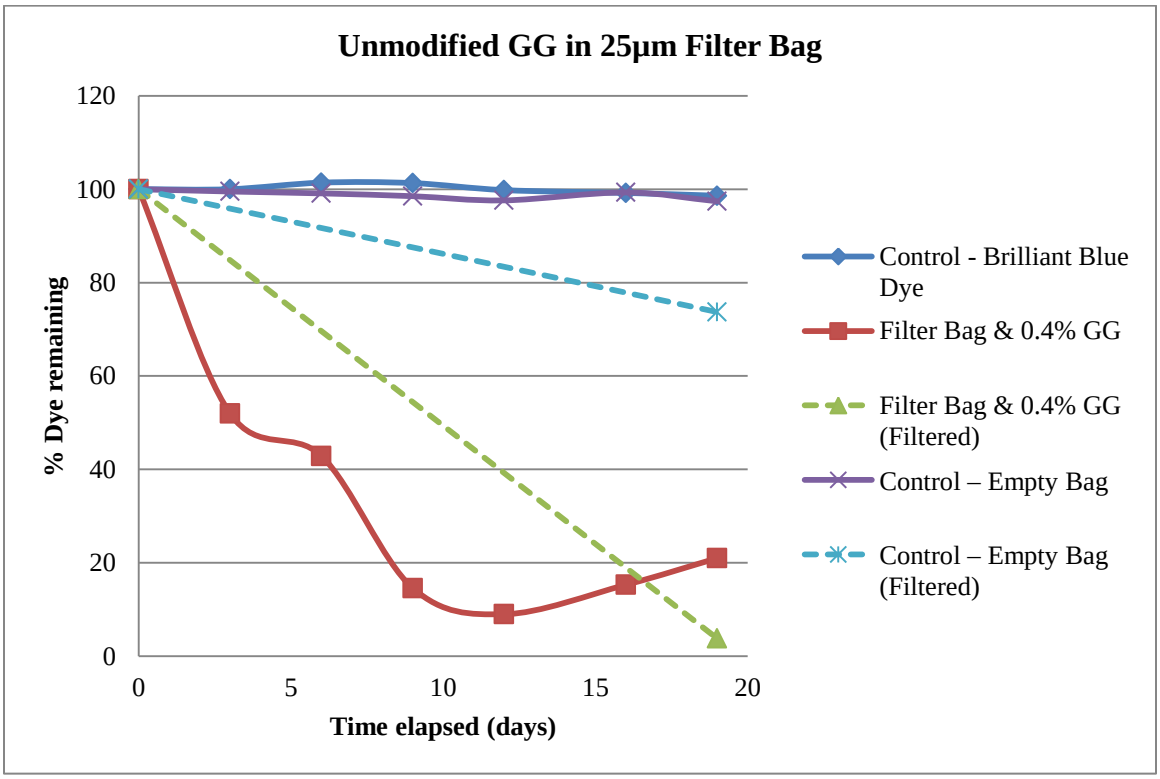



**Figure 31. Brilliant Blue Adsorption with Unmodified GG in Filter Bag**

A larger bottle test comparing 0.2% GG (1 gram) of TIC and Fisher brand GG with brilliant blue dye indicated the TIC brand outperformed the Fisher, and removed

approximately 30% after 2 weeks. These test results are compared to the effectiveness of a dried GG sample and summarized in Table 11.

**Brilliant Blue: Cleaned or Dried Guar Gum**

0.2% GG (1 gram) of TIC and Fisher brand GG were dried in a vacuum oven and tested against the same quantity of unmodified GG. The TIC GG demonstrated less than 10% variation between samples. The cleaned Fisher GG outperformed the unmodified Fisher after 1 week; after 2 weeks, the cleaned Fisher GG demonstrated nearly 20% improvement in dye removal. Throughout the test period, the unmodified Fisher GG removed less than 5% of the dye, however, the modified Fisher GG removed 20% after 2 weeks and 28% after 3 weeks. Additionally, the same equilibrium value was reached by the cleaned Fisher and both TIC samples. Results are summarized in Table 11 and Figure 32.

**Table 11. Brilliant Blue with Unmodified and Dried GG**

| Percent Brilliant Blue (4 ppm) Remaining: Unmodified GG, Dried GG Comparison | | | | | |
|---|---|---|---|---|---|
| **Time Elapsed (days)** | **Control Brilliant Blue Dye (filtered)** | **Unmodified Fisher GG** | **Dried Fisher GG** | **Unmodified TIC GG** | **Dried TIC GG** |
| 0.1 | 94.4 | 100.1 | 98.8 | 94.4 | 96.0 |
| 5 | 92.2 | 97.3 | 98.6 | 96.1 | 98.4 |
| 7 | 101.9 | 107.0 | 92.9 | 95.0 | 95.8 |
| 14 | 107.7 | 98.5 | 78.3 | 64.6 | 62.5 |
| 15 | 109.1 | 99.4 | 80.9 | 72.9 | 75.8 |
| 21 | 109.8 | 95.6 | 71.8 | 71.1 | 73.8 |
| 24 | 106.6 | 96.4 | 72.0 | 76.0 | 74.2 |
| 37 | 107.8 | 98.1 | 70.9 | 71.9 | 77.3 |
| 45 | 106.5 | 98.7 | | 73.0 | 69.8 |
| 58 | 105.2 | 94.3 | 75.2 | 73.7 | 66.4 |

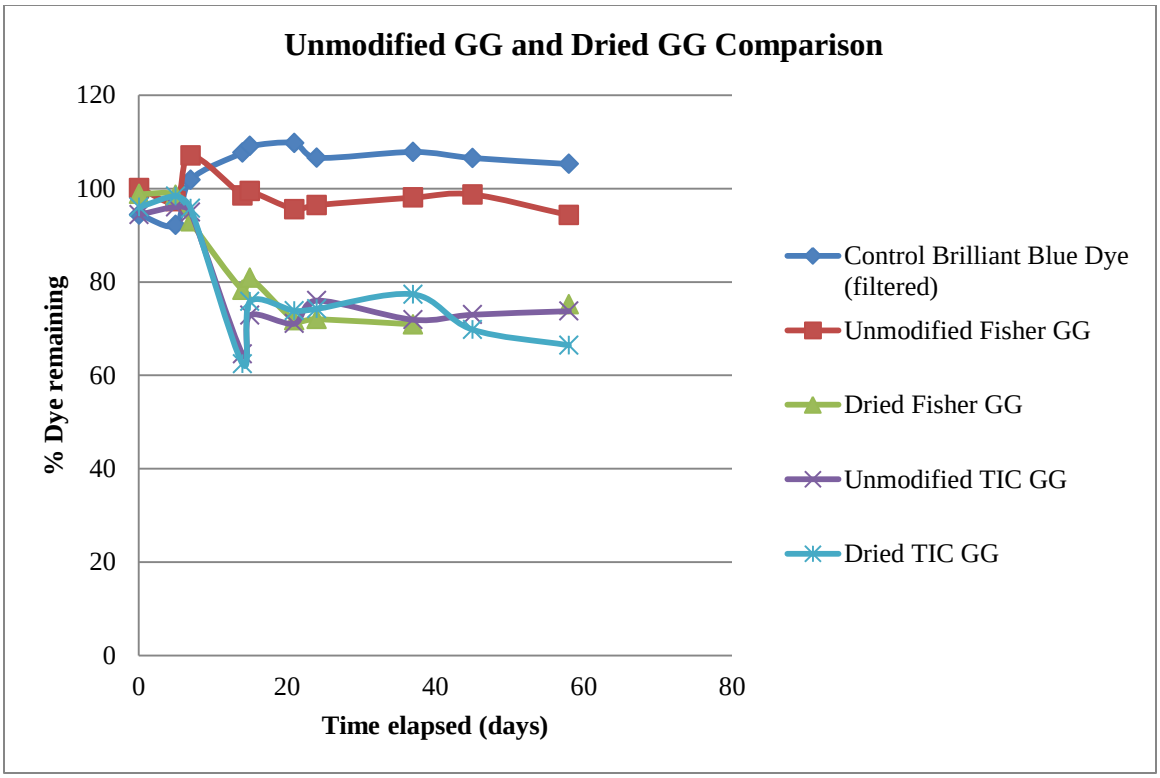



**Figure 32. Brilliant Blue with Unmodified and Dried GG**

Another test was conducted using Fisher GG that had been cleaned with hexane and then dried. Unmodified GG and the cleaned GG were then pre-hydrated for 4 hours and added to a Brilliant Blue mixture. Both products performed similarly, and neither product demonstrated more than 5% removal compared to the dye standard over a 4 day test period. Increasing the pH resulted in substantial improvement, and will be discussed further in the next section.

Furthermore, a pre-hydrated sample of TIC GG was mixed with hexane as a cleaning method, and an initial test comparing the performance over several hours demonstrated that the unmodified GG removed 14% more dye than the cleaned product. This was compared to the same % GG quantity using dry GG, and as shown in the

images of Figure 33, both hydrated GG types adsorbed substantially more dye than the dry powder application.

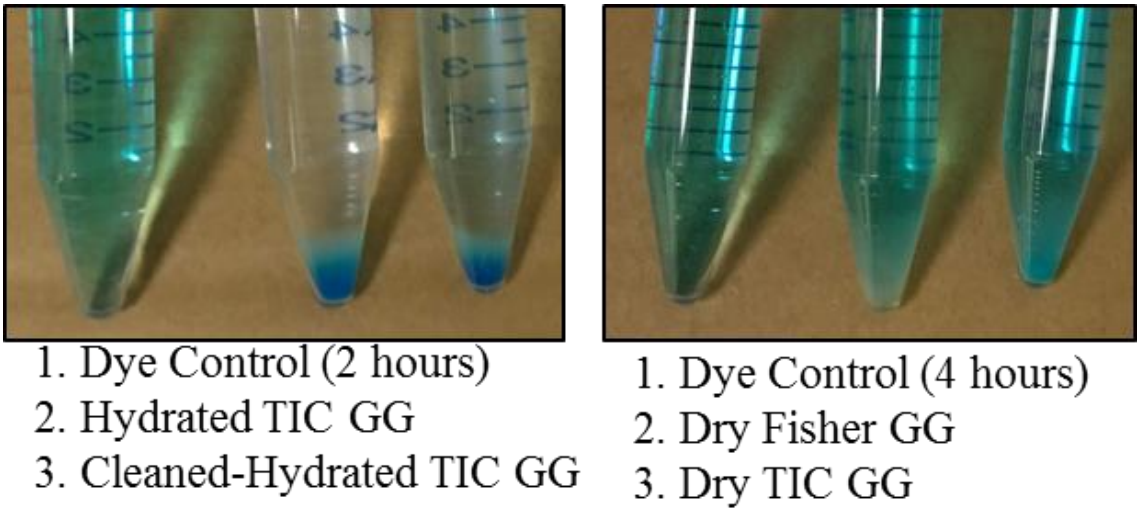



**Figure 33. Comparison of Samples Using Unmodified, Hydrated, and Dried GG Products**

**Brilliant Blue: Hydrated Guar Gum**

As noted in the previous summary of cleaned GG testing, unmodified pre-hydrated GG was more effective than the same % GG quantity using dry GG. Further testing with large batch solutions was conducted; this test evaluated pre-hydrated TIC and Fisher GG's, pre-hydrated TIC that was several days old, pre-hydrated cleaned Fisher GG product (described in previous section), and the impact of pH modification. The percent of dye remaining for each sample is included in Table 12 and Figure 34. Most interestingly, the older TIC GG showed nearly complete dye removal within 2 hours, and the higher pH modification resulted in rapid dye adsorption over the test period. An interesting trend emerged; against an anionic substance, the adsorption was most effective with the older GG typically associated with a lower pH. However, the fresh GG modified to a higher pH steadily decreased to nearly the same level during the test period.

This occurrence may warrant additional research to understand the mechanisms at work, and determine optimum pH conditions.

**Table 12. Brilliant Blue Comparison of Hydrated GG Samples**

| Percent Brilliant Blue (4 ppm) Remaining: 0.5% Hydrated GG | | | | | | | |
|---|---|---|---|---|---|---|---|
| **Time elapsed (hours)** | **Control - Brilliant Blue dye** | **Hydrated TIC GG (>10days)** | **Hydrated TIC GG (4hrs)** | **Hydrated, Regular Fisher GG (4hrs)** | **Hydrated, Cleaned Fisher GG (4hrs)** | **Low pH & Regular Fisher GG (4hrs)** | **High pH & Regular Fisher GG (4hrs)** |
| 2 | 93.9 | < 0 | 95.9 | 108.6 | 109.3 | 100.3 | 95.3 |
| 16 | 97.8 | 5.5 | 98.6 | 106.8 | 109.3 | 102.3 | 77.9 |
| 24 | 96.8 | 2.1 | 105.6 | 109.0 | 109.8 | 105.8 | 75.7 |
| 40 | 91.9 | 4.8 | 87.6 | 93.1 | 106.6 | 97.8 | 44.2 |
| 48 | 97.1 | 4.1 | 101.7 | 93.6 | 109.0 | 104.5 | 34.2 |
| 64 | 97.5 | 5.2 | 98.1 | 106.7 | 103.1 | 108.7 | 23.7 |
| 72 | 98.5 | 6.4 | 97.9 | 110.6 | 97.8 | 107.8 | 19.6 |
| 93 | 98.1 | 13.6 | 87.2 | 103.2 | 103.5 | 102.3 | 13.8 |
| Std Dev: 93hr sample | 0.2 | 0.5 | 0.5 | 0.5 | 0.1 | 0.4 | 0.5 |

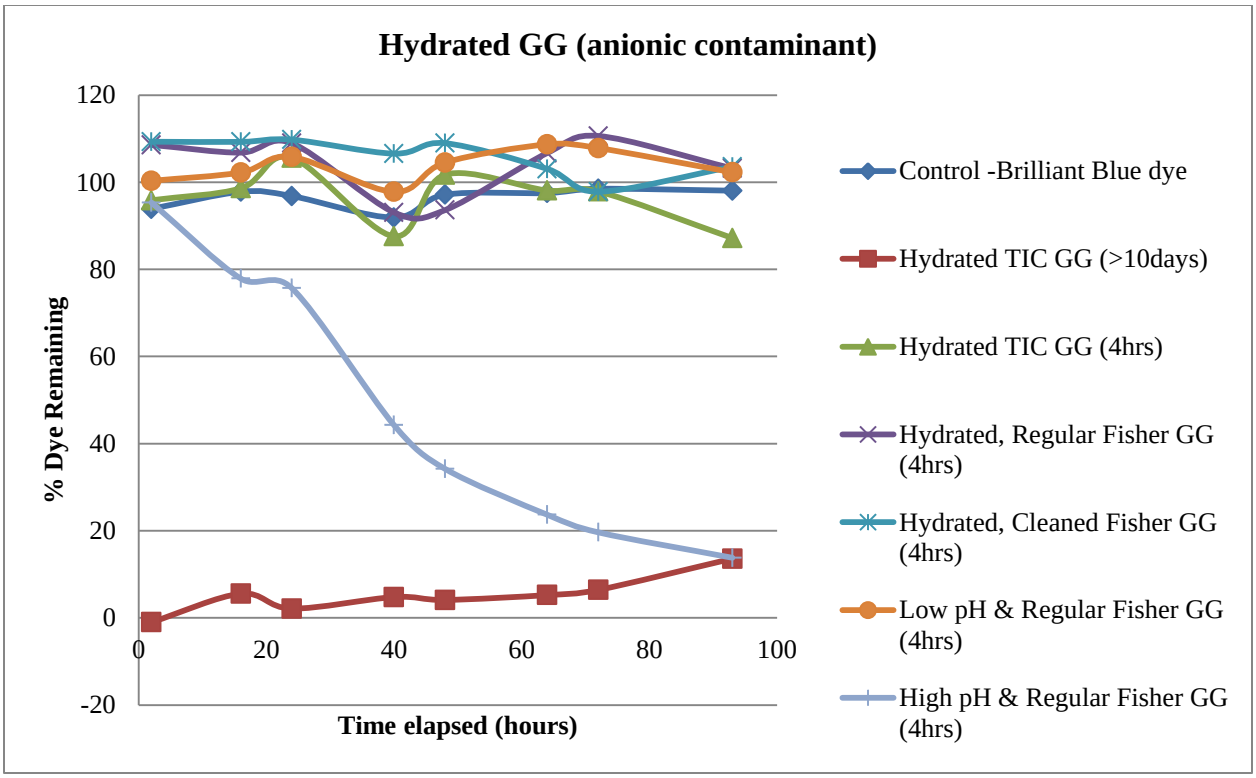
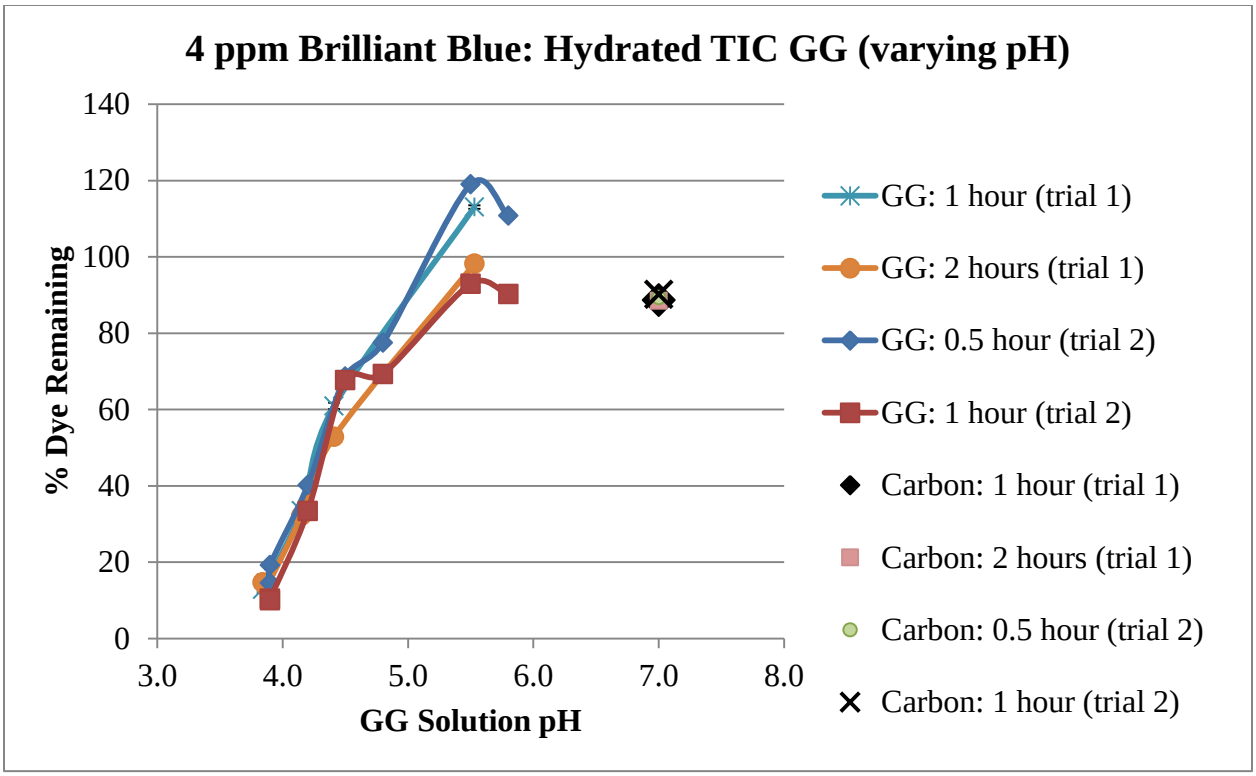



**Figure 34. Brilliant Blue Comparison of Hydrated GG Samples**

Based on the older TIC GG hydrate increased rate of adsorption, this experiment was followed by short term comparisons of GG of varying age and pH values, included in Figure 35 and Figure 36. The TIC brand performed substantially better than the Fisher brand, and adsorption may be correlated to the solution pH. Averaging the 1 hour samples, the 1 day old TIC GG did not remove any dye while the 2 week old sample removed an average of 88%. The fresh Fisher GG also removed no dye, and the 2 week Fisher GG removed an average of 15%. Both outperformed a similar weight of carbon which demonstrated an average 10.6% removal after 1 hour.



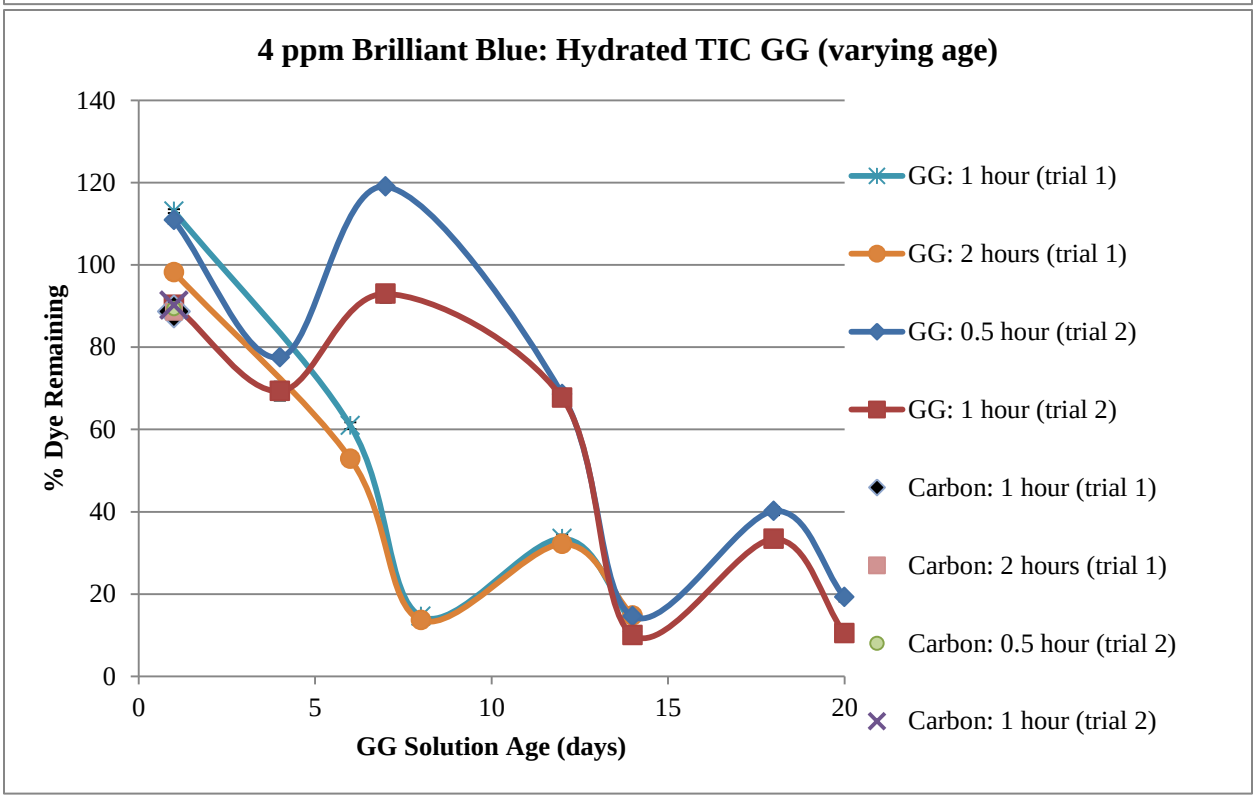
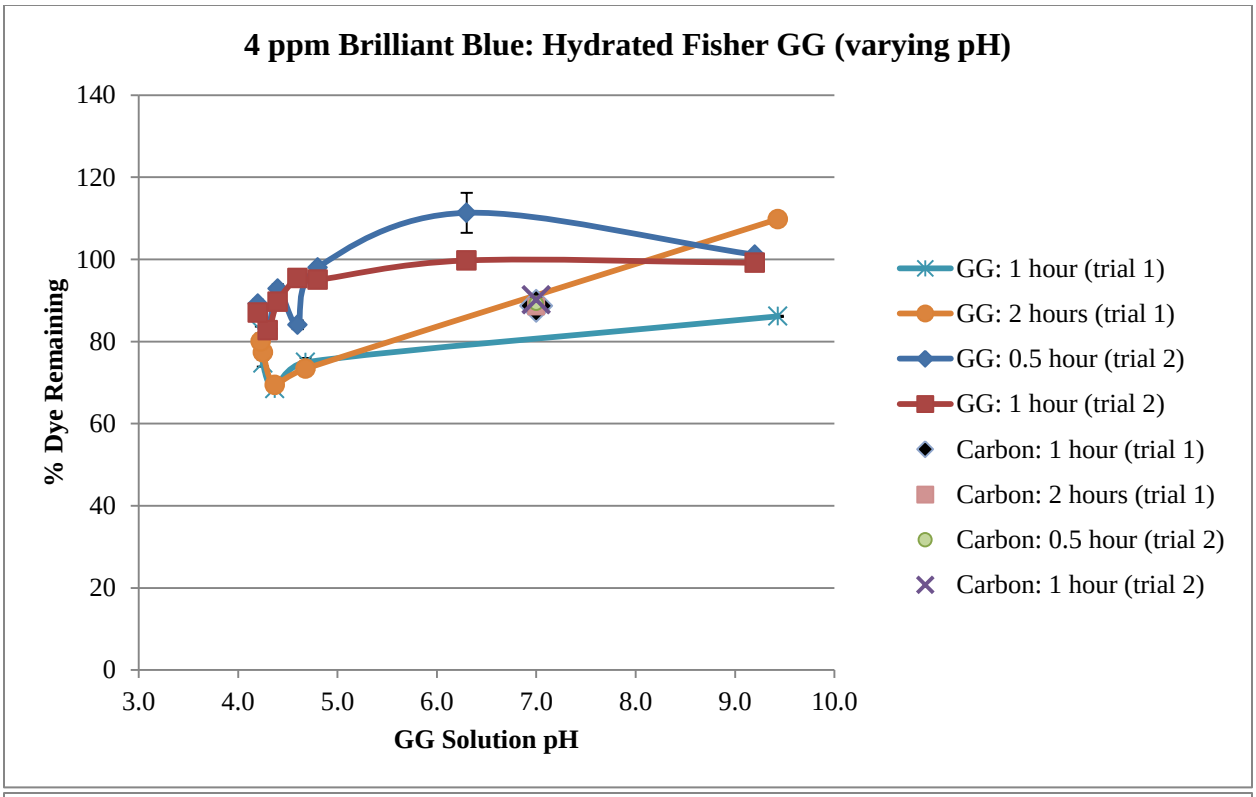




**Figure 35. TIC Adsorption of Brilliant Blue, Comparison of GG Solution pH and Age**



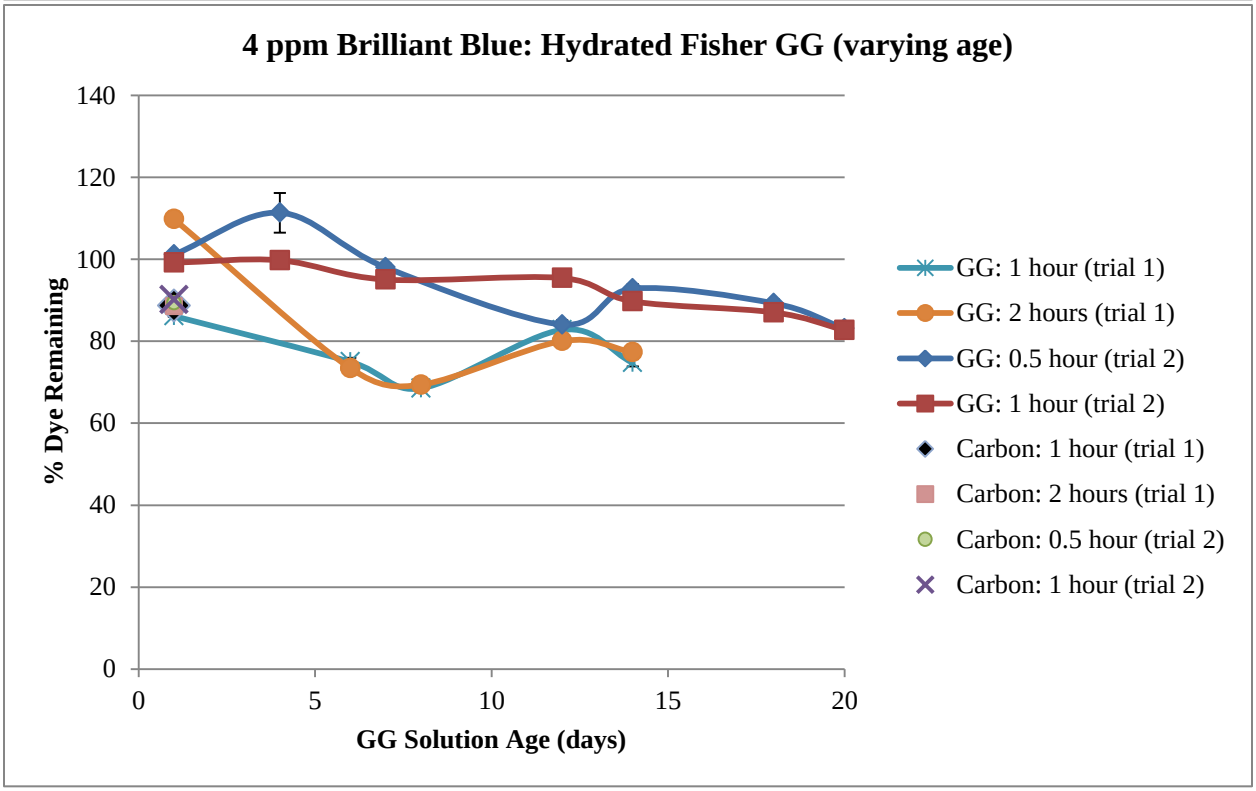




**Figure 36. Fisher Adsorption of Brilliant Blue, Comparison of GG Solution pH and Age**

**Brilliant Blue: Guar Gum with Salting-Out Solution**

GG matrix collapse in dye solution was tested using Brilliant Blue dye. Images of this process are included in Figure 37. While the salt-out collapse was possible using both borax and boric acid, the borax-initiated collapse only removed 11% of the dye and the boric acid-initiated collapse removed 10%. Using a larger percentage of pre-hydrated GG or longer mixing time may enhance this reaction. Further testing which placed the dried collapsed matrix back into a water solution resulted in a change of appearance to a hard rubbery gel and demonstrated desorption of the dye within 24 hours, potentially showing that the dye was not strongly bound within the collapsed gel matrix or the matrix was rapidly decomposing; eventually, the matrix broke down completely.

