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SYNTHESIS AND CHARACTERIZATION OF THIOL-GRAFTED CHITOSAN BEADS FOR MERCURY REMOVAL

By

John D. Merrifield

B.S. University of Maine, 2000

A THESIS

Submitted in Partial Fulfillment of the
Requirements for the Degree of
Master of Science
(in Civil Engineering)

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SYNTHESIS AND CHARACTERIZATION OF THIOL-GRAFTED CHITOSAN BEADS FOR MERCURY REMOVAL

By John D. Merrifield

Thesis Advisor: Dr. Aria Amirbahman

An Abstract of the Thesis Presented
in Partial Fulfillment of the Requirements for the
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This study describes the synthesis and characterization of thiol-grafted chitosan beads for use as mercury (Hg) adsorbents. Chitosan flakes were manipulated into beads using a phase inversion technique, then crosslinked to improve porosity and chemical stability. Cysteine was grafted onto the beads in order to improve the adsorption affinity of Hg to the beads. The beads possessed an average diameter of 3.2 mm, porosity of 0.9, specific surface are of ~100 m^2/g, average pore size of ~120 Angstroms, and specific gravity of 2. The beads exhibited a high adsorption capacity for Hg: 2, 2.5, 3.5 and 8 mmol/g dry at pH values of 2.2, 4, 5,and 7, respectively. By comparison ungrafted chitosan had a capacity of ~1.2 mmol/g dry at pH 4. Adsorption of Hg onto the beads was modeled using the Freundlich isotherm. Hg adsorption kinetics was modeled as radial diffusion into an infinite sphere. The beads exhibited a high initial uptake rate comparable to other published chitosan bead data followed by a slower uptake rate suggesting pore diffusion as the rate-determining step.

ACKNOWLEDGEMENTS

Excessive efforts have been made to render this text consistent with the guidelines of the Graduate School at the University of Maine.

A foolish consistency is the hobgoblin of little minds, adored by little statesman and philosophers and divines. With consistency a great soul has simply nothing to do.
-Ralph Waldo Emerson

[L XXXVII III]

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Chapter 1

INTRODUCTION

1.1. Mercury and Chitosan

Human activities are intimately tied to the environment, and harmful behaviors often have harmful consequences. In order to ensure a healthful environment for the future of humanity it is necessary to reduce the harm done to the environment through anthropogenic activities. Metals such as Hg are recognized as having serious negative effects on ecological health and researching ways to mitigate these risks is of great importance. Human activities often produce a great deal of waste, and it is of both economical and environmental importance to attempt to recover and reuse the materials present in waste streams.

The slaughter of shelled sea creatures represents a significant source of waste since humans are primarily interested in the edible portions of these life forms. Chemical processing allows for the transformation of chitin containing crustacean exoskeletons into a more reactive form, chitosan. In an effort to provide partial solutions to both Hg wastes and shellfish wastes research has been conducted to develop an adsorbent for Hg based upon the chitosan derived from shellfish waste.

1.2. Scope of Study

In order to develop an effective means of Hg removal utilizing chitosan it was necessary to synthesize chitosan beads, and then to perform experiments to characterize the beads. Several sets of experiments were performed in order to investigate kinetic and equilibrium properties of the beads. The beads were also analyzed to determine their physical characteristics.

1.3. Arrangement of Thesis

This thesis is divided into five chapters: Introduction, Literature Review, Materials and Methods, Results, and Discussion. This, the first chapter, provides a brief overview of the entire work. The second chapter describes the current body of knowledge on Hg, chitosan and adsorbents engineered for metal removal. The third chapter describes the procedures and equipment used to conduct the experimental research. The fourth chapter presents the collected data, while the fifth chapter discusses the data and includes recommendations for future work.

Chapter 2

LITERATURE REVIEW

2.1. Mercury

Mercury exists as a silvery liquid at room temperature, and volatilizes with ease. It is quite dense (~13.5 g/cm^3), toxic and conducts electricity. [1] These factors all contribute to the popularity of Hg for a wide variety of purposes. Electrical switches, batteries, lamps, thermometers and other instruments, dental amalgams, medicines, poisons and many other products all can contain Hg.[2,3] Hg has also been used for many diverse industrial applications, from the processing of gold ore to its use as a substitute for water in industrial boilers.[4]

Mercury occurs naturally with sulfur in an ore called cinnabar (HgS).[5] It can also be found as a dissolved ion at oxidation states of +1 and +2 and combined with methyl groups in methylated species. These ionic species of Hg form a wide variety of salts.[6]

