DIFFUSION TESTING AND DEVELOPMENT OF A WATER FILTRATION SYSTEM USING BIODEGRADABLE CROSSLINKED POLYMERIC FILMS

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I dedicate this research and work to my family, friends, and colleagues whom have supported me over the past few years through the both my undergraduate and graduate careers. Thank you and God bless you.

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ABSTRACT

In this particular study, several polymeric films composed of polyvinyl alcohol and ionic liquid modified clays were crosslinked in the presence of glutaraldehyde to develop a water filtration system. The goal was to create a functional, biodegradable, environment friendly filtration system in which water contaminants such as dye could easily be removed from a potential water source. Throughout this study, several tests were conducted in order to fully understand how each clay modifier would affect the swelling characteristics of the film, the crystalline and melting characteristics of the film, and finally the diffusion of ions or dye through the film. It was concluded that these components were vital when attempting to understand and develop a potential water filtration system because each modification maintained differing diffusion trends regarding dye removal. Furthermore, by removing contaminates such as dye from a polluted water source, this study exemplified how other hazardous aromatic hydrocarbons could possibly be removed on a grander scale. All analyses regarding both clay and film modifications were completed using DSC, ISE, X – ray diffraction, and UV – Vis.

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CHAPTER 1 INTRODUCTION

Polymeric hydrogels, microspheres, and films have all been used in a wide variety of applications including biomedical, industrial, and environmental products. Such products include coatings, adhesives, emulsifiers, colloidal stabilizers, drug delivery systems, and possible watershed management devices.^{2, 5} Several studies have been performed to understand how the tensile strength, adsorption properties, and swelling capacities of these polymers participate in these applications. In addition, clays have also been studied for similar uses as well.¹⁰ Clays are not only excellent, inexpensive, abundant adsorbents for removing wastewater contaminants, but also clays act as carriers, barriers, and support scaffolds in many pharmaceutical applications.⁴ In the past, such clays like bentonite, kaolinite, and sepiolite along with polymers like polyvinyl alcohol and poly acrylamide have been studied independently. However, in this study the type of materials focused upon involved polymer - clay composite films. These films consisted of a blend between polyvinyl alcohol and ionic liquid modified clays encapsulated into a plastic. Even though this was not the first study of its kind, what mainly differentiated this study from the work by Ekici et al. involving poly acrylamide hydrogels with sepiolite⁴ was the fact the clays in this study were modified with both aliphatic and aromatic substituents on phosphonium based ionic liquids. By subjecting the clays and films produced in this study to either hydrophilic or hydrophobic ionic liquids, the modifications most helpful with facilitating the removal of dye from a contaminated water source could be determined. Additionally, the cationic dye of choice used in this study was malachite green rather than methylene blue, nile blue, or methyl violet; the type of clay used was sodium montmorillonite not sepiolite; and also all samples were made as polyvinyl alcohol films, not poly acrylamide hydrogels.⁴

As shown in **Figure 1**, polyvinyl alcohol is a biodegradable, hydrophilic, isotactic, semi crystalline polymer that incorporates repeating ethanol units maintaining a molecular weight of 44.00 g/mole.⁵ Also the hydroxyl groups for this polymer are aligned on the same side of the main chain.^{5,7} The polyvinyl alcohol utilized in this study maintained the molecular weight of approximately 22,000 grams per mole with an 88% degree of hydrolysis.⁵ Furthermore, polyvinyl alcohol was used in this study because unlike poly acrylamide, it allowed for the diffusion of small ions through its amorphous medium.⁵⁻⁶ Polyvinyl alcohol, a member of the porous membrane class, maintains a prolonged release micro matrix that affects the diffusion rate of ions through the polymer by inducing separation through the discrimination of particle size.⁷ Small ions can easily diffuse through the polymer; whereas, larger ions become entrapped. For this reason, due to polyvinyl alcohol's ability to size exclude, it was the better polymer to deal with the removal of a dye from a contaminated water source. Also polyvinyl alcohol when it degrades produces non – hazardous waste. When poly acrylamide degrades, the acrylamide subunits that form, drastically affect the environment by acting as neurotoxins to both humans and animals.4,8



Figure 1: **Polyvinyl Alcohol**. Polyvinyl alcohol is a hydrophilic semi – crystalline polymer that maintains several repeating ethanol units in which the alcohol groups attached are aligned on the same side of the main chain.⁵⁻⁷ The repeating units maintain a molecular weight of 44.00 g/mole.⁵

As previously mentioned, the type of clay adsorbent used in this experiment was sodium montmorillonite. As displayed in **Figures 2** – **3**, sodium montmorillonite is a smectite clay layered with a 2:1 expandable lamellar structure containing sodium aluminosilicate particles.⁹

Smectite clays form from the condensation of aluminum oxide or magnesium oxide octahedral sheets between two tetrahedral silicon dioxide sheets.¹⁰ The octahedral oxide sheets contain metallic defects with lower electron valences resulting in an overall negative charge for the clay.¹⁰ For this reason, in naturally occurring montmorillonite clays this charge is balanced with exchangeable inorganic cations, such as calcium or sodium. By balancing the charge of the clay with smaller alkali cations such as sodium, this renders the clay surface more hydrophilic allowing for the montmorillonite to be more easily dispersed into the polyvinyl alcohol matrix. Furthermore, this can lead to extensive film stability, improved stiffness, better chemical resistance, extensive permeability with heightened tensile strength, and an increased cation exchange capacity given the combine nature of each component.^{4, 9, 11} Also by incorporating smaller cations, cationic displacement interactions within the internal clay gallery is possible as well. As the malachite green organic cations interacted with the oxygen atoms aligning the internal clay gallery within the sodium montmorillonite, greater removal efficiency of the cationic dye is possible with enhanced adsorption properties as well because the smaller sodium cations can be displaced by larger organic cations. Therefore, sodium montmorillonite was chosen to be used for this study because it allows for larger organic molecules to wedge themselves between the internal clay galleries either through aromatic – pi, cationic – pi, or cationic displacement interactions.



Figure 2 -3: **Sodium Montmorillonite**. Montmorillonite is a smectite nanocomposite belonging to the 2:1 phyllosilicates family.^{9, 11} The crystal lattice of this structure maintains two dimensional octahedral sheets composed of alumina fused to the external silica tetrahedral sheets.¹⁰⁻¹¹ Specifically, the type of montmorillonite used in this experiment was sodium montmorillonite: $Na_{0.33}Al_2Si_4O_{10}$ (OH)₂ (H₂O)₁₀ and 549.07 g / mole respectively.¹¹

Aside from the polyvinyl alcohol and sodium montmorillonite being used in this study, the ionic liquids included hexyl triphenyl phosphonium bromide (HxPh₃PBr), tributyl hexadecyl phosphonium bromide (Bu₃HdPBr), and hexadecyl triphenyl phosphonium bromide (1-HdPh₃PBr), **Figures 4 – 6**.¹⁴⁻¹⁶ Ionic liquids are biodegradable salts in which poorly coordinated ions lead to limited crystal stability and melting points below 100° C.¹⁷⁻¹⁸ Due to the extreme differences between the anions and cations found within ionic liquids, stable crystal lattices are unable to form because one ion participates as a delocalized charge; whereas, the other ion acts as a stable weak base in solution.¹⁷ In comparison to one another, both the Bu₃HdPBr and HdPh₃PBr ionic liquids were more hydrophobic than that of the HxPh₃PBr ionic liquid because these two ionic liquids maintained elongated hydrocarbon chains in their molecular structures. Also all films were crosslinked with glutaraldehyde, **Figure 7**.



Figure 4: **Hexyl Triphenyl Phosphonium Bromide** (HxPh₃PBr). HxPh₃PBr is an aromatic hydrophilic phosphonium based ionic liquid. ¹⁴ HxPh₃PBr has three aromatic rings and a hexane hydrocarbon chain.¹⁴ The molecular weight of HxPh₃PBr is 427.36 g / mole respectively.¹⁴



Figure 5: **Tributyl Hexadecyl Phosphonium Bromide (Bu₃HdPBr)**. Bu₃HdPBr is an aliphatic hydrophobic phosphonium based ionic liquid. ¹⁵ Bu₃HdPBr has three butane hydrocarbon chains and a hexadecane hydrocarbon chain. ¹⁵ The molecular weight of Bu₃HdPBr is 507.65 g / mole respectively.¹⁵



Figure 6: Hexadecyl Triphenyl Phosphonium Bromide (HdPh₃PBr). $1 - HdPh_3PBr$ is an aromatic hydrophobic phosphonium based ionic liquid. ¹⁶ $1 - HdPh_3PBr$ has three aromatic rings and a hexadecane hydrocarbon chain. ¹⁶ The molecular weight of $1 - HdPh_3PBr$ is 567.62 g / mole respectively. ¹⁶

Glutaraldehyde is a toxic crosslinking agent that facilitates the formation of acetal linkages between monomer units of a polymer.⁴ Glutaraldehyde participates as both a strong irritant, aggravating the human eyes, the skin, and respiratory track, along with an antiseptic

topical medicine used to treat planar warts.^{4,44} As displayed in Figure 7, when the

glutaraldehyde was added to the polyvinyl alcohol films, new ring like structures formed

between the polymer monomer units leading to increased stability regarding the scaffolding or

internal infrastructure of the films.⁴ Therefore, by crosslinking each film, this not only can encapsulate the clays within the polymer, but also will minimize the dissolution of the films when placed in other aqueous solutions.⁴ However, by adding glutaraldehyde to polymer – clay composite films, not only do the swelling capabilities of the film become inhibited, but also the tensile strength and elasticity of the films are limited as well.^{1,4}



Figure 7: **Glutaraldehyde Crosslinking Reaction**. In order to encapsulate various materials, each polyvinyl alcohol film underwent a crosslinking reaction. By using glutaraldehyde as the crosslinking agent as shown in the schematic above, new acetal linkages developed within each polyvinyl alcohol film stabilizing the internal infrastructure of the films while minimizing dissolution in other aqueous substances.⁴

Focusing upon dye adsorption, the type of organic dye used in this experiment was malachite green oxalate or Basic Green 4, **Figure 8.**¹² Malachite green oxalate is a hydrophilic, cationic, triarylmethane dye exploited by textile companies to color silk, cotton, leather, jute, and paper.¹²⁻¹³ The leuco form of malachite green is colorless; whereas, the salt versions of the dye sustain an intense blue green color regarding the aromatic cations formed through resonance.¹³ In many cases malachite green oxalate is utilized as either a parasiticide, fungicide, acid – base indicator, or biological staining agent for blood and tissues samples regarding forensic science.¹²⁻¹³ Not only can malachite green oxalate destroy microorganisms in wood, plastics, and swimming pools, but also the dye can be used to develop inorganic phosphate assays for environmental purposes.¹³ Unfortunately, malachite green oxalate is also viewed as a hazardous

carcinogen and controversial aquaculture agent. ¹³ Malachite green oxalate drastically affects the fish population – crippling seafood supplies – and also causes severe damage to the human eyes and reproductive organs.¹² In many cases, there are reported instances of malachite green oxalate being released into the environment by textile manufacturers resulting in extensive water contamination. Malachite green oxalate was chosen for this study because it not only was a model textile dye, but also its structure resembled that of other hazardous wastewater pollutants known as polycyclic aromatic hydrocarbons (PAHs). Most importantly, the goal of this study was to develop a biodegradable water filtration devise capable of removing the dye without potentially harming an aquatic environment. Overall, the varied polymer – clay composite films produced participated as the filtration materials or plastic barriers between the fresh water and contaminated water samples within the model diffusion cell.



Figure 8: **Malachite Green Oxalate**. Malachite green, originally synthesized by Fisher Scientific in 1877, is a textile dye that stems from the condensation of benzaldehyde with dimethylaniline.¹² Although, the dye maintains two salt forms – chloride or oxalate – in this study, the salt form of malachite green utilized was malachite green oxalate. Malachite green oxalate not only maintains an intense blue green color, but also a strong absorption band at 618nm with an extinction coefficient of 150,000 M⁻¹ cm⁻¹.¹²

In essence, there are four potential ways in which malachite green oxalate can likely adsorbed to either the modified clays or polymer – clay composite films. The first adsorption pathway involves cationic displacement interactions, **Figure 9**. Cationic displacement interactions are single replacement reactions in which one cation potentially replaces another in a compound either through size exclusion or differences in electron affinity. ¹⁹ The reason why cationic displacement interactions occur is due to the compound's ability to maintain a greater

affinity for one cation versus the other given similar characteristics. For example, an increasingly hydrophobic compound will maintain a greater affinity or attraction towards larger hydrophobic cations in comparison to smaller hydrophilic cations. The fact that both the cation and the compound maintain less of an affinity for water due to their hydrophobicity leads to potential cationic displacement interactions. Furthermore, as an example, smaller hydrophilic cations will get replaced by the larger hydrophobic cations because of their size – potentially greater ability to freely dissociate in aqueous solutions – and most importantly differences in electron affinity in comparison.