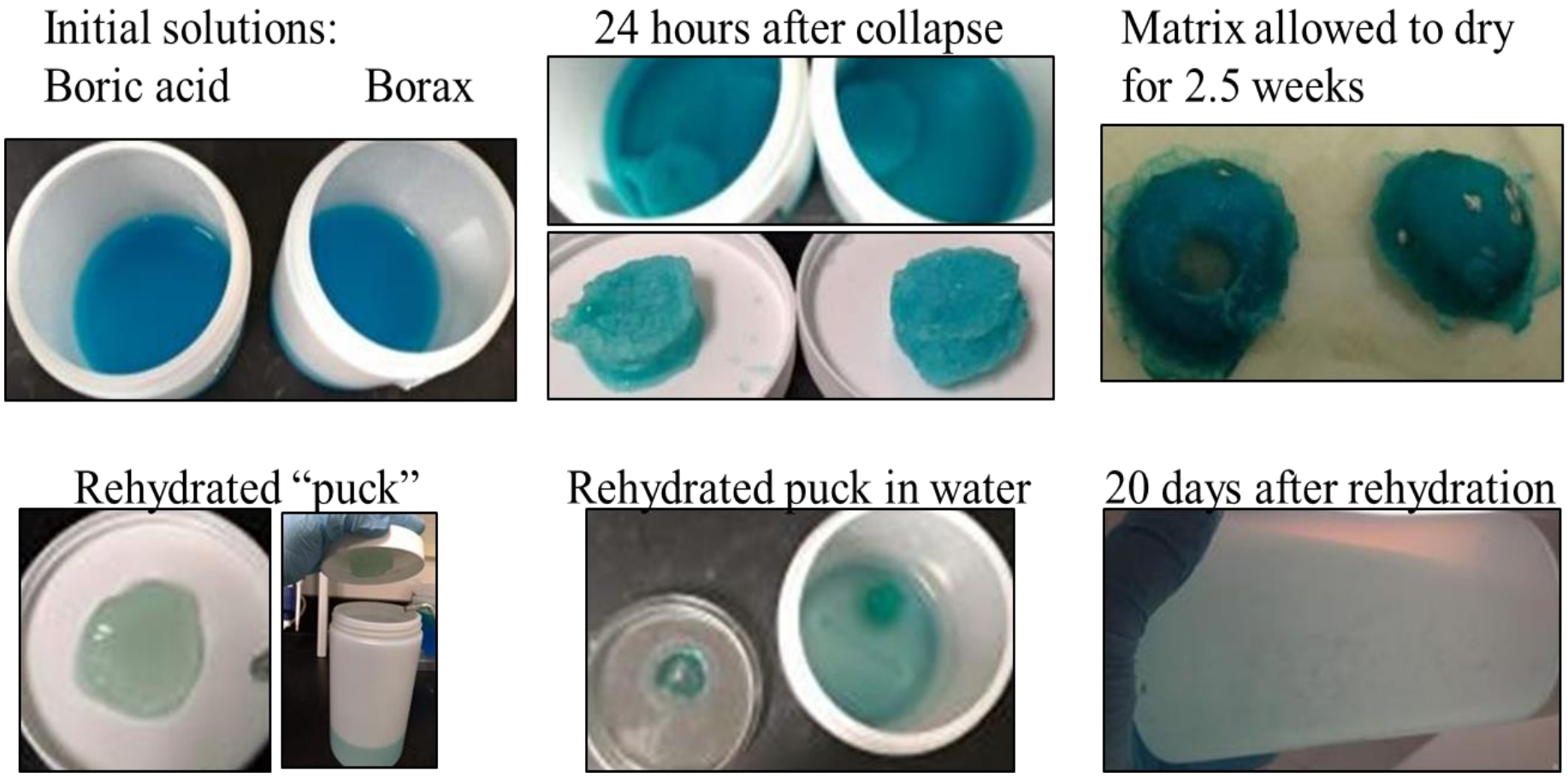



**Figure 37. Brilliant Blue Salt-out Pictures**

## Erythrosine B Results

### Erythrosine B: Unmodified, Dry Guar Gum

One test was conducted using Erythrosine B dye and 0.4% GG (1 gram) of dry unmodified GG placed in a filter bag. This contaminant is unique in that the dye naturally breaks down in UV light. Photodegradation of the dye presented a confounding factor in this experiment, and sample results were standardized using the method listed in Equation 6 rather than using a specific calibration curve.

The initial UV-Vis absorbance ($C_0$) value used the dye control standard measurement from day 3, meaning that any adsorption which occurred prior to day 3 was not accounted for. Table 13 and Figure 38 present the results of this test. Although the dye control standard degraded over time, the sample with GG demonstrated faster dye removal and complete removal by day 9. The sample with the empty bag demonstrated slower adsorption than the other Erythrosine B samples, however, this may be attributed to its location on the tumbler and potential for less impact by direct light.

**Table 13. Erythrosine B Adsorption with Unmodified GG in Filter Bag**

| Percent Erythrosine B (9 ppm) Remaining*: Unmodified GG in Filter Bag | | | |
|---|---|---|---|
| **Time Elapsed (Days)** | **Control - Erythrosine B Dye** | **Filter Bag & 0.4% GG** | **Control – Empty Bag** |
| 3 | 100 | 110.8 | 122.9 |
| 6 | 68.2 | 49.4 | 94.3 |
| 9 | 31.9 | < 0 | 70.4 |
| 12 | 14.2 | < 0 | 54.0 |
| 16 | 6.6 | < 0 | 32.9 |
| 19 | 3.4 | < 0 | 20.6 |

*Note: all samples were normalized using the Day 3 Control Dye UV-Vis absorbance value.

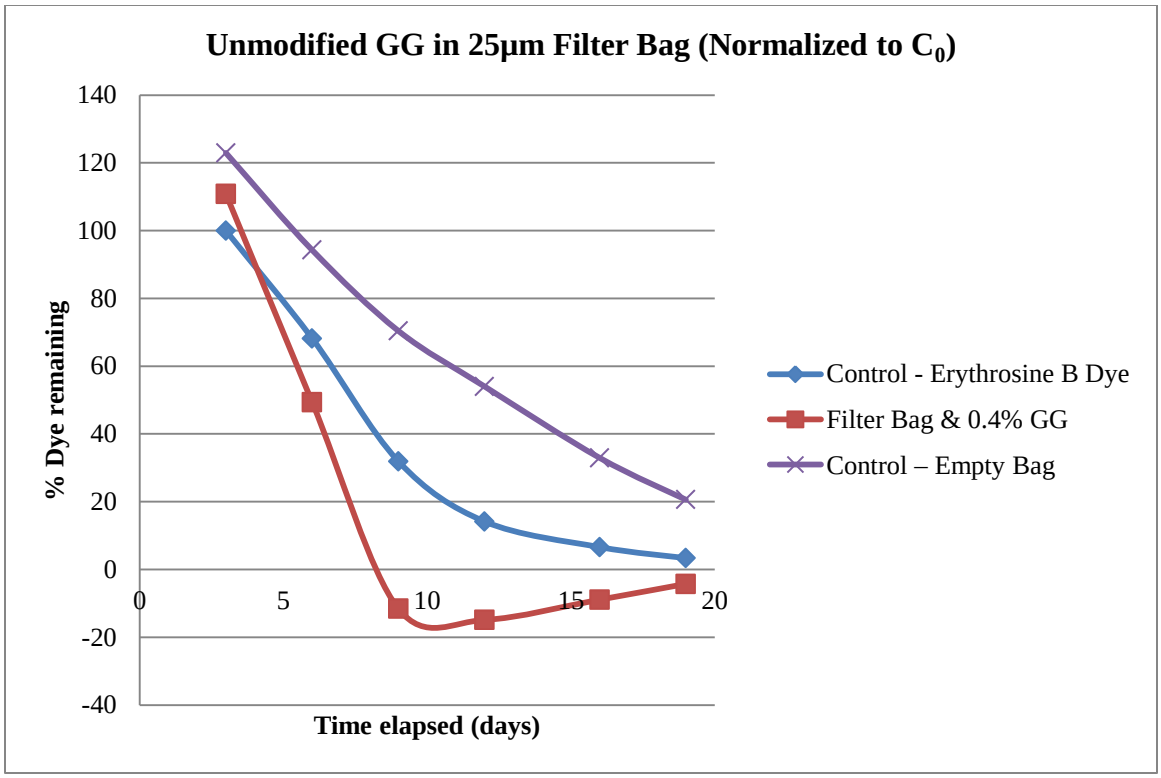



**Figure 38. Erythrosine B Adsorption with Unmodified GG in Filter Bag**

**Erythrosine B: Crosslinked Guar Gum**

Dye was stored in opaque jars for the duration of the test in order to mitigate UV photodegradation described earlier. Varying percentages of GG were crosslinked with borax to form either a small (15mL) or a large (150mL) gel volume. The small volume gel samples were not effective in removing the dye, and showed less than a 5% variation in UV-Vis absorbance compared to the control sample over a 5 month period. Ultimately, the gels that comprised less than 0.0264% or 264 ppm GG in solution were unsuccessful.

However, several samples using a larger volume of crosslinked gels did remove the Erythrosine B dye. Table 14 and Figure 39 demonstrate the results of this test. The highest GG quantity tested (a gel comprised of 1% GG, in solution where GG was

ultimately 0.25%), resulted in an 86% dye decrease by day 27, and substantially better performance than other concentrations after 1 month. A gel comprised of 0.3% GG (ultimately 0.075% GG in solution) was required for any notable change. This experiment did not have paired control samples or control subtraction; it simply compared the UV-Vis absorbance values to the dye control standards, and thus the calibration curve calculation may underestimate total percent removal. Also, it was interesting to note that the sample with the greatest removal of dye also had bacterial growth the same color as the dye used, as shown in Figure 40 and Figure 41.

**Table 14. Erythrosine B Adsorption using Crosslinked GG**

| **Percent Erythrosine B (5.5 ppm) Remaining: Crosslinked increasing % GG Comparison** | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| % GG in Solution | 0% | 0.00002% | 0.0002% | 0.002% | 0.025% | 0.07% | 0.12% | 0.17% | 0.25% |
| **Time elapsed (day)** | **Control - Dye, 100mL water, 50mL Borax** | **Gel 1: 0.001g GG** | **Gel 2: 0.01g GG** | **Gel 3: 0.05g GG** | **Gel 4: 0.1g GG** | **Gel 5: 0.3g GG** | **Gel 6: 0.5g GG** | **Gel 7: 0.7g GG** | **Gel 8: 1.0g GG** |
| 7 | 100.0 | 103.8 | 102.7 | 103.3 | 100.7 | 162.6 | 154.2 | 140.0 | 120.2 |
| 10 | 103.2 | 101.5 | 101.3 | 103.2 | 102.6 | 139.9 | 134.5 | 135.2 | 119.0 |
| 14 | 99.9 | 100.2 | 98.6 | 101.2 | 101.0 | 120.0 | 115.5 | 131.1 | 119.8 |
| 20 | 102.2 | 100.5 | 100.4 | 103.7 | 105.4 | 111.7 | 103.4 | 96.6 | 58.3 |
| 27 | 101.5 | 101.0 | 101.7 | 103.3 | 104.6 | 113.5 | 79.3 | 79.2 | 14.0 |
| 33 | 101.2 | 101.4 | 101.4 | 105.8 | 103.6 | 88.0 | 71.4 | 55.5 | 12.0 |
| 40 | 98.5 | 99.7 | 100.9 | 101.2 | 102.1 | 89.9 | 66.2 | 44.1 | 14.5 |
| 47 | 99.1 | 99.8 | 102.4 | 102.0 | 103.3 | 86.3 | 59.2 | 39.9 | 18.4 |
| 54 | 98.9 | 100.9 | 102.3 | 102.8 | 103.4 | 92.5 | 63.1 | 42.8 | 9.1 |
| 63 | 102.0 | 102.1 | 102.1 | 103.8 | 106.6 | 89.0 | 92.6 | 37.9 | 8.7 |
| 76 | 99.0 | 99.4 | 100.4 | 101.5 | 102.5 | 92.9 | 92.5 | 40.0 | 14.7 |
| 94 | 100.9 | 89.9 | 102.5 | 102.6 | 102.4 | 93.9 | 105.7 | 32.3 | 8.7 |

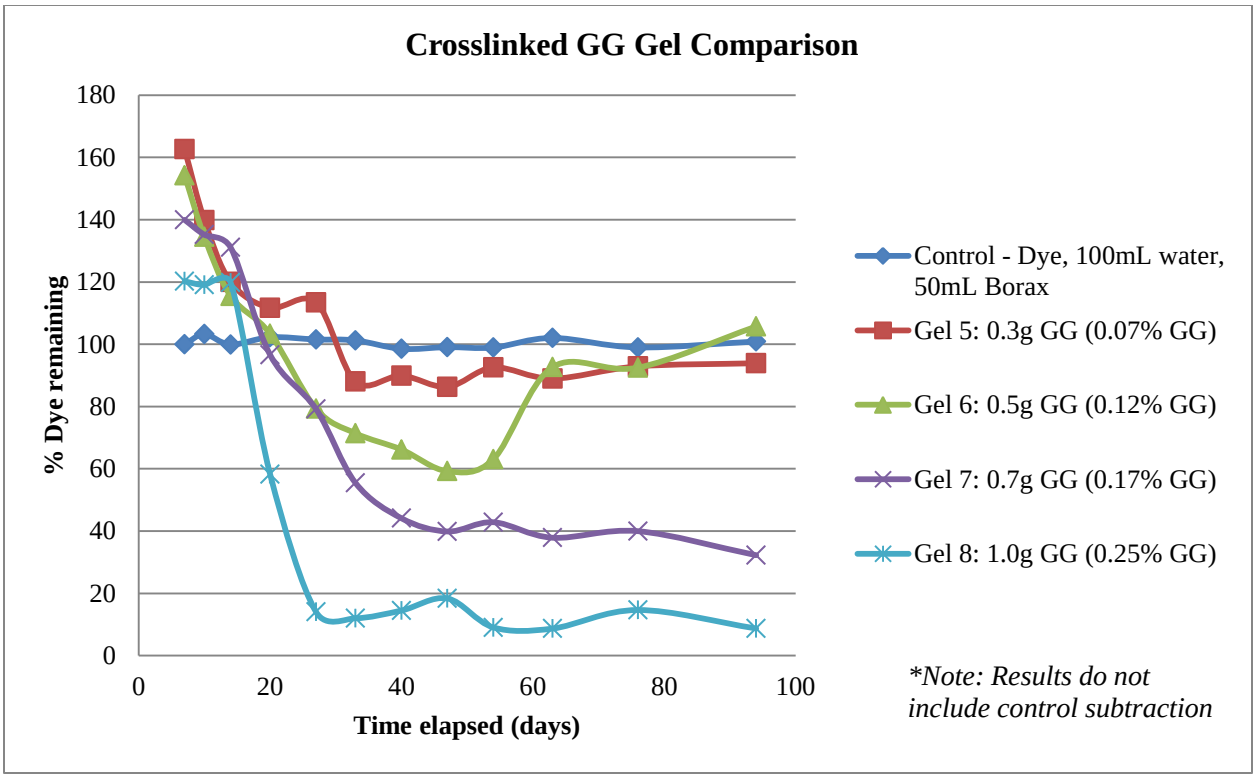



**Figure 39. Erythrosine B Adsorption using Crosslinked GG**

**Figure 40. Photograph of Erythrosine B Samples: Dye Control, and Gels 8, 7, and 6 after 6 months**

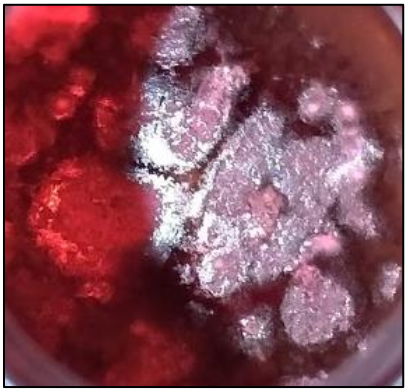


**Figure 41. Photograph of Microbial Growth in Gel 8 Sample Container**

## Fast Green Results

### Fast Green: Unmodified, Dry Guar Gum

One test was conducted using Fast Green dye. This test evaluated the effectiveness of 0.4% GG w/v (1 gram) of dry, unmodified GG placed in a filter bag. Table 15 and Figure 42 present the results of this test. Based on the calibration curve, the percentage of dye remaining decreased to 33.5% on day 12 (indicating 66.5% dye was removed) and then began increasing. Although the sample UV-Vis absorbance increased after that, a filtered sample collected on day 19 indicated that nearly 78% of the dye had been removed. Additionally, the percentage of dye removed by the filter was measured; the paired sample on day 19 demonstrated the filter removed 16% of the dye, however, subsequent samples demonstrated an average removal by the filter of only 7.5%. This variation could be due to filter type or age, and new filters were available after the day 19 sampling occurred.

**Table 15. Fast Green Adsorption with Unmodified GG in Filter Bag**

| Percent Fast Green (4 ppm) Remaining: Unmodified GG in 25µm filter bag | | | | | |
|---|---|---|---|---|---|
| **Time Elapsed (Days)** | **Control - Fast Green Dye** | **Filter Bag & 0.4% GG** | **Filter Bag & 0.4% GG (Filtered)** | **Control – Empty Bag** | **Control – Empty Bag (Filtered)** |
| 3 | 100.6 | 99 | | 107.3 | |
| 6 | 104.6 | 66.5 | | 105.5 | |
| 9 | 103.9 | 11.6 | | 104.6 | |
| 12 | 104.2 | 11.4 | | 102.7 | |
| 16 | 103.4 | 33 | | 102.8 | |
| 19 | 102.5 | 36.8 | 22.3 | 100.9 | 83.4 |

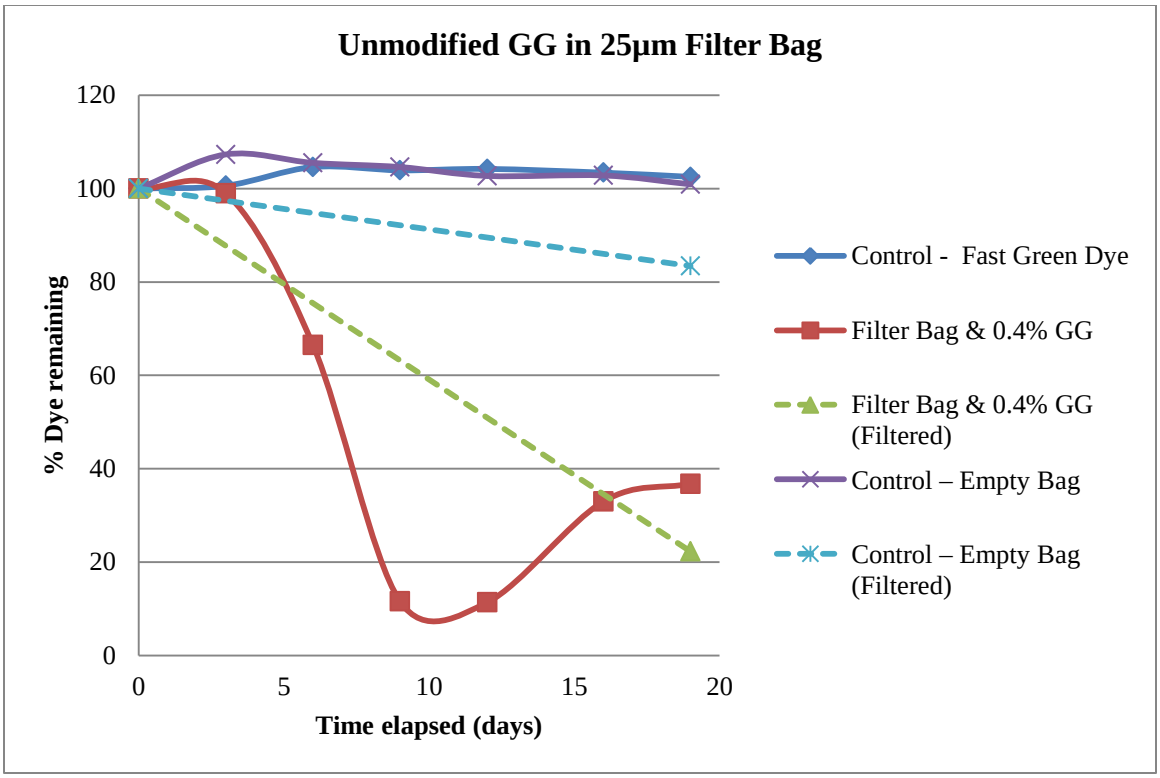



**Figure 42. Fast Green Adsorption with Unmodified GG in Filter Bag**

## Tartrazine Results

### Tartrazine: Unmodified, Dry Guar Gum

Tartrazine is unique in that the dye has 2 characteristic peaks, at 427nm and 258nm, which demonstrate approximately the same UV-Vis absorbance values. The interference from the GG baseline shift is less pronounced at the higher wavelengths, and syringe filters are also much more effective for removing the interference at higher wavelengths. Despite the challenges associated with interpreting adsorption at the lower wavelengths, the results are included for completeness and transparency of analysis. Preliminary testing indicated that at the higher wavelength, 0.4% GG w/v (1 gram) of dispersed GG removed 80% of the dye, and GG in a cotton filter bag removed 98% of the

dye within 3 weeks; analysis of the lower wavelength indicated 68% removal from the dispersed GG and 42% removal with GG in a filter bag. Based on these results, an experiment was conducted using 25µm filter bags, and the use of a syringe filter. Parameters tested included both brands of GG, impact of mixing, heat, and percentage of GG in solution. Testing spanned a month-long period, and samples appeared to reach equilibrium within 2 weeks.

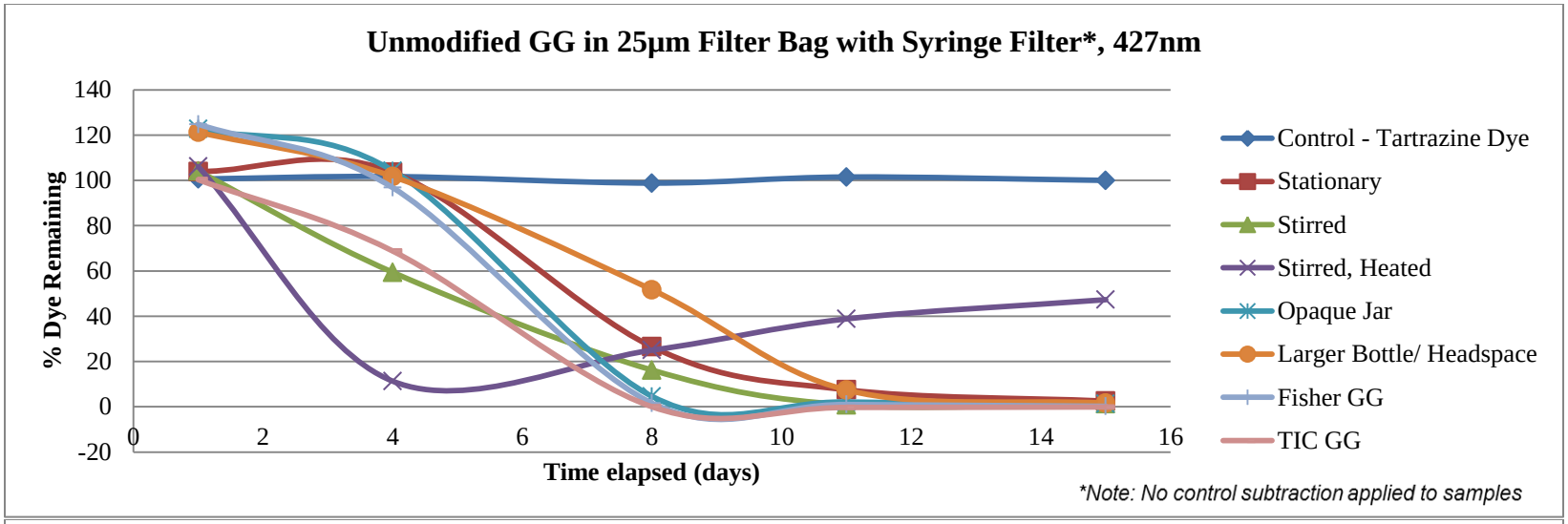
At the higher wavelength, the stirred and heated sample displayed the most rapid adsorption, however, its UV-Vis absorbance increased after 8 days, possibly due to degradation of the GG. The stationary sample and sample with larger headspace showed slower adsorption than other samples. Interestingly, a 1% GG w/v application seemed optimum, and more GG did not correlate to more or faster dye removal. This could be due to pH changes caused by GG, increased hydration time, or kinetic impacts less space and flow through the filter bag. Additionally, the TIC GG performed better than the same quantity of Fischer GG until day 8 when both appeared to reach equilibrium. Data are summarized in Table 16, Table 17, and Figure 43.