Mercury is also emitted from a number of anthropogenic sources, including coal-fired power plants. Hg can be found in the waste streams of processes that create Hg-containing products, streams from processes that exclude Hg from the final product and in many products meant for consumer use.[7] In addition to Hg use in products such as lamps and in such processes as chlorine production, Hg is also used extensively as a biocide.[8] The deliberate injection of Hg containing vaccines and medicines into humans remains an important problem, but is only tangentially related to pollution prevention.[9]

Mercury is toxic and can cause many health problems including neurological impairments, sensory impairments, psychological impairments and rashes.[10] These effects have long been known, but the usefulness of the elusive shiny liquid metal has kept it in circulation. New research concerning the links between autism and Hg may help to dissuade people from using Hg, or at least focus attention on the problem.[11]

2.2. Mercury Removal by Sorption

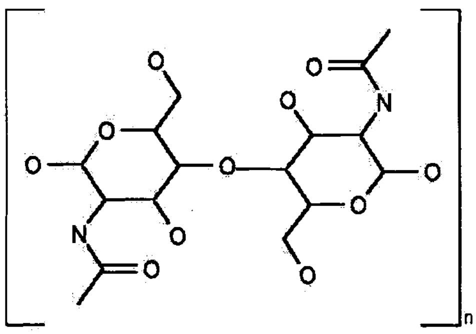
In order to minimize the adverse effects of Hg in the environment, it behooves us to find ways to capture it before it becomes a problem. Several techniques are available for this including precipitation, ion exchange and adsorption.[12] Precipitation is effective within a narrow pH range and results in large volumes of Hg-containing sludge, while ion exchange is effective for wastes with low dissolved solids concentrations. Adsorbents can be designed that are specific to Hg and whose volume is much less than an amorphous sludge. Bailey et al. reviewed several adsorbents and their applications for Hg removal and found that several natural materials were capable of adsorbing moderately high amounts of Hg.[13]

The ability of a material to capture metals is controlled in part by the number of available functional groups used for binding metals. Functional groups with a known affinity for specific metals can be attached to other substances in order to create an effective adsorbent.[14] The thiol (-SH) group is known to form stable complexes with soft heavy metals of high polarizability such as Hg, Ag, Au, and to a lesser extent, Cd and Zn, while failing to coordinate well with the more abundant smaller, lighter metals such as Ca, Na, and Mg.[15] Some of the compounds used to improve the adsorption capacity of designed sorbents include amino[16] and polyamino acids[17,18], mercaptopropylsilane[19], thiourea[20] and poly(ethylene imine).[21] Various materials have been used as the support structure for functional groups including clays[22,23,] glass beads[24], chitosan[25,26] and silica gels.[27]

Chitin (poly(D-acetylglucosamine)) and chitosan (poly(D-glucosamine)) have been investigated as adsorbents for metal removal by researchers worldwide. Chitosan based adsorbents have been investigated for the removal of arsenic[28], cadmium[29,30,31,32], chromium[33,34,35], cobalt[36], copper[37,38, 39,40,41,42,43,44,45], gold[46], lead[47,48,49], Hg[50, ,51, ,52,53], molybdenum[54,55,56], nickel[57,58,59], platinum[60], vanadium[61,62], uranium[63], and zinc[64,65,66]. These chitosan-based adsorbents have the advantage of using waste products as raw material.

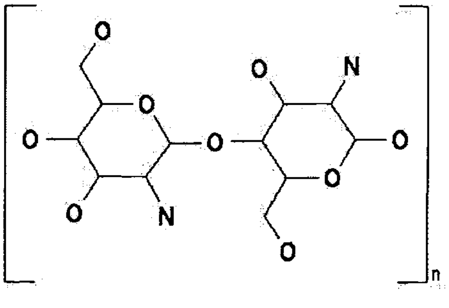
2.3. Chitosan

Chitin and chitosan are natural polysaccharides found in fungi[67]. Chitosan is also produced by deacetylation of chitin that is found in the shells of crustaceans.[68] Shellfish waste represents the source of most commercially available chitosan. Figure 2.1 shows the structure of chitin and Figure 2.2 shows the structure of chitosan.



chitin

Figure 2.1. Chitin.



chitosan

Figure 2.2. Chitosan.

Chitosan has found a great many uses in a wide variety of fields. It can be used as a protective coating on food and seeds, to clarify suspensions by coagulation, to capture and reclaim metals or proteins and to serve as a time-release structure for medicines or poisons.[69,70] The intended use of the chitosan influences its method of preparation. Table 2.1 shows typical conditions for producing chitosan.