$A + BC \rightarrow B + AC$

Figure 9: **Cationic Diplacement Interactions**. Cationic displacement interactions are single replacement reactions in which one cation gets replaced by another within a compound.¹⁹ Overall, due to differences in electron affinity, reactivity, and the overall ability of both the polymers and clays to size exclude, some of the phosphonium based ionic liquids were displaced by the malachite green oxalate cation due to the greater affinity of the oxygen atoms towards the nitrogen versus the phosphorus cations.

The second potential adsorption pathway regarding malachite green oxalate involves polar – π interactions. Polar – π interactions are reactions that occur between polar molecules and quadrupole moments in highly conjugated π systems.²¹ In this study, potential polar – π interactions can develop between the polymer - clay films and the phenyl rings within the malachite green structure. Overall, the top layer or skin of the polymer can help to determine the transport rate of the dye or contaminate; whereas, the incorporated clay particles can participate as scaffolds or support systems for the polymeric matrix.⁷ Additionally, for each polymer – clay composite film being used as a barrier between the two water sources within the diffusion cell, potentially different malachite green dye permeation rates can be established. Overall, due to permeation rates being inversely proportional to the thickness of each actual barrier, potentially higher permeation rates given the clay modifiers incorporated within the films may lead to symmetric membranes of comparable thickness and size due to increased swelling capabilities.⁷



Figure 10: Polar – π Interactions. Polar – π interactions are interactions that occur between polar molecules and quadrupole moments in highly conjugated π systems.²¹ Polar – π interactions developed between the clays, the polymeric films, and the phenyl rings maintained in the malachite green dye. As an example, when the polyvinyl alcohol hydroxyl groups encountered the phenyl rings within the malachite green structure, a reaction occurred which led to the facilitation as well as incorporation of the dye into the polymeric films through surface adsorption.

Cationic – π interactions are another potential adsorption pathway in which malachite green oxalate can be adsorbed to either the clays or polymer – clay films synthesized throughout the study. Cationic – π interactions are reactions in which cationic monopoles complex with quadrupole moments in highly conjugated π systems.²¹ Potential cationic – π interactions develop especially between non – exchanged clays and the phenyl rings within the malachite green oxalate structure. By interacting malachite green dye with the sodium cations within the montmorillonite composite, dye adsorption occurs within the internal clay gallery due to ionic bonds forming between the cationic monopoles and quadrupole moments of the malachite green dye. Furthermore, by interfacing the malachite green oxalate phenyl rings with the sodium cations found within sodium montmorillonite, both of these entities can possibly wedge themselves between the tetrahedral and octahedral sheets of the clay composite facilitating dye adsorption, **Figure 11**.



Figure 11: **Cationic** – π **Interactions**. Cationic – π interactions are reactions in which ionic bonds form between cationic monopoles and quadrupole moments in a highly conjugated π systems.²¹ Cationic – π interactions developed between the sodium ions within the non – exchanged clays and the phenyl rings maintained in the structure of malachite green oxalate. When the sodium ions encountered the phenyl rings within the malachite green structure, a reaction occurred leading to the facilitation, incorporation, and adsorption of dye into the internal clay gallery.

The final adsorption pathway in which malachite green oxalate could potentially infiltrate and adsorb to the modified clays or polymer – clay composite films within this experiment was through aromatic - π interactions. Aromatic - π interactions are reactions that involve aromatic – π stacking through the formation of covalent bonds between two quadrupole moments in highly conjugated π systems of two different species.²¹ The exchanged clays and films containing the HxPh₃PBr and HdPh₃PBr ionic liquids, potentially allowed for aromatic - π interactions due to the two types of aromatic species present in solution. In essence, when the highly conjugated aromatic systems of both the malachite green dye and the aromatic phosphonium based ionic liquids encounter one another, dye adsorption can occur through increased aromatic – π stacking, **Figure 12**. However, in some cases, not all films and clays are able to incorporate aromatic – π interactions as potential dye adsorption pathways because some phosphonium based ionic liquids lack conjugated aromatic systems. Modified clays and polymer – clay composite films exchanged with aliphatic phosphonium based ionic liquids – such as Bu₃HdPBr – rather than

aromatic phosphonium based ionic liquids are unable to facilitate dye adsorption specifically through aromatic – π interactions for this reason.



Figure 12: Aromatic – π Interactions. Aromatic – π interactions are reactions in which covalent bonds form between two quadrupole moments in highly conjugated π systems stemming from two different species.²¹ Aromatic – π interactions developed when the HxPh₃PBr and 1- HdPh₃PBr ionic liquids encountered the phenyl rings within the malachite green oxalate structure, leading to the facilitation, incorporation, and adsorption of the dye through aromatic – π stacking within the clay gallery. However, for the ionic liquid, Bu₃HdPBr, no aromatic – π interactions occurred due to limited aromatic species and quadrupole moments within this structure.

CHAPTER 2 MATERIALS AND METHODS

<u>Chemicals Provided:</u> The polyvinyl alcohol, MW: 22,000 grams / mole with an 88% degree of hydrolysis, used during this experiment was purchased from MP Biomedicals LLC. The 8% wt. glutaraldehyde solution was obtained from the Sigma – Aldrich Company. HPLC grade water, 99% wt. 1-bromohexane, 98% wt. 1 – hexadecyl triphenyl phosphonium bromide, and 200 proof OmniPur ethanol solutions were purchased from JT Baker, Acros Organics, Alfa Aesar, and Calbiochemical. The sodium montmorillonite sample (NaMT) was kindly donated by Southern Clay Products Inc. All other analytical grade chemicals used throughout this experiment: 95 - 98% wt. sulfuric acid, 99.5% wt. ethyl acetate, 99.8% wt. acetonitrile, 90% wt. sodium sulfate anhydrous, 97% wt. tributyl hexadecyl phosphonium bromide, 95% wt. malachite green oxalate, sodium bicarbonate, triphenylphosphine, and 1N hydrochloric acid were purchased from the Sigma – Aldrich or Fisher Scientific chemical companies.

Synthesis of Ionic Liquids: The ionic liquid, hexyl triphenyl phosphonium bromide (HxPh₃PBr), was synthesized using a one – step quaternization reaction. Approximately 10 grams of triphenylphosphine, 3.30mL of 1 – bromohexane, and 35mL of acetonitrile were placed into a 100mL round bottom flask and refluxed at a temperature of 110°C for a total of three days. On the third day, the reaction flask was removed from the condenser and allowed to cool to room temperature. The cooled reaction mixture was added dropwise to a beaker containing 300 mL ethyl acetate to crash out the quaternized product. The contents within the beaker were then collected using vacuum filtration and Whatman 41 filter paper. To ensure that all precipitate crystals formed were completely cleaned, purified, and dried; the crystals were washed over several times with ethyl acetate for approximately two minutes and then left on the vacuum

pump for an additional ten minutes to dry. Afterwards, the sample was placed into the oven to dry overnight on a watch glass at 90°C. DSC and X-Ray samples were taken of the HxPh₃PBr ionic liquid to assess its yield and purity, **Appendix C.** The same spectroscopic analyses were also conducted on the other ionic liquids purchased and utilized within this experiment.

Synthesis of Ionic Liquid Exchanged Clays: Once all ionic liquids were prepared and examined using spectroscopic techniques, approximately 2.75 grams of sodium montmorillonite clay was added to four closed cap bottles containing 50 mL of 50:50 HPLC grade water to ethanol. There were a total of four closed cap beakers filled with sodium montmorillonite clay on account that there were four different clay exchanges that occurred. A designated amount of ionic liquid was added to each beaker filled with clay given the exchange rate desired. After capping each beaker tightly, the clay samples were allowed to stir for approximately one week. At the end of the week, each clay exchanged sample was collected using vacuum filtration with 0.2µm Nylon filter paper. Afterwards, all clay samples were spread in thin layers over individual watch glasses and dried in an oven at 90°C overnight. Once dried, the ionic liquid exchanged clay was sampled for powder X – Ray diffraction analyses to determine how the ionic liquid exchanges affected the clay. (Ionic liquid exchange calculations can be found in chapter 3.)

Synthesis of Biodegradable PVA 22K Films: Although there were a wide variety of polymers and protocols able to create different polymeric films, the type of polymer used in this experiment was polyvinyl alcohol. Each film synthesized, used approximately 1 gram of polyvinyl alcohol. In approximately ten small 10mL beakers, 1 gram of polyvinyl alcohol (PVA 22K) was added along with various clays to prepare each modified film. The clay amounts used

to produce each film ranged from 1 – 10% in weight. The varieties of clays used to produce each film were either non – exchanged, 50% exchanged, or 100% exchanged. **Table 1** reveals the abbreviations used in this paper for the clays and films. To obtain each modified film, 7mL of water added to each beaker to homogeneously dispense the contents throughout the liquid medium. Also the solutions were heated at 75°C for 15 minutes to ensure that the polyvinyl alcohol was dissolved and the clay was well dispersed. Once each solution containing the various film modifications cooled down to room temperature, 0.5mL of both 8% wt glutaraldehyde solution and 1N hydrochloric acid were added to each beaker. Afterwards, the contents in each beaker were again stirred and poured into Teflon dishes in thin layers to produce films. All samples were allowed to dry in the fume hood overnight to remove excess water.

Cross-linking Biodegradable PVA 22K Films: To render the films insoluble and maintain film integrity and tensile strength, each polymeric film underwent a cross-linking process preserving the film structure for further examination. To crosslink the modified polymeric films established throughout this experiment, three solutions were required. For the first cross-linking solution, about 3.33 grams of sodium sulfate anhydrous was dissolved in 150mL of distilled water in order to form a 0.15M heated cross-linking solution. However, before heating this solution at 80°C for approximately 15 minutes, 15mL of concentrated sulfuric acid was also added to the solution. Overall, the sodium sulfate participated as a "salting out" agent for the polymer, minimizing sample dissolution prior to cross-linking; and the sulfuric acid participated as the catalyst. For the second cross-linking solution, 1.5mL of concentrated hydrochloric acid was weighed out by mass and placed in 150mL of distilled water to produce a 1% wt. hydrochloric acid solution. Additionally, this 1% wt. hydrochloric acid solution was also heated at 80°C for 15 minutes as well. Finally, for the third solution required, about 2.55 grams

of sodium bicarbonate was added to 150mL of distilled water to produce a 0.2M basic neutralizing solution. The sodium bicarbonate neutralized any excess acid remaining within the film sample. When attempting to crosslink each film, all heated solutions were monitored using a thermometer ensuring that temperature remained above 80°C for the cross-linking process.

When placing each individual film in the first cross-linking solution containing the sodium sulfate and sulfuric acid mixture, each film was heated along with gently stirred in solution for approximately one hour. After the one hour period ended, the films were then dipped in distilled water as a rinse solution and then placed in the 1% wt. hydrochloric acid solution for 30 minutes to be heated and gently stirred again. Once the 30 minute period ended, each film was again dipped in distilled water as a rinse solution and finally placed in the 0.2M sodium bicarbonate solution to neutralize any hydrochloric acid residue remaining in the film. The films were allotted 15 minutes to sit the in sodium bicarbonate solution before being removed and again rinsed with distilled water. Before storing each film in closed cap beakers of distilled water for short periods of time, X - Ray samples were taken of the films in order to observe how the various film modifications had affected crystallinity each film. Afterwards, all films were stored in closed cap beakers filled with distilled water keeping the films moist, limiting cracking, and increased rigidity accompanied with film dryness.

<u>PVA 22 K & Clay Equilibrium Adsorption Capacities:</u> In order to determine how differing solutions – distilled water versus malachite green – affect the crystal lattice and adsorption capacities of differing polymeric films, a natural diffusion study was conducted to determine the maximum loading capacity of each liquid medium into each polymeric film. In two small 15mL Falcon tubes, for each type of modified polymeric film, two small samples were cut and weighed to determine the original mass of each film sample before placing them in either

12mL of distilled water or a 4.82×10^{-5} M malachite green solution. Once weighed, each cut film sample was placed into one of the two liquid mediums. After a 24 hour period, the film samples were then retrieved from the small Falcon tubes using a pair of tweezers. All excess solution left behind in each Falcon tube was then discarded in a designated waste container. After quickly drying each sample with a paper towel, each cut film sample was then placed on a small weighing boat to naturally and fully dry over a period of 3 days. On the third day, each cut film sample was weighed again to obtain the dry weights of the film. Once both the swollen and dry masses of the film samples were collected, the adsorption capacities for each polymeric film were calculated. Additionally, this study was also conducted in a diffusion cell for a 20 hour period in order to see if and when the films would reach equilibrium or a maximum loading capacity in which no more malachite green dye could be adsorbed. After a 20 hour period, a distilled water sample, a malachite green sample, and a polymeric film measurement was taken to determine adsorption capacities. Before calculating the adsorption capacity, the samples were analyzed using UV - V is to determine the maximum loading capacity of malachite green dye for each particular polymeric film.

The same procedure was repeated for the ionic liquid modified clays as well; however, only 0.25 grams of clay were weighed out and added to each small 15mL Falcon tube. Also in addition, each Falcon tube was centrifuged for a period of ten minutes after the 20 hour malachite green exchange to ensure that all clay particles were no longer suspended in solution. Again before calculating the adsorption capacity, the clay samples were analyzed using UV – Vis to determine the maximum loading capacity and adsorption tactics of malachite green dye for each particular clay sample synthesized. (An example equilibrium adsorption calculation

is listed in chapter 3; whereas, an example equilibrium adsorption capacity table is listed in chapter 4.)