**Table 16. Tartrazine Adsorption with Unmodified GG in Filter Bag and Syringe Filter (based on 427nm UV-Vis peak)**

| **Percent Tartrazine (5 ppm, 427nm) Remaining: Unmodified GG in 25µm filter bag**<br>*Note: No control subtraction applied to samples | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| % GG/Brand of GG | | 0.5% Fisher GG | 0.5% Fisher GG | 0.5% Fisher GG | 0.5% Fisher GG | 0.5% Fisher GG | 0.5% Fisher GG | 0.5% TIC GG |
| **Time Elapsed (days)** | **Control - Tartrazine Dye** | **Stationary** | **Stirred** | **Stirred, heated** | **Opaque Jar** | **Larger bottle/ headspace** | **Fisher GG** | **TIC GG** |
| 1 | 100.6 | 103.9 | 104.1 | 106.1 | 122.8 | 121.3 | 124.8 | 100.3 |
| 4 | 101.7 | 103.6 | 59.4 | 11.3 | 104.3 | 101.7 | 96.8 | 68.8 |
| 8 | 98.8 | 26.5 | 16.2 | 25 | 4.6 | 51.7 | 1.6 | 0 |
| 11 | 101.5 | 7.5 | 0.8 | 38.8 | 2.1 | 7.4 | 1 | < 0 |
| 15 | 100 | 2.5 | 1.3 | 47.3 | 1.3 | 1.6 | 0.2 | < 0 |

**Table 17. Tartrazine Adsorption with Varying Percentages of Unmodified GG in Filter Bag and Syringe Filter (based on 427nm UV-Vis peak)**

| **Percent Tartrazine (5 ppm, 427nm) Remaining: Unmodified GG in 25µm filter bag** | | | | | | |
|---|---|---|---|---|---|---|
| **Time Elapsed (days)** | **0.5% TIC GG** | **0.5% Fisher GG** | **1% Fisher GG** | **1.5% Fisher GG** | **2% Fisher GG** | **3% Fisher GG** |
| 1 | 87.8 | 84 | 47.6 | 116.2 | 69.8 | 57 |
| 4 | 55.4 | 82.4 | 25.7 | 41 | 55.4 | 77 |
| 8 | < 0 | < 0 | < 0 | < 0 | < 0 | < 0 |
| 11 | < 0 | < 0 | < 0 | < 0 | < 0 | < 0 |
| 15 | < 0 | < 0 | < 0 | < 0 | < 0 | < 0 |



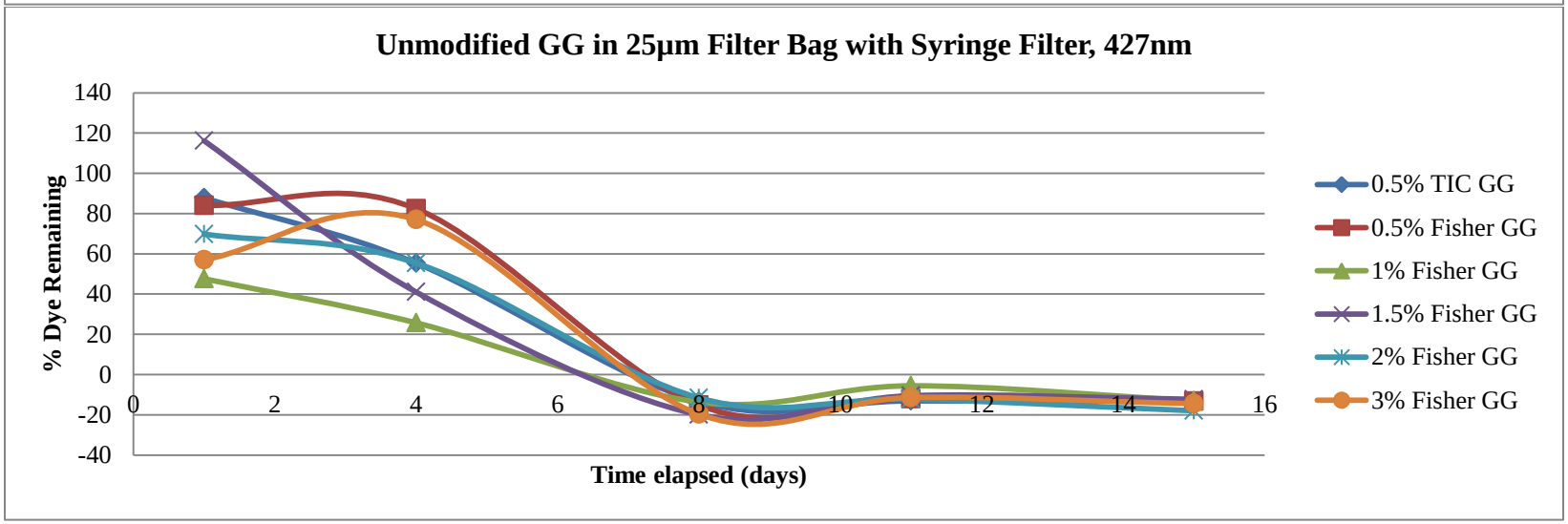




**Figure 43. Tartrazine Adsorption with Unmodified GG in Filter Bag (based on 427nm UV-Vis peak)**

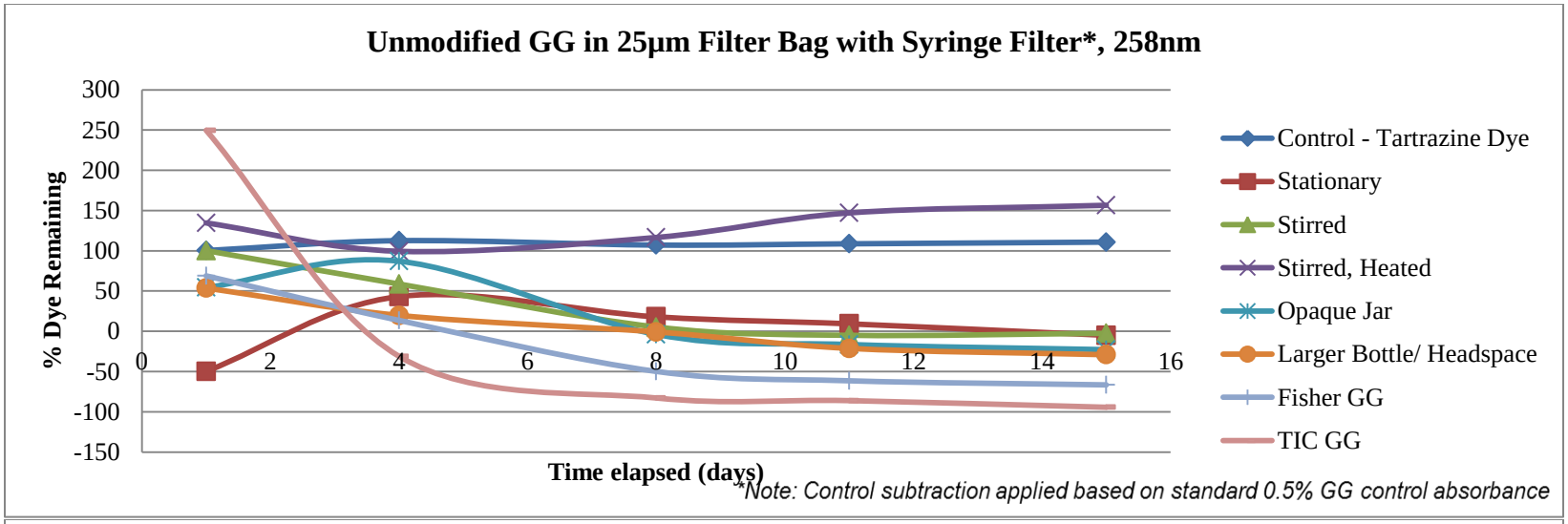
At the lower wavelength, the TIC brand GG was most effective. It was the only sample with a lower UV-Vis absorbance than dye control at this wavelength (before control subtraction occurred); however, Fischer GG is more effective after day 8 due to the higher absorbance value of the control samples when using the control subtraction method. The heated sample had the highest absorbance at this wavelength, and was relatively stable through the test duration. Additionally, it was observed that more GG resulted in higher UV-Vis absorbance values. Analysis was challenging at this wavelength since not all samples were associated with a paired control sample. A filter mitigated the issue at the higher wavelength, however, the native GG spectrum peak at the lower wavelength presented a confounding factor. Samples used the generic 0.5% GG control for control subtraction at this wavelength. This may not be perfectly representative of the samples that were stirred, stationary, heated, or placed in a different container type. With this limitation in mind, all samples, except for the heated sample demonstrated an UV-Vis absorbance lower than the GG/water control by day 8 indicating complete dye removal. Results are summarized in Table 18, Table 19, and Figure 44.

**Table 18. Tartrazine Adsorption with Unmodified GG in Filter Bag and Syringe Filter (based on 258nm UV-Vis peak)**

| **Percent Tartrazine (5 ppm, 258nm) Remaining: Unmodified GG in 25µm filter bag**<br>*Note: Control subtraction applied based on standard 0.5% GG control UV-Vis absorbance | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| % GG/Brand of GG | | 0.5% Fisher GG | 0.5% Fisher GG | 0.5% Fisher GG | 0.5% Fisher GG | 0.5% Fisher GG | 0.5% Fisher GG | 0.5% TIC GG |
| **Time Elapsed (days)** | **Control - Tartrazine Dye** | **Stationary** | **Stirred** | **Stirred, heated** | **Opaque Jar** | **Larger bottle/ headspace** | **Fisher GG** | **TIC GG** |
| 1 | 100.3 | < 0 | 100.3 | 134.6 | 54.4 | 53.8 | 68.9 | 249.7 |
| 4 | 112.6 | 43.2 | 58.7 | 99.4 | 87.1 | 19.8 | 13.6 | < 0 |
| 8 | 107.1 | 18.0 | 5.3 | 116.6 | < 0 | < 0 | < 0 | < 0 |
| 11 | 108.7 | 9.3 | < 0 | 147.1 | < 0 | < 0 | < 0 | < 0 |
| 15 | 110.8 | < 0 | < 0 | 156.6 | < 0 | < 0 | < 0 | < 0 |

**Table 19. Tartrazine Adsorption with Varying Percentages of Unmodified GG in Filter Bag and Syringe Filter (based on 258nm UV-Vis peak)**

| **Percent Tartrazine (5 ppm, 258nm) Remaining: Unmodified GG in 25µm filter bag** | | | | | | |
|---|---|---|---|---|---|---|
| **Time Elapsed (days)** | **0.5% TIC GG** | **0.5% Fisher GG** | **1% Fisher GG** | **1.5% Fisher GG** | **2% Fisher GG** | **3% Fisher GG** |
| 1 | 46.2 | 68.9 | 34.7 | 91.4 | 29.8 | 29.7 |
| 4 | 9.1 | 13.6 | 43.4 | 89.2 | 16.7 | 203 |
| 8 | < 0 | < 0 | 52.7 | < 0 | 18.7 | 107.6 |
| 11 | < 0 | < 0 | 117 | < 0 | 36.4 | 95.3 |
| 15 | < 0 | < 0 | 134.2 | < 0 | 24 | 94.3 |



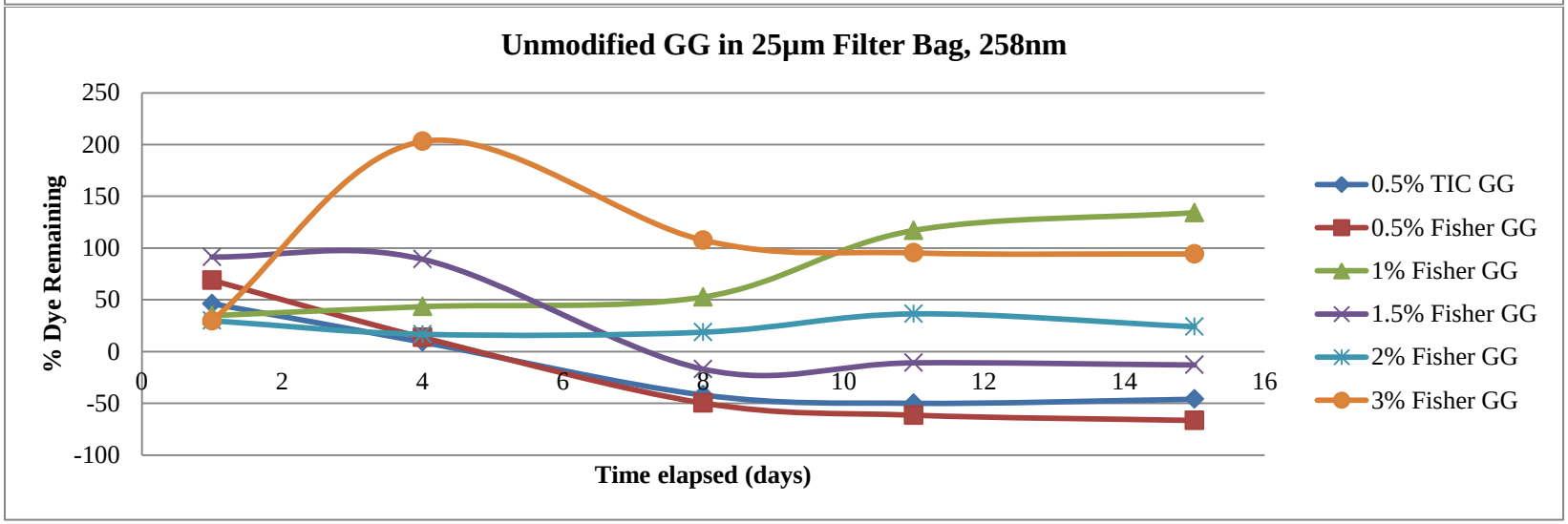




**Figure 44. Tartrazine Adsorption with Unmodified GG in Filter Bag (based on 258nm UV-Vis peak)**

**Tartrazine: Crosslinked Guar Gum**

Preliminary tests attempted to crosslink GG onto glass pellets, evaluate pre-hydrating GG in borax, as well as assess placing the GG in bags to pre-hydrate in borax, or to place GG in bags to pre-hydrate in water and dip in borax. At the higher Tartrazine wavelength, these treatments did not outperform the results noted for unmodified GG, and in fact the crosslinking on beads only removed 30% compared to 80% removal using unmodified and uncontained GG. At the lower wavelength, the modified samples behaved similarly to the unmodified GG versions.

**Tartrazine: Guar Gum with Salting-Out Solution**

Two tests based on the salification effect were conducted for Tartrazine. The first test used a low quantity of GG, the percentage of 0.025%, and no matrix collapse occurred. The subsequent test using 0.5% GG did enable the matrix collapse to occur. Results comparing the performance of boric acid, concentrated borax powder, diluted 0.02M borax, and unmodified GG at the higher and lower wavelengths are summarized in Table 20. For this contaminant, unmodified GG may have been more effective than a salt-out solution. Water control scans did show that the boric acid collapse decreased some of the GG baseline shift typically present above 500nm; however, other GG spectrum anomalies were still present, indicating not all GG was removed from the modified solutions.

**Table 20. Tartrazine Adsorption Using Salt-Out Solution**

| Percent Tartrazine (5 ppm) Remaining: 0.4% GG; Salt-out | | | | |
|---|---|---|---|---|
| **427nm (Filtered)** | **Boric Acid, GG, Salt** | **Borax powder (concentrated), GG, Salt** | **0.02M Borax solution (diluted), GG, Salt** | **GG, salt (no borate ions)** |
| 24 hours post-collapse; normalized% compared to dye control standard | 84.7 | 90.9 | 108.7 | 84.3 |
| 4 days post collapse; normalized% compared to dye control standard | 87.3 | 87.0 | 86.6 | 77.3 |
| **Percent Tartrazine (5 ppm) Remaining: 0.4% GG; Salt-out** | | | | |
| **258nm (Filtered)** | **Boric Acid, GG, Salt** | **Borax powder (concentrated), GG, Salt** | **0.02M Borax solution (diluted), GG, Salt** | **GG, salt (no borate ions)** |
| 24 hours post-collapse; normalized% compared to dye control standard | 63.9 | 71.4 | 75.2 | 66.9 |
| 4 days post collapse; normalized% compared to dye control standard | 59.6 | 65.4 | 61.6 | 46.6 |

## Methylene Blue Results

### Methylene Blue: Cleaned or Dried Guar Gum

A test was conducted using Fisher GG that had been cleaned with hexane and then dried. Unmodified GG and the cleaned GG were pre-hydrated for 4 hours and added to a Methylene Blue mixture. Both Fisher GG products performed similarly, outperforming the unmodified TIC brand gum and demonstrating over 90% removal over a 4 day test period. Increasing the pH resulted in significant improvement for the TIC GG, and will be discussed further in the next section. Additionally, it was determined

that syringe filters removed nearly all the Methylene Blue dye, and centrifuging samples proved most effective in limiting UV interference caused by dissolved GG.

**Methylene Blue: Hydrated Guar Gum**

Batch tests were conducted to compare various pre-hydrated GG products This test evaluated pre-hydrated TIC and Fisher GGs, pre-hydrated TIC that was several days old, pre-hydrated/cleaned Fisher GG product (described in previous section), and the impact of pH modification. The percent of dye remaining for each sample is included in Table 21 and Figure 45. Most interestingly, the older TIC GG showed nearly no color removal during the duration of the test, and the TIC GG that had been hydrating for 4 hours demonstrated nearly 20% removal within 2 hours, while the sample modified to a higher pH resulted in over 80% removal within 2 hours. This indicates that pH may have a dominant role in driving the adsorption processes.

**Table 21. Methylene Blue Comparison of Hydrated GG Samples**

| Percent Methylene Blue (2 ppm) Remaining: 0.5% Hydrated GG | | | | | | | |
|---|---|---|---|---|---|---|---|
| **Time elapsed (hours)** | **Control - Methylene Blue Dye** | **Hydrated TIC GG (>10 days)** | **Hydrated TIC GG (4hrs)** | **Hydrated, Regular Fisher GG (4hrs)** | **Hydrated, Cleaned Fisher GG (4hrs)** | **Low pH & Hydrated TIC GG (4hrs)** | **High pH & Hydrated TIC GG (4hrs)** |
| 2 | 96.5 | 99.2 | 80.9 | 40.6 | 38.8 | 101.0 | 19.5 |
| 16 | 101.2 | 102.7 | 83.1 | 41.1 | 47.1 | 103.3 | 23.0 |
| 24 | 98.1 | 98.9 | 83.4 | 42.3 | 52.3 | 101.6 | 24.1 |
| 40 | 96.0 | 101.3 | 50.1 | 30.6 | 51.0 | 84.2 | 3.9 |
| 48 | 97.4 | 102.0 | 39.7 | 31.4 | 44.0 | 78.2 | < 0 |
| 64 | 98.8 | 101.3 | 46.2 | 43.8 | 45.2 | 69.4 | < 0 |
| 72 | 101.3 | 107.8 | 36.7 | 39.9 | 43.1 | 65.4 | < 0 |
| 93 | 95.5 | 91.9 | 38.2 | 9.1 | 7.5 | 75.4 | < 0 |
| Std Dev: 93hr sample | 0.4 | 0.7 | 0.6 | 0.5 | 0.8 | 0.8 | 0.6 |

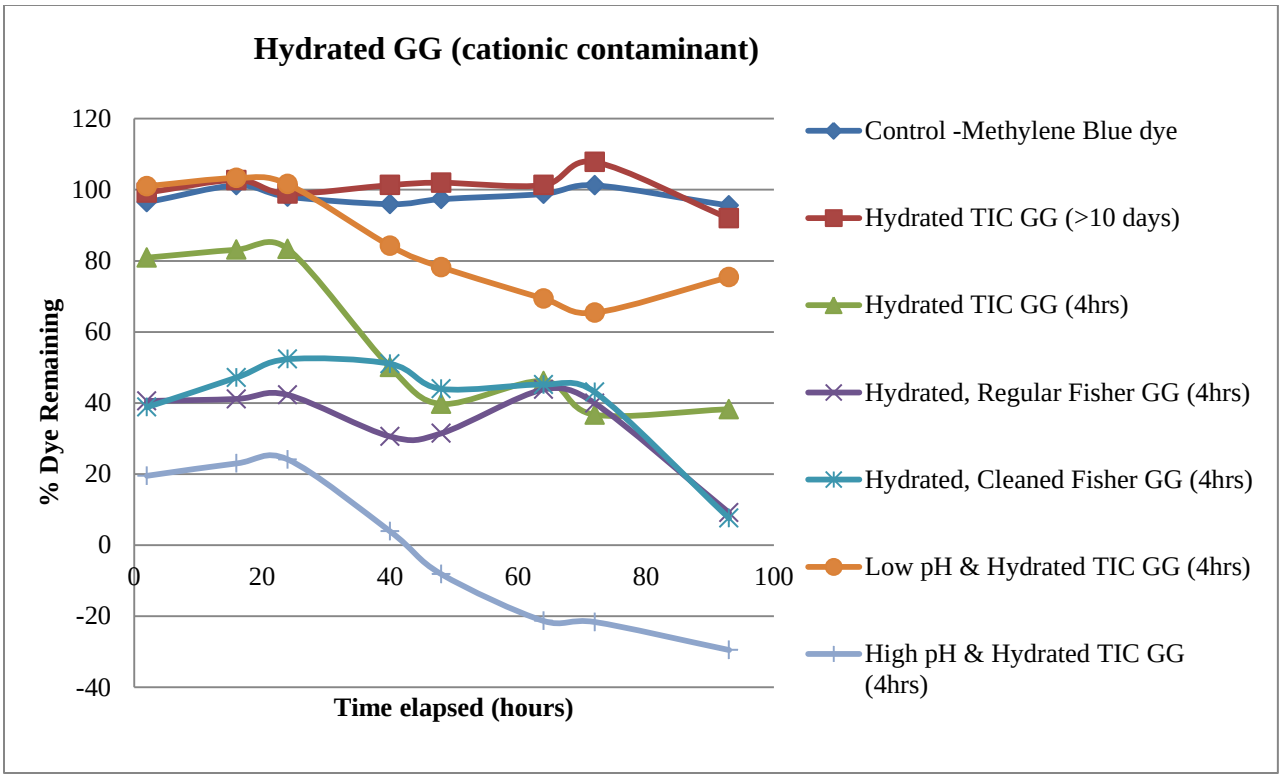



**Figure 45. Methylene Blue Comparison of Hydrated GG Samples**

Based on the wide variability noted between GG solutions of different ages, this experiment was followed by short term comparisons of GG solutions of varying age and pH values, included in Figure 46 and Figure 47. As a cationic dye, the results for Methylene Blue were contrary to those identified for the anionic Brilliant Blue and Allura Red dyes. The youngest Fisher brand GG solution, associated with the highest pH, performed better than the other samples. Within 2 hours, the 1 day old TIC GG did not remove any dye while the 2 week old sample removed 32%. The fresh Fisher GG removed 38%, and the 2 week old Fisher GG removed 13%. However, a similar weight of carbon surpassed the GG samples and demonstrated an average 45% removal after 2 hours.