Step	Time	Temperature	Solution	Concentration
Deproteinization	0 .5-72 hours	room - 100C	Base, Usually NaOH	1%-15%
Demineralization	0.5-48 hours	-20 - 25 C	Acid, Usually HCl	2.5%-90%
Deacetylation	0.33 - 144 hours	30 -150 C	Base, Usually NaOH	39%-60%

Table 2.1. Typical Chitosan Production Conditions, from No, et al.[71]

The first step in producing chitosan from crustacean shells is to remove the chitin from the shell. In addition to chitin, shells are composed of proteins and calcium carbonate.[72] Proteins are extracted through the use of a basic solution, and calcium carbonate is removed by an acidic solution. The concentration of the acid and base solutions, the temperature, and the duration of processing can all vary depending on the shell type and the intended products.[73] After the removal of proteins and minerals, the chitin must be processed further to yield chitosan.

Chitosan is the deacetylated form of chitin.[74] The acetyl groups are removed from the chitin exposing the amine groups. This is done by processing chitin in a basic solution at an elevated temperature.[75] This deacetylation step requires much more concentrated solutions than those needed for protein removal.[76] As a result, this step also provides a potential hazard to workers and the environment.

2.4. Chitosan Manipulation

Chitosan can be manipulated into engineered forms through various methods. Several solvents[77] and organic acids[78] can be used to dissolve chitosan. The dissolved chitosan can then be formed into the desired shape: beads, membranes, ground particles or others.[79] Acidic solutions of chitosan are generally gelled using a basic solution while solvents are either evaporated or substituted with water. Unless the product is to be used wet, it must be dried after the casting process. Freeze drying tends to preserve the structure of the pores better, but air drying may be suitable if the intended use does not require extensive internal microporosity.[80]

One useful form of chitosan is the bead. Chitosan beads have been studied by several groups and descriptions of their preparation are readily available.[81,82,83,84,85] The general process is to dissolve the chitosan in acetic acid and to drop it into a casting bath of base. The beads can then be crosslinked to improve their physical characteristics such as porosity and resistance against solubility.

Porosity and related characteristics can be manipulated using cryogenic phase separation[86], poregens such as silica[87], the addition of cross-linking agents[88], incorporating spacer metals that can later be removed[89], or by adjusting the concentration of the base solution in the casting bath.[90] Other possible modifications include the inclusion of magnetic particles[91], the inclusion of hydrocarbons such as nonanyl chloride to reduce hydrophobic effects by disrupting the organization of water molecules[92], and the grafting of other compounds containing functional groups to the chitosan.[93]

Cross-linking is the process of chemically or physically binding a portion of a molecule to another molecule or portion of itself. This process has many effects on the physiochemical properties of a polymeric structure. Cross-linking agents act as spacers and ties between the chains of a polymer, creating rigid chemical bridges, which affect the polymeric structure. The bridges provide some measure of chemical stability, prevent the dissolution of the cross linked chitosan in acidic media and also provide a degree of resistance to biodegradation.[94] Increasing levels of cross-linking can increase the internal surface area of a polymer. However, it results in a reduction of mechanical (crushing) strength.[95] Cross-linking consumes some of the reactive sites on a polymer, and this can reduce the loading capacity of the structure.[96]

The inclusion of cross-linking agents can also improve the accessibility of reactive sites on a polymer, which could increase the loading capacity.[97]

Cross-linking agents work by binding to the functional groups on a polymer. Cross-linking agents are generally composed of functional groups separated by some spacing molecules. The active sites on a given cross-linking compound may be the same or different from each other. The molecules in between can be structured in various forms (rings, straight chains, branched chains), be of varying lengths and contain other active sites than those involved in cross-linking. Various substances have been used to cross link chitosan. They include alginate[98], (chloromethyl)oxirane[99], epichlorohydrin[100,101], esters[102], ethers[103], glutaraldehyde[104,105], glycine[106]and pectin[107].

2.5. Engineered Hg Sorbents

Many natural substances possess the ability to adsorb Hg, but often possess other characteristics that make their use prohibitive in an engineered system (i.e. poor porosity, putrescible constituents, highly variable chemical contents, etc.). Attempts can be made to optimize the characteristics of substances in order to best achieve the desired result. In the case of engineered Hg sorbents, care is taken to optimize surface area, concentration of useful functional groups and potential ease of application. In general, a "skeleton" possessing high surface area is chosen, and the number of useful functional groups is increased, either through the addition of new groups or modification of existing groups. Table 2.2. shows properties of some engineered Hg sorbents. The sorbents characterized in Table 2.2. are characteristic of the current state of engineered Hg sorbents.