PVA 22K Film Diffusion Studies: In order to determine how quickly a wastewater contaminant can be removed from a possible watershed using a water filtration membrane, a type of diffusion study was conducted over a given interval of time to understand if and when an equilibrium period could be reached using differing polymeric films. In this study, malachite green dye was used to represent a type of wastewater contaminant. In order to generate a concentrated malachite green dye solution in which the UV – Vis absorbance value was equivalent to 1.00, first an increasingly concentrated malachite green stock solution was prepared. About 76.20 mg of malachite green dye was dissolved in 45mL of HPLC grade water within a large 50mL Falcon tube to generate a 5.45×10^{-3} M malachite green stock solution. Afterwards, several dilutions were made from this stock solution in order to evaluate which concentration provided a UV – Vis absorbance equivalent to the absorbance value of 1.00. Once this concentration was reached, a 1L stock solution of this particular concentration was established. After careful evaluation and examination, it was concluded that a 4.82×10^{-5} M malachite green stock solution provided an absorbance value equivalent to that of 1.00 (~ 0.962). Therefore, a malachite green stock solution maintaining a 4.82×10^{-5} M concentration was prepared in a 1L volumetric flask with HPLC grade water. (Beer's law and dilution calculations listed in chapter 3.)

To fully conduct this natural diffusion study over a given period of time, each film was placed in the 15mm PermaGear diffusion chamber in which one side of the chamber was filled with 10mL of distilled water and the other side of the chamber was filled with 10mL of 4.82×10^{-5} M malachite green solution. As the solutions were stirred and flow within the diffusion

chamber was developed, over a period of one hour, several samples were taken to determine the loading capacity or removal of the dye solution given the modified polymeric film being used. Samples were taken of the malachite green solution at intervals of 1 minute, 5 minutes, 10 minutes, 30 minutes, and 60 minutes. Between each interval and sampling, not only was a UV – Vis spectrum generated, but also each sample was returned to the diffusion chamber before the next sample was taken at a given interval. This ensured that not only was the volume within the diffusion chamber was maintained, but also that the one hour loading capacity was reached for each type of modified polymeric film accurately. Due to the time required to acquire a UV-Vis spectrum, the 5 minute interval was eliminated. Once the one hour diffusion period ended, not only was a final sample of the malachite green solution taken, but also a distilled water sample was taken to determine if any malachite green dye had leached through the polymeric film, contaminating the freshwater chamber in the diffusion cell. Furthermore, UV - Vis spectrums were taken of the distilled water sample after one hour, the malachite green sample after one hour, and the polymeric film after one hour to determine the one hour loading capacity of the dye for each particular polymeric film. The same process for each film was also repeated again; however, the malachite green exchange period was lengthened from a 1 hour exchange period to a 20 hour exchange period.

Instrumentation and Protocols: To conduct all testing regarding DSC, ISE, X-Ray Diffraction, and UV - Vis spectroscopic analyses, several parameters had to be set for each experimental test. The UV – Vis spectrophotometer used was a Shimadzu 200 UV - Vis Spectrophotometer. The parameters set for this instrument included an absorbance wavelength range of 200 - 800nm. Malachite green oxalate samples exhibit strong absorption bands at 618nm and 421nm. Additionally, when examining the presence of phenyl rings in the ionic

liquids, typically phenyl rings for most aromatic samples maintain strong absorption bands between 250 – 255nm. For differential scanning calorimetry (DSC), TA Instruments Q-2000 Calorimeter was used. The parameters set for this instrument included an equilibration period of approximately two minutes at 0°C for each sample; a ramping up of the sample temperature from 0° - 240°C at a rate of 10°C per minute; an isotherm period at 240°C for two minutes; a ramping down of the sample temperature from 240° - 0°C at a rate of 10°C per minute; and again a isotherm period at 0°C for an additional two minutes. The heating and cooling cycles were repeated a second time for each sample. For the Ion Selective Electrode used (ISE), a Thermo Scientific Orion Ross Sodium Ion Selective Electrode was used along with a Thermo Scientific pH Meter to conduct sodium cation concentration measurements. Finally, a Rigaku Miniflex II Diffractometer was used to collect X-Ray diffraction data. The parameters set for this instrument included an initial start angle at 2 degrees, a stop angle at 40 degrees, a scan speed of 1.0 degree per second, and a sampling width of 0.5 degrees. (Sodium ion selective electrode calculations listed in chapter 3.)

CHAPTER 3 EXPERIMENTAL CALCULATIONS

Ionic Liquid Calculations:

 $(262.69 \text{ g/mole Triphenylphosphine}) / (427.39 \text{ g/mole HxPh}_3PBr) * 10 \text{g} \text{ product desire} = 6.1460 \text{g} \text{ Triphenylphosphine}$ $(165.07 \text{ g}/\text{mole 1 - Bromohexane}) / (427.39 \text{ g}/\text{mole HxPh}_3PBr) * 10 \text{ g} \text{ product desire} = 3.8620 \text{g} \text{ 1 - Bromohexane}$ 3.8620 g 1 - Bromohexane * (1 mL / 1.17 g 1 - Bromohexane) = 3.301 mL 1 - Bromohexane

Ionic Liquid Clay Exchange Calculations:

2.7500 g NaMT x (92 meqv/100 g NaMT) x (1 mol $HxPh_3PBr$ /1000 meqv) x (50/100%) x (427.39 g $HxPh_3PBr$ /1 mol $HxPh_3PBr$) = 0.5407 g Hexyl Triphenyl Phosphonium Bromide ($HxPh_3PBr$)

2.7500 g NaMT x (92 meqv/100 g NaMT) x (1 mol $HxPh_3PBr$ /1000 meqv) x (<u>100/100%</u>) x (427.39 g $HxPh_3PBr$ /1 mol $HxPh_3PBr$) = 1.0813 g Hexyl Triphenyl Phosphonium Bromide ($HxPh_3PBr$)

2.7500 g NaMT x (92 meqv/100 g NaMT) x (1 mol Bu_3HdPBr /1000 meqv) x (<u>100/100%</u>) x (507.75 g Bu_3HdPBr /1 mol Bu_3HdPBr) = 1.2846 g Tributyl Hexadecyl Phosphonium Bromide (Bu_3HdPBr)

1.5000 g NaMT x (92 meqv/100 g NaMT) x (1 mol **1 - HdPh₃PBr** /1000 meqv) x (<u>100/100%</u>) x (567.69 g **1 - HdPh₃PBr** /1 mol **1 - HdPh₃PBr**) = 0.7834 g 1 – Hexadecyl Triphenyl Phosphonium Bromide (**1 - HdPh₃PBr**)

Malachite Green Dilution Calculations:

 $(0.0762 \text{ g Malachite Green}) / (310.95 \text{ g/mole Malachite Green}) = 2.45 * 10^{-4} \text{ moles Malachite Green}$ $(2.63* 10^{-4} \text{ moles Malachite Green}) / (0.045L \text{ HPLC Grade H}_2\text{O}) = 5.45 * 10^{-3} \text{ M Malachite Green solution}$ Stock Solution Concentration – 5.45* 10⁻³ M Malachite Green $\mathbf{M_1V_1} = \mathbf{M_2V_2}$ $(4.82 * 10^{-5} \text{ M Malachite Green}) \times 1L = (5.45 * 10^{-3} \text{ M Malachite Green}) \mathbf{V_2}$ $\mathbf{V_2} = \underline{8.84mL} \text{ Needed For Dilution}$ (Eq. #1)

UV - Vis Calculations:

| $\frac{\text{Beer's Law: }}{\mathbf{A} = \mathbf{Ebc}}$ $\mathbf{A} = \text{Absorbance } \mathbf{E} = \text{Molar Absorbtivity (M -1 cm -1)}$ $\mathbf{b} = \text{Pathlength (cm) } \mathbf{c} = \text{Concentration (M)}$ | (Eq. #2) |
|--|----------|
| EXAMPLE: | |
| $C = A / Eb Malachite Green Oxalate E = 162,149 M^{-1} cm^{-1} C = (0.962) / (162,149 M^{-1} cm^{-1} * 1 cm) \qquad C = 5.93 * 10^{-5} M \text{ solution (theoretical)}$ | |

Experimental Error Calculations:

| Percent Error: = [(Theoretical - Experimental) / Theoretical] * 100% | (Eq. #3) |
|--|------------|
| EXAMPLES: | |
| Theoretical Malachite Green Oxalate $\mathcal{E} = 150,000 \text{ M}^{-1} \text{ cm}^{-1}$ Experimental Malachite Green Oxalate $\mathcal{E} = 162,149 \text{ M}^{-1} \text{ cm}^{-1}$ | |
| $[(162,149 \text{ M}^{-1} \text{ cm}^{-1} - 150,000 \text{ M}^{-1} \text{ cm}^{-1}) / (150,000 \text{ M}^{-1} \text{ cm}^{-1})] * 100\% = 8.1\% \text{ Error} \text{ (Malachite Green Oxalate 8)}$ | E) |
| Theoretical Malachite Green Oxalate = $(5.93 \times 10^{-5} \text{ M concentration / 1L}) = 0.01844 \text{ grams MG}$ Experimental Malachite Green Oxalate = $(4.82 \times 10^{-5} \text{ M concentration / 1L}) = 0.01499 \text{ grams MG}$ | |
| [(0.01844 grams – 0.01499 grams) / (0.01844 grams)] * 100% = 18.7% Error (Malachite Green Oxalate Conce | entration) |

Adsorption Capacity Study Calculations:

| | | , |
|-------|--|---------|
| 1.1 | | |
| i | | |
| 1.1 | [(Swollen polymer weight – Dry polymer weight) / Dry Polymer Weight] * 100% (Eq. # | ·4) I |
| 1.1 | | - í - I |
| ÷ | | |
| 1. | EXAMPLE: | |
| 1. | | |
| i | | 1 |
| 1 - E | [(0.12726 g PVA 22K Film - 0.05597 g PVA 22K Film) / 0.05597 g PVA 22K Film] * 100 - 127% Swell PVA 22K Film | m |
| 1 - E | $\left[\left(0.12720\text{g}^{-1}^{-1}\text{v}^{-2}\text{c}^{-1}\text{m}^{-1}\right)^{-1}^{-1}^{-1}\text{o}^{-1}\text{c}^{$ | |
| 1 | | |
| L | | |

Malachite Green Removal Efficiency Calculations:

| [| [(Initial MG Concentration – Equilibrium MG Concentration) / (Equilibrium MG Concentration)] * 100% (Eq. #5) | |
|---|--|--|
| | EXAMPLE: | |
| | Initial Malachite Green Concentration = 15.00 mg / L Final Malachite Green Solution Concentration (20hrs) = 5.02 mg / L | |
| | [(15.00 mg / L - 5.02 mg / L) / (15.00 mg / L)] * 100% = 67% MG Removal Efficiency (PVA 22K Film) | |

Malachite Green Binding Ratio Calculations:

- - - -

| | $\mathbf{R} = (\mathbf{C}_{\mathbf{B}} / \mathbf{P})$ $\mathbf{C}_{\mathbf{B}} = \text{Equilibrium Concentration of Solute in Adsorbent (M)}$ $\mathbf{R} = \text{Binding Ratio } \mathbf{P} = \text{Moles of Monomer Unit (M)}$ | (Eq. #6) |
|----|--|----------|
| Į. | EXAMPLE: | |
| | R (_{PVA 22K Film}) = [($2.5*10^{-3}$ M Malachite Green) / ($3.05M$ PVA Monomer Unit)] R (_{PVA 22K Film}) = 0.81 mM of malachite green dye / mole of monomer unit of polyvinyl alcohol (PVA) | |

- - - - -

X-Ray Diffraction Calculations:

| $\lambda = 2d^*sin\Theta$ $\lambda = Wavelength of X - ray radiation (nm)$ $d = Spacing between diffraction lattice planes (nm)$ | (Eq. #7) |
|--|----------|
| Θ = Diffraction or glancing angle EXAMPLE: | |
| $d = (\lambda / 2*\sin\Theta) \text{ NaMT } 2\Theta \text{ Angle} = 7.15^{\circ} \lambda = 0.15418 \text{ nm} (\textbf{X-Ray value designated})$ NaMT $\Theta \text{ Angle} = (7.15^{\circ} / 2) = 3.58^{\circ} d = (0.15418 / 2*\sin(3.58)) d_{\text{(sodium montmorillonite internal lattice)}} = 1.24 \text{ nm}$ | |

Sodium Ion Selective Electrode Calculations:

| | y = 19 x = Concentra y = Ion selection | .403ln(x) - 186.2 ation of sodium i ive electrode read | 29 ons (ppm) ding (mV) | (Eq. #8) |
|--|--|--|-------------------------------------|--|
| EXAMPLE: | | | | |
| $\mathbf{y}_{(\text{Sodium Montmorillonite Clav Sample})} = -78.5 \text{ n}$ -78.5 = 19.403ln(x) - 186.29 107.7 | mV 9 = 19.403ln(x) | $5.555 = \ln(x)$ | $\mathbf{x} = e^{(-5.555)}$ | x = 259 ppm Na ⁺ ions in solution |

CHAPTER 4 FIGURES AND TABLES

| ABBREVIATION | SAMPLE NAME | |
|-----------------------|---|--|
| MG | Malachite Green Oxalate | |
| PVA 22K | Polyvinyl Alcohol MW: 22,000 grams / mole | |
| NaMT | Sodium Montmorillonite | |
| HxPh ₃ PBr | Hexyl Triphenyl Phosphonium Bromide | |
| Bu ₃ HdPBr | Tributyl Hexadecyl Phosphonium Bromide | |
| HdPh ₃ PBr | Hexadecyl Triphenyl Phosphonium Bromide | |

Table 1: Abbreviations. This table represents and defines all abbreviations used throughout this research.