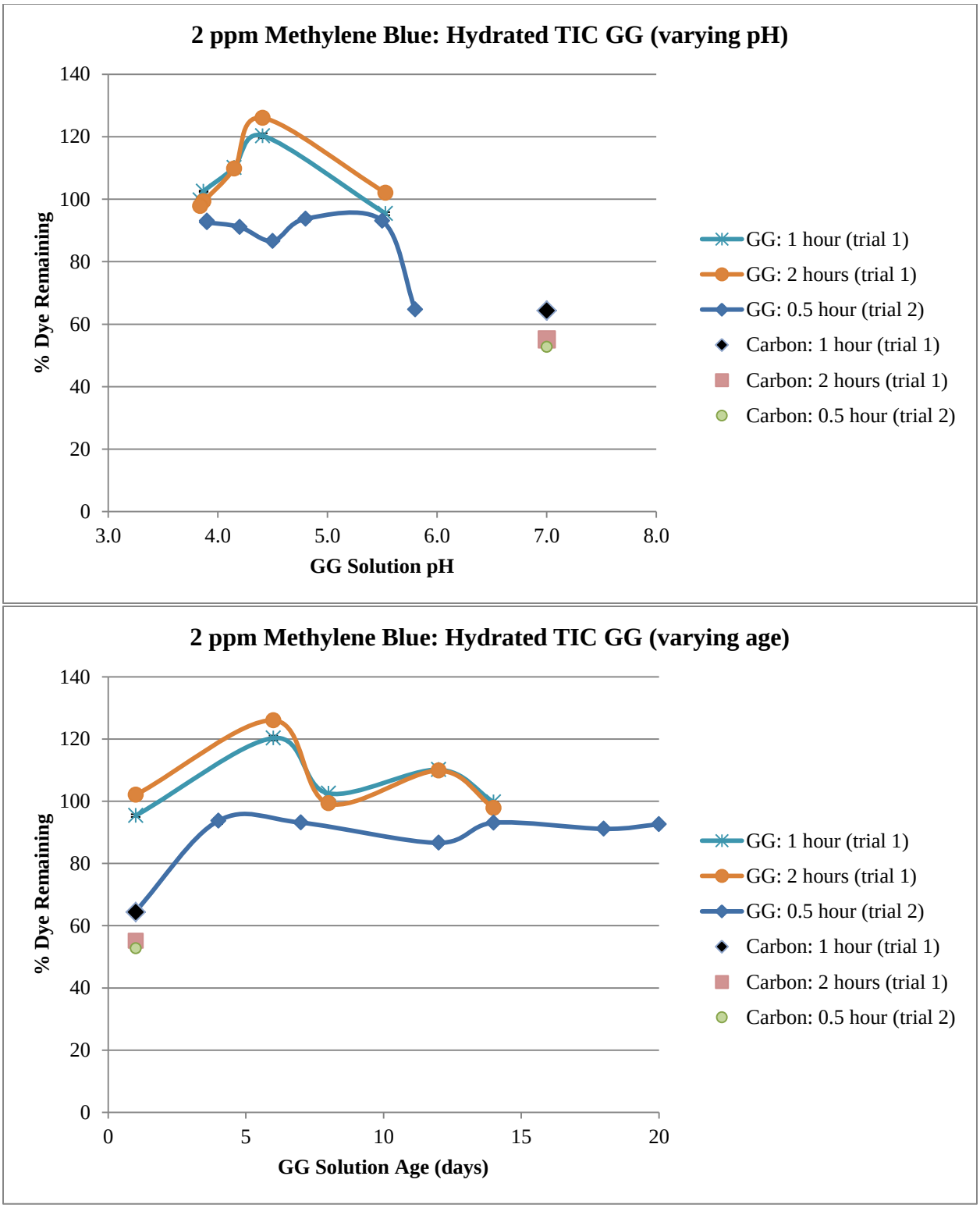
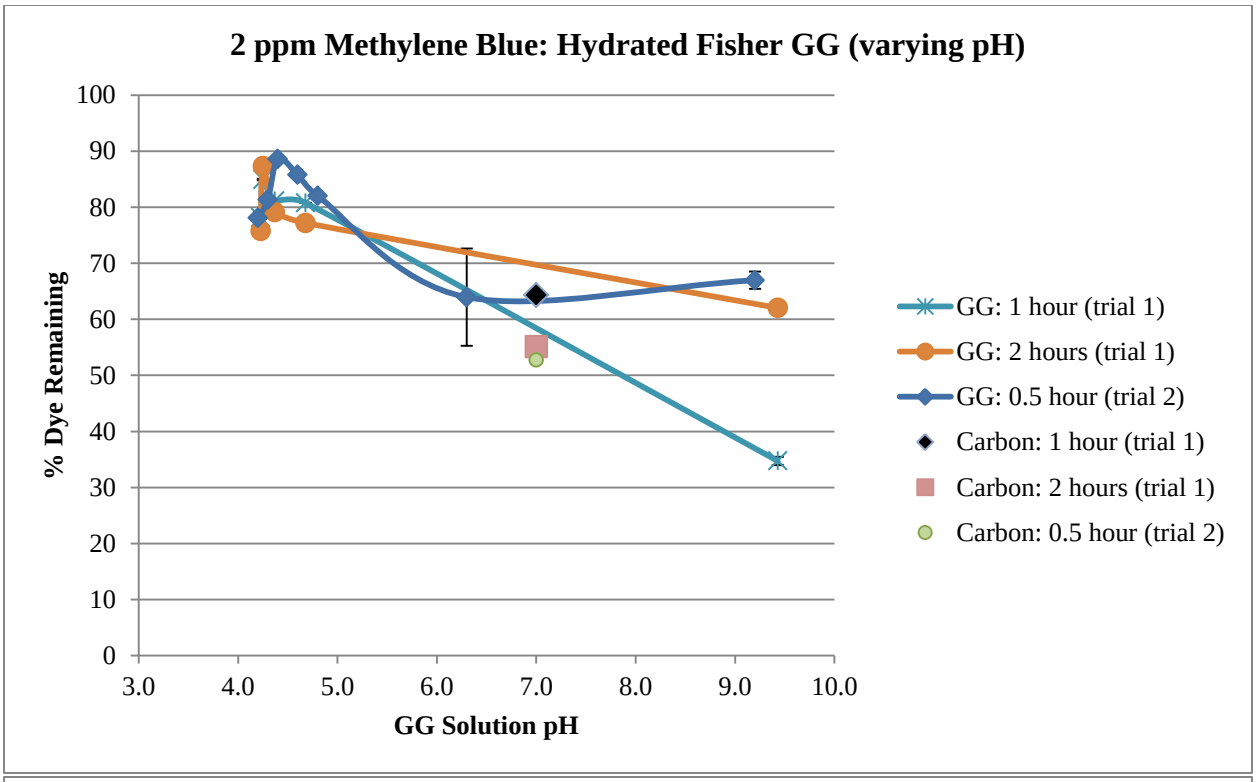



**Figure 46. TIC Adsorption of Methylene Blue, Comparison of GG Solution pH and Age**



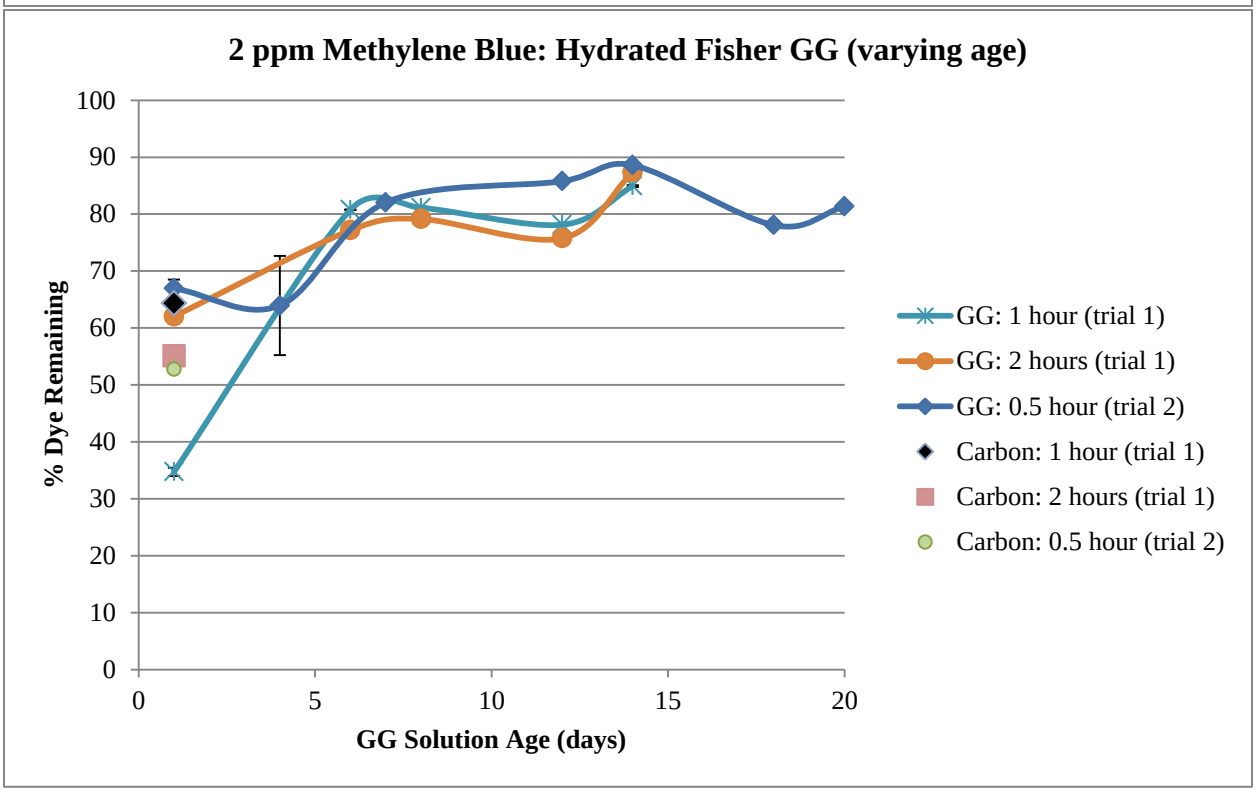




**Figure 47. Fisher Adsorption of Methylene Blue, Comparison of GG Solution pH and Age**

## 2,4-Dinitrotoluene Results

DNT was challenging to analyze since the syringe filter removes a majority of the contaminant, and its characteristic peak is located at a low wavelength, meaning it can be impacted by the GG baseline interference.

### DNT: Unmodified, Dry Guar Gum

Preliminary evaluations of 0.4% GG in filter bags appeared to remove over 80% of the DNT within 2 weeks. This was further explored, and dry unmodified samples of 0.5% GG, were placed in filter bags. Table 22, Table 23, and Figure 48 demonstrate the results of this test. Interestingly, the sample with the lower quantity of GG performed better, and had completely removed 10 ppm of DNT by day 15. Additionally, the percentage of DNT removed by the filter bag was less than 5% on average. Another test conducted using a very low quantity of GG, 0.01%, was not effective in removing DNT, and no samples demonstrated 10% removal or better over a 2 month period.

**Table 22. DNT Adsorption with Unmodified GG in Filter Bag**

| Percent DNT (10 ppm) Remaining: Unmodified GG in 25µm filter bag | | | | |
|---|---|---|---|---|
| **Time Elapsed (days)** | **Control - DNT Standard** | **Control - DNT, empty bag** | **0.5%GG (1.25g) Filter bag** | **0.75% GG (1.9g) Filter bag** |
| 0.2 | 96.0 | 92.1 | 72.0 | 80.3 |
| 1 | 95.3 | 87.7 | 124.7 | 87.8 |
| 3 | 92.8 | 87.8 | 44.9 | 52.3 |
| 6 | 98.1 | 90.4 | 1.7 | 25.7 |
| 8 | 95.3 | 88.1 | 13.4 | 37.1 |
| 13 | 96.2 | 89.5 | 3.0 | 46.6 |
| 15 | 94.5 | 88.5 | < 0 | 35.8 |
| 17 | 99.6 | 92.3 | < 0 | 33.3 |

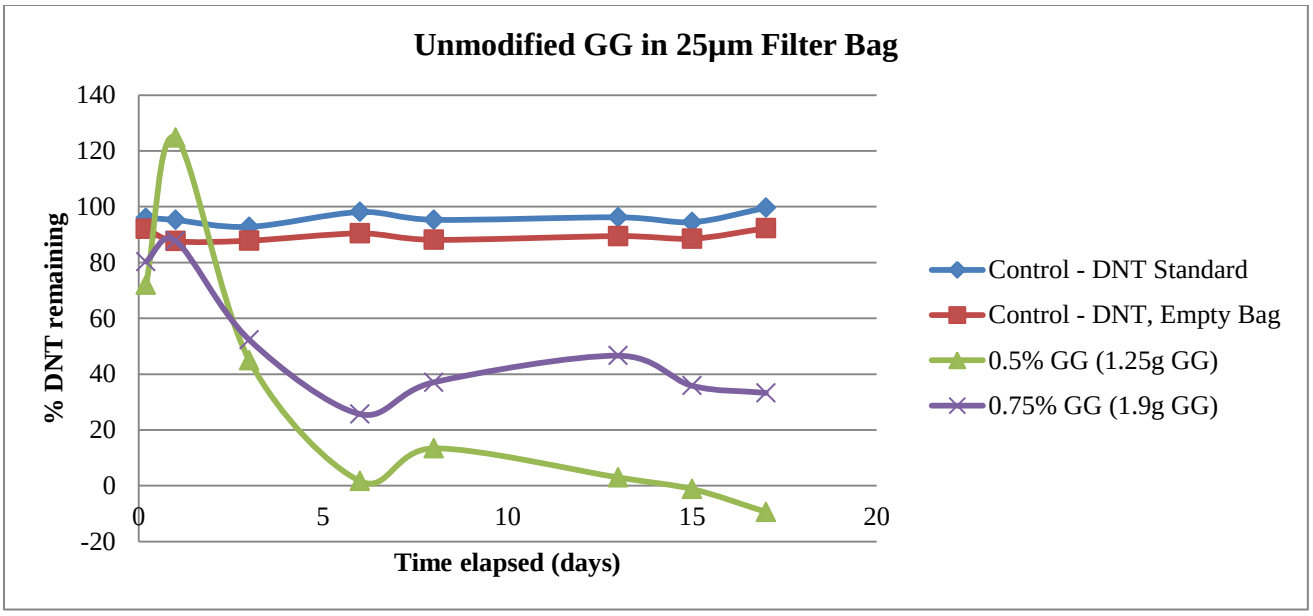



**Figure 48. DNT Adsorption with Unmodified GG in Filter Bag**

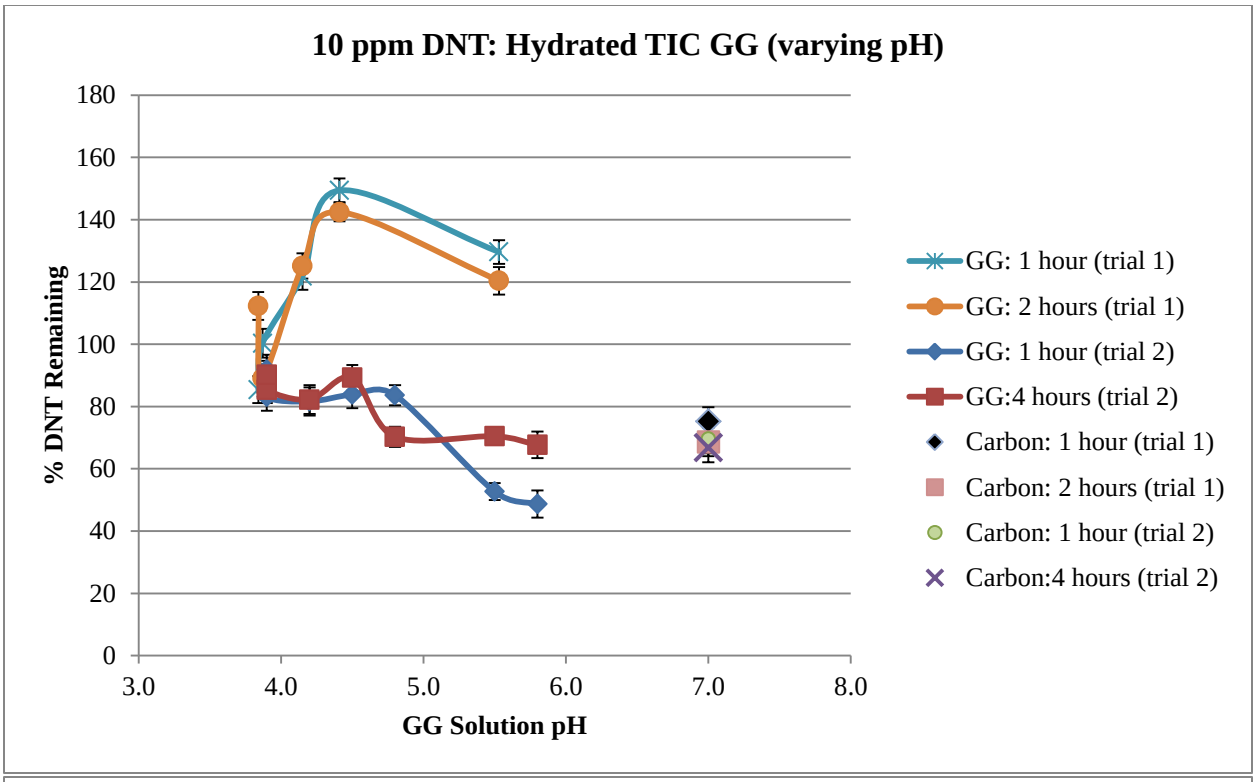
**Table 23. pH Measurements of GG and DNT Samples**

| pH Measurements of DNT and Unmodified GG Samples in Filter Bags | | | | | | |
|---|---|---|---|---|---|---|
| **Time elapsed (days)** | **Control - DNT standard** | **Control – DNT, empty bag** | **Control – 0.5% GG (1.25g), water** | **Control – 0.75% GG(1.9g), water** | **0.5% GG* (1.25g), DNT** | **0.75% GG* (1.9g), DNT** |
| 6 | 6.7 | 6.2 | 4.4 | 4.3 | 4.5 | 4.3 |
| 8 | 7.1 | 7.2 | 4.5 | 4.3 | 4.6 | 4.2 |
| 13 | 7.5 | 7.1 | 4.4 | 4.2 | 4.3 | 4.3 |
| 15 | 7.0 | 6.8 | 4.5 | 4.4 | 4.5 | 4.4 |
| 17 | 7.0 | 6.7 | 4.5 | 4.4 | 4.5 | 4.3 |
| Average Std Dev* | 0.93 | 0.33 | 0.01 | 0.01 | 0.01 | 0.01 |

*Average Standard Deviation is based on replicate pH readings collected each sampling event.

### DNT: Hydrated Guar Gum

Short term comparisons of GG of varying age and pH values are included in Figure 49 and Figure 50. Results varied throughout this test and no clear trend based on GG brand, pH, or age was apparent. Carbon outperformed a majority of the GG samples; however, there were a few individual GG samples that demonstrated better adsorption than the same weight of carbon.



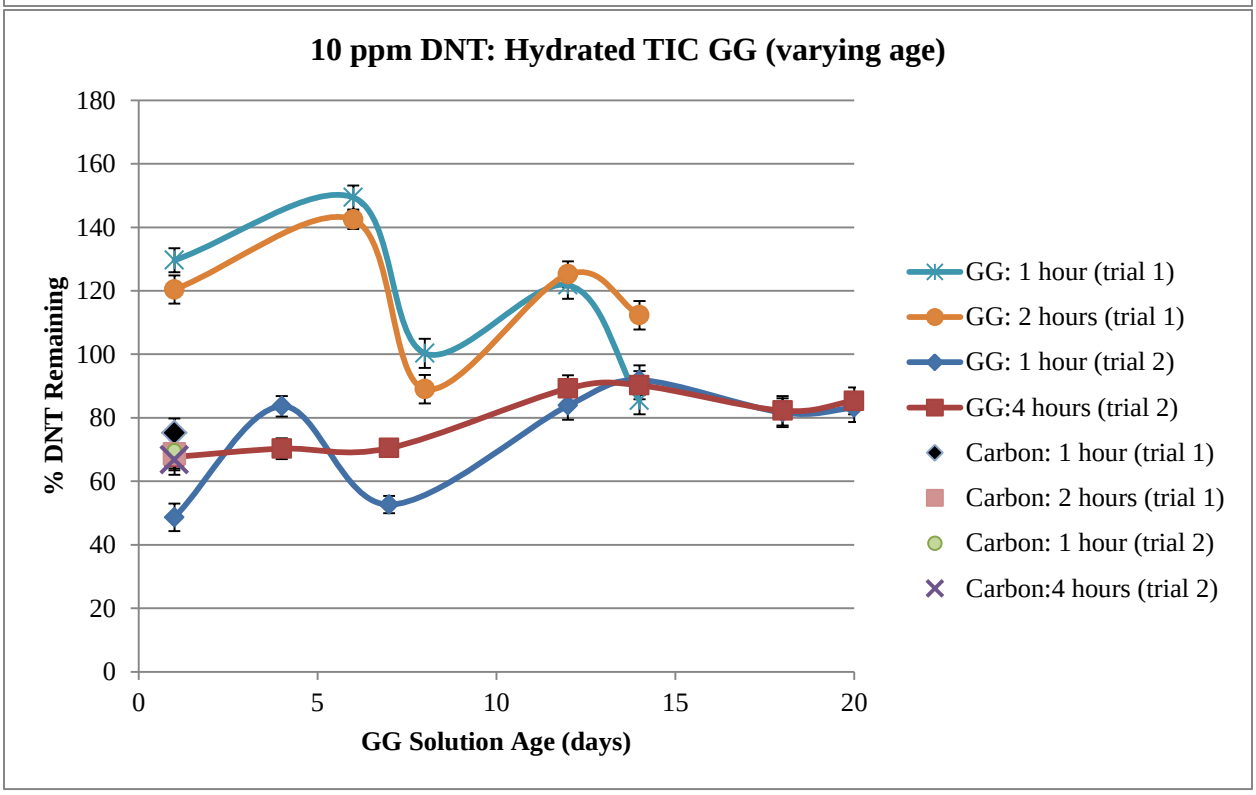
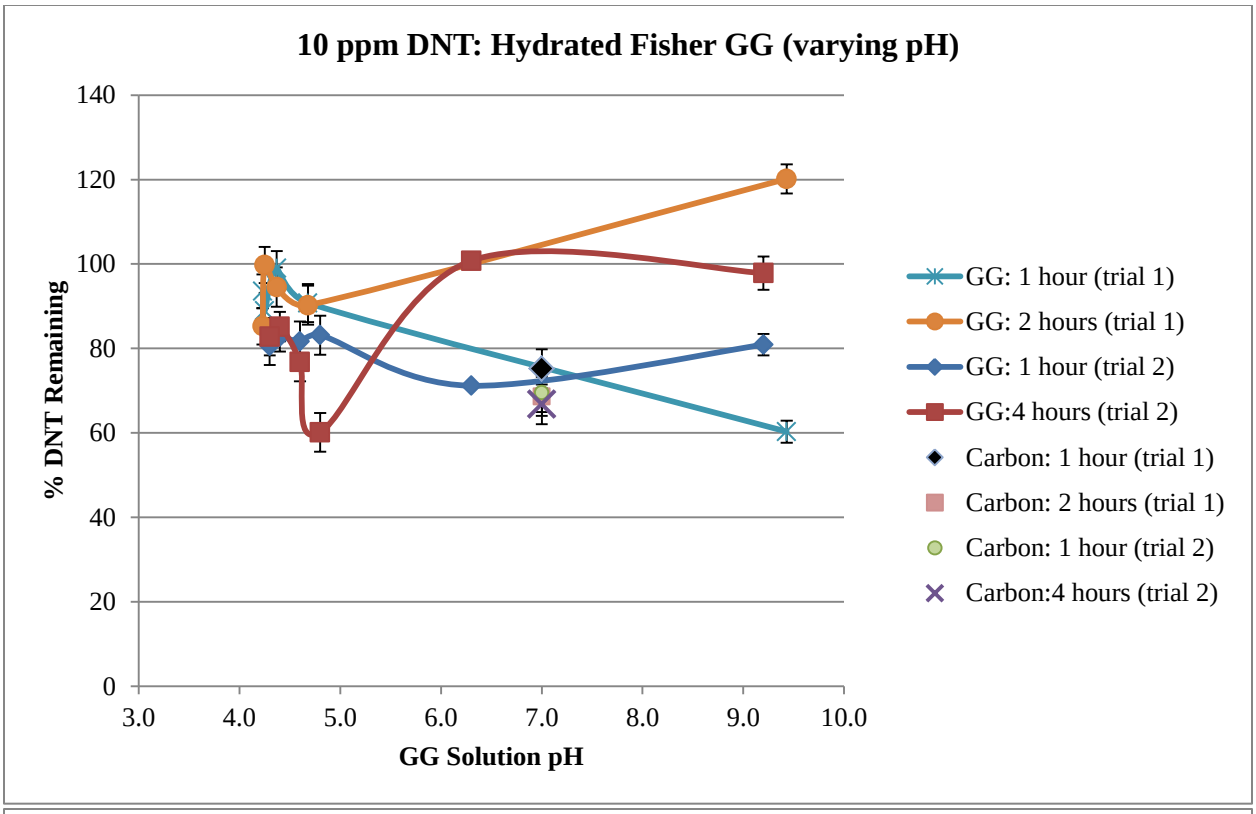




**Figure 49. TIC Adsorption of DNT, Comparison of GG Solution pH and Age**



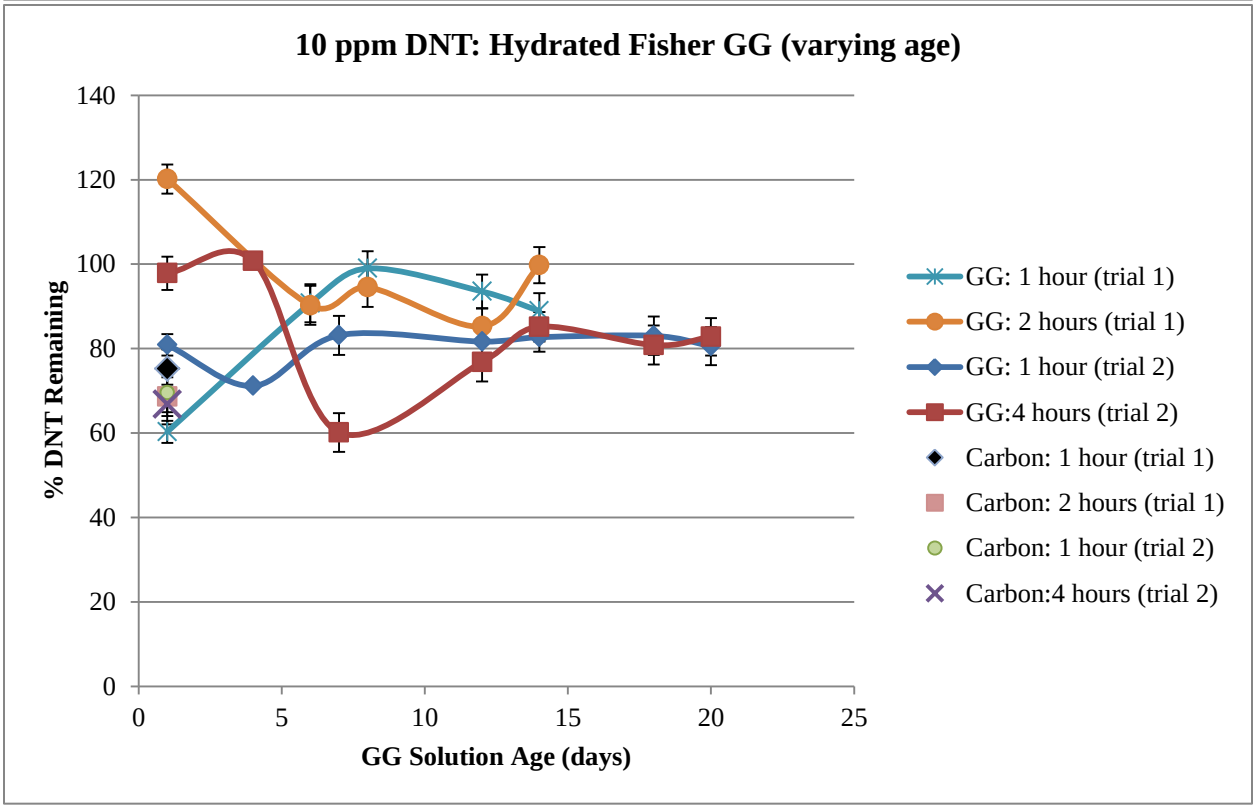




**Figure 50. Fisher Adsorption of DNT, Comparison of GG Solution pH and Age**

## Toluene Results

### Toluene: Unmodified, Dry Guar Gum

Toluene proved challenging to work with as over 50% of the toluene volatilized within 6 hours. Additionally, syringe filters removed a majority of the toluene, and it was noted during one experiment, that the centrifuged samples demonstrated an average 20% lower UV-Vis absorbance when compared to a non-centrifuged sample after the same period of time, likely due to further volatilization. Furthermore, the characteristic peak of 10 ppm of toluene is fairly small, and is located at a lower wavelength, meaning that the baseline interference caused by GG was substantial. The GG baseline UV-Vis absorbance at this wavelength was between 4 and 12 times the size of the toluene peak size. Using the calibration curve analysis, small changes in absorbance would appear as large "%remaining" changes. To mitigate these problems, samples were normalized based on their original UV-Vis absorbance, at $C_0$.