Researcher	Engineered Sorbent	Hg adsorption capacity (mmole/g dry)	Experimental Conditions	
			[Hg]	pH
Kawamura et al.	PEI-CS Polyaminated Highly Porous Chitosan Beads	10.5	<= 50 mM	not reported
Elmahadi et al.	Cysteine Functionalized Controlled Pore Glass Beads	8.86	25 mM	6.5
Ohga et al.	(Chloromethyl)oxirane Crosslinked Cd-Complexed Chitosan	2.6	<= 10 mM	5
Feng et al.	FMMS, Thiol Functionalized Mesoporous Silica	2.5	not reported	not reported
Brown et al.	Mercaptopropyl-Functionalized Silica Mesostructures	2.3	<= 0.1 mM	not reported
Ritchie et al.	Polycysteine Functionalized Cellulose Filter	0.13	<= 0.38 mM	6

Table 2.2. Some Engineered Sorbents and Their Properties, from Kawamura et al.[108], Elmahadi et al.[109], Ohga et al.[110], Feng et al.[111], Brown et al.[112], and Ritchie et al.[113]

Chapter 3

MATERIALS AND METHODS

3.1. Chitosan Bead Synthesis

3.1.1. Solution Preparation

Chitosan (4% by mass), acetic acid (4 % by mass) and deionized water (DIW) were mixed with an impeller (Fischer Scientific Jumbo Stirrer) for 30 minutes at approximately 500 rpm. The impeller was used in conjunction with a Powerstat (Superior Electric Company) rheostat control. A Monarch Pocket-Tach 100 tachometer was used to measure the speed of the impeller. The chitosan mixture was kept in a plastic beaker in order to reduce the possibility of breakage of the container. The highly viscous mixture was then transferred to 0.5 L wide mouthed low-density polyethylene bottle (LDPE) bottles and shaken vigorously for a week to ensure dissolution of the chitosan and to reduce the viscosity. The synthesis of chitosan beads in this study was based upon the procedures described by Rorrer and Hsien.[114].

3.1.2. Bead Casting

After shaking, the chitosan solution was transferred to 60-mL plastic syringes with 18 gauge x 38 mm hypodermic needles. The acidic chitosan mixture was pumped into a 1 L plastic beaker containing 900 mL of 0.5 M

NaOH using a syringe pump (Harvard Apparatus cat. # 55-2314) at a rate of 4 mL/hr. This pumping rate was chosen based on the fastest rate possible for this particular setup. The beaker was shaken at 50 rpm in a LabLine model 3540 orbital shaker bath. Stirring prevented beads from sticking to one another. The distance between the needle and the surface of NaOH solution was approximately 180 mm. Figure 3.1 shows a drop of chitosan just prior to falling.

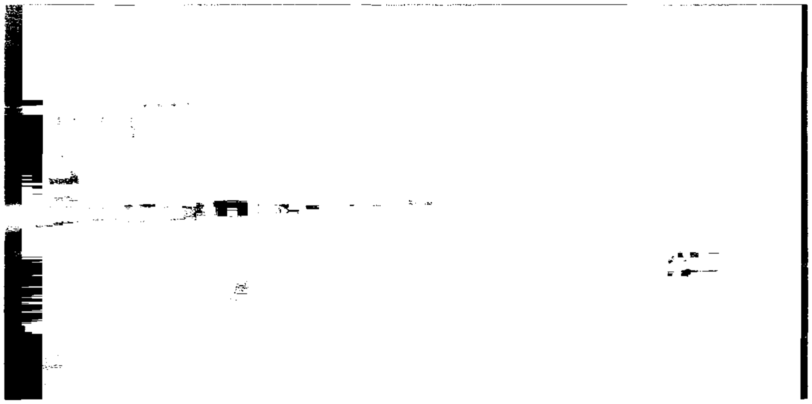


Figure 3.1. Wet Chitosan Drop.

3.1.3. Crosslinking

After gelling for a minimum of 16 hours in the 0.5 M NaOH solution, the beads were rinsed to a neutral pH with DIW. The wet beads were then placed in a 2.5 % (w/w) glutaraldehyde solution. A ratio of 1.5 mL of cross-linking solution to 1 g wet bead was used. This corresponds with a 1:1 glutaraldehyde-amine ratio. This mixture was shaken at 150 rpm, 25 °C for 48 hours. The beads were then rinsed with DIW to remove any free glutaraldehyde. This step links the chitosan polymer chains in the beads to each other. Some glutaraldehyde may also attach to the chitosan with one end while leaving the other end free in solution. Cross-linking is illustrated in Figure 3.2, while the second possible configuration is illustrated in Figure 3.3.