Figure 13: **Different Ionic Liquids**. This figure represents the various ionic liquids used throughout this experiment to modify both the clays and the polyvinyl alcohol – clay films. For the HxPh₃PBr and HdPh₃PBr ionic liquids, two peaks appeared between the wavelengths of 250 - 255nm indicating the presence of phenyl rings. If these peaks surface after clay or film exchanges with the malachite green dye, then as a result cationic displacement interactions have occurred.



Figure 14: **Different Ionic Liquid Modified Clays after MG Exchange (20hrs).** This figure represents the results of the ionic liquid modified clays after being exchanged with the malachite green dye for a period of 20 hours. Only one clay sample revealed the presence of phenyl rings stemming from the displacement one of the aromatic phosphonium based ionic liquids. Overall, due to these peaks surfacing after 50 and 100 CEC NaMT – HxPh₃PBr clay exchanges with the dye malachite green, it was concluded that cationic displacement interactions occurred.



Figure 15: **Different Ionic Liquid Modified Clays X-Ray**. This figure represents the plain sodium montmorillonite composites after being exchanged with various ionic liquids. For each of these ionic liquid exchanged clays, one can easily determine the D-spacing values and structural formations the internal clay galleries given the 2 Θ angles designated.



Figures 16 – 17: **Clay Formations and Structures**. These figures represent the different formations in which an ionic liquid can aggregate between the interlayer of the clays or polymer – clay films. Overall, ionic liquid incorporation maintains a great influence on D-spacing between the clay or polymer layers leading to four different interlayer configurations. The four different interlayer formations are: (a) lateral monolayer, (b) lateral bilayer, (c) paraffin – monolayer, and (d) paraffin – bilayer. For the sodium montmorillonite clay, the sodium ions intertwined within the tetrahedral and octahedral sheets of the montmorillonite structure maintain a lateral bilayer formation.



Figure 18: Malachite Green Clay Exchanges (1hr) X - Ray. This figure represents the various ionic liquid exchanged clays interfaced with the malachite green dye after a one hour adsorption period. For each of these ionic liquid exchanged clays, one can easily determine the D-spacing values and structural formations of the internal clay galleries after the one hour adsorption period given the 2 Θ angles designated.

| X Diffraction Data | | | | | | | |
|----------------------------|---------|--------------------------|------------------------------|-----------------------------------|--|--|--|
| SAMPLE | Clay 20 | <u>D-spacing</u> (nm) | <u>Malachite</u> Green 20 | Malachite Green D-spacing (nm) | | | |
| NaMT Clay | 7.15 | 1.24 | 6.98 | 1.27 | | | |
| 50 CEC NaMT - | 5.07 | 1.74 | 5.23 | 1.68 | | | |
| HxPh ₃ PBr Clay | 9.95 | 0.89 | 9.85 | 0.90 | | | |
| 100 CEC NaMT - | 5.05 | 1.75 | 4.94 | 1.79 | | | |
| HxPh ₃ PBr Clay | 9.99 | 0.89 | 9.85 | 0.90 | | | |
| 100 CEC NaMT - | 4.06 | 2.18 | 4.13 | 2.14 | | | |
| Bu ₃ HdPBr Clay | 8.09 | 1.09 | 8.20 | 1.08 | | | |
| | 2.84 | 3.11 | 2.97 | 2.97 | | | |
| 100 CEC NaMT - | 4.71 | 1.88 | 4.62 | 1.91 | | | |
| HdPh ₃ PBr Clay | 9.20 | 0.96 | 9.35 | 0.95 | | | |

Table 2: **X-Ray Diffraction Data**. This table represents the changes in the D-spacing values for all ionic liquid modified clays after being exchanged with either ionic liquids or malachite green dye. Typically the literature D-spacing value for sodium montmorillonite is roughly about 1.24nm.^{11, 23} Also regardless of the type of exchange, an increase in D-spacing leads to better intercalcation or exfoliation of the layers within polymer and clay composites leading to more improved physical and chemical properties.²⁴ Additionally, the presence of overtone peaks as highlighted above indicated the presence of well organized spatial arrangement as well within the modified clay structures.²⁴ Therefore, from this table both the structural arrangements of the clay layers can be uncovered given the ionic liquid or dye modifications present.

| PVA 22K Film Swelling Capacities | | | | | | |
|---|---|---------------------------|--|--|--|--|
| SAMPLE | H ₂ O Swelling Percentage | MG Swelling Percentage | | | | |
| PVA 22K Film | 77% | 95% | | | | |
| 1% wt. NaMT PVA 22K Film | 108% | 109% | | | | |
| 1% wt. 50 CEC NaMT – HxPh ₃ PBr PVA 22K Film | 149% | 151% | | | | |
| 1% wt. 100 CEC NaMT – HxPh ₃ PBr PVA 22K Film | 255% | 273% | | | | |
| 1% wt. 100 CEC NaMT – Bu₃HdPBr PVA 22K Film | 131% | 139% | | | | |
| 1% wt. 100 CEC NaMT – HdPh ₃ PBr PVA 22K Film | 99% | 125% | | | | |

Table 3: **PVA 22K Film Swelling Capacities**. This table represents the swelling capacity of each film in two different mediums over a 20 hour period given their various ionic liquid and clay modifications. After 3 days, a dry mass of each film was collected in order to fully understand how the swelling capacity of either water or malachite green into the polymeric films affects thickness and film transport abilities. Also as a side note, by incorporating ionic liquids and ionic liquid exchanged clays into the films, this overall affected the swelling capacity of each film because the extent of swelling depended upon the length of the alkyl chain incorporated. Overall, the introduction of ionic liquids into the clays and polymeric films within this experiment led to increased polar – π , aromatic – π , cationic- π , and cationic displacement interactions.

| PVA 22K Malachite Green Film Diffusion Studies (20hrs) | | | | | | | |
|--|---|---------------------------------|--------------------|--|------------------------|---|------------------------------|
| SAMPLE | <u>Monomer</u> <u>Concentration</u> (<u>M)</u> | MG Film Concentration (M) | MG Film (mg) | <u>H₂O</u> <u>solution</u> (mg) | MG solution (mg) | <u>MG</u> <u>Binding</u> <u>Ratio</u> (mM) | <u>Removal</u> Efficiency |
| PVA 22K Film | 3.05 | 2.5E-03 | 7.67 | 2.30 | 5.02 | 0.81 | 67% |
| 1% wt. NaMT PVA 22K Film | 3.06 | 3.2E-03 | 9.86 | 3.07 | 3.95 | 1.04 | 74% |
| 1% wt. 50 CEC NaMT – HxPh ₃ PBr | | | | | | | |
| PVA 22K Film | 3.05 | 1.3E-03 | 4.15 | 5.06 | 5.79 | 0.44 | 61% |
| NaMT – HxPh ₃ PBr PVA 22K Film | 3.15 | 2.0E-03 | 6.10 | 4.03 | 4.87 | 0.62 | 68% |
| 1% wt. 100 CEC NaMT – Bu ₃ HdPBr | 2.05 | 1.55.00 | 5.00 | 2.04 | 5.04 | 0.55 | <00/ |
| PVA 22K Film 1% wt. 100 CEC | 3.05 | 1.7E-03 | 5.22 | 3.84 | 5.94 | 0.55 | 60% |
| PVA 22K Film | 3.14 | 2.7E-03 | 8.52 | 1.88 | 4.60 | 0.87 | 69% |

Table 4: **PVA 22K Malachite Green Film Diffusion Studies (20hrs)**. This table represents the amount of malachite green dye present in solution after an equilibrium study was hosted for each polymeric film. In most cases, the malachite green dye leached through the polymeric film barriers and contaminated the freshwater samples in the diffusion cell. However, some films removed more dye than others through adsorption as shown above. Also the binding ratio of malachite green per PVA monomer unit of the polymeric – clay composite films was determined as well.

CHAPTER 5 RESULTS AND DISCUSSION

In this experiment, several ionic liquid modified clays and polymer – clay composite films were synthesized. Given their vastly changing sizes, molecular weights, and alkyl chain lengths, when each of these phosphonium based ionic liquids were integrated into the sodium montmorillonite clays or polyvinyl alcohol films, these substances directly impacted the clays and films examined leading to several new theories and implications germane to malachite green dye adsorption. For instance, in **Figures 13 - 14**, when these ionic liquids were introduced into the internal clay galleries after being exchanged for a 20 hour period with the cationic dye, several possible dye adsorption pathways emerged. Given the ionic liquids present within the montmorillonite clay composites, each dye adsorption pathway was not only uniquely different, but also solely significant to the clay modifier being used. For the ionic liquids that contained aromatic or phenyl rings within their structures, these modifiers facilitated the adsorption of dye through mostly aromatic - π or cationic displacement interactions; whereas, for the ionic liquids that consisted solely of aliphatic hydrocarbon chains or sodium ions, these particular substances were only was able to facilitate the adsorption of dye through limited cationic displacement interactions, minimal cationic $-\pi$ interactions, or not at all.

The three main phosphonium based ionic liquids used throughout this study – HxPh₃PBr, Bu₃HdPBr, and HdPh₃PBr – were monitored using UV absorption as shown in **Figure 13**. Specifically focusing upon the HxPh₃PBr and the HdPh₃PBr ionic liquids, there were two peaks that appeared between the wavelength range of 250 – 255nm on the UV – Vis spectrum generated. These two peaks indicated the presence of phenyl rings for each ionic liquid. Contrarily, for the ionic liquid, Bu₃HdPBr, which lacked aromatic rings no peaks appeared within the given wavelength range for this particular substance. When examining **Figure 14**, after a 20 hour exchange period with the malachite green cationic dye, the clays incorporating the HxPh₃PBr ionic liquids within their clay galleries, lost their important phenyl peaks in the spectrum indicating cationic displacement interactions within the montmorillonite composites. Due to the close proximity of oxygen and nitrogen atoms on the periodic table, the oxygen atoms aligning the edges of the internal clay galleries maintained a greater affinity towards the positively charged nitrogen cations in the malachite green oxalate dye, more so than the phosphorus cations within the ionic liquid structures.¹⁹ Therefore, in this situation, the HxPh₃PBr ionic liquid was displaced from internal clay galleries of both the 50% and 100% exchanged clays in order to form more stable ionic bonds between the oxygen and the nitrogen atoms stemming from the internal clay galleries and malachite green oxalate dye.

Conversely, for the clay incorporating the ionic liquid HdPh₃PBr within its structure, the phenyl peaks remained present within the spectrum even after the dye exchange period ended – an indication that cationic displacement interactions did not occur. Therefore, due to the continued presence of phenyl rings within this clay, it was concluded that the dye adsorption pathway used to facilitate the removal of malachite green dye from the contaminated water source was actually done through aromatic – π interactions instead. When the highly conjugated aromatic systems of malachite green oxalate and the HdPh₃PBr ionic liquid encountered one another, a complex formed between the two types of phenyl rings leading to the minimal steric hindrance through increased aromatic - π stacking within the internal clay gallery, **Figure 12**. By sandwiching together the two types of phenyl rings, the removal efficiency of the malachite green oxalate dye skyrocketed for the HdPh₃PBr ionic liquid modified clay. Overall, by using aromatic - π stacking as the dye adsorption pathway, these interactions allotted for increased dye adsorption through expanded clay layer exfoliation.

Regarding the plain sodium montmorillonite clay in **Figure 14**, no phenyl peaks appeared for this composite as well because this composite lacked aromatic rings within its internal clay gallery; however, a small peak did appear around 621 nm indicating that not all of the malachite green dye was removed from the contaminated water source for this particular clay composite. Even though sodium montmorillonite was not an ionic liquid modified clay, cationic displacement interactions were still able to take place as one possible adsorption pathway. Also another potential adsorption pathway for this composite included cationic – π interactions as well. In order to determine if cationic displacement interactions occurred in comparison to cationic $-\pi$ interactions, measurements were taken to determine the concentration of sodium ions present in aqueous solutions before and after the malachite green dye exchange. Originally before the dye exchange, the amount of sodium ions present in solution was less than 1 ppm; whereas, after the dye exchange, the concentration of sodium ions present in solution increased to 259 ppm. Therefore, cationic displacement interactions occurred between the malachite green dye and the sodium montmorillonite composite as well. Again as previously mentioned, the oxygen atoms aligning the internal clay gallery had a greater affinity for the positively charged nitrogen cations versus the sodium cations present due to the close proximities between oxygen and nitrogen atoms on the periodic table.¹⁹ Furthermore, even though cationic displacement interactions occurred between the malachite green dye and the sodium montmorillonite clay, the full amount of malachite green dye was unable to be removed from the contaminated water source likely due to reaching an equilibrium. This could be determined by resoaking the clay in fresh malachite green solution, but this is outside the scope of this study.