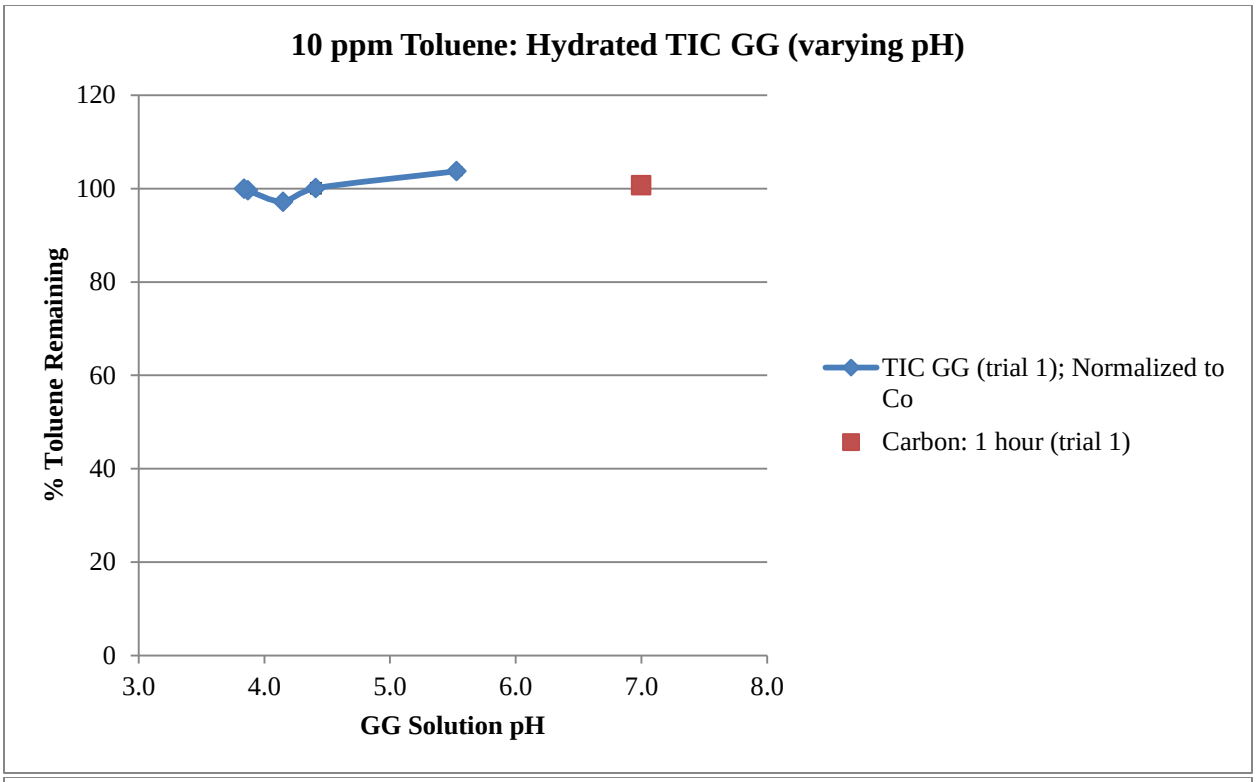
Two experiments using 0.5% dry GG powder with 10 ppm toluene were conducted. In both tests, the toluene control sample degraded faster than the sample with GG.

### Toluene: Hydrated Guar Gum

Short term comparisons of GG of varying age and pH values, were compared for effectiveness with toluene at 10 ppm and 50 ppm. The pH did not appear to have a strong correlation to adsorption, and no clear trend was apparent. As discussed in the previous section, toluene has a very low UV-Vis absorbance compared to dissolved GG, and samples were normalized based on their initial concentration, $C_0$. The first test evaluated adsorption of 10 ppm toluene between a 1 and 2 hour period. Between 1 and 2 hours, the

toluene control sample decreased 0.6%, the TIC GG showed no removal, and the Fisher GG showed an average 2.6% removal. However, one sample, the 1 day old Fisher GG showed 12% removal of the toluene. This was compared to the same weight of carbon, which also demonstrated no removal of toluene during the sample period.

Additional tests used a higher concentration, 50 ppm toluene, and longer sample time for clarity in the analysis. The normalized results compared the adsorption that potentially occurred between 1 and 4 hours and are summarized in Figure 51 through Figure 54. The distribution curves of both GG brands have a similar shape, but at different pH profiles. Based on this analysis, 23% of the toluene in the control sample volatilized during the test period; only one GG sample demonstrated more advanced removal, the 4 day old Fisher GG, which demonstrated 32% removal. Additionally, carbon performed best, and removed 44% between 1 and 4 hours.



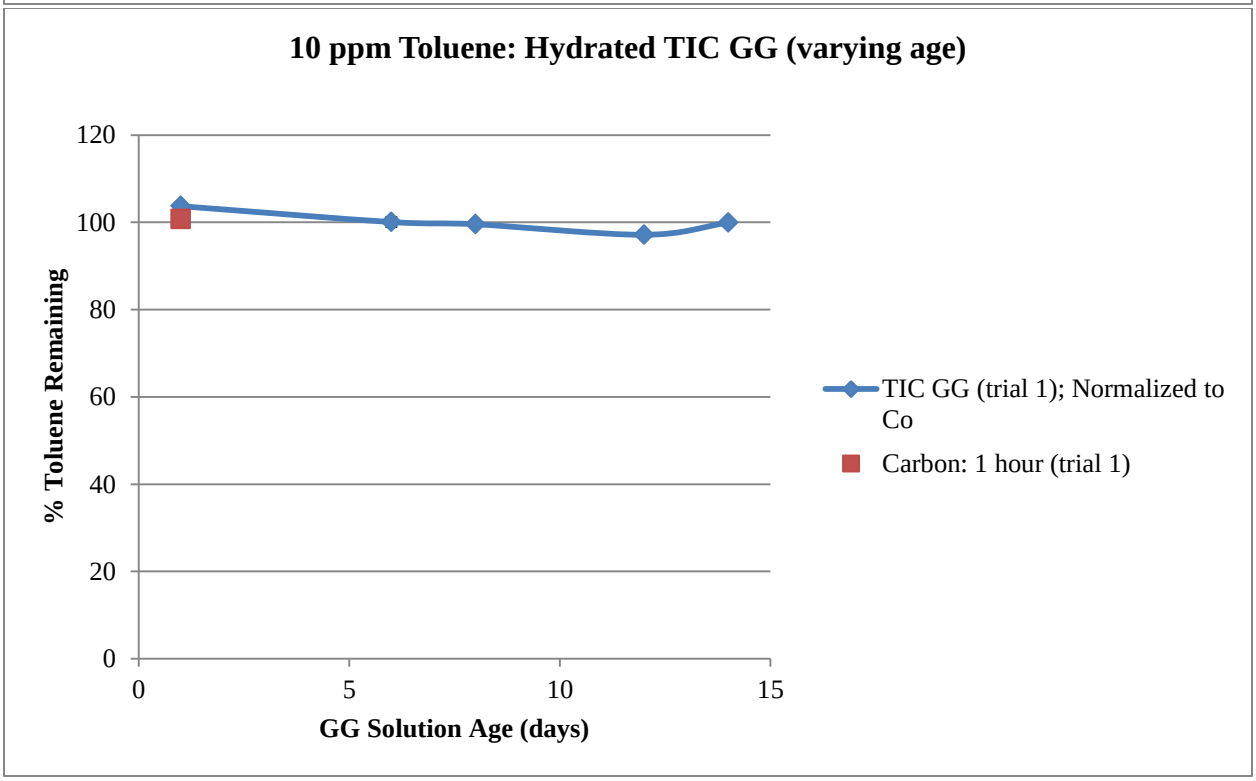
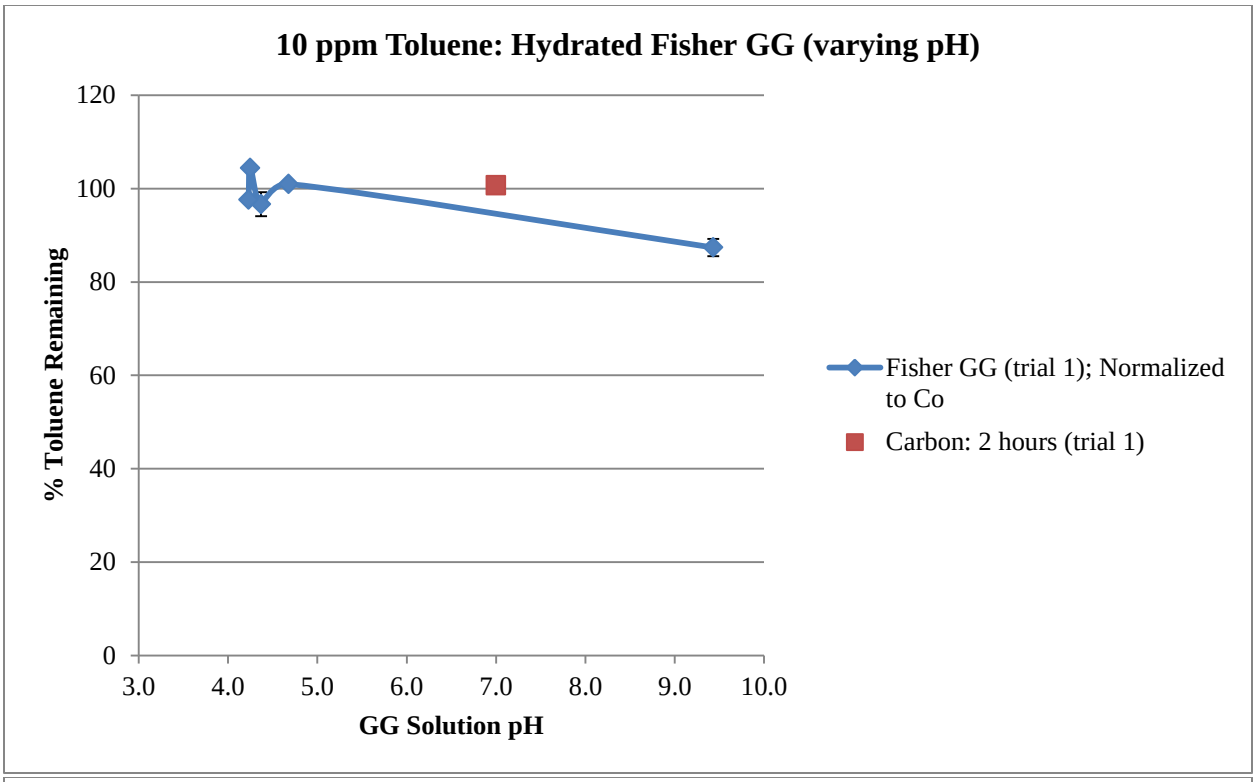




**Figure 51. TIC Adsorption of 10 ppm Toluene, Comparison of GG Solution pH and Age**



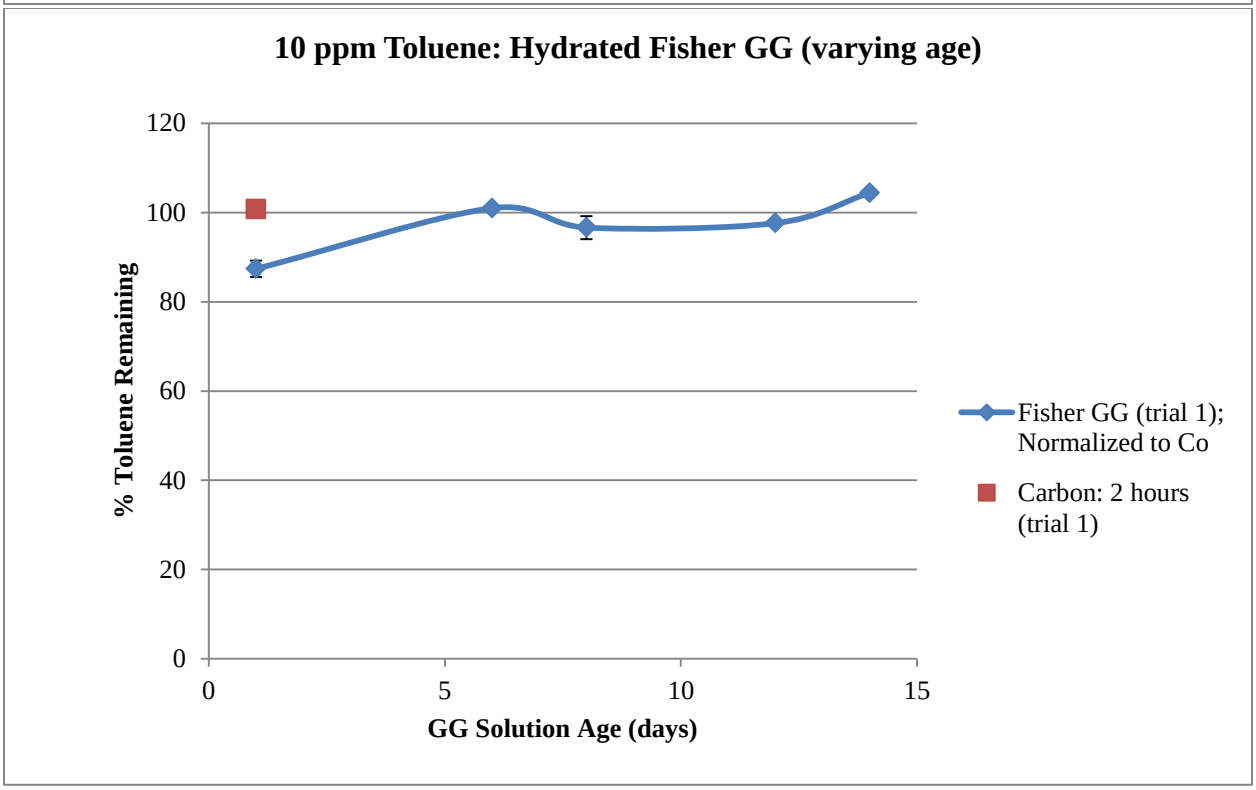
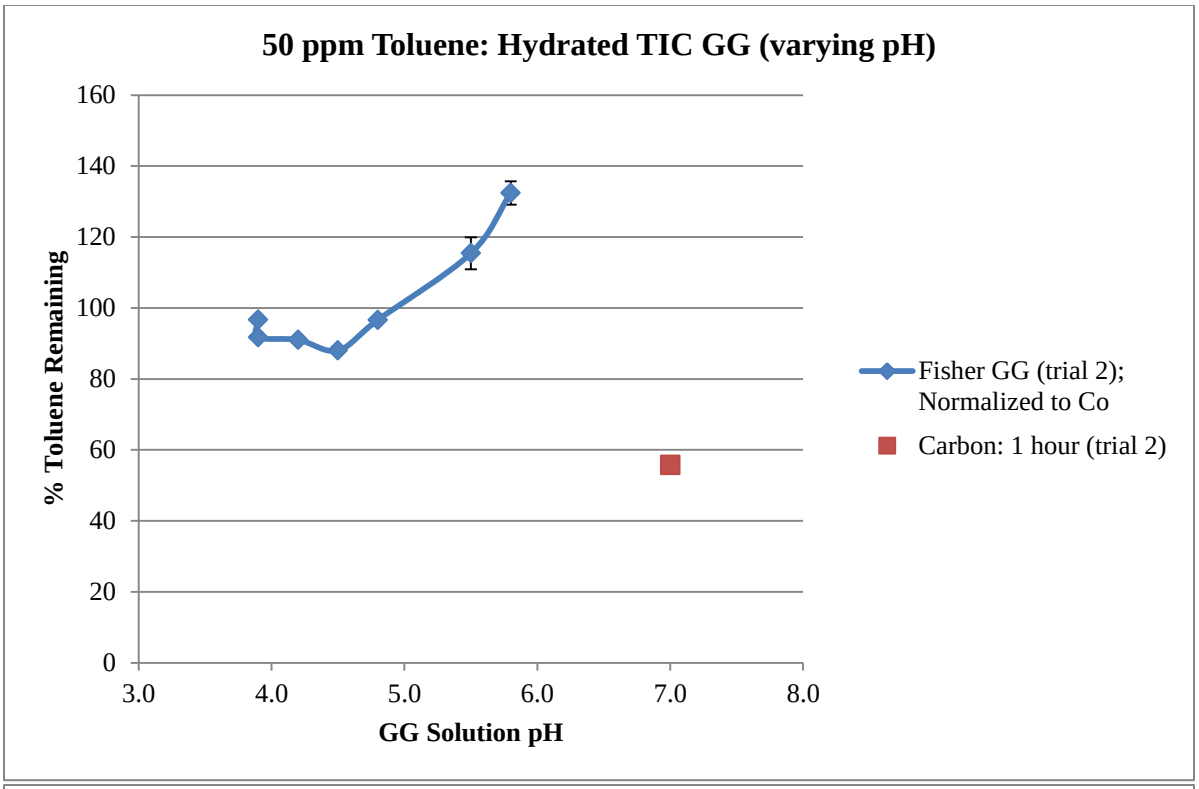




**Figure 52. Fisher Adsorption of 10 ppm Toluene, Comparison of GG Solution pH and Age**



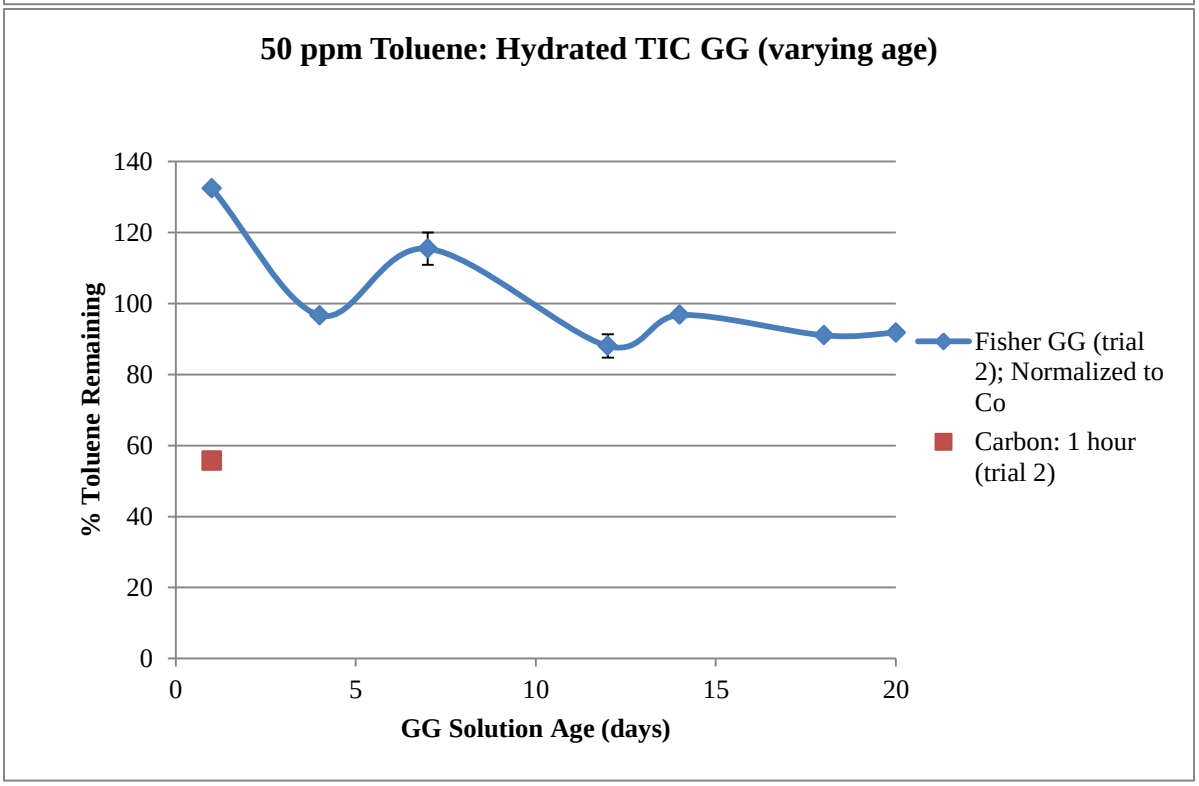
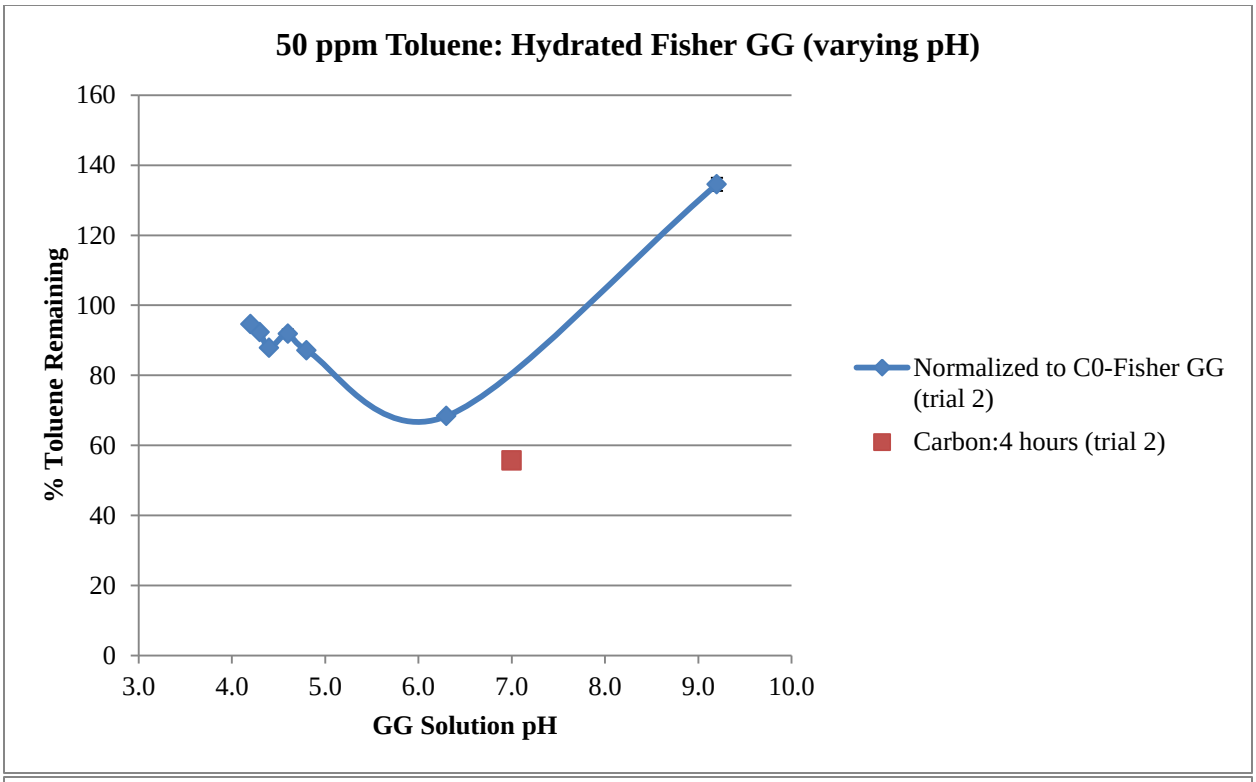




**Figure 53. TIC Adsorption of 50 ppm Toluene, Comparison of GG Solution pH and Age**



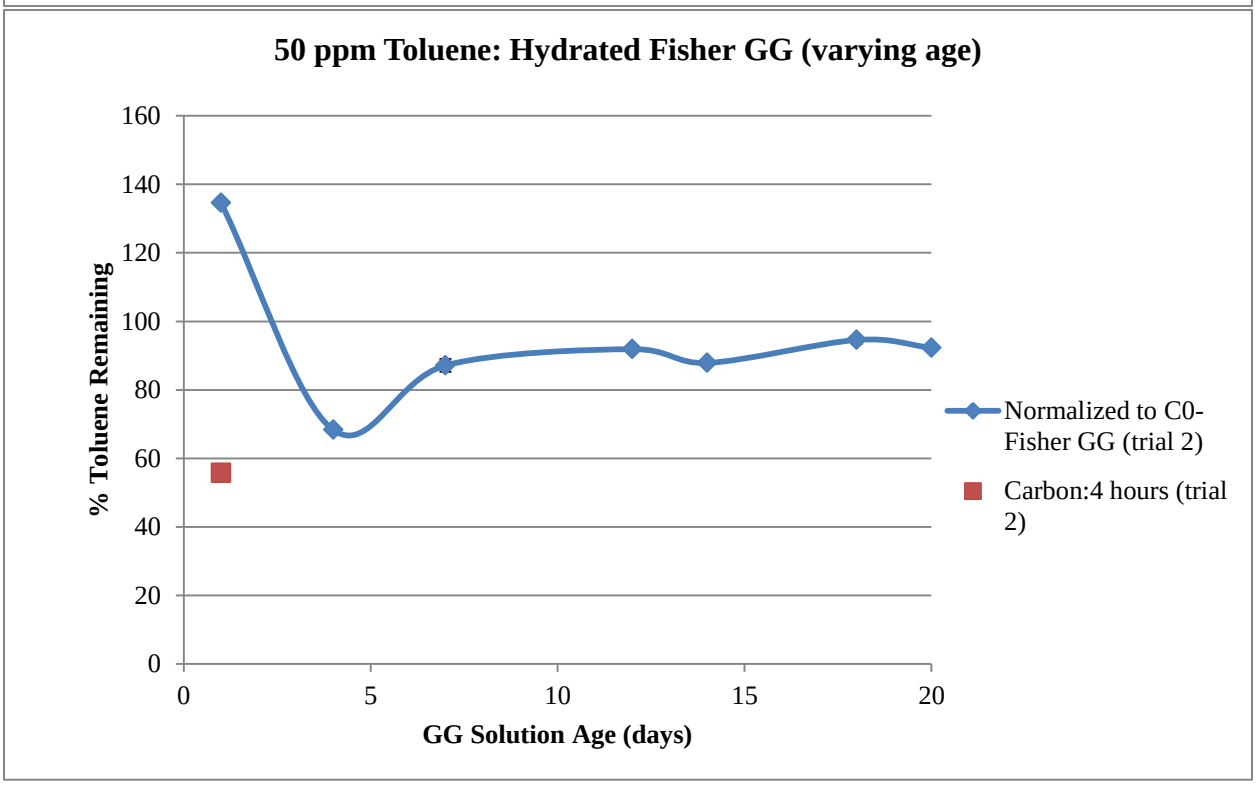




**Figure 54. Fisher Adsorption of 50 ppm Toluene, Comparison of GG Solution pH and Age**

## Summary

This chapter explored the effectiveness of 5 different application methods using GG with 8 contaminants. Although a variety of experimental conditions were assessed, some general trends emerged. GG was determined to decrease a solutions' pH over time, attributed to the likely production of a member of the carboxylic acid family. pH may also have a significant impact on the performance of GG as an adsorbent. Overall, GG was least effective removing toluene; due to the volatile nature of the contaminant. The application of pre-hydrated GG significantly outperformed other GG treatment techniques evaluated, and in some instances demonstrated better adsorption than an equivalent amount of carbon. Dry unmodified GG powder demonstrated adsorption ability; however, it required a much longer period of time (1-4 weeks) to demonstrate the same effectiveness. Additionally, the other applications of cleaning/drying GG, crosslinking, and generating a salt-out matrix collapse removed some of the contaminants but did not appear substantially more effective than using the unmodified product.