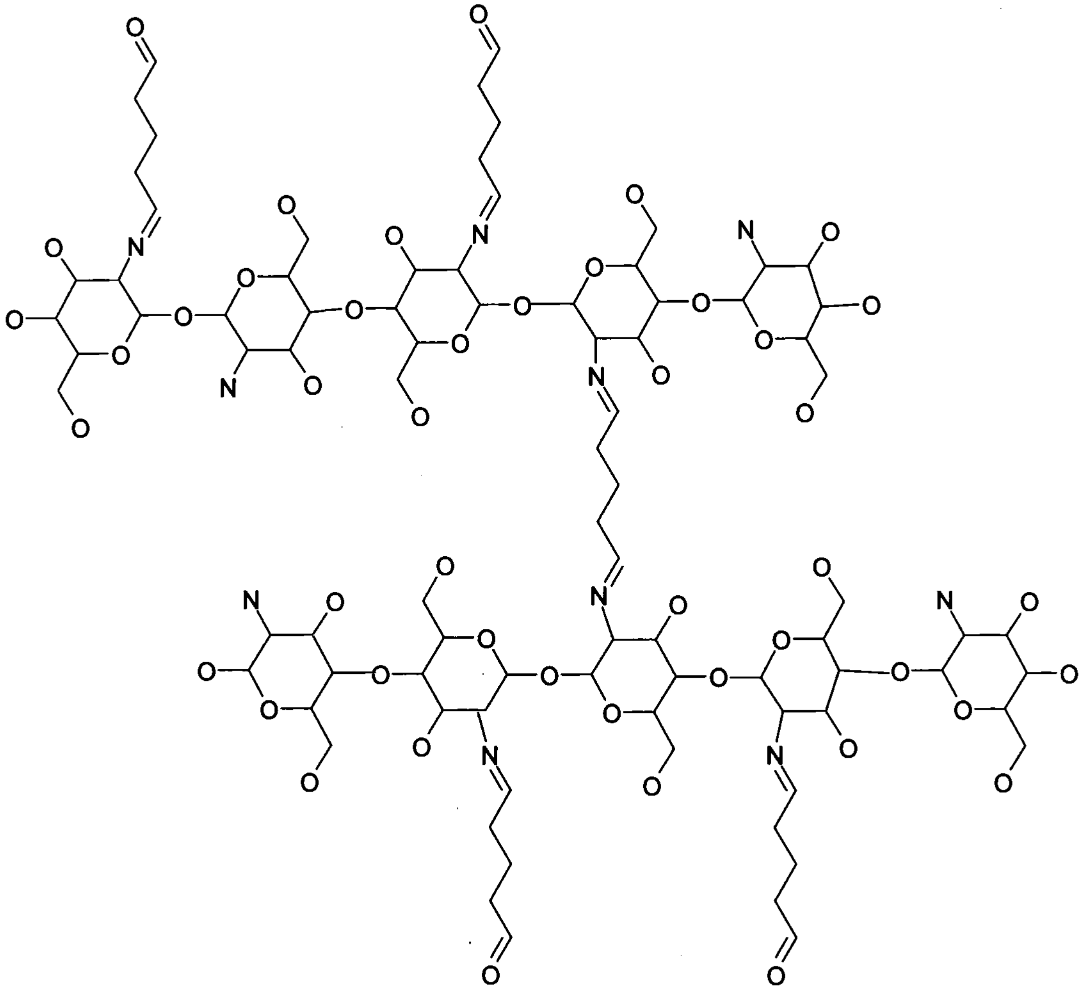


Figure 3.2. Crosslinked Chitosan Strands.