Finally, for the Bu₃HdPBr ionic liquid modified clay, although the clay composite appeared to be colored after the dye exchange, it could not be pinpointed exactly as to how the

dye was incorporated into the internal clay gallery. The Bu₃HdPBr ionic liquid modified clay lacked aromatic rings within its structure; therefore, cationic displacement interactions could have occurred, but one would not be able to support this theory most definitely because no indication was provided by the UV - V is spectrum, **Figure 14**. All that could be determined was that somehow the dye infiltrated into the clay composites possibly in the form of tactoids or disorganized layer arrangements. The same 20 hour exchange period was repeated again with the malachite green dye regarding the polymer - clay films. Although in the case of the polymer clay film samples synthesized, several possible dye adsorption pathways occurred simultaneously due to a new adsorption pathway introduced, polar – π interactions. When highly conjugated aromatic systems of malachite green oxalate encountered the polar hydroxyl groups aligning the edges of polyvinyl alcohol chain, polar – π interactions surfaced leading to increased dye adsorption through aromatic $-\pi$ stacking within the top layers of the polymer. Given the ionic liquid modifiers and clays integrated within each polymer - clay film, not only did combinations of dye adsorption pathways emerge, but also each adsorption pathway combination was uniquely different and solely significant to the polymer - clay film being used. For each distinctive polymer – clay film sample produced throughout the study participating as a barrier between the model diffusion cell, again the facilitated removal of dye was done through either combinations of polar – π interactions, aromatic – π interactions, cationic – π interactions, or cationic displacement interactions.

After subjecting the sodium montmorillonite clays to both aliphatic and aromatic phosphonium based ionic liquids, X-Ray diffraction samples were taken of the modified clays to analyze the new d-spacing generated, as shown in **Figure 15**. In most cases like in **Table 2**, as the 2Θ angles decreased, the d-spacing values increased indicating the presence of phosphonium

based ionic liquids within the internal clay galleries between the tetrahedral and octahedral sheets of the montmorillonite structures. In essence, the oxygen atoms aligning the two sheets donated their electrons to the phosphorus based cations within the ionic liquids to establish new ionic bonds between the clay layers. When these new ionic bonds developed, the original sodium cations were then displaced from the internal clay galleries of the montmorillonite structures leading to limitations in the surface area available to adsorb malachite green dye. However, given the presence of these new ionic bonds formed within the clays, not only was the d-spacing heightened, but also better intercalcation and layer exfoliation within the polymer developed.²⁴ Intercalcation occurs when hydrophilic cations are eliminated from the internal clay galleries through the displacement of these substances by larger organic cations; as a result, these insertions help to establish more organized multilayer formations within the clay galleries.²¹ In addition, as depicted in Table 15, all clay samples experienced better intercalcation due to the establishment of more hydrophobic clay galleries from the phosphonium based ionic liquids. Furthermore to illustrate a highly ordered structure was established, all clay X-Ray diffraction samples experienced overtone peaks, Figure 15 and Table 2. Overtone peaks are secondary ordered peaks that occur in X-Ray diffraction samples pinpointing the presence of well organized spatial arrangements within the internal clay layers.¹¹ Overtone peaks can be identified by either doubling the original 2 Θ angles or dividing the d-spacing values by $\frac{1}{2}$.¹¹ Within **Table** 2, each clay exhibited the presence of overtone peaks showing that by exchanging out the hydrophilic sodium cations with bulky organic cations, the hydrated phyllosilicate clays became more ordered. The expansion of the d-spacing within the polymer films showed that the clays became increasingly organophilic as well – allowing for the enhanced dye removal of such hazardous organics like malachite green oxalate.¹¹

Focusing upon the spatial arrangements as shown in **Figure 16**, ideally when sodium montmorillonite composites lack organic modifying cations within its internal clay gallery, the dspacing values calculated mirror that of 1.18 nm with a lateral monolayer formation.^{11, 23, 24} However, when intertwined with sodium cations, the d-spacing for the montmorillonite composite slightly escalates to roughly 1.23 or 1.24 nm respectively, Figure 17 and Table 2.^{11,23} This evidence again was also supported by examining Figure 15. In Figure 15, for the sodium montmorillonite composite, this clay attained one X - Ray diffraction peak. The peak appeared around the 2 Θ angle of 7.15 degrees which corresponded to the literature d-spacing value of 1.24 nm.^{11,23} This value was also indicative of a lateral bilayer arrangement for the sodium montmorillonite clay as well.⁴³ Due to the negatively charged oxygen atoms aligning the tetrahedral and octahedral sheets of the internal clay gallery, for each individual oxygen atom an individual sodium cation was used to counterbalance the charge by allowing each oxygen atom to donate a lone pair of electrons to each sodium cation forming new ionic bonds. Furthermore, due to sodium cations maintaining relatively small atomic sizes, these cations were able to laterally stack on top of one another without too much steric interference surfacing within the internal clay gallery; in essence, forming a lateral bilayer spatial arrangement, Figure 16. In regards to the other ionic liquid modified clays produced throughout this study, each clay not only its attained its own significant spatial arrangements within the internal clay gallery, but also vastly differing d-spacing measurements emerged as well. Most importantly, in all cases one would expect the d-spacing values for all modified clays to be greater than that of 1.24 nm, because as previously mentioned all modified clay samples experienced better layer expansion due to the establishment of new ionic bonds formed between the phosphonium based ionic liquids and the oxygen atoms within the internal clay galleries.²⁴

For the 50% and 100% ionic liquid exchanged clays containing the HxPh₃PBr ionic liquid, these clays both attained two X - Ray diffraction peaks as shown in **Figure 15** and **Table 2.** For the 50% exchanged clay, the first peak appeared around the 2Θ angle of 5.07 degrees; whereas, the second peak appeared around the 2Θ angle of 9.95 degrees. The peak at 5.07 degrees corresponded to the d-spacing of 1.74 nm; whereas, the peak at 9.95 degrees corresponded to the d-spacing of 0.89 nm. In regards to the 100% exchanged clay, the first peak appeared around the 2 Θ angle of 5.05 degrees; whereas, the second peak appeared around the 2 Θ angle of 9.99 degrees. The peak at 5.05 degrees corresponded to the d-spacing of 1.75 nm; whereas, the peak at 9.99 degrees corresponded to the d-spacing of 0.89 nm. Overall, when comparing the two peaks generated to one another for both modified clays, the peaks that appeared around the 2O angles of 9.95 and 9.99 degrees were not only roughly similar in value, but also viewed as overtone peaks. Again as previously mentioned, the presence of overtone peaks within X-Ray diffraction samples pinpoint the formation of well organized spatial arrangements within the internal clay galleries.¹¹ To determine if these two peaks were indeed overtones, the d-spacing values found regarding each angle was roughly ¹/₂ the original d-spacing values calculated from the smaller angles denoted within the clays. Also in comparison to one another, both the 50% and 100% HxPh₃PBr modified clays maintained not only similar dspacing values, but also the same spatial arrangements within the internal clay gallery. Seeing as though the d-spacing values as depicted in **Table 2** for the 50% and 100% HxPh₃PBr modified clays increased by 0.50 nm in comparison to the sodium montmorillonite composite, far smaller than the length of the hexyl chain, it was concluded that the spatial orientation of the ionic liquid within the clay galleries retained a lateral monolayer formation as shown in **Figure 16.** Due to increased strain between oxygen and phosphorus atoms when forming ionic bonds between the

clay sheets, the phenyl rings located on HxPh₃PBr ionic liquid formed tetrahedral arrangements in order to minimize the steric hindrance present. Additionally, when the phenyl rings within the HxPh₃PBr modified clays formed tetrahedral arrangements; this limited the upward protrusion of the small hexyl chain. Instead the small hexane alkyl chain, although rigid, laid flattened against the oxygen atoms aligning the clay sheets to allow for minimal steric hindrance between the internal clay layers.

In regards to the 100% ionic liquid exchanged clays containing either the Bu₃HdPBr or HdPh₃PBr ionic liquids, these clays too attained two or three X - Ray diffraction peaks as shown in Figure 15 and Table 2. However in comparison to one another, even though both 100% ionic liquid modified clays encompassed elongated hexadecane hydrocarbon chains with hydrophobic tendencies, both clays attained vastly different spatial arrangements within their internal clay galleries. For instance, for the 100% Bu₃HdPBr exchanged clay, the first peak appeared around the 2 Θ angle of 4.06 degrees; whereas, the second peak appeared around the 2 Θ angle of 8.09 degrees. For the peak that appeared around the 2O angle of 8.09 degrees, again this peak was viewed as overtone peak because by roughly doubling the smaller 20 angle of 4.06 degrees, one would receive a 2Θ angle value relatively similar to that of 8.09 degrees. Additionally, for the peak at 4.06 degrees, it corresponded to the d-spacing value of 2.18 nm; whereas, the peak at 8.09 degrees corresponded to the d-spacing of 1.09 nm. In general, this ionic liquid modified clay maintained a spatial orientation of a lateral bilayer configuration as shown in **Figure 16**. Due to increased rigidity of the small butane alkyl chains, in order to decrease the strain between the oxygen and phosphorus atoms when forming ionic bonds between the clay sheets, the clay gallery expanded enough to fit an adjacent head group. Overall, the expansion of the clay gallery only increased by about 0.4nm which was approximately the size of a phosphorus cation.⁴²⁻⁴³ As

a result of increased steric hindrance, the small rigid butane chains ended up protruding outwards into the clay gallery; whereas, the elongated hexadecane hydrocarbon chain ended up lying along the clay surface, **Figure 16**.

Analyzing the X-Ray diffraction sample of the 100% HdPh₃PBr modified clay, the first peak appeared around the 2Θ angle of 2.84 degrees; whereas, the second peak appeared around the 2O angle of 4.71 degrees. Additionally, a third X-Ray diffraction peak appeared for this particular clay as well at the 2O angle of 9.20 degrees. Although a third diffraction peak surfaced for this particular clay, again it was ruled to be an overtone peak because by halving the dspacing value calculated for the 2 Θ angle of 4.71 degrees, the new d-spacing value calculated was similar to that of 2O angle of 9.20 degrees. The peak at 2.84 degrees corresponded to the dspacing of 3.11 nm; the peak at 4.71 degrees corresponded to the d-spacing of 1.88 nm; and finally the peak at 9.20 degrees corresponded to the d-spacing of 0.96 nm. In comparison to the Bu₃HdPBr ionic liquid modified clay, this particular ionic liquid modified clay maintained two spatial orientations: a lateral bilayer configuration similar to that of the Bu₃HdPBr exchanged clay, and a paraffin monolayer configuration as shown in **Figure 16**. Due to increased strain between oxygen and phosphorus atoms when forming ionic bonds between the clay sheets, the phenyl rings located on HdPh₃PBr ionic liquid again formed tetrahedral arrangements in order to minimize the steric hindrance present. When the phenyl rings within the HdPh₃PBr modified clays formed tetrahedral arrangements; as a result, more compact bilayer arrangements formed with slight decreases in the d-spacing values relative to the Bu₃HdPBr ionic liquid and its small butyl groups. These compact structures greatly increased the hydrophobic repulsions between the hexadecyl coated clay surfaces, causing the formation of some paraffin layer arrangements. The ionic liquid then had to slant at a 45° degree angle in order to remain within the internal clay

gallery while allotting for various other adsorption interactions and minimal steric hindrance. Furthermore, this behavior stemming from the repulsion of and between increasingly hydrophobic clay surfaces as sodium ions get replaced, has been observed for other hexadecyl ammonium exchanged clays as well.⁴²⁻⁴³ The d-spacing was consistent with a monolayer paraffin arrangement with an expansion to nearly the length of a hexadecyl chain. Also in several cases, when dealing with clay interlayer exfoliation or intercalcation through the introduction of ionic liquids such as the HdPh₃PBr ionic liquid, disordered conformations or gauche is more preferred than trans or all ordered conformations.¹¹

Finally, in regards to Figure 18 and again Table 2, by exchanging these ionic liquid modified clays with the malachite green oxalate dye, not only were new dye adsorption pathways introduced, but most importantly, the d-spacing values and spatial orientations of the internal clay galleries remained roughly the same. For the 50% and 100% HxPh₃PBr ionic liquid modified clays, the spatial orientations of the internal clay galleries remained as lateral monolayer formations after the 20 hour dye exchange period as shown in Figure 16. For these particular clays, as previous mentioned, cationic displacement interactions occurred in which the malachite green dye displaced the ionic liquids between the clay layers, **Figure 14.** As a result, due to the presence of phenyl rings within the malachite green structure, the phenyl rings flattened or sandwiched together within the internal clay galleries minimizing the amount of steric hindrance present, but also to facilitating the removal and adsorption of the dye from a contaminated water source, Figure 18 and Table 2. For the 100% ionic liquid modified clays attaining both the Bu₃HdPBr and HdPh₃PBr ionic liquids, the spatial orientations of the internal clay galleries remained as either lateral monolayer formations or paraffin monolayer formations after the 20 hour dye exchange period as shown in Figure 16. Regarding the Bu₃HdPBr ionic

liquid modified clay, it was not exactly concluded as to how the dye infiltrated into the clay composite given the various adsorption pathways, **Figure 14**; however, regardless as to whether the dye was adsorbed in the form of tactoids or disorganized layer arrangements, this clay still retained the spatial orientation of a lateral monolayer after the 20 hour dye exchange period,

Figure 16. Finally, for the 100% HdPh₃PBr ionic liquid modified clay, the spatial orientations of the internal clay galleries incorporated both lateral monolayer and paraffin monolayer formations after the 20 hour dye exchange period, **Figures 16** and **18.** Again as a result, due to the presence of two types of aromatic species within the internal clay layers, malachite green oxalate versus the HdPh₃PBr ionic liquid, the phenyl rings present complexed together by flattening or sandwiching together within the internal clay gallery minimizing the amount of steric hindrance present. Furthermore, through aromatic – π stacking and interactions, this clay was able to facilitate the removal of dye from a contaminated water source through this adsorption pathway, **Table 2**. Although X-Ray diffraction samples were taken of the polymer – clay composite films before and after the dye exchange process, no significant polymer - clay arrangements could be determined given the low clay concentrations from the tight packing and strong crosslinked characteristics of each film.