# V. Conclusions and Recommendations

## Chapter Overview

Emerging contaminants and changing regulatory limits require that new and innovative water treatment technologies be developed. This chapter summarizes the impact, conclusion and recommendations for future action generated by this research. Experimental studies investigated the potential of GG as a novel treatment against a variety of contaminants, and research objectives included evaluating how GG behaved in

water, its ability to adsorb dyes, and its applicability to treat other organic contaminants. GG performance was also compared to the industry standard for water treatment, granular activated carbon. The hydrated GG outperformed carbon with the anionic dyes, Allura Red and Brilliant Blue; this demonstrates the significant potential of the low cost, biodegradable material as a water treatment option.

**Conclusions of Research**

The novel use of GG as an adsorbent was studied using 5 different application techniques and 8 different contaminants. GG treatment demonstrated some effectiveness against all contaminants tested: Allura Red dye, Brilliant Blue dye, Erythrosine B dye, Fast Green dye, Methylene Blue dye, Tartrazine dye, toluene, and 2,4 DNT. The use of pre-hydrated GG significantly outperformed other treatment techniques and demonstrated faster adsorption than an equivalent amount of carbon in short term tests with some anionic contaminants. Dry unmodified GG powder demonstrated adsorption ability, however it required a longer period of time, in excess of 1 week, to demonstrate the same effectiveness. Placing the dry GG powder into filter bags helped eliminate the impact of turbidity during UV-Vis analysis caused by GG freely dispersed in solution. Ultimately, other applications of cleaning/drying GG, crosslinking with borate ions, and generating a salt-out matrix collapse removed some of the contaminants but did not appear substantially more effective than using the unmodified GG product. GG was least effective for adsorbing toluene, which rapidly volatilizes. Of the stable contaminants tested, the TIC brand gum tended to be more effective with anionic products and the Fisher brand gum with cationic substances. While the precise reason for this observation

is unknown, it may be due to differences in the GG brand mesh size, age, source, or the refining or bleaching processes used by the manufacturers.

When dissolved in water, GG has some unique spectrum characteristics, which often present non-uniform peaks and rises at wavelengths below 300 nm. These artifacts are most likely due to electronic transitions caused by the absorption of UV light, and can vary based on the quantity, the age, and the brand of GG used. GG also decreases the solution pH over time, potentially due to the production of a member of the carboxylic acid family. The natural pH change and influence of manipulated pH of solutions may also have a dramatic impact on performance. Older GG solutions, associated with lower pH values, were most effective against anionic substances, while younger GG mixtures, with higher pH values, were more effective against cationic contaminants. Alternatively, preliminary testing which increased the pH of fresh GG solutions, improved performance in both cationic and anionic environments. Additionally, GG solutions demonstrate rapid microbial growth within a few weeks. This may be beneficial when considering bioremediation procedures. However, it is also apparent that while biological processes may play a role in GG adsorption, other factors are also involved.

Three broad hypotheses were posited prior to the start of this research; however, methodologies and investigative questions evolved throughout the research process as new techniques and considerations developed, which were not originally considered. Re-visiting the original objectives and hypotheses, it was determined that GG can be detected with the UV-Vis and does demonstrate a UV-Vis baseline shift compared to water; alternatively, this shift proved more challenging than anticipated to remove. The hypotheses that 1 gram of unmodified GG will demonstrate at least 50% adsorption of

dyes and other contaminants tested were further refined during specific experiment initiatives. Overall, the use of GG in some manner did demonstrate greater than 70% adsorption of 7 of the 8 contaminants tested. While further research is needed to optimize the treatment approach and effectively remove GG itself from a water source, this research demonstrated that GG has the potential to become an effective treatment approach to remove water contaminants.

**Significance of Research**

Overall, this research has shown that GG may be effective in removing a variety of nonvolatile, aromatic organic water contaminants. Although several different approaches were evaluated, the most successful were using pre-hydrated gum solutions and the unmodified gum products. Treatment technologies based on this research may prove valuable against emerging contaminants and changing regulatory limits. GG may also be effective in treating waste streams from a number of industries; unmodified GG may be an ideal passive remediation treatment if it could be left in-place, without the costs associated with transporting, treating, or disposal after its use. However, the environmental impact of GG degradation and the associated pH decrease must be fully considered before this could be implemented as a viable treatment approach.

Since GG is already considered non-toxic, and is regularly added to food and personal products, it may eventually be viable in drinking or waste water treatment. In several instances, the hydrated GG performed better than granular activated carbon. This may be valuable when considering the cost-effectiveness of potential treatments. While the price of GG varies seasonally and in response to other market pressures, the largest

GG producer, India, demonstrated that GG costs less than 10,000 Rupees per quintal, the equivalent to US $1.40 per kilogram, throughout 2018; further trend analysis from 2003 to 2015 indicate the highest spike in India's GG price was approximately US $4.21 per kilogram [54], [55]. This is substantial if comparing to the market price cost of commercial activated carbon, currently about US $20 per kilogram [56].

While this research demonstrated GG as a promising new adsorbent, many of the initial tests were not as successful as anticipated. Time requirements and GG behavior in water presented several challenges. Although certain applications of the unmodified GG have potential, more research is needed to evaluate the secondary impacts, life-cycle cost, source variability, and statistical analysis to determination if GG is truly a cost-effective, biodegradable, and viable approach to contaminant removal.

**Recommendations for Future Research**

Much of this research was method development, and follow-on research should focus on standardization and uniformity across tests. Repeating several of the most promising tests, and conducting thorough statistical analysis is recommended to create a more complete picture of GG treatment efficiency. Best practices included: using filter bags if using dry GG, centrifuging or syringe filtration of samples (assuming bags, centrifuge and filters themselves do not substantially remove the contaminant of concern), constant stirring or mixing of the sample, using the semi-micro UV-Vis quartz cuvette, and scanning the entire UV-Vis spectrum to identify unique characteristics or changes. While this analysis used 0.2µm syringe filters, a larger pore size may be similarly effective and result in faster analysis with less waste.

Future research should also focus on determining the ideal usage parameters: GG quantity, pH, isotherms/kinetics involved, and the most effective mesh sizes or GG type. The impact of other water chemistry parameters should also be evaluated such as hardness, total organic carbon, oxygen demand, turbidity, etc. pH may have a significant impact on GG performance, and further testing should be conducted regarding the effectiveness of pH buffering and impact of various ages and pH of GG solutions. Furthermore, older solutions with a lower pH, proved to be much more effective with anionic dyes; perhaps crosslinking with borax would create a more effective crosslinked product than those seen during this research. Additionally, it may be beneficial to pursue an understanding of the decomposition of GG over time, and determine what products are being formed. It was suggested that a member of the carboxylic acid family is produced based on the pH shifts, odor, and gas-formation caused by GG dissolution in water, but further research would be needed for confirmation.

The treatment technique may also be modified; for example, rather than using a stir plate or the tumbler to mix GG solutions, a rotator or stator mixer may shorten hydration time and increase dispersion. More effective mixing may allow for the use of higher quantities of GG and could also decrease variability between samples. The concept of using raw GG is appealing considering the potential cost-savings and biodegradation properties; however, additional modification may improve performance. As summarized in Chapter 2, various methods using GG derivatives, grafting, (co)polymerization, depolymerization, oxidation, interpenetrating networks, or nanomaterials, may enhance the performance of GG as an adsorbent.

One of the biggest future research needs is the ability to completely remove GG from a solution. This would eliminate concerns about GG being in the finished water product, and would make it possible to use more sensitive analytical equipment. The ability to use sensitive items such as the Gas Chromatograph, Liquid Chromatograph, and Mass Spectrometer would improve the ability to evaluate GG's effectiveness against varying concentrations of numerous potential contaminants. This research found that fresh solutions of GG resulted in decreased sensitivity of the analytical equipment, however, it may be beneficial to test older GG solutions which are associated with lower viscosity. Otherwise, the use of filter aids like diatomaceous earth, perlite, or cellulose may also prove effective. Alternatively, functionalized alumina membrane microfiltration as describe by Samuel Maguire-Boyle, et al. or grafting GG with iron oxides for removal via magnetic field might be work-intensive but effective in removing GG from solution [57], [47].

There may also be other methods to measure the amount of GG present in solution using food-grade assays for gums/hydrocolloids/polysaccharides, galactose, mannose, or proteins. These tests might be more effective in determining how GG changes and degrades as well as the overall mass-balance of the system. Eventually, if GG continues to demonstrate promising application as an adsorbent, it may be beneficial to test GG as part of a treatment train or within a column test.

**Summary**

This research has highlighted promising results using GG as a novel adsorbent for a variety of organic contaminants. While several methodologies were evaluated, the most

effective was using hydrated GG or unmodified GG powder. Most importantly, in some studies, it adsorbed contaminants faster than activated carbon. GG has demonstrated that it is a cost- effective and biodegradable product; further research should be pursued in order to fully explore its effectiveness and determine the ideal parameters for its use.

# Appendix A

## TIC Brand Guar Gum Certificate of Analysis:

Texture Innovation Center
10552 Philadelphia Road | White Marsh, MD 21162 USA
(800) 899-3953 | (410) 273-7300 | (410) 335-4935 Fax
Operations
4609 Richlynn Drive | Belcamp, MD 21017 USA
(800) 221-3953 | (410) 273-7300 | (410) 273-0289 Fax
ticgums.com

TIC GUMS
We're your Gum Guru

GuarNT® USA 8/22

CERTIFICATE OF ANALYSIS

This product, or the ingredients used to make this product, has/have been demonstrated to conform with current Food Chemical Codex requirements.

NON GMO Project VERIFIED nongmoproject.org

**Lot:** 37395
**Mfg Date:** 06/20/2017
**Retest After:** 06/20/2019

| CHARACTERISTICS | STANDARDS | | | LAB RESULTS | | |
|---|---|---|---|---|---|---|
| | MIN | MAX | | Pass | Comments | |
| **Bacteriological** | | | | | | |
| Aerobic Plate Count (AOAC 988.18, 2.5g) | 0 | 2500 | cfu | YES | 435 | cfu |
| Total Coliforms (AOAC 989.11) | 0 | 9 | /g | YES | <10 | /g |
| E. coli (AOAC 989.11, 2.5g) | Negative /g | | | YES | Negative /g | |
| Salmonella - 375g (AOAC 2013.01 ) | Negative /375g | | | YES | Negative /375g | |
| S. aureus (BAM) | Negative /10g | | | YES | Negative /10g | |
| Combined Yeast and Mold (BAM) | 0 | 200 | /g | YES | <17 | /g |
| **Mesh** | | | | | | |
| USS#100 Mesh On | 0 | 5 | % | YES | 0.8 | % |
| USS#200 Mesh Through | 85 | 100 | % | YES | 92.2 | % |
| **Physical and Chemical** | | | | | | |
| Powder Color (Visual) | Creamy White | | | YES | Creamy White | |
| Flavor (Typical) | Bland | | | YES | Bland | |
| Moisture (Infrared) | 0 | 15 | % | YES | 5.52 | % |
| Odor (Typical) | Nearly Odorless | | | YES | Nearly Odorless | |
| pH (viscosity solution) | 5.4 | 7.0 | pH | YES | 5.75 | pH |
| Texture (Qualitative) | Free Flowing Powder | | | YES | Free Flowing Powder | |
| Viscosity (1.0%,RV@20rpm,25C) | 4000 | 6000 | cps | YES | 4752 | cps |

Jessica Harrilal, QA Supervisor

Jessica Harrilal

1/14/2019

GUAR USA 8/22

**Appendix B.**

# Experimental Summaries

Supplement to data included previously in Evaluation of Guar Gum as a Novel Adsorbent Thesis.

All data results presented in % contaminant remaining based on calibration curve.

**Supplement 1.**

| GG Application (Methodology) | Contaminant | Concentration of Contaminant | % Ratio GG Used (w/v) | Sample Size | UV-Vis Wavelength | Type of mixing | Any Pre-treatment |
|---|---|---|---|---|---|---|---|
| Unmodified, Dry GG; Crosslinked GG | Allura Red | 5 ppm; 0.01mM | 0.2% GG, 2020 ppm | 500mL | 505nm | Stationary | Varied - periodic syringe filter |

**Week 2**

Sample Order:

1. Crosslinked filter
2. GG
3. Carbon
4. Dye Standard

**Week 4**

Sample Order:

1. Dye Standard
2. Carbon
3. GG
4. Crosslinked filter

**Week 6**

Sample Order:

1. Dye Standard
2. Carbon
3. GG
4. Crosslinked filter

*Note, testing of Carbon and GG crosslinked filter samples discontinued after week 6

| Time Elapsed (days) | %Dye with 1g GG (subtract cntrl) | %Dye with 1g GG (Filtered) | %Dye with 1.0g Carbon (subtract cntrl) | %Dye with GG Crosslinked filter (subtract cntrl) |
|---|---|---|---|---|
| 7 | 70.11 | | 7.96 | 97.42 |
| 14 | 16.3 | | 3.52 | 96.34 |
| 21 | 0.16 | | 0.71 | 96.52 |
| 28 | -26.88 | | 0.37 | 96.43 |
| 35 | 4.99 | | 0.67 | 98.36 |
| 42 | 3.56 | | 0.35 | 94.94 |
| 49 | 2.59 | | | |
| 56 | 14.27 | | | |
| 63 | 5.8 | | | |
| 69 | 17.27 | | | |
| 76 | 11.53 | | | |
| 83 | 19.01 | 3.45 | | |
| 90 | 3.23 | 10.72 | | |
| 96 | 1.99 | 4.11 | | |
| 103 | 10.85 | 11.52 | | |
| 111 | 9.56 | 11.64 | | |
| 118 | 1.37 | 12.62 | | |
| 125 | 2.95 | 15.66 | | |
| 146 | -1.57 | 13.47 | | |
| 153 | -11.44 | 11.3 | | |
| 167 | -9.66 | 11.17 | | |
| 174 | -5.14 | 11.21 | | |
| 181 | -1.53 | 11.14 | | |
| 194 | -1.08 | 9.43 | | |
| 209 | -3.33 | 9.61 | | |
| 223 | -1.43 | 9.27 | | |
| 240 | -1.38 | 8.67 | | |
| 252 | 0.19 | 9.77 | | |

**Supplement 2.**

| GG Application (Methodology) | Contaminant | Concentration of Contaminant | % Ratio GG Used (w/v) | Sample Size | UV-Vis Wavelength | Type of mixing | Any Pre-treatment |
|---|---|---|---|---|---|---|---|
| Unmodified, Dry GG; Crosslinked GG | Allura Red | 5 ppm; 0.01mM | 0.2-0.4% GG, 4000 ppm | 250mL | 505nm | Tumbler | Varied - some in filter bags, periodic syringe filter |

| Time Elapsed (Days) | %Dye with 1g GG (subtract cntrl) | %Dye with 1g GG (filtered) | %Dye with filter bag & 1g GG (subtract cntrl) | %Dye with filter bag & 1g GG (filtered) | %Dye with 0.5g Crosslinked GG Powder (subtract cntrl) | %Dye with 0.5g Crosslinked GG Powder (filtered) |
|---|---|---|---|---|---|---|
| 3 | 100.55 | | 111.2 | | 99.49 | |
| 6 | 142.32 | | 87.87 | | 93 | |
| 11 | -44.29 | | 6.17 | | 120.08 | |
| 13 | -39.03 | | 32.66 | | 42.64 | |
| 16 | -14.94 | | 24.01 | | 19.68 | |
| 20 | -45.49 | | 12.17 | | 15.82 | |
| 23 | -94.31 | | 17.2 | | 20.39 | |
| 27 | -92.05 | | -23.97 | | 9.27 | |
| 30 | -89.68 | | -24.38 | | -5.57 | |
| 35 | -101.01 | 11.59 | 3.89 | 10.44 | 17.68 | |
| 42 | -110.12 | 11.57 | 17.19 | 9.02 | 26.36 | 78.87 |
| 47 | -60.81 | 3.2 | 26.48 | 2 | 34.46 | 77.82 |
| 53 | -38.57 | 4.71 | 1.48 | 2.85 | 23.42 | |
| 60 | -35.14 | 9.14 | 37.43 | 9.26 | -0.81 | |

**1g (0.4%) GG dry powder/no bag (i.e. flocculent)**

Picture Sample container order:

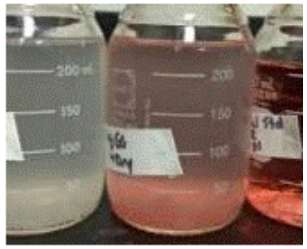
1. Control: GG, water
2. GG sample, Dye
3. Dye control standard

3 days

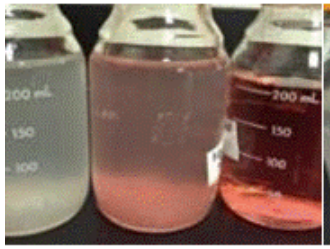
6 days

11 days

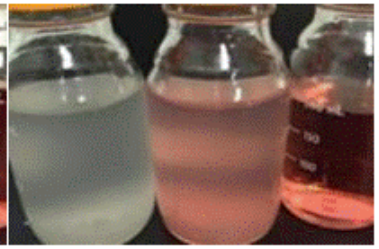
13 days



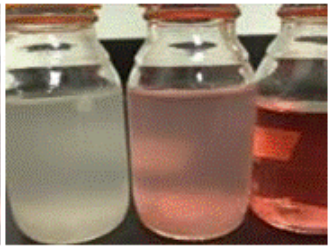
16 days



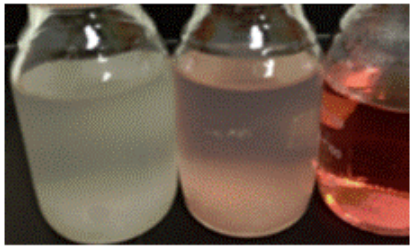
20 days



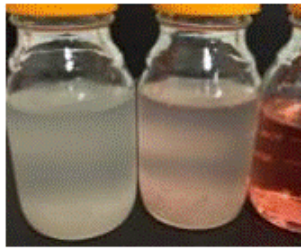
23 days



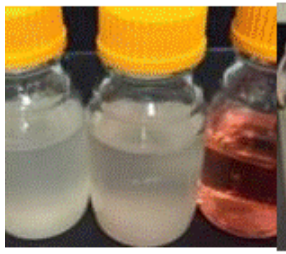
27 days



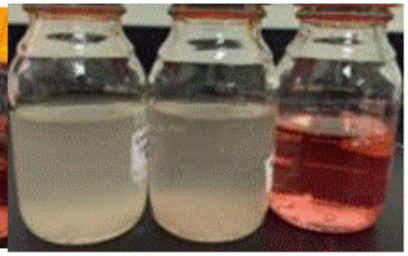
30 days



35 days

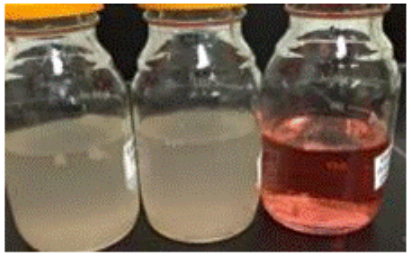


42 days

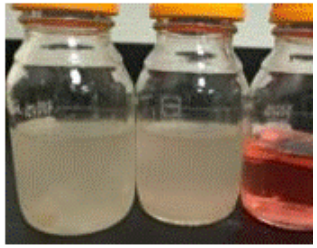


47 days

53 days



60 days



Picture Sample container order:

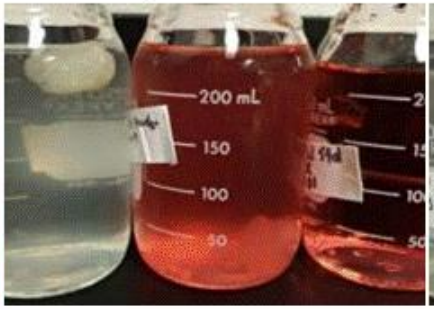
1. Control: GG, water
2. GG sample, Dye
3. Dye control standard

**0.5g (0.2%) Crosslinked GG powder**

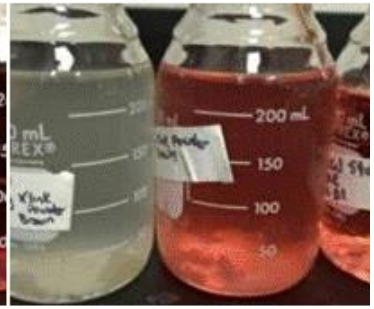
3 days

6 days

11 days




13 days




16 days

20 days

23 days

27 days

30 days

35 days

42 days

47 days

53 days

**Filter bag: 1g (0.4%) GG dry powder**

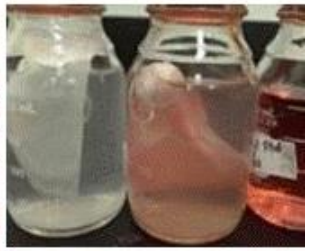
Picture Sample container order:
1. Control: GG, water
2. GG sample, Dye
3. Dye control standard

3 days

6 days

11 days

13 days



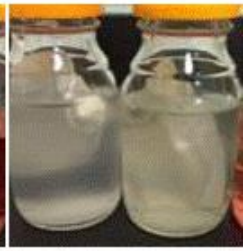
16 days

20 days

23 days

27 days

30 days



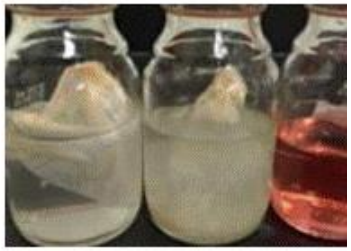
35 days

42 days

47 days

53 days

60 days



**Supplement 3.**

| GG Application (Methodology) | Contaminant | Concentration of Contaminant | % Ratio GG Used | Sample Size | UV-Vis Wavelength | Type of mixing | Any Pre-treatment |
|---|---|---|---|---|---|---|---|
| Unmodified, Dry GG; Cleaned or Dried GG | Allura Red | 5 ppm; 0.01mM | 0.2% GG, 2000 ppm | 500mL | 505nm | Stationary | Varied - periodic syringe filter |

**Syringe Filtered Samples**

| Time Elapsed (days) | 100% AR, Dye Std | %Dye with 1g GG, Fridge | %Dye with 1g GG, Room Temp | %Dye with 1g GG, Heated | %Dye with 1g GG & Ethanol | %Dye with 1g GG & 0.1mL Bleach | %Dye with 1g GG & 0.5mL Bleach | %Dye with 1g burnt GG | %Dye with 1g dehydrated GG | %Dye with 1g GG & 1%H2O2 |
|---|---|---|---|---|---|---|---|---|---|---|
| 13 days (filtered) | | | | | | | | | 72.08 | 30.82 |
| 20 days (filtered) | 98.19 | | 30.97 | 11.88 | 22.1 | 58.33 | 1.72 | 117.05 | 52.82 | 26.34 |
| 27 days (filtered) | 88.8 | 88.47 | 15.49 | 4.35 | 12.35 | 34.59 | 2.54 | 115.33 | 43.29 | 17.61 |
| 34 days (filtered) | 86.98 | | 7.14 | 2.38 | 16.75 | 11.22 | 2.75 | 121.84 | 27.31 | 12.65 |
| 38 days (filtered) | 103.94 | 92.9 | 4.19 | 1.84 | 6.93 | 4.77 | 3.05 | 119.27 | 19.28 | 12.63 |
| 41 days (filtered) | 99.47 | 96.97 | 1.47 | 0.07 | 5.06 | 1.56 | 0.76 | 119.71 | 28.2 | 10.83 |
| 45 days (filtered) | 102.49 | 101.54 | 3.44 | 5 | 5.61 | 3.79 | 2.19 | 121.03 | 34.85 | 10.34 |
| 52 days (filtered) | 104.7 | 95.35 | 3.05 | 4.75 | 5.29 | 2.61 | 1.85 | 121.07 | 5.69 | 8.68 |
| 59 days (filtered) | 100.36 | 96.37 | 3.71 | 3.63 | 3.68 | 5.54 | 0.74 | 121.33 | 1.6 | 4.95 |
| 80 days (filtered) | 105.06 | 102.61 | 15.61 | 7.2 | 12.6 | 5.73 | 3.32 | 125.5 | 6.81 | 4.13 |
| 101 days (filtered) | 101.37 | 94.88 | 18.15 | 2.87 | 10.9 | 3.2 | 0.34 | 123.13 | 1.78 | 1.46 |
| 115 days (filtered) | | 92.73 | 4.8 | 4.28 | 2.58 | 3.43 | 0.55 | 120.63 | -6.68 | -6.82 |
| 150 days (filtered) | 103.66 | 102.98 | 6.61 | 11.44 | 4.82 | 10.11 | 1.48 | 130.97 | 6.05 | -0.42 |
| 175 days (filtered) | 103.46 | 95.29 | 4.62 | 2.81 | 4.49 | 6.51 | 1.70 | 128.26 | -1.76 | -7.43 |

## 1g (0.2%) GG Powder: Refrigerated, Room Temp, Hot Plate

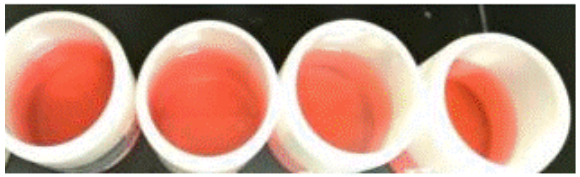
Picture Sample container order:

1. GG/Fridge
2. GG/room temp
3. GG/heated
4. Dye control standard

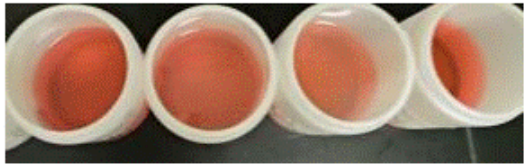
6 days

10 days

13 days

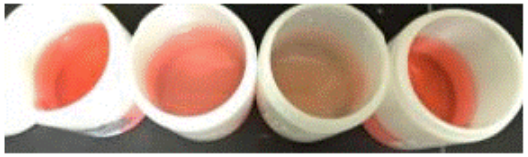


17 days

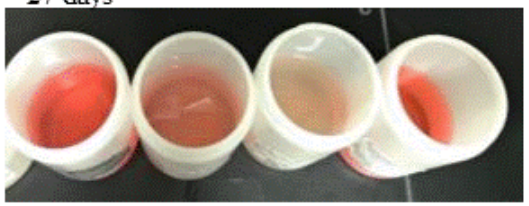


20 days

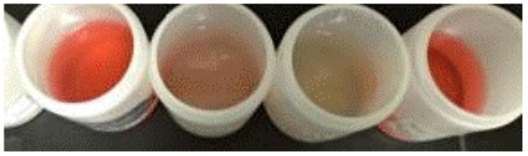
24 days



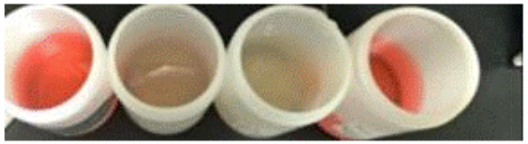
27 days



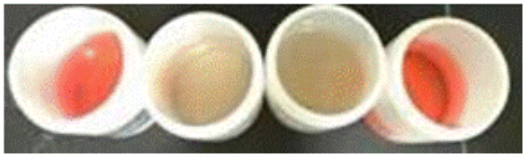
34 days



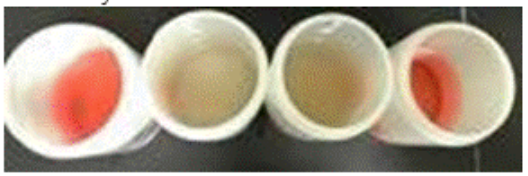
38 days



45 days

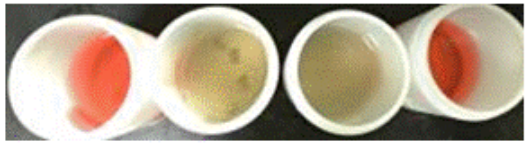


59 days

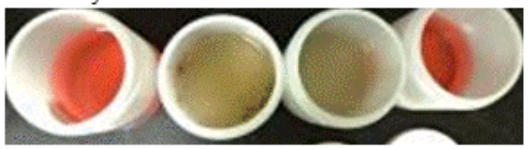


80 days

115 days



150 days



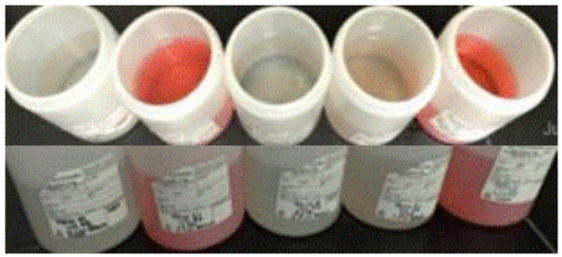
## 1g (0.2%) GG with Low & High Concentration Bleach Disinfectant

Picture Sample container order:

1. Control: low bleach, Dye
2. GG, low bleach, Dye
3. Control: high bleach, Dye
4. GG, high bleach, Dye
5. Dye control standard

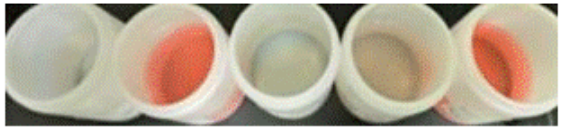
6 days

13 days



17 days

20 days



27 days

31 days

38 days

45 days

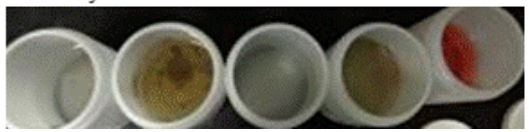
52 days

59 days

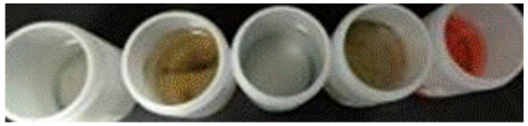
80 days

115 days

150 days



175 days

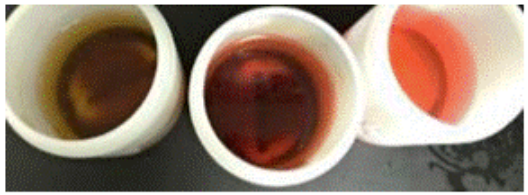


## 1g (0.2%) GG Baked/Burnt Powder

Picture Sample container order:

1. Control: Baked GG, water
2. Baked GG, Dye
3. Dye control standard

10 days



17 days

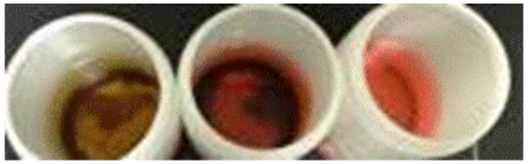
20 days

27 days

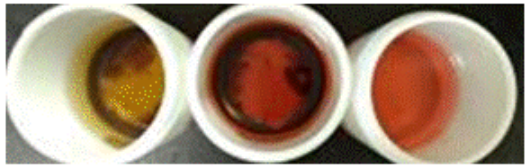
31 days

38 days

59 days



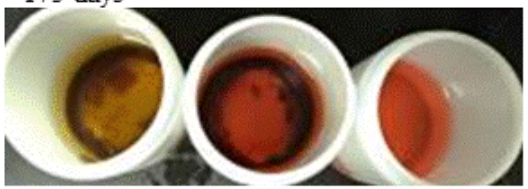
80 days



115 days

150 days

175 days



## 1g (0.2%) Dried/Dehydrated GG

Picture Sample container order:

1. Control: Dehydrated GG, Water
2. Dehydrated GG, Dye
3. Dye control standard

6 days

13 days

17 days

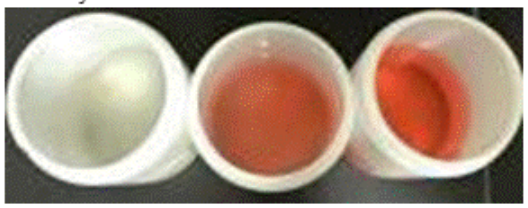
20 days

24 days

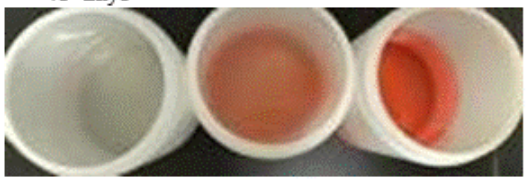
27 days

31 days

38 days



45 days



52 days

59 days

80 days

115 days

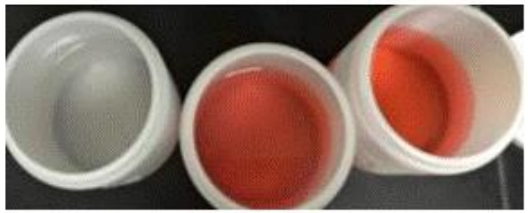
150 days

## 1 g (0.2%) GG with 1% Peroxide (H2O2)

Picture Sample container order:

1. Control: GG, Peroxide, Water
2. GG, Peroxide, Dye
3. Dye control standard

6 days



13 days

17 days

20 days

24 days

27 days

31 days

38 days

45 days

52 days

59 days

80 days

115 days

150 days

**Supplement 4.**

| GG Application (Methodology) | Contaminant | Concentration of Contaminant | % Ratio GG Used (w/v) | Sample Size | UV-Vis Wavelength | Type of mixing | Any Pre-treatment |
|---|---|---|---|---|---|---|---|
| Unmodified, Dry GG | Allura Red | 5 ppm; 0.01mM | 0.2% GG, 2000 ppm | 50mL | 505nm | Stationary | Varied - periodic syringe filter |

| Time Elapsed (Days) | %Dye with GG, Fischer (subtract cntrl) | %Dye with GG, TIC (subtract cntrl) | %Dye with Gellan (subtract cntrl) | %Dye with GG & Xanthan (subtract cntrl) | %Dye with Konjac & Xanthan (subtract cntrl) |
|---|---|---|---|---|---|
| 0 | 100 | 100 | 100 | 100 | 100 |
| 7 | 41.42 | 76.41 | 93.87 | 94.97 | 88.68 |
| 11 | 30.56 | 73.94 | 96.59 | 69.62 | 95.46 |
| 14 | 37.38 | 60.52 | 92.06 | 50.34 | 77.03 |
| 18 | 26.20 | 41.70 | 96.25 | 25.33 | 77.13 |
| 21 | 20.07 | 38.71 | 93.91 | 40.24 | 49.11 |
| 28 | 23.95 | 101.71 | 94.51 | 41.75 | 42.97 |
| 32 | 17.31 | 5.64 | 92.19 | 14.74 | 40.57 |
| 35 | 11.59 | 48.96 | 106.25 | 42.01 | 11.51 |
| 39 | 21.86 | 10.02 | 91.04 | 71.67 | -10.65 |
| 46 | 541.02 | 137.92 | 88.24 | -33.52 | -17.54 |
| 53 | -388.55 | 57.64 | 88.47 | 57.76 | 148.77 |

**Syringe Filtered Samples:**

| Time Elapsed (Days) | %AR Dye Std | %Dye with GG, Fischer | %Dye with GG, TIC | %Dye with Gellan | %Dye with GG & Xanthan | %Dye with Konjac & Xanthan |
|---|---|---|---|---|---|---|
| 7 (filtered) | 101.87 | 48.26 | 89.01 | 96.34 | | |
| 28 (filtered) | | 30.97 | 22.78 | 88.39 | 31.00 | |
| 32 (filtered) | 100.62 | 21.34 | 14.05 | 91.45 | 29.35 | |
| 35 (filtered) | 99.09 | 13.77 | 4.13 | 93.34 | 30.91 | |
| 39 (filtered) | | 4.58 | 1.54 | 88.81 | 21.77 | |
| 46 (filtered) | 100.28 | 6.27 | 3.07 | 83.95 | 13.00 | 10.55 |
| 53 (filtered) | | 3.16 | 2.93 | 82.54 | 8.41 | 5.47 |

**Supplement 5.**

| GG Application (Methodology) | Contaminant | Concentration of Contaminant | % Ratio GG Used (w/v) | Sample Size | UV-Vis Wavelength | Type of mixing | Any Pre-treatment |
|---|---|---|---|---|---|---|---|
| Unmodified, Dry GG; Crosslinked GG | Tartrazine | 5.3 ppm; 0.01mM | 0.4% GG, 4000 ppm | 250mL | 427nm, and 258nm | Stationary | Varied - some in filter bags, periodic syringe filter |

| **427 nm** Time Elapsed (Days) | 100% TR, Dye Std | Cntrl: %Dye with empty bag | Cntrl: %Dye with unmodified beads | subtract cntrl: %Dye with 1g GG | %Dye with 1g GG (filtered) | subtract cntrl: %Dye with 1g GG & 30mL Borax | subtract cntrl: %Dye with bag, 1g GG& 30mL water | subtract cntrl: %Dye with bag, 1g dry GG | %Dye with Filter Bag & 1g GG (filtered) | subtract cntrl: %Dye with bag, 1g GG & 50mLwater +Borax | subtract cntrl: %Dye with beads, 1.0g GG & 30mLBorax | subtract cntrl: %Dye with beads, 1.0g GG & 30mL water + Borax | subtract cntrl: %Dye with 1g Carbon |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 8 | 99.93 | 106.63 | 102.66 | 62.58 | | 79.80 | 72.71 | 65.53 | | 60.13 | 92.00 | 72.78 | -10.46 |
| 11 | 95.22 | 109.00 | 98.89 | 35.37 | | 73.49 | 68.72 | -7.35 | | -10.33 | 84.59 | 76.65 | -13.35 |
| 15 | 97.75 | 107.93 | 99.52 | 30.69 | | 75.85 | 56.42 | -0.42 | | -26.41 | 66.74 | 74.88 | -12.63 |
| 18 | 99.57 | 109.38 | 101.37 | 22.13 | | 75.31 | 51.53 | 0.56 | | -5.42 | 63.40 | 73.56 | -11.71 |
| 22 | 101.01 | 109.74 | 102.88 | 19.99 | | 28.98 | 40.82 | 1.73 | | -2.43 | 20.85 | 70.11 | -11.77 |
| 26 | 96.67 | 109.71 | 102.83 | 19.83 | | 28.89 | 40.85 | 1.70 | | -2.28 | 20.91 | 70.21 | -11.71 |
| 29 | 100.65 | 107.20 | 99.76 | 20.82 | | -17.77 | 6.27 | -3.12 | | 112.53 | 98.64 | 66.67 | -10.67 |
| 34 | 97.75 | 108.94 | 100.71 | 11.74 | | -1.31 | 8.49 | -2.00 | | -29.94 | 52.72 | 60.03 | -11.83 |
| 43 | 102.10 | 106.40 | 100.47 | 2.23 | | -27.84 | 2.33 | -0.72 | | 9.10 | 51.54 | 59.32 | -11.72 |
| 49 | 95.58 | 105.72 | | -12.39 | | | | -15.73 | | | | | |
| 56 | 97.03 | 104.01 | | -33.12 | | | | -47.56 | | | | | |
| 63 | 96.09 | 104.60 | | -34.86 | 4.54 | | | -15.35 | 4.54 | | | | |
| 70 | 94.16 | 101.23 | | -100.50 | 8.72 | | | -4.88 | 5.87 | | | | |

| **258 nm** Time Elapsed (Days) | 100% TR, Dye Std | Cntrl: %Dye with empty bag | Cntrl: %Dye with unmodified beads | subtract cntrl: %Dye with 1g GG | %Dye with 1g GG (filtered) | subtract cntrl: %Dye with 1g GG & 30mL Borax | subtract cntrl: %Dye with bag, 1g GG& 30mL water | subtract cntrl: %Dye with bag, 1g dry GG | %Dye with Filter Bag & 1g GG (filtered) | subtract cntrl: %Dye with bag, 1g GG & 50mLwater +Borax | subtract cntrl: %Dye with beads, 1.0g GG & 30mLBorax | subtract cntrl: %Dye with beads, 1.0g GG & 30mL water + Borax | subtract cntrl: %Dye with 1g Carbon |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 8 | 112.56 | 124.37 | 105.07 | 64.96 | | 59.11 | 34.30 | 45.93 | | 90.69 | 93.39 | 11.43 | -14.99 |
| 11 | 99.22 | 126.69 | 99.39 | 37.29 | | 122.21 | 52.66 | -3.07 | | -9.92 | 62.05 | 31.00 | -19.08 |
| 15 | 99.59 | 123.82 | 99.57 | 25.12 | | 99.04 | 64.15 | 49.93 | | -32.11 | 40.44 | 32.24 | -17.66 |
| 18 | 102.56 | 125.62 | 102.93 | 25.52 | | 134.00 | 59.27 | 50.40 | | 9.09 | 9.88 | 29.27 | -16.26 |
| 22 | 102.93 | 125.32 | 104.71 | 32.04 | | 58.26 | 59.53 | 57.68 | | 14.79 | -30.56 | 22.74 | -16.39 |
| 26 | 99.59 | 125.15 | 104.78 | 32.19 | | 58.11 | 59.59 | 57.74 | | 14.78 | -30.41 | 22.56 | -16.33 |
| 29 | 103.67 | 122.46 | 101.77 | -22.81 | | 14.56 | 14.84 | 47.11 | | 159.90 | 144.50 | 25.05 | -14.02 |
| 34 | 102.19 | 123.24 | 102.59 | -77.11 | | 6.46 | 21.16 | 52.39 | | -29.78 | 59.72 | 21.53 | -16.18 |
| 43 | 94.04 | 121.21 | 103.24 | -241.61 | | -54.67 | -52.20 | 59.18 | | 46.86 | 24.27 | 41.71 | -16.17 |
| 49 | 99.96 | 119.56 | | -846.24 | | | | 29.36 | | | | | |
| 56 | 100.70 | 118.25 | | -1066.86 | | | | 43.26 | | | | | |
| 63 | 99.30 | 118.62 | | -1111.09 | 221.67 | | | 91.57 | 474.38 | | | | |
| 70 | 100.92 | 113.34 | | -1088.04 | 276.28 | | | 394.42 | 583.72 | | | | |

**1g (0.4%) GG dry powder/no bag (i.e. flocculent)**

Picture Sample container order:

1. Control: GG, water
2. GG sample, Dye
3. Dye control standard

Day 8

Day 11

Day 15

Day 18

Day 22

Day 29

Day 34

Day 43

Day 49

Day 56

Day 63

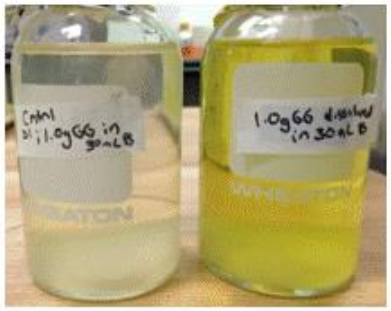
Day 70

## 1g (0.4) GG pre-hydrated in 30mL Borax/no bag

Picture Sample container order:

1. Control: GG, water
2. GG sample, Dye
3. Dye control standard

Day 8



Day 11

Day 15

Day 18

Day 22

Day 26

Day 29

Day 34

*Note, testing was discontinued after Day 34

**Filter bag: 1g GG (0.4%) pre-hydrated in 50 mL DI, dipped in Borax**

Picture Sample container order:

1. Control: GG, water
2. GG sample, Dye
3. Dye control standard

Day 8

Day 11

Day 15

Day 18

Day 22

Day 26

Day 29

Day 34

*Note, testing was discontinued after Day 34

**Filter bag: 1g (0.4%) GG prehydrated in 30 mL Borax**

Picture Sample container order:

1. Control: GG, water
2. GG sample, Dye
3. Dye control standard

Day 8

Day 11

Day 15

Day 18

Day 22

Day 26

Day 29

Day 34

*Note, testing was discontinued after Day 34

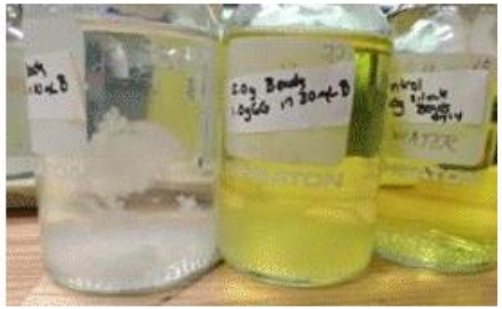
**1g (0.4%) GG mixed in 30mL Borax & 5g glass beads**

Picture Sample container order:

1. Control: GG, water
2. GG sample, Dye
3. Dye control standard

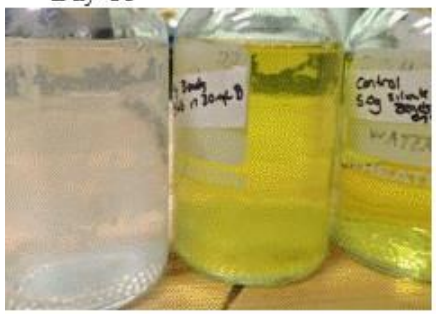
Day 8

Day 11



Day 15

Day 18



Day 26

Day 29

Day 34

*Note, testing was discontinued after Day 34

**1g (0.4%) GG mixed in 30 mL DI & 5g glass beads; dipped in B**

Picture Sample container order:

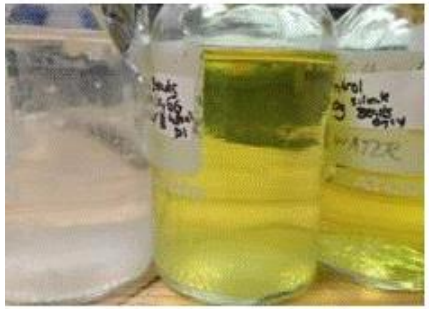
1. Control: GG, water
2. GG sample, Dye
3. Dye control standard

Day 8

Day 11

Day 15

Day 18



Day 26

Day 29

Day 34

*Note, testing was discontinued after Day 34

## 1g (0.4%) Carbon dry powder/no bag (i.e. flocculent)

Picture Sample container order:

1. Control: GG, water
2. Carbon sample, Dye
3. Dye control standard

Day 0

Day 8

Day 11

Day 15

Day 18

Day 22

Day 26

Day 29

Day 34

*Note, testing was discontinued after Day 34

**Supplement 6.**

| GG Application (Methodology) | Contaminant | Concentration of Contaminant | % Ratio GG Used (w/v) | Sample Size | UV-Vis Wavelength | Type of mixing | Any Pre-treatment |
|---|---|---|---|---|---|---|---|
| Unmodified, Dry GG | Tartrazine | 5.3 ppm; 0.01mM | 0.5-3% GG, 5000-30000 ppm | 250mL | 427nm, and 258nm | Tumbler | Filter bags, syringe filter |

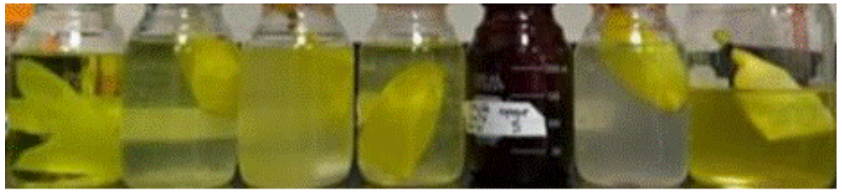
Data summarized in Tables 14-17

Picture Sample container order:

1. Dye control standard
2. 1.25g (0.5%) GG sample, Dye, Stationary
3. 1.25g (0.5%) GG sample, Dye, Stirred
4. 1.25g (0.5%) GG sample, Dye, Stirred+low heat
5. 1.25g (0.5%) GG sample, Dye, Opaque container, Tumbler
6. 1.25g (0.5%) TIC Gum GG, Dye, Tumbler
7. 1.25g (0.5%) GG sample, Dye, Larger bottle/headspace, Tumbler

4 Day

8 days



11 days

15 days

22 days

25 days

29 days

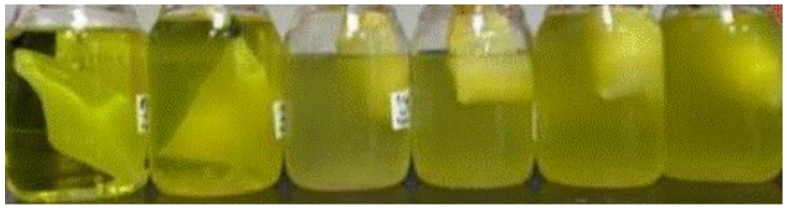
| GG Application (Methodology) | Contaminant | Concentration of Contaminant | % Ratio GG Used (w/v) | Sample Size | UV-Vis Wavelength | Type of mixing | Any Pre-treatment |
|---|---|---|---|---|---|---|---|
| Unmodified, Dry GG | Tartrazine | 5.3 ppm; 0.01mM | 0.5-3% GG, 5000-30000 ppm | 250mL | 427nm, and 258nm | Tumbler | Filter bags, syringe filter |

Data summarized in Tables 14-17

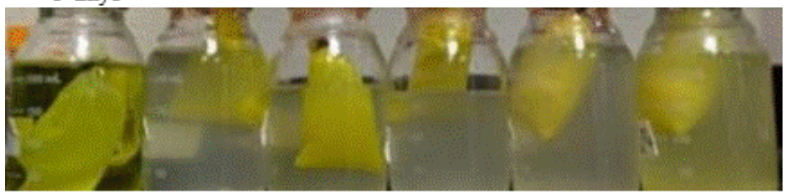
Picture Sample container order:

1. Dye control standard
2. 1.25g (0.5%) GG sample, Dye
3. 2.5g (1%) GG sample, Dye
4. 3.75g (1.5%) GG sample, Dye
   **Note:1.5% GG sample bottle broke on day 22*
5. 5g (2%) GG sample, Dye
6. 7.5g (3%) GG sample, Dye

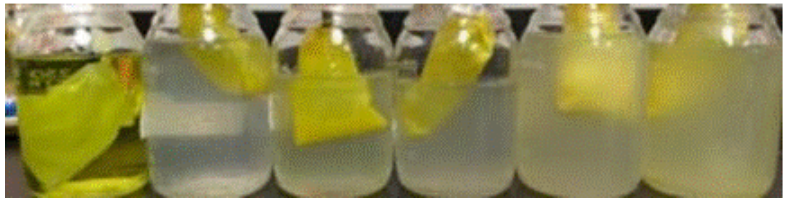
4 Day



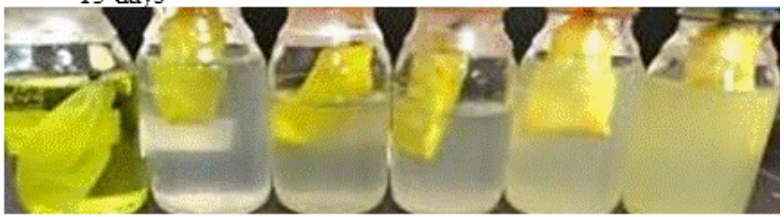
8 days



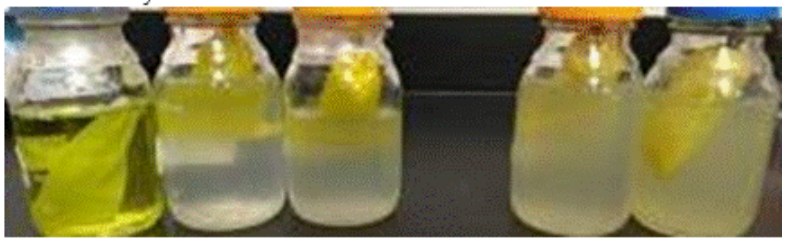
11 days



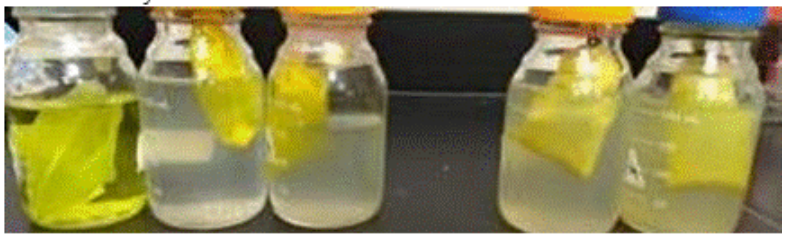
15 days



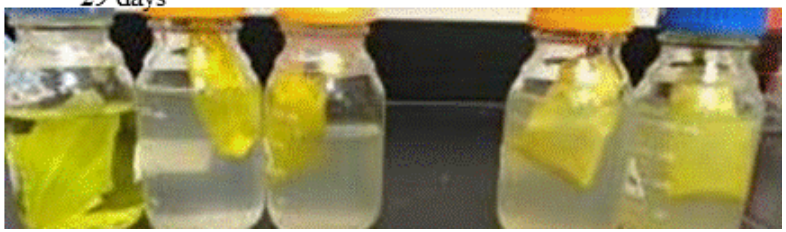
22 days



25 days



29 days



**Control Samples**

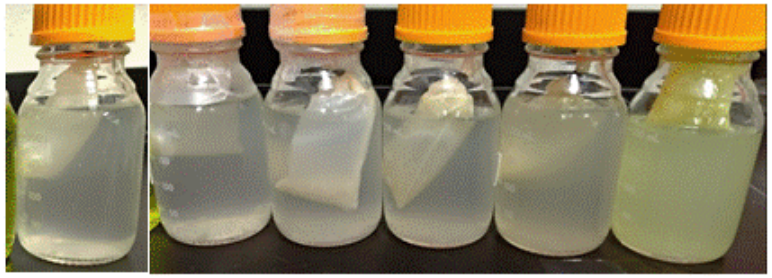
Picture Sample container order:

1. Control: 1.25g (0.5%) GG sample, Dye
2. Control: 2.5g (1%) GG sample, Dye
3. Control: 3.75g (1.5%) GG sample, Dye
4. Control: 5g (2%) GG sample, Dye
5. Control: 7.5g (3%) GG sample, Dye