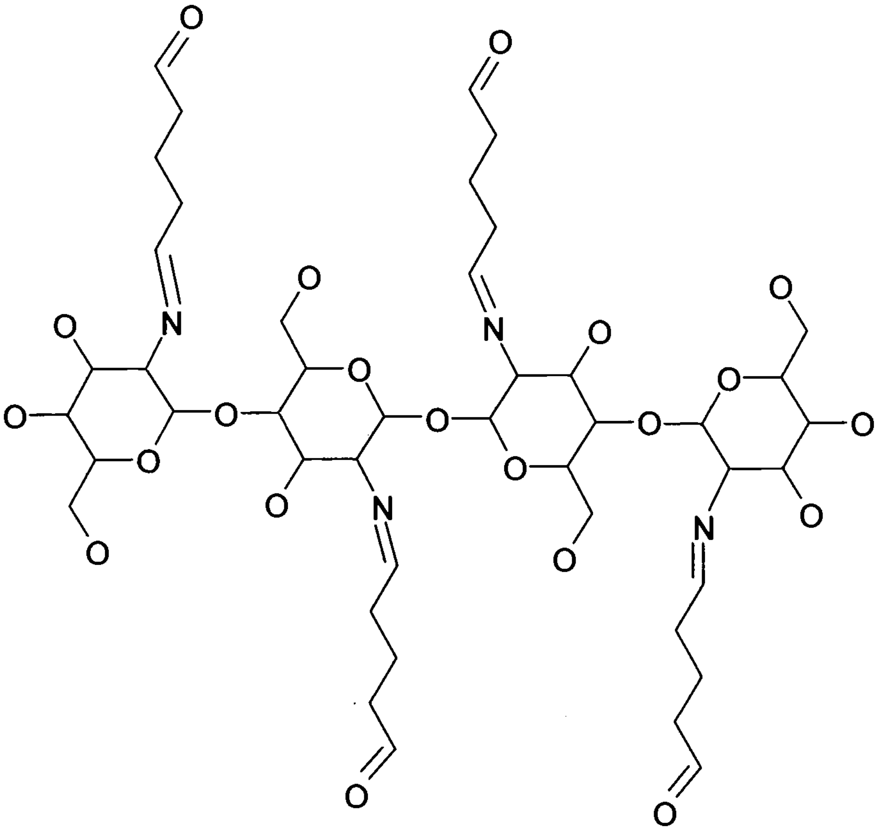


Figure 3.3. Chitosan Strand with Free Hanging Glutaraldehyde.

3.1.4. Cysteine Grafting

After rinsing, the beads were placed in a 2% (w/w) cysteine solution at a ratio of 1.5 ml cysteine solution / gram wet bead. The solution was shaken for 24 hr at 150 rpm, 25 °C. During this process the amino group of the cysteine attaches to the aldehyde group of the free hanging glutaraldehyde via a Schiff base reaction mechanism similar to that used in the attachment of cysteine to silanized controlled pore glass beads by Elhamadi et al.[115] After grafting them with cysteine, the off white colored chitosan beads became red colored as seen in Figure 3.4. An idealized product of this reaction is shown in Figure 3.5. Care was taken to completely rinse the beads with DIW to remove any free cysteine.

Figure 3.4. Plain and Cysteine Grafted Chitosan Beads.