Throughout this experiment, not only were equilibrium diffusion studies hosted on the ionic liquid modified clays, but also on the modified polymer – clay composite films as well. In **Table 3**, after subjecting the modified polymer – clay films to two different liquid mediums over a period of 20 hours, both the thickness and swelling capacities of each film were measured in order to fully understand film transport and dye adsorption abilities. As previous mentioned, by utilizing a polymer such a polyvinyl alcohol to encapsulate the ionic liquid modified clays, the new dye adsorption pathway introduced included polar – π interactions. All polymer – clay

composite films in **Table 3**, experienced polar $-\pi$ interactions when interfaced with either water or malachite green oxalate solutions as liquid mediums. Contrarily, given the other modifiers integrated within each polymer - clay film, various combinations of dye adsorption pathways emerged. For each dye adsorption pathway combination that surfaced, all were uniquely different and solely significant to the polymer – clay film being used. When examining Table 3, it was also noted that by incorporating ionic liquids and ionic liquid modified clays into the films, this overall affected the swelling capacity and dye adsorption capabilities of each film. The extent of film swelling mainly depended upon the electron affinity of each ionic liquid and the length of the alkyl chain for each modifier. For instance, due to plain polyvinyl alcohol sustaining no other modifications regarding clay or ionic liquid additions, the film swelling capacity ranged between 77-95% given the liquid mediums being used. The plain polyvinyl alcohol film experienced solely polar – π interactions as the dye adsorption pathway. However, for the sodium montmorillonite based film, the film swelling capacity escalated – ranging from 108-109% given the liquid mediums being used. As a result of the hydrophilic clay additions, this film experienced polar – π interactions and cationic displacement interactions as the two main dye adsorption pathways in comparison. The increased hydrophilicity of both substances led to a greater incorporation of water and subsequently more swelling.

The HxPh₃PBr ionic liquid based films obtained the film swelling capacity ranges between 149-151% for the 50% exchanged film and 255-273% for the 100% exchanged film due to the presence of aromatic rings within their ionic liquid structures. By incorporating aromatics within these two films, even though the hexane alkyl chains were more hydrophobic than sodium ions found within the sodium montmorillonite based film, not only were polar – π interactions able to take place, but also aromatic – π interactions occurred as well leading to heightened dye

adsorption. The hexyl chains were short enough to maintain a relatively polar clay gallery. Therefore, the expanded clay layers could hold more water leading to greater swelling. For the 100% Bu₃HdPBr and HdPh₃PBr ionic liquid based films, both of these films were extremely hydrophobic in comparison. For this reason, the swelling capacities regarding these two films ranged between 131-139% (Bu₃HdPBr) and 99-125% (HdPh₃PBr). What made these two films increasing hydrophobic was the presence of the elongated hexadecane hydrocarbon chains integrated into the ionic liquid structures. The hydrophobic chain not only inhibited the swelling capacities of both films, but also limited the amount of surface area available for dye adsorption. Furthermore, even though both films maintained hydrophobic ionic liquids, these films were still able to facilitate the removal of a dye from a contaminated water source because both films allotted for polar – π interactions. Additionally, for the HdPh₃PBr ionic liquid based film, polar – π interactions and aromatic – π interactions were able to take place due to the presence of phenyl rings. Most importantly, regardless of the modifications provided, the swelling capacities of each polymer – clay film emulated from the adsorption of water more so than dye from the contaminated aqueous solutions.

After conducting a 20 hour equilibrium diffusion study on all polymer – clay films, in **Table 4** not only was the binding ratio of malachite green oxalate per polyvinyl alcohol monomer unit determined, but also film stability and dye removal efficiency was addressed as well. In most cases within **Table 4**, all films reached a dynamic equilibrium or maximum loading capacity after the 20 hour dye exchange period; however, not all films removed all of the malachite green dye present within the contaminated water sample without leaching the dye into the freshwater sample either. At first glance the sodium montmorillonite based film technically removed more malachite green oxalate dye from solution than all the other films produced. The

sodium montmorillonite based film adsorbed approximately 9.86 mg of malachite green dye from solution corresponding to a 74% removal efficiency. Also the binding ratio of malachite green oxalate to each polymer monomer unit within this film was 1.04 mM. The reason this film was able to easily facilitate extensive dye adsorption was again because this film allotted for both polar – π and cationic displacement interactions. Due to polyvinyl alcohol's ability to size exclude as a porous membrane and relatively small atomic sizes of the sodium cations, the sodium cations were able to easily diffuse through the polymer; whereas, the larger malachite green oxalate cations became entrapped through the discrimination of particle size induced by polyvinyl alcohol.⁷ For this reason, the sodium montmorillonite based film was viewed as the better sample to more effectively purify a contaminated water source containing dye. Contrarily, at one point this film too reached a dynamic equilibrium and leached malachite green dye into the freshwater sample within the model diffusion cell – similar to that of the HxPh₃PBr based films and the Bu₃HdPBr based film.

Referring to **Table 4**, The HdPh₃PBr based film in comparison adsorbed approximately 8.52 mg of malachite green dye from solution corresponding to a 69% removal efficiency. Also the binding ratio of malachite green oxalate to each polymer monomer unit for this film was 0.87 mM. Overall, this film allotted for both polar – π and aromatic – π interactions. Aromatic – π interactions were viewed as stronger dye adsorption pathways because the phenyl rings within this ionic liquid were not only able to stack by sandwiching together, but also this type of aromatic – π stacking fostered the formation of resonance and stability regarding the covalent π – π bonds formed between the phenyl rings. Additionally, films that solely experienced cationic displacement interactions as the main dye adsorption pathway tended to reach a dynamic equilibrium more quickly and readily than films utilizing other dye adsorption pathways such as

aromatic – π interactions. For the HdPh₃PBr based film not only did this film maintain aromatic – π interactions facilitating dye adsorption and removal from a contaminated water source, but also the presence of an extremely large hydrophobic substituent ensured that solely hydrophobic components were desired from the contaminated aqueous solution. For instance, the phenyl rings within the HdPh₃PBr ionic liquid maintained somewhat of an affinity for water, but the elongated hexadecane hydrocarbon chain incorporated lacked an affinity for water. Conversely, both substituents within the ionic liquid attained greater electron affinities towards other organophilic components such as malachite green oxalate; therefore, in comparison to all other ionic liquid based clays and polymer – clay films, this particular sample reached equilibrium more slowly and prevented more malachite green were standardized to the number of exchange sites on the clay, the HdPh₃PBr based film would actually be the better sample to effectively purify a contaminated water source containing dye.

CHAPTER 6 CONCLUSION

Overall by conducting a study in which clays and polymers were combined together versus studied independently, one was able to fully understand how a blend of these two substances could potentially lead to the development of a functional, biodegradable, environment friendly water filtration system capable of purifying a contaminated water source. Allowing for the integration of clays into polymers affected the swelling characteristics of the film, the crystalline and melting characteristics of the film, and the diffusion of ions through the film through the enhancement of film stability regarding improved stiffness, enhanced chemical resistance, heightened tensile strength, and increased cationic exchange capacity. Most importantly, regardless of the types of clays utilized within this study, all clays incorporated within the polyvinyl alcohol films were shown to be beneficial, especially when examining differing diffusion trends regarding the removal of malachite green oxalate. Additionally, by subjecting both the clays and polymer – clay films to additional modifications regarding either hydrophilic or hydrophobic ionic liquids, this allowed for higher dye adsorption rates and removal efficiencies stemming from the introduction of certain dye adsorption pathways.

The types of dye adsorption pathways available within this study included polar – π interactions, aromatic – π interactions, cationic – π interactions, and cationic displacement interactions. Given the ionic liquids present within the montmorillonite clay composites, each dye adsorption pathway was not only uniquely different, but also solely significant to the clay modifier being used. Also given the ionic liquid modified clays introduced within each polyvinyl alcohol film, not only were combinations of simultaneous dye adsorption pathways available, but also each dye adsorption combination was uniquely different and solely significant to the polymer – clay film being used. Regarding the sodium montmorillonite clay and film, cationic

displacement interactions took place within the clay; whereas, cationic displacement and polar – π interactions took place within the film. For the HxPh₃PBr modified clays and films, cationic displacement interactions and some aromatic– π interactions took place within the clays; whereas, cationic displacement and polar – π interactions took place within the films. As for the HdPh₃PBr modified clay and film, aromatic - π interactions took place within the clay; whereas, of aromatic - π and polar – π interactions took place within the clay; whereas, of aromatic - π and polar – π interactions took place within the film. Finally, for the Bu₃HdPBr modified clay and film, the specific dye adsorption pathways were unable to be determined because the presence of this particular ionic liquid could not be monitored experimentally. Furthermore, regardless of the adsorption pathways utilized to facilitate the removal of malachite green dye from a contaminated water source, both clay and film samples experienced varying spatial arrangements after the dye exchange periods with heightened removal efficiencies.

Regarding the sodium montmorillonite clay, given the presence and ability to undergo cationic displacement interactions, the sodium cations were arranged in a lateral bilayer formation within the montmorillonite internal clay gallery. For the HxPh₃PBr modified clays, given the presence and ability to undergo cationic displacement interactions more so than aromatic – π interactions because the small hexane alkyl chain was more hydrophilic, the HxPh₃PBr cations were arranged in a lateral monolayer formations within the montmorillonite internal clay gallery. These ionic liquids were partially displaced when interfaced with the malachite green oxalate dye. Regarding the HdPh₃PBr cations were arranged in both lateral monolayer and paraffin monolayer formations within the montmorillonite internal clay gallery. The phenyl rings regarding this ionic liquid used were arranged parallel to the clay surface, resulting in minimal d-spacing changes in the formation of a monolayer. However, by

incorporating the large rigid hexadecane alkyl chain within the clay surface, this modification led to increased layer expansion and heightening of the d-spacing within the clay gallery as a lateral bilayer arrangement. Although, the same process was repeated for the ionic liquid modified polymer – clay films, the d-spacing and spatial orientations of the clays within the polymers could not be unveiled given the tight packing and strong crosslinked characteristics of each film.

At some point throughout the study, several films reached dynamic equilibriums in which a maximum dye loading capacity value was determined. Additionally, for some films, dye leaching occurred due to high solubility of malachite green in water. The films that experienced leaching included the more hydrophilic composites: 50% exchanged HxPh₃PBr based film, 100% exchanged HxPh₃PBr based film, the polyvinyl alcohol film, and the sodium montmorillonite based film. In regards to the other two films maintaining the ionic liquids of Bu₃HdPBr and HdPh₃PBr, the incorporation of these ionic liquid modifiers actually helped to trap malachite green dye increasing hydrophobicity and slower diffusion which limited the amount of dye leaching occurring. Contrarily, HdPh₃PBr modified film was better than both the Bu₃HdPBr and HxPh₃PBr modified films likely because the ionic liquid modifier within this film allowed for aromatic - π stacking to occur between the two phenyl ring species in solution. Also due to the increased hydrophobicity of this particular ionic liquid modifier, in comparison to the hydrophilic ionic liquid of the HxPh₃PBr, the HdPh₃PBr modified film solely maintained a greater electron affinity towards the organophilic component of malachite green oxalate.