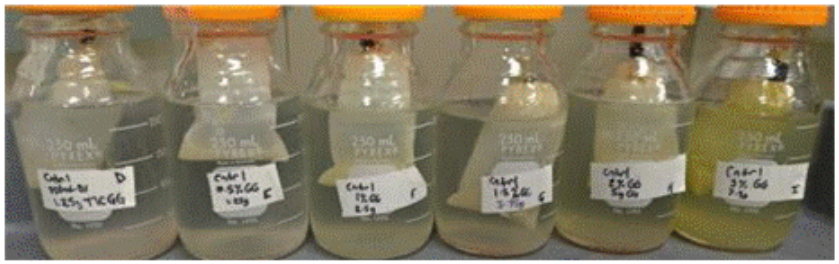
4 days

22 days

18 days



40 days



**Supplement 7.**

| GG Application (Methodology) | Contaminant | Concentration of Contaminant | % Ratio GG Used (w/v) | Sample Size | UV-Vis Wavelength | Type of mixing | Any Pre-treatment |
|---|---|---|---|---|---|---|---|
| Cleaned or Dried GG; Hydrated GG | Brilliant Blue | 2 ppm; 0.0025mM | 0.5% GG, 5000 ppm | 6mL | 630nm | None | Centrifuge |

| Time elapsed (hours) | Blank | 100% BB Dye Std | subtract cntrl: %Dye with unmodified GG | subtract cntrl: % Dye with Cleaned GG |
|---|---|---|---|---|
| 2 | -0.07 | 100.14 | 8.10 | 23.59 |
| 6 | -0.53 | 99.13 | 6.78 | 20.49 |
| 28.5 | -0.63 | 101.32 | 10.34 | 24.46 |

**Filtered Samples**

| Time elapsed (hours) | Blank | 100% BB Dye Std | subtract cntrl: %Dye with unmodified GG | subtract cntrl: %Dye with Cleaned GG |
|---|---|---|---|---|
| 2 (filtered) | 0.05 | 100.64 | 0.40 | 22.75 |
| 6 (filtered) | -0.42 | 99.59 | 8.02 | 19.54 |
| 28.5 (filtered) | -0.52 | 102.97 | 9.34 | 21.34 |

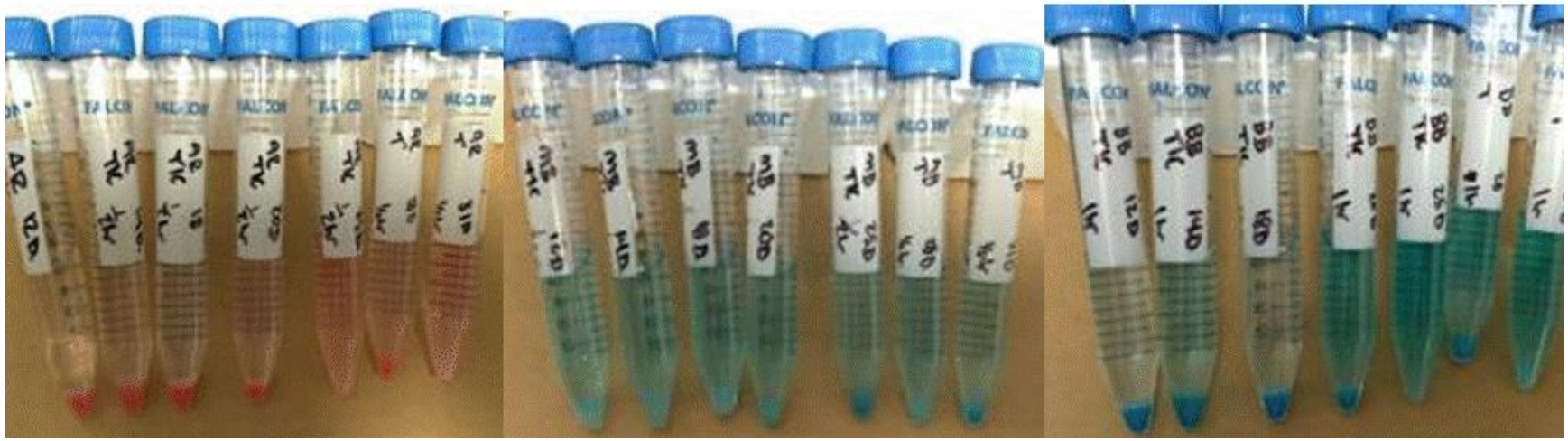
**Supplement 8-10 Images**

**Oldest GG → Youngest GG**

*Allura Red (Anionic)* *Methylene Blue (Cationic)* *Brilliant Blue (Anionic)*

Fisher Brand GG

TIC Brand GG



**Supplement 8.**

| GG Application (Methodology) | Contaminant | Concentration of Contaminant | % Ratio GG Used (w/v) | Sample Size | UV-Vis Wavelength | Type of mixing | Any Pre-treatment |
|---|---|---|---|---|---|---|---|
| Hydrated GG | Allura Red | AR: 4.96 ppm; 0.01mM | 0.5% GG, 5000 ppm | 6mL | AR: 505nm | Stationary | Centrifuge |

| Sample Type | GG age (days) | Avg pH of GG used | subtract cntrl: %Dye After 1 hour (trial 1) | subtract cntrl: %Dye After 2 hours (trial 1) | Std Dev, % 1hr | Std Dev % 2hr |
|---|---|---|---|---|---|---|
| blank | N/A | N/A | -0.3 | -0.5 | 6.8 | 6.9 |
| AR Dye Cntrl | N/A | N/A | 98.0 | 97.1 | 6.9 | 6.8 |
| TIC GG | 14 | 3.8 | -2.4 | 2.6 | 6.5 | 6.5 |
| TIC GG | 12 | 4.2 | 28.0 | 24.0 | 6.2 | 5.5 |
| TIC GG | 8 | 3.9 | 8.6 | -0.8 | 6.3 | 6.5 |
| TIC GG | 6 | 4.4 | 59.0 | 70.6 | 5.9 | 6.0 |
| TIC GG | 1 | 5.5 | 94.3 | 90.9 | 6.4 | 6.8 |
| Fisher GG | 14 | 4.3 | 59.2 | 70.5 | 6.0 | 2.4 |
| Fisher GG | 12 | 4.2 | 61.8 | 55.6 | 6.3 | 6.7 |
| Fisher GG | 8 | 4.4 | 50.6 | 44.3 | 6.8 | 6.8 |
| Fisher GG | 6 | 4.7 | 55.1 | 52.9 | 6.7 | 6.8 |
| Fisher GG | 1 | 9.4 | 61.4 | 109.4 | 5.3 | 6.3 |
| Carbon | N/A | N/A | 79.6 | 72.2 | 6.8 | 6.9 |

| Sample Type | GG age (days) | Avg GG pH | subtract cntrl: %Dye After 0.5 hour (trial 2) | subtract cntrl: %Dye After 1 hour (trial 2) | Std Dev, % 0.5hr | Std Dev % 1hr |
|---|---|---|---|---|---|---|
| blank | N/A | N/A | -14.1 | -12.8 | 6.9 | 6.9 |
| AR Dye Cntrl | N/A | N/A | 90.5 | 90.5 | 6.9 | 6.9 |
| TIC GG | 20 | 3.9 | 0.6 | -8.1 | 6.9 | 6.5 |
| TIC GG | 18 | 4.2 | 17.4 | 5.9 | 6.8 | 6.3 |
| TIC GG | 14 | 3.9 | 0.3 | -4.2 | 6.6 | 6.6 |
| TIC GG | 12 | 4.5 | 37.8 | 34.8 | 6.4 | 6.6 |
| TIC GG | 7 | 5.5 | 159.8 | 82.8 | 5.5 | 4.9 |
| TIC GG | 4 | 4.8 | 63.8 | 83.0 | 3.9 | 3.4 |
| TIC GG | 1 | 5.8 | 76.4 | 72.1 | 6.8 | 6.7 |
| Fisher GG | 20 | 4.3 | 48.9 | 47.8 | 6.9 | 6.8 |
| Fisher GG | 18 | 4.2 | 67.9 | 60.6 | 6.8 | 6.9 |
| Fisher GG | 14 | 4.4 | 76.0 | 67.0 | 6.8 | 2.6 |
| Fisher GG | 12 | 4.6 | 75.9 | 76.1 | 6.7 | 6.9 |
| Fisher GG | 7 | 4.8 | 81.4 | 84.2 | 6.8 | 6.7 |
| Fisher GG | 4 | 6.3 | 87.3 | 89.6 | 12.0 | 4.5 |
| Fisher GG | 1 | 9.2 | 94.4 | 82.8 | 3.8 | 6.1 |
| Carbon | N/A | N/A | 73.8 | 75.9 | 6.9 | 6.8 |

**Supplement 9.**

| GG Application (Methodology) | Contaminant | Concentration of Contaminant | % Ratio GG Used (w/v) | Sample Size | UV-Vis Wavelength | Type of mixing | Any Pre-treatment |
|---|---|---|---|---|---|---|---|
| Hydrated GG | Methylene Blue | MB:1.87 ppm; 0.005mM | 0.5% GG, 5000 ppm | 6mL | MB: 665nm | Stationary | Centrifuge |

| Sample Type | GG age (days | Avg pH of GG used | subtract cntrl: %Dye After 1 hour (trial 1) | subtract cntrl: %Dye After 2 hours (trial 1) | Std Dev, % 1hr | Std Dev % 2hr |
|---|---|---|---|---|---|---|
| blank | N/A | N/A | 1.3 | 1.1 | 0.0 | 0.0 |
| MB Dye Control | N/A | N/A | 101.0 | 101.8 | 0.1 | 0.2 |
| TIC GG | 14 | 3.8 | 99.7 | 97.8 | 0.1 | 0.2 |
| TIC GG | 12 | 4.2 | 110.1 | 109.8 | 0.6 | 0.7 |
| TIC GG | 8 | 3.9 | 102.5 | 99.3 | 0.2 | 0.7 |
| TIC GG | 6 | 4.4 | 120.3 | 126.0 | 0.8 | 0.9 |
| TIC GG | 1 | 5.5 | 95.4 | 102.0 | 0.5 | 0.4 |
| Fisher GG | 14 | 4.3 | 84.9 | 87.4 | 0.1 | 0.0 |
| Fisher GG | 12 | 4.2 | 78.1 | 75.8 | 0.2 | 0.1 |
| Fisher GG | 8 | 4.4 | 81.1 | 79.1 | 0.2 | 0.1 |
| Fisher GG | 6 | 4.7 | 80.8 | 77.2 | 0.0 | 0.0 |
| Fisher GG | 1 | 9.4 | 34.7 | 62.0 | 0.7 | 0.6 |
| Carbon | N/A | N/A | 64.3 | 55.1 | 0.0 | 0.3 |

| Sample Type | GG age (days) | Avg GG pH | subtract cntrl: %Dye After 0.5 hour (trial 2) | Std Dev, % 0.5hr |
|---|---|---|---|---|
| blank | N/A | N/A | -2.6 | 0.1 |
| MB Dye Control | N/A | N/A | 98.7 | 0.2 |
| TIC GG | 20 | 3.9 | 92.6 | 0.1 |
| TIC GG | 18 | 4.2 | 91.1 | 0.4 |
| TIC GG | 14 | 3.9 | 93.1 | 0.1 |
| TIC GG | 12 | 4.5 | 86.6 | 0.2 |
| TIC GG | 7 | 5.5 | 93.1 | 0.5 |
| TIC GG | 4 | 4.8 | 93.7 | 1.0 |
| TIC GG | 1 | 5.8 | 64.7 | 0.1 |
| Fisher GG | 20 | 4.3 | 81.4 | 0.1 |
| Fisher GG | 18 | 4.2 | 78.1 | 0.1 |
| Fisher GG | 14 | 4.4 | 88.6 | 0.2 |
| Fisher GG | 12 | 4.6 | 85.8 | 0.1 |
| Fisher GG | 7 | 4.8 | 82.0 | 0.1 |
| Fisher GG | 4 | 6.3 | 64.0 | 8.7 |
| Fisher GG | 1 | 9.2 | 67.0 | 1.6 |
| Carbon | N/A | N/A | 52.7 | 0.1 |

**Supplement 10.**

| GG Application (Methodology) | Contaminant | Concentration of Contaminant | % Ratio GG Used (w/v) | Sample Size | UV-Vis Wavelength | Type of mixing | Any Pre-treatment |
|---|---|---|---|---|---|---|---|
| Hydrated GG | Brilliant Blue | BB: 3.96 ppm; 0.005mM | 0.5% GG, 5000 ppm | 6mL | BB: 630 nm | Stationary | Centrifuge |

| Sample Type | GG age (days) | Avg pH of GG used | subtract cntrl: %Dye After1 hour (trial 1) | subtract cntrl: %Dye After 2 hours (trial 1) | Std Dev, % 1hr | Std Dev % 2hr |
|---|---|---|---|---|---|---|
| blank | N/A | N/A | 0.1 | -0.1 | 1.0 | 1.1 |
| BB Dye Control | N/A | N/A | 99.3 | 96.1 | 0.3 | 1.9 |
| TIC GG | 14 | 3.8 | 12.9 | 14.7 | 1.0 | 1.1 |
| TIC GG | 12 | 4.2 | 33.5 | 32.2 | 1.0 | 0.6 |
| TIC GG | 8 | 3.9 | 14.6 | 13.7 | 0.9 | 1.0 |
| TIC GG | 6 | 4.4 | 60.9 | 52.9 | 0.8 | 0.1 |
| TIC GG | 1 | 5.5 | 113.1 | 98.2 | 0.5 | 0.9 |
| Fisher GG | 14 | 4.3 | 74.7 | 77.3 | 0.9 | 0.9 |
| Fisher GG | 12 | 4.2 | 82.8 | 80.0 | 0.8 | 0.7 |
| Fisher GG | 8 | 4.4 | 68.5 | 69.4 | 1.0 | 1.0 |
| Fisher GG | 6 | 4.7 | 75.0 | 73.4 | 1.0 | 0.9 |
| Fisher GG | 1 | 9.4 | 86.1 | 109.8 | 0.2 | 0.8 |
| Carbon | N/A | N/A | 88.6 | 88.5 | 1.0 | 0.4 |

| Sample Type | GG age (days) | Avg GG pH | subtract cntrl: %Dye After 0.5 hour (trial 2) | subtract cntrl: %Dye After 1 hour (trial 2) | Std Dev, % 0.5 hr | Std Dev % 1 hr |
|---|---|---|---|---|---|---|
| blank | N/A | N/A | -2.3 | -1.8 | 1.1 | 1.1 |
| BB Dye Control | N/A | N/A | 91.8 | 96.9 | 1.0 | 1.0 |
| TIC GG | 20 | 3.9 | 19.2 | 10.5 | 1.0 | 1.0 |
| TIC GG | 18 | 4.2 | 40.2 | 33.4 | 0.9 | 0.9 |
| TIC GG | 14 | 3.9 | 14.6 | 10.0 | 1.1 | 1.0 |
| TIC GG | 12 | 4.5 | 68.6 | 67.7 | 1.0 | 1.0 |
| TIC GG | 7 | 5.5 | 119.0 | 93.0 | 0.7 | 2.1 |
| TIC GG | 4 | 4.8 | 77.5 | 69.3 | 0.3 | 2.3 |
| TIC GG | 1 | 5.8 | 110.8 | 90.2 | 0.9 | 1.0 |
| Fisher GG | 20 | 4.3 | 83.1 | 82.7 | 1.1 | 0.9 |
| Fisher GG | 18 | 4.2 | 89.2 | 87.0 | 1.0 | 1.0 |
| Fisher GG | 14 | 4.4 | 92.8 | 89.7 | 1.1 | 0.6 |
| Fisher GG | 12 | 4.6 | 84.1 | 95.4 | 1.1 | 1.1 |
| Fisher GG | 7 | 4.8 | 98.0 | 95.0 | 1.0 | 1.0 |
| Fisher GG | 4 | 6.3 | 111.3 | 99.7 | 4.9 | 0.7 |
| Fisher GG | 1 | 9.2 | 101.1 | 99.2 | 0.1 | 0.7 |
| Carbon | N/A | N/A | 89.3 | 90.2 | 1.0 | 1.0 |

**Supplement 11.**

| GG Application (Methodology) | Contaminant | Concentration of Contaminant | % Ratio GG Used (w/v) | Sample Size | UV-Vis Wavelength | Type of mixing | Any Pre-treatment |
|---|---|---|---|---|---|---|---|
| Hydrated GG | DNT | DNT:10 ppm | 0.5% GG, 5000 ppm | 6mL | DNT: 250nm | Stationary | Centrifuge |

| Sample Type | GG age (days) | Avg pH of GG used | subtract cntrl: %DNT After 1 hour (trial 1) | subtract cntrl: %DNT After 2 hours (trial 1) | Std Dev, % 1hr | Std Dev % 2hr |
|---|---|---|---|---|---|---|
| blank | N/A | N/A | 0.4 | 0.4 | 4.7 | 4.7 |
| DNT Control Standard | N/A | N/A | 99.0 | 98.5 | 4.0 | 4.5 |
| TIC GG | 14 | 3.8 | 85.4 | 112.3 | 4.3 | 4.5 |
| TIC GG | 12 | 4.2 | 121.8 | 125.2 | 4.3 | 4.1 |
| TIC GG | 8 | 3.9 | 100.3 | 89.0 | 4.6 | 4.5 |
| TIC GG | 6 | 4.4 | 149.4 | 142.4 | 3.8 | 2.9 |
| TIC GG | 1 | 5.5 | 129.6 | 120.4 | 3.8 | 4.4 |
| Fisher GG | 14 | 4.3 | 88.9 | 99.8 | 4.2 | 4.3 |
| Fisher GG | 12 | 4.2 | 93.5 | 85.3 | 4.0 | 4.3 |
| Fisher GG | 8 | 4.4 | 99.0 | 94.5 | 4.1 | 4.7 |
| Fisher GG | 6 | 4.7 | 90.8 | 90.3 | 4.5 | 4.6 |
| Fisher GG | 1 | 9.4 | 60.3 | 120.2 | 2.6 | 3.4 |
| Carbon | N/A | N/A | 75.2 | 68.7 | 4.6 | 4.6 |

| Sample Type | GG age (days) | Avg GG pH | subtract cntrl: %DNT After 1 hour (trial 2) | subtract cntrl: %DNT After 4 hours (trial 2) | Std Dev, % 1hr | Std Dev % 4hr |
|---|---|---|---|---|---|---|
| blank | N/A | N/A | -9.2 | -9.2 | 4.7 | 4.7 |
| DNT Control Standard | N/A | N/A | 92.3 | 90.8 | 4.5 | 4.7 |
| TIC GG | 20 | 3.9 | 83.1 | 85.3 | 4.5 | 4.2 |
| TIC GG | 18 | 4.2 | 81.6 | 82.2 | 4.5 | 4.6 |
| TIC GG | 14 | 3.9 | 91.9 | 90.3 | 4.7 | 4.4 |
| TIC GG | 12 | 4.5 | 83.8 | 89.2 | 4.4 | 4.2 |
| TIC GG | 7 | 5.5 | 52.7 | 70.5 | 2.7 | 2.7 |
| TIC GG | 4 | 4.8 | 83.7 | 70.3 | 3.2 | 3.2 |
| TIC GG | 1 | 5.8 | 48.7 | 67.7 | 4.4 | 4.2 |
| Fisher GG | 20 | 4.3 | 80.6 | 82.8 | 4.5 | 4.4 |
| Fisher GG | 18 | 4.2 | 83.0 | 80.8 | 4.5 | 4.6 |
| Fisher GG | 14 | 4.4 | 82.7 | 85.2 | 3.5 | 3.5 |
| Fisher GG | 12 | 4.6 | 81.7 | 76.8 | 4.7 | 4.6 |
| Fisher GG | 7 | 4.8 | 83.2 | 60.1 | 4.6 | 4.6 |
| Fisher GG | 4 | 6.3 | 71.2 | 100.8 | 0.3 | 1.6 |
| Fisher GG | 1 | 9.2 | 80.9 | 97.9 | 2.5 | 4.0 |
| Carbon | N/A | N/A | 69.5 | 66.8 | 4.6 | 4.7 |

**Supplement 12.**

| GG Application (Methodology) | Contaminant | Concentration of Contaminant | % Ratio GG Used (w/v) | Sample Size | UV-Vis Wavelength | Type of mixing | Any Pre-treatment |
|---|---|---|---|---|---|---|---|
| Hydrated GG (Trial 1) | Toluene | Toluene: 10 ppm | 0.5% GG, 5000 ppm | 6mL | Toluene: 261nm | Stationary | Centrifuge |
| Hydrated GG (Trial 2) | Toluene | Toluene: 50 ppm | 0.5% GG, 5000 ppm | 6mL | Toluene: 261nm | Stationary | Centrifuge |

| Sample Type | GG age (days) | Avg pH of GG used | Between 1 & 2 hrs (trial 1); Normalized to Co | Std Dev |
|---|---|---|---|---|
| Toluene Control Standard | N/A | N/A | 99.4 | 0.5 |
| TIC GG | 14 | 3.8 | 99.9 | 0.2 |
| TIC GG | 12 | 4.2 | 97.2 | 0.4 |
| TIC GG | 8 | 3.9 | 99.6 | 0.2 |
| TIC GG | 6 | 4.4 | 100.1 | 1.1 |
| TIC GG | 1 | 5.5 | 103.7 | 0.9 |
| Fisher GG | 14 | 4.3 | 104.4 | 0.4 |
| Fisher GG | 12 | 4.2 | 97.6 | 0.5 |
| Fisher GG | 8 | 4.4 | 96.6 | 2.6 |
| Fisher GG | 6 | 4.7 | 101.0 | 0.3 |
| Fisher GG | 1 | 9.4 | 87.4 | 1.8 |
| Carbon | N/A | N/A | 100.7 | 1.7 |

| Sample Type | GG age (days) | Avg GG pH | Between 1 and 4 hrs (trial 2); Normalized to Co | Std Dev |
|---|---|---|---|---|
| Toluene Control Standard | N/A | N/A | 77.1 | 0.6 |
| TIC GG | 20 | 3.9 | 91.7 | 0.3 |
| TIC GG | 18 | 4.2 | 91.0 | 0.1 |
| TIC GG | 14 | 3.9 | 96.7 | 0.1 |
| TIC GG | 12 | 4.5 | 88.0 | 0.4 |
| TIC GG | 7 | 5.5 | 115.4 | 3.3 |
| TIC GG | 4 | 4.8 | 96.6 | 4.5 |
| TIC GG | 1 | 5.8 | 132.4 | 0.5 |
| Fisher GG | 20 | 4.3 | 92.3 | 0.4 |
| Fisher GG | 18 | 4.2 | 94.6 | 0.1 |
| Fisher GG | 14 | 4.4 | 87.9 | 1.2 |
| Fisher GG | 12 | 4.6 | 91.9 | 0.1 |
| Fisher GG | 7 | 4.8 | 87.1 | 0.2 |
| Fisher GG | 4 | 6.3 | 68.4 | 1.9 |
| Fisher GG | 1 | 9.2 | 134.5 | 0.5 |
| Carbon | N/A | N/A | 55.7 | 0.2 |

**Supplement 13.**

| GG Application (Methodology) | Contaminant | Concentration of Contaminant | % Ratio GG Used (w/v) | Sample Size | UV-Vis Wavelength | Type of mixing | Any Pre-treatment |
|---|---|---|---|---|---|---|---|
| Crosslinked GG; GG with Salting-Out | Allura Red | 2.5 ppm; 0.005mM | 0.3% GG, 3000 ppm | 200mL | 505nm | Stirred | Varied - periodic syringe filter and centrifuge |

**Centrifuged or Filtered samples**

| Time elapsed | subtract cntrl: %Dye with wet puck (9.1g) | subtract cntrl: %Dye with dried puck (0.7g) | subtract cntrl: %Dye with crosslink powder 1 (0.6g) | subtract cntrl: %Dye with crosslink powder 2 (0.6g) | subtract cntrl: %Dye with crosslink gel (50.6g) |
|---|---|---|---|---|---|
| 2 hr; filter | -12.12 | 57.05 | 75.97 | 66.1 | 65.57 |
| 3hr; centrifuge | 73.72 | 78.86 | 82.5 | 83.37 | 71.19 |
| 24hrs; centrifuge | 75.37 | 76.89 | 84.83 | 23.16 | 63.83 |
| 50hrs; centrifuge | 76.02 | 77.88 | 101.47 | 18.45 | 22.73 |
| 71.5hrs; centrifuge | 74.05 | 77.78 | 124.52 | 18.15 | 71.89 |
| 5 day; centrifuge | 82.51 | 75.09 | 98.57 | -118.68 | 21.35 |
| 9 day; centrifuge | 58.86 | 74.98 | 12.36 | 82.02 | 37.83 |
| 12 day; centrifuge | 65.71 | 63.35 | -8.74 | 20.49 | 31.46 |
| 12 day; centrifuge & filter | 45.06 | 11.44 | -1.22 | 60.6 | 33.89 |
| 15 day; centrifuge | 52.44 | 68.62 | 37.46 | 72.1 | 105.56 |
| 15 day centrifuge & filter | 37.06 | 5.29 | -11.88 | 60.62 | 30.99 |
| 18 day; centrifuge | 38.08 | 52.26 | 82.96 | 82.86 | 81.28 |
| 20 day; centrifuge | 45.17 | 41.33 | 49.77 | 122.06 | 61.67 |
| 24 day; centrifuge | 31.80 | 22.85 | 64.13 | 78.56 | 64.98 |
| 30 day; centrifuge | 23.92 | 49.08 | 81.93 | 46.31 | 111.91 |
| 34 day; centrifuge | 37.49 | 64.89 | 116.84 | 74.21 | 148.52 |

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**14. ABSTRACT**
Guar gum (GG) is a promising product increasingly used in a variety of industries. It is nontoxic, inexpensive, and biodegradable. This research evaluated novel approaches using GG to adsorb aromatic organic water contaminants. Two brands of GG were tested using 5 different GG treatment strategies. Various experiments demonstrated nearly complete removal of Allura Red, Brilliant Blue, Erythrosine B, Methylene Blue, and Tartrazine dyes, as well as 2,4-dinitrotoluene; 78% adsorption was observed for Fast Green dye. GG typically removed less than 10% of toluene, which rapidly volatilizes. The application of pre-hydrated GG outperformed other GG treatment techniques, and in some instances demonstrated faster adsorption than an equivalent amount of granular activated carbon. Comparatively, usage of dry GG powder required over 1 week to demonstrate appreciable results; methods of GG cleaning, crosslinking, and salification were possible, but not substantially better than using unmodified gum. When dissolved in water, GG has unique spectrum characteristics at wavelengths below 300 nm, likely due to electronic transitions, which vary based on the quantity, age, and brand of GG used. Furthermore, adsorption may be linked to pH, and GG usage results in solution pH decrease, possibly due to production of a member of the carboxylic acid family.

**15. SUBJECT TERMS**
Guar gum, Allura Red, Brilliant Blue, Erythrosine B, Fast Green, Methylene Blue, Tartrazine Dye, Toluene, 2,4-Dinitrotoluene, DNT, biodegradable, adsorbent

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