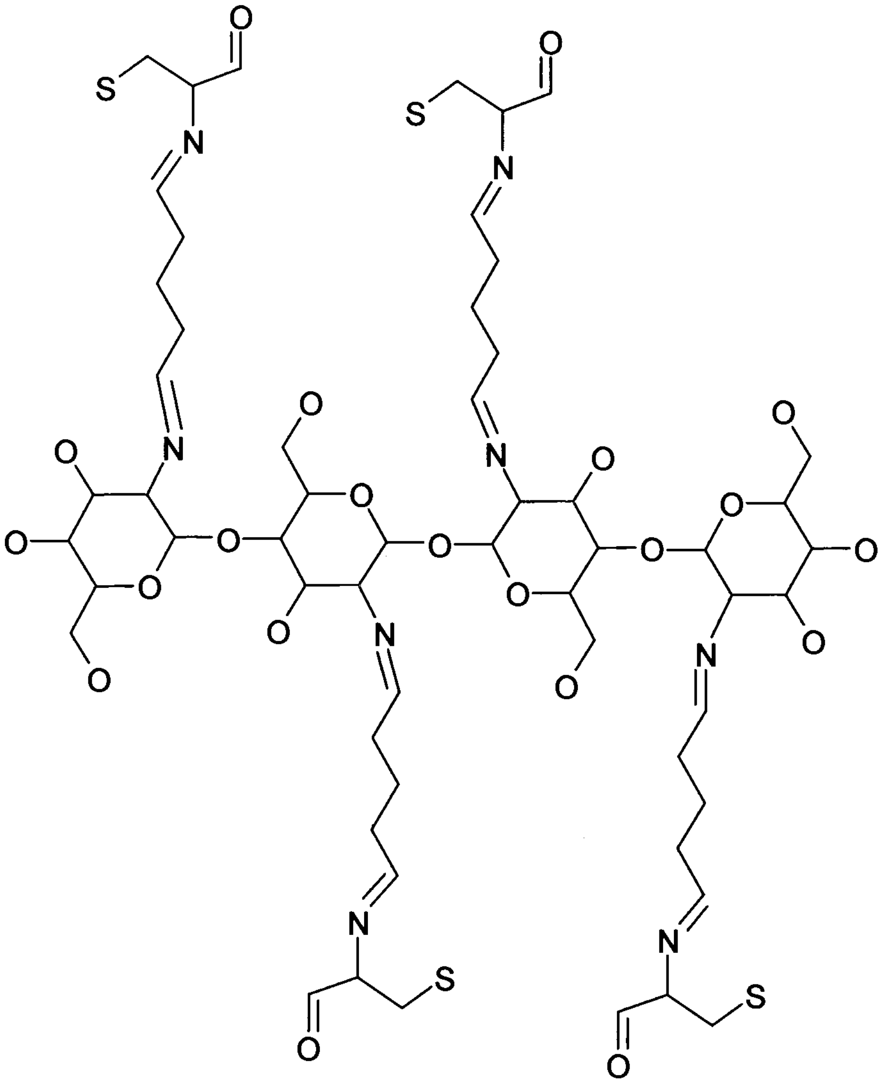


Figure 3.5. Cysteine Attached to Chitosan via Glutaraldehyde.

3.1.5. Gel Bead Drying

The wet gel beads were prepared for storage and analysis by removing the water through sublimation using a lyophilizer (Virtis Freezemobile 25SL). This is commonly referred to as "freeze drying" since samples are usually frozen before lyophilization. The beads were placed in the drying chamber without prior freezing. Trials conducted with prior freezing of the gel beads showed that the freezing process destroyed the pore structure of the beads. A duration of 24 hr under a 100-micron Hg vacuum was sufficient to remove the water from the beads. This process preserved the pore structure and also greatly reduced the mass of the beads. Wet beads were stored in DIW in the dark at 4°C. Dry beads were stored in a desiccator at room temperature. Figure 3.6. shows some lyophilized beads. Comparison with Figures 3.1 and 3.4. shows how the shape of the beads remains virtually unchanged from the original liquid drop. It is important to note that beads dried under conditions that preserve the structural characteristics of the gel beads retain the same ability to adsorb metals.[116]

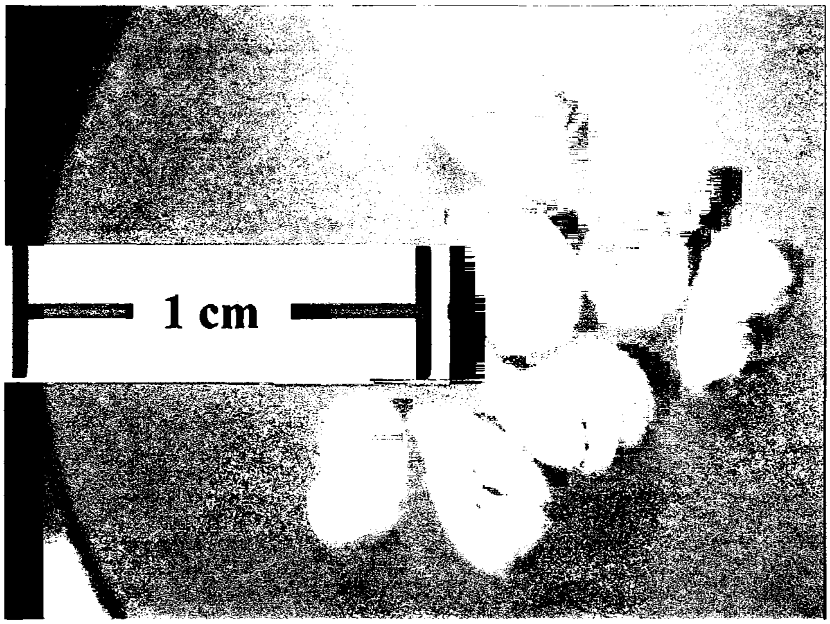


Figure 3.6. Lyophilized Beads.

3.2. Adsorption Experiments

3.2.1. Reaction Vessels

All adsorption experiments were conducted in 125 mL and 500 mL amber glass bottles. Background experiments were performed to ensure that no adsorption to the glass walls was taking place. Most glassware containing Hg was washed in a 10% HCl bath followed by triple rinsing with DIW. Glassware used to prepare high concentration stock solutions was washed separately in order to maintain the integrity of the acid bath.

3.2.2. Hg Solutions

Mercury stock solutions were prepared fresh for each experiment from the $HgCl_2$ salt. Nitric acid (10%) was used to dissolve the salt. Calibration standards and the experimental solutions were prepared from the same stock.

Calibration standards were prepared for each experiment with the same background constituents as the experimental solutions.