The sodium montmorillonite based film attained the highest removal efficiency rate in comparison to all other films. This occurred because this extremely hydrophilic film allotted for polar - π and cationic displacement interactions and also because polyvinyl alcohol had size exclusion abilities allowing relatively small sodium cations to easily perforate through the

polymer; while entrapping the larger malachite green oxalate cations. For this reason, the sodium montmorillonite based film was viewed as the better sample to more effectively purify a contaminated water source containing a dye even though this film reached dynamic equilibrium more readily and quickly than other films. On the other hand, if amount of malachite green were standardized to the number of montmorillonite exchange sites within the internal clay galleries, then the HdPh₃PBr based film would have actually removed and adsorbed more malachite green oxalate dye given the strong dye adsorption pathway regarding aromatic $-\pi$ stacking and interactions. Furthermore, through the execution of this study and examination of the removal process germane to organic contaminates such as dye within a by removing organic contaminates such as dye from a polluted water source, this study overall exemplified how other hazardous aromatic hydrocarbons could possibly be removed on a grander scale.

CHAPTER 7 FUTURE WORK

After conducting this study, there were several other aspects of research taken into account that should have been pursued as well. For instance, to fully understand the thermal stability of each polymeric film along, thermo gravimetric analyses (TGA) should be conducted to confer that the ionic liquids within the clays follow the given aggregation patterns previously mentioned. In regards to the presence of highly ordered structures within both clays and films, Transmission Electron Microscopy (TEM) analyses should be conducted as well. Also High Performance Liquid Chromatography (HPLC) should be employed to quantify the amount of Bu₃HdPBr found in solution before and after clay and film equilibrium studies with malachite green. In addition, desorption studies should be conducted over 20 hour periods to determine if the malachite green cationic dye can be recovered and possibly recycled for future use. New crosslinking methods should also assessed as well because as previously mentioned glutaraldehyde is a strong irritant.^{4,44} Therefore, another crosslinking process such as freeze – thaw should be examined to determine if the films will still maintain increased stability, better permeability, improved stiffness, enhanced chemical resistance, heightened tensile strength, and similar cationic exchange capacities. Also in the future, other ionic liquids, polymers, clays, and dyes should be analyzed in order to understand in more depth how the adsorption properties and pathways change given new modifications.

APPENDIX A UV – VIS IMAGES AND DATA



Figure 19: **Malachite Green Oxalate Standards**. This figure represents the various concentrations of malachite green oxalate, 0 - 20 ppm, tested in order to reach the maximum absorbance of 1.00. The concentration of malachite green needed to reach the maximum absorbance of 1.00 respectively was 15.00 ppm malachite green. The actual absorbance attained from this malachite green solution was 0.962. Therefore, a stock solution of 4.82×10^{-5} M or 15 ppm malachite green oxalate was prepared in order to further test the diffusion of this dye through other types of polymeric matrices.



Figure 20: **Malachite Green Oxalate Experimental Molar Absorptivity**. The literature value for malachite green oxalate regarding its molar absorbtivity or extinction coefficient was 150,000 cm⁻¹.¹¹However, in this experiment, the molar absorbtivity for malachite green oxalate was found to be 162,149 M⁻¹ cm⁻¹. Therefore, there was an 8.1% error or difference between the known literature molar absorbtivity value and experimental molar absorbtivity value for malachite green oxalate.



Figure 21: **PVA 22K MG Film Exchange (1hr)**. This figure represents the concentration and time period in which the malachite green dye was adsorbed to the PVA 22K film. The initial concentration of malachite green concentration used for this 1 hour diffusion analysis was 4.82×10^{-5} M (~ 15 ppm). Samples were taken of the malachite green dye solution within the diffusion cell at 1 min, 5 min, 10 min, 30 min, and 60 min intervals. Additionally, a water sample was taken at the end of the 60 min period to determine if any malachite green dye leached from the polymer into the freshwater sample. The amount of malachite green dye adsorbed into the polymeric film was calculated as well.



Figure 22: **NaMT PVA 22K MG Film Exchange (1hr)**. This figure represents the concentration and 1 hour time period in which the malachite green dye was adsorbed to the 1% wt. NaMT PVA 22K film. The initial concentration of malachite green concentration used for this 1 hour diffusion analysis was 4.82×10^{-5} M (~ 15 ppm). Samples were taken of the malachite green dye solution within the diffusion cell at 1 min, 5 min, 10 min, 30 min, and 60 min intervals. Additionally, a water sample was taken at the end of the 60 min period to determine if any malachite green dye leached from the polymer into the freshwater sample. The amount of malachite green dye adsorbed into the polymeric film was calculated as well.



Figure 23: **50 CEC NaMT – HxPh₃PBr PVA 22K MG Film Exchange (1hr)**. This figure represents the concentration and 1 hour time period in which the malachite green dye was adsorbed to the 1% wt. 50 CEC NaMT – HxPh₃PBr PVA 22K film. The initial concentration of malachite green concentration used for this 1 hour diffusion analysis was 4.82×10^{-5} M (~ 15 ppm). Samples were taken of the malachite green dye solution within the diffusion cell at 1 min, 5 min, 10 min, 30 min, and 60 min intervals. Additionally, a water sample was taken at the end of the 60 min period to determine if any malachite green dye leached from the polymer into the freshwater sample. The amount of malachite green dye adsorbed into the polymeric film was calculated as well.



Figure 24: 100 CEC NaMT – HxPh₃PBr PVA 22K MG Film Exchange (1hr). This figure represents the concentration and 1 hour time period in which the malachite green dye was adsorbed to the 1% wt. 100 CEC NaMT – HxPh₃PBr PVA 22K film. The initial concentration of malachite green concentration used for this 1 hour diffusion analysis was 4.82×10^{-5} M (~ 15 ppm). Samples were taken of the malachite green dye solution within the diffusion cell at 1 min, 5 min, 10 min, 30 min, and 60 min intervals. Additionally, a water sample was taken at the end of the 60 min period to determine if any malachite green dye leached from the polymer into the freshwater sample. The amount of malachite green dye adsorbed into the polymeric film was calculated as well.



Figure 25: 100 CEC NaMT – Bu_3HdPBr PVA 22K MG Film Exchange (1hr). This figure represents the concentration and 1 hour time period in which the malachite green dye was adsorbed to the 1% wt. 100 CEC NaMT – Bu_3HdPBr PVA 22K film. The initial concentration of malachite green concentration used for this 1 hour diffusion analysis was 4.82×10^{-5} M (~ 15 ppm). Samples were taken of the malachite green dye solution within the diffusion cell at 1 min, 5 min, 10 min, 30 min, and 60 min intervals. Additionally, a water sample was taken at the end of the 60 min period to determine if any malachite green dye leached from the polymer into the freshwater sample. The amount of malachite green dye adsorbed into the polymeric film was calculated as well.



Figure 26: **100 CEC NaMT – HdPh₃PBr PVA 22K MG Film Exchange (1hr)**. This figure represents the concentration and 1 hour time period in which the malachite green dye was adsorbed to the 1% wt. 100 CEC NaMT – HdPh₃PBr PVA 22K film. The initial concentration of malachite green concentration used for this 1 hour diffusion analysis was 4.82×10^{-5} M (~ 15 ppm). Samples were taken of the malachite green dye solution within the diffusion cell at 1 min, 5 min, 10 min, 30 min, and 60 min intervals. Additionally, a water sample was taken at the end of the 60 min period to determine if any malachite green dye leached from the polymer into the freshwater sample. The amount of malachite green dye adsorbed into the polymeric film was calculated as well.



Figure 27: **PVA 22K MG Film Exchange (20hr)**. This figure represents the concentration and time period in which the malachite green dye was adsorbed to the PVA 22K film in order to reach a dynamic a dynamic equilibrium point. The initial concentration of malachite green concentration used for this equilibrium analysis was 4.82×10^{-5} M (~ 15 ppm). Samples were taken of the malachite green dye solution within the diffusion cell at the 20 hour interval. Additionally, a water sample was taken at the end of the 20 hour time period to determine if any malachite green dye leached from the polymer into the freshwater sample.



Figure 28: **NaMT PVA 22K MG Film Exchange (20hr)**. This figure represents the concentration and time period in which the malachite green dye was adsorbed to the 1% wt. NaMT PVA 22K film in order to reach an a dynamic equilibrium point. The initial concentration of malachite green concentration used for this equilibrium analysis was 4.82×10^{-5} M (~ 15 ppm). Samples were taken of the malachite green dye solution within the diffusion cell at the 20 hour interval. Additionally, a water sample was taken at the end of the 20 hour time period to determine if any malachite green dye leached from the polymer into the freshwater sample. Overall, specifically this film did reach an a dynamic equilibrium point after the 20 hour time period.



Figure 29: **50 CEC NaMT – HxPh₃PBr PVA 22K MG Film Exchange (20hr)**. This figure represents the concentration and time period in which the malachite green dye was adsorbed to the 1% wt. 50 CEC NaMT – HxPh₃PBr PVA 22K film in order to reach an a dynamic equilibrium point. The initial concentration of malachite green concentration used for this equilibrium analysis was 4.82×10^{-5} M (~ 15 ppm). Samples were taken of the malachite green dye solution within the diffusion cell at the 20 hour interval. Additionally, a water sample was taken at the end of the 20 hour time period to determine if any malachite green dye leached from the polymer into the freshwater sample. Overall, specifically this film did reach an a dynamic equilibrium point after the 20 hour time period.



Figure 30: 100 CEC NaMT – HxPh₃PBr PVA 22K MG Film Exchange (20hr). This figure represents the concentration and time period in which the malachite green dye was adsorbed to the 1% wt. 100 CEC NaMT – HxPh₃PBr PVA 22K film in order to reach an a dynamic equilibrium point. The initial concentration of malachite green concentration used for this equilibrium analysis was 4.82×10^{-5} M (~ 15 ppm). Samples were taken of the malachite green dye solution within the diffusion cell at the 20 hour interval. Additionally, a water sample was taken at the end of the 20 hour time period to determine if any malachite green dye leached from the polymer into the freshwater sample. Overall, specifically this film did t reach a dynamic equilibrium point after the 20 hour time period.



Figure 31: **100 CEC NaMT – Bu₃HdPBr PVA 22K MG Film Exchange (20hr)**. This figure represents the concentration and time period in which the malachite green dye was adsorbed to the 1% wt. 100 CEC NaMT – Bu_3HdPBr PVA 22K film in order to reach an a dynamic equilibrium point. The initial concentration of malachite green concentration used for this equilibrium analysis was 4.82 * 10⁻⁵ M (~ 15 ppm). Samples were taken of the malachite green dye solution within the diffusion cell at the 20 hour interval. Additionally, a water sample was taken at the end of the 20 hour time period to determine if any malachite green dye leached from the polymer into the freshwater sample. Overall, specifically this film did reach an a dynamic equilibrium point after the 20 hour time period.



Figure 32: 100 CEC NaMT – HdPh₃PBr PVA 22K MG Film Exchange (20hr). This figure represents the concentration and time period in which the malachite green dye was adsorbed to the 1% wt. NaMT – HdPh₃PBr PVA 22K film in order to reach an a dynamic equilibrium point. The initial concentration of malachite green concentration used for this equilibrium analysis was 4.82×10^{-5} M (~ 15 ppm). Samples were taken of the malachite green dye solution within the diffusion cell at the 20 hour interval. Additionally, a water sample was taken at the end of the 20 hour time period to determine if any malachite green dye leached from the polymer into the freshwater sample. Overall, specifically this film did not reach an a dynamic equilibrium point after the 20 hour time period.



Figure 33: **Different PVA 22K MG Films (20hr)**. This figure represents the amount of malachite green dye adsorbed at equilibrium into each of the polymeric films given their various modifications. As exemplified in this figure, the polyvinyl alcohol – clay film maintaining the ionic liquid 1 – HdPh₃PBr, absorbed the greatest amount of malachite green dye due to the presence and facilitation of aromatic – π stacking along with polar - π interactions that occurred.



APPENDIX B X-RAY DIFFRACTION IMAGES & DATA

Figure 34: **Different PVA 22K Films X-Ray**. This figure represents the various ionic liquid exchanged clays placed in the polyvinyl alcohol micro matrices to form polymeric films. For each of these polymeric films, one can easily determine the basal spacing value and structural formation of the internal polymer layers, given the 2 Θ angles designated.



Figure 35: **Different PVA 22K MG Films (1hr)**. This figure represents the various ionic liquid exchanged polyvinyl alcohol – clay films interfaced with the malachite green dye after a one hour adsorption period. For each of these polyvinyl alcohol – clay films, one can easily determine the basal spacing value and structural formation of the internal clay galleries after the one hour adsorption period, given the 2 Θ angles designated.

| PVA 22K Malachite Green Film Diffusion Studies (1hr) | | | | | | | |
|---|--------------|--------------|---------------|---------------|---------------|------------|-------------------|
| SAMPLE | <u>0 min</u> | <u>1 min</u> | <u>10 min</u> | <u>30 min</u> | <u>60 min</u> | Water Cell | <u>MG</u> Film |
| PVA 22K Film | 14.99 | 14.33 | 13.92 | 13.88 | 12.43 | 2.78 | 0.22 |
| 1% NaMT PVA 22K Film | 14.99 | 7.65 | 7.33 | 6.81 | 6.62 | 4.26 | 4.11 |
| 1% 50 CEC NaMT – HxPh ₃ PBr PVA 22K Film | 14.99 | 13.21 | 7.31 | 5.16 | 4.83 | 2.91 | 7.24 |
| 1% 100 CEC NaMT – HxPh ₃ PBr PVA 22K Film | 14.99 | 11.81 | 5.91 | 3.76 | 3.43 | 1.82 | 9.73 |
| 1% 100 CEC NaMT – Bu ₃ HdPBr PVA 22K Film | 14.99 | 11.54 | 10.60 | 8.53 | 6.79 | 1.61 | 6.59 |
| 1% 100 CEC NaMT – HdPh ₃ PBr PVA 22K Film | 14.99 | 14.82 | 12.98 | 10.20 | 10.51 | 1.21 | 3.27 |

APPENDIX C SUPPLEMENTAL TABLES & GRAPHS

Table 5: **PVA 22K Malachite Green Film Diffusion Studies (1hr)**. This table represents the 1 hour time period in which the malachite green dye was adsorbed to the various polyvinyl alcohol – clay composite films. Samples were taken of the malachite green dye solution in the diffusion cell at 1 min, 5 min, 10 min, 30 min, and 60 min intervals. Water samples were taken at the end of the 60 min period to determine if any malachite green dye leached through the polymers into the freshwater samples. The ionic liquid samples containing the HxPh₃PBr substances removed dye more readily and quickly than the other ionic liquids during the one hour period; however, at some point all films reached dynamic equilibriums limiting the amount malachite green uptake into their polymeric matrices.



Figure 36: **Crude HxPh₃PBr Synthesized**. This figure represents the crude product of hexyl triphenyl phosphonium bromide (HxPh₃PBr) synthesized with the experiment. Overall, this ionic liquid was not only relatively pure, but used to modified clays and polyvinyl alcohol films in the study. The HxPh₃PBr ionic liquid maintained a molecular weight of 427.36 g / mole and an experimental melting point of 202.4°C.



Figure 37: **Sodium Ion Selective Electrode Standards**. This figure represents the concentrations of sodium standards, 0 – 750 ppm, tested in order to determine the sodium concentration of unknown modified clays and films exchanged with malachite green oxalate. The purpose of this ion selective electrode test was to discover if cationic displacement interactions occurred after a 20 hour dye exchange period. For the sodium montmorillonite non – exchanged clay sample, a -78.5 mV value was uncovered indicating an approximate concentration of 259 ppm sodium ions were detected after a 20 hour dye exchange period – cationic displacement interactions occurred for this particular clay with similar results reflected for the clay based film.

REFERENCES

- 1. Nath, D. C.; Fabrication of High Strength Biodegradable Composite Films of Poly (Vinyl Alcohol) and Fly Ash Crosslinked with Glutaraldehyde. *International Journal of Polymeric Materials*, **2011**, *60*, 852 861.
- 2. Georgieva, N.; Bryaskova, R.; Tzoneva, R.; New Polyvinyl Alcohol Based Hybrid Materials for Biomedical Applications. *Material Letters*, **2012**, *88*, 19 22.
- 3. Differential Scanning Calorimetry: First and Second Order Transitions in Polymers. http://www.colby.edu/chemistry/PChem/lab/DiffScanningCal.pdf (accessed March 4, 2014).
- 4. Ekici, S.; Isikver, Y.; Saraydin, D. Poly (Acrylamide Sepiolite) Composite Hydrogels: Preparation, Swelling, and Dye Adsorption Properties. *Polymer Bulletin*, **2006**, *57*, 231-241.
- 5. Polymer Processing.com. Poly (vinyl) Alcohol. <u>http://www.polymerprocessing.com/polymers/PVOH.html</u> (accessed March 4, 2014).
- 6. Varshosaz, J.; Koopaie, N.; Cross linked Poly (vinyl alcohol) Hydrogel: Study of Swelling and Drug Release Behaviour. *Iranian Polymer Journal*, **2002**, *11*, 123 131.
- 7. Mulder, M. Basic Principles of Membrane Technology, 2nd ed.; Kluwer Academic Publishers: Boston, 2003.
- 8. Technology Transfer Network Air Toxics Website. Acrylamide. http://www.epa.gov/ttnatw01/hlthef/acrylami.html (accessed May 6, 2014).
- 9. Kokabi, M.; Sirousazar, M.; Hassan, Z. M. PVA clay Nanocomposite Hydrogels for Wound Dressing. European Polymer Journal, **2007**, *43*, 773 881.
- 10. Arbeloa, F. L.; Tapia Estevez, M. J.; Arbeloa, T. L.; Arbeloa, I. L. Spectroscopic Study of the Adsorption of Rhodamine 6G on Clay Minerals in Aqueous Suspensions. *J. Clay Minerals*, **1997**, *32*, 97 106.
- 11. Alexandre, M.; Dubois, P. Polymer Layered Silicate Nanocomposites: Preparation, Properties, and Uses of a New Class of Materials. *J. Materials Sciences and Engineering*, **2000**, *28*, 1 63.
- 12. Sigma Aldrich Company. Malachite Green Oxalate Salt. http://www.sigmaaldrich.com/catalog/product/sigma/m9015?lang=en®ion=US (accessed March 4, 2014)
- 13. Chemical Index Database: Drug Future. Malachite Green. <u>http://www.drugfuture.com/chemdata/malachite-green.html</u> (accessed May 6, 2014)
- 14. Chemical Book. Hexyl Triphenyl Phosphonium Bromide. <u>http://www.chemicalbook.com/Search_EN.aspx?keyword=hexyl%20triphenyl%20phosphonium%20bromide</u> (accessed May 6, 2014)
- 15. Chemical Book. Tributyl Hexadecyl Phosphonium Bromide. <u>http://www.chemicalbook.com/Search_EN.aspx?keyword=tributyl%20hexadecyl%20phosphonium%20bromid</u> <u>e</u> (accessed May 6, 2014)
- 16. Chemical Book. Hexadecyl Triphenyl Phosphonium Bromide. <u>http://www.chemicalbook.com/Search_EN.aspx?keyword=%20hexadecyl%20triphenyl%20phosphonium%20b</u> <u>romide</u> (accessed May 6, 2014)
- 17. Johnson Matthey Catalysis and Chiral Technologies. Ionic Liquids. <u>http://www.organic-chemistry.org/topics/ionic-liquids.shtm</u> (accessed May 6, 2014).

- Sigma Aldrich Company. Ionic Liquids. <u>https://www.sigmaaldrich.com/chemistry/chemistry-products.html?TablePage=16255866</u> (accessed May 6, 2014)
- 19. Petras, T. Mr. P. Chemistry. Single Replacement Reactions Tutorial. <u>http://www.sartep.com/chem/tutorials/tutprint.cfm?tutorial=Single%20Replacement%20Reactions</u> (accessed May 6, 2014)
- 20. Meyer, E. A.; Castellano, R. K.; Diederich, F. Synthesis and Properties of New Poly (Dimethylsiloxane) Nanocomposites. *Chemistry of Materials*, **1995**, *7*, 1597 1560.
- 21. Burnside, S. D.; Giannelis, E. P. Interactions with Aromatic Rings in Chemical and Biological Recognition. *Angewandte Chemie*, **2003**, *42*, 1210 1250.
- 22. Aowda, S. A; Jafar Al-Mulla, E. A.; Baqir, S. J. Modification of Montmorillonite using Different Phosphonium Salts: Study Their Effect upon Structure. Ph.D. Dissertation, Babylon University, Babylon.
- 23. He, H.; Frost, R. L.; Deng, F.; Zhu, J.; Wen, X.; Yuan, P. Conformation of Ionic liquid Molecules in the Interlayer of Montmorillonite Studied by ¹³C Mas NMR. *Clays and Clay Minerals*, **2004**, *52*, 350 356.
- 24. Singla, P.; Mehta, R.; Upadhyay, S. N. Clay Modification by the Use of Organic Cations. *Green and Sustainable Chemistry*, **2012**, *2*, 21 25.
- 25. He, H.; Ma, Y.; Zhu, J.; Yuan, P.; Qing, Y. Organoclays Prepared from Montmorillonites with Different Cation Exchange Capacity and Ionic liquid Configuration. *Applied Clay Science*, **2010**, *48*, 67 72.
- 26. Xue, W.; He, H.; Zhu, J.; Yuan, P. FTIR Investigation of CTAB Al Montmorillonite Complexes. *Spectrochimica Acta Part A*, 2007, 67, 1030 1036.
- 27. Kumpf, R.; Dougherty, D. A Mechanism for Ion Selectivity in Potassium Channels: Computational Studies of Cation Pi Interactions. *Science*, **1993**, *261*, 1708 1710.
- 28. Dougherty, D. A. Cation pi Interactions in Chemistry and Biology: A New View of Benzene, Phenylalanine, Tyrosine, and Tryptophan. *Science*, **1996**, *271*, 163 168.
- 29. Geise, G. M.; Freeman, B. D.; Paul, D. R. Sodium Chloride Diffusion in Sulfonated Polymers for Membrane Applications. J. Membrane Science. 2013, 427, 186 196.
- 30. Cadene, A.; Durand-Vidal, S.; Turq, P.; Brendle, J.; Study of Individual Na-montmorillonite Particles Size, Morphology and Apparent Charge. *J Colloid Interface Sci.*, **2005**, *285*, 719 730.
- 31. Gohil, J.M.; Bhattacharya, A.; Ray, P. Studies on the Cross linking of Poly (Vinyl Alcohol). J. Polymer Research. 2006, 13, 161 169.
- 32. Tudorachi, N.; Cascaval, C.N.; Rusu, M.; Pruteanu, M.; Testing of Polyvinyl Alcohol and Starch Mixtures as Biodegradable Polymeric Materials. *Polymer Testing*, **2000**, *19*, 785 799.
- Sirousazar, M.; Kokabi, M.; Hassan, Z.M.; Bahramain, A. R. Mineral Kaolinite Clay for Preparation of Nanocomposite Hydrogels. J. Applied Poly. Sci., 2012, 125, E122 – E130.
- 34. Strawhecker, K.E.; Manias, E. Structure and Properties of Poly (vinyl alcohol)/Na⁺ Montmorillonite Nanocomposites. *Chem Mater*, **2000**, *12*, 2943 2949.

- 35. Kesting, R. E. *Synthetic Polymer Membranes: A Structural Perspective*, 2nd ed.; John Wiley & Sons Inc: Irvine, California 1985.
- 36. FPO IP Research & Communities. Plasticized polyvinyl compositions. http://www.freepatentsonline.com/2399456.html (accessed April 24, 2013)
- 37. Polymer Science Learning Center, University of Southern Mississippi. Differential Scanning Calorimetry. http://pslc.ws/macrog/dsc.htm (accessed March 4, 2014).
- 38. X-Ray Diffraction. http://web.pdx.edu/~pmoeck/phy381/Topic5a-XRD.pdf (accessed March 4, 2014)
- 39. Montmorillonite Crystal Lattice, <u>http://pubs.usgs.gov/of/2001/of01-041/htmldocs/clays/smc.htm</u> (accessed March 4, 2014).
- 40. Prahl, S. Oregon Medical Laser Center. Malachite Green. http://omlc.ogi.edu/spectra/PhotochemCAD/html/030.html (accessed May 6, 2014).
- 41. Soriyan, O.; Owoyomi, O.; Ogunniyi, The Basic Hydrolysis of Malachite Green in β Cyclodextrin / Cetyltrimethlammonium Bromide (CTAB) Mixed System. *Acta Chim. Slov.*, **2008**, *55*, 613 616.
- 42. Ganguly, S.; Dana, K.; Parya, T. K; Mukhopadhyay, T. K; Ghatak, S. Organic Inorganic Hybrids Prepared from Alkyl Phosphonium Salts Intercalated Montmorillonites. *Ceramics Silikáty*, **2012**, *56*, 306 313.
- 43. Li, Z.; Jiang, W.; Hong, H. An FTIR Investigation of Hexadecyltrimethylammonium Intercalation into Rectorite. *Spectrochemica Acta Part A: Molecular and Biomolecular Spectroscopy*, **2008**, *71*, 1525 1534.
- 44. ScienceLab.com: Chemicals and Laboratory Equipment. Materials Data Safety Sheet: Glutaraldehyde Solution. http://www.sciencelab.com/msds.php?msdsId=9924161 (accessed May 6, 2014)
- 45. Ozdemir, A. and Keskin, C. S. "Removal of A Binary Dye Mixture of Congo Red and Malachite Green From Aqueous Solutions Using a Bentonite Adsorbent." Journal of Clays and Clay Minerals **2009**, 57, 695-705
- 46. UV-Vis Absorption Spectroscopy. <u>http://teaching.shu.ac.uk/hwb/chemistry/tutorials/molspec/uvvisab3.htm</u> (accessed 11/26/12), part of Sheffield Hallam University. http://www.shu.ac.uk/(accessed 11/26/12).
- 47. Yu, Y. H.; Lin, C. Y.; Yeh, J. M.; and Lin, W. H. "Preparation and Properties of Poly (vinyl) alcohol clay Nanocomposite Materials." *Journal of Polymers* **2003**, *44*, 3553-60.