3.2.3. Buffers and Ionic Strength

Buffers at 0.01 M concentration were used to control the pH in the range of 4-10. Acetate buffers were used for experiments conducted in the 4-5 pH range. HEPES buffer was used initially for the 6-10 pH range, but was discontinued due to the formation of floating precipitates and measured decreases in Hg concentration. Subsequently phosphate buffers were used for experiments in the 6-10 pH range. Experiments conducted outside the pH 4-10 range had stable pH values due to an excess of H^+ at low pH and an excess of OH^- at high pH values. A background salt concentration of 0.01 M KNO_3 was used for all experiments other than the varied Cl- investigation.

3.2.4. Temperature and Mixing Rates

The experiments were conducted in a combined temperature controlled bath-shaker table (LabLine model 4862). Mixing rates and temperature were digitally controlled.

3.2.5. Adsorption Equilibrium

Mercury solutions of the desired concentrations were prepared and buffered to the desired pH and ionic strength. 100 mL of Hg solution was poured into 125 mL amber glass bottles and enough beads were added to remove approximately one half of the aqueous Hg. The bottles were then shaken in the 25°C water bath until equilibrium was achieved. The solutions were sampled before the addition of the beads as well as at equilibrium in order to determine the Hg concentrations. Control blanks were also run without beads to check for removal of Hg through other mechanisms than adsorption to the beads. Reactors used to investigate Cl^- interference, to evaluate the performance of beads grafted with different cysteine concentrations, and for the pH edge all had initial Hg concentrations of 0.5 mM.

3.2.6. Adsorption Kinetics

Mercury solutions of desired concentrations were made and buffered to the desired pH and ionic strength. 500 mL of the Hg solution was placed in a 1 L amber glass bottle and sampled for initial concentration. Enough beads were added to remove approximately half of the Hg by the end of the run, and the solution was placed in the shaker bath. The solutions were sampled periodically and analyzed for Hg content. Samples of 1 mL were taken for solutions containing less than 1 mM Hg while aliquots of 0.25 mL were taken for more concentrated solutions. 0.75 mL of DI was added to the smaller samples in order to maintain dilution ratios. Initial and final solution volumes were within 5% of each other and the ratio of liquid to solid remained essentially constant.

3.3. Chemical Analysis

3.3.1. Hg Analysis

A colorimetric technique was determined to be the most effective method of measuring Hg in this work. Aliquots (usually 1 mL) were taken from the reaction vessels and placed in 50 mL Fisherbrand polypropylene centrifuge bottles. One mL of the zincon (2-carboxy-2'-hydroxy-5'-sulphoformazylbenzene) coloring reagent (1 mL 2 M NaOH and 0.13 g zincon diluted to 100 mL) described by Morris[117] and 10 mL of 0.1 M HEPES buffer solution at pH 7.2 were then added to this solution. The vials were recapped and shaken to ensure complete mixing. Hg concentrations were determined using a diode array spectrophotometer (HP 8452A). This colorimetric method was chosen over other available methods due to the ease with which it could be used at high concentrations. The spectrophotometer was set to measure in the range of 516-716 nm and readings were recorded at 616 nm.

Cold Vapor Atomic Absorbance Spectrometry (CVAAS) was used initially using a Merlin Mercury Fluorescence Detector. Multiple serial dilutions were required to reduce the working concentrations to the levels at which the CVAAS instrument could accurately measure. The dilution procedure, however, required an excessive amount of time and exposure to 10% nitric acid. Hg measurement using the CVAAS was therefore abandoned.

3.3.2. Cysteine and Total S Analysis

The concentration of the cysteine solution was measured using a Brinkmann 746 VA Trace Analyzer. Samples taken throughout the grafting period were diluted to the working range of the instrument with DIW. The cysteine content of the dried beads was derived from the total S content of the beads.

The total S measurements were performed at Huffman Laboratories of Golden, Colorado. It has been assumed that the only source of S is the added cysteine, although some trace amounts of S may be associated with the other constituents. Only thiol-grafted beads were tested for total S.

3.4. Physical Analysis

Analysis of the physical characteristics of the freeze-dried beads, including surface area, pore volume and pore diameters, was performed by Micromeritics Instrument Corporation of Norcross, GA. Additionally, a graduated cylinder and balance were used to determine bulk density, solid density, specific gravity and porosity. Porosity was approximated by a comparison of wet volume to that of the oven dried beads. Chitosan beads that are dried without a vacuum collapse and become quite dense and hard. 50 freeeze-dried beads were measured with a caliper in order to determine average length and diameter. Each bead was measured twice, once from tip to tail and also in the perpendicular direction. Figure 3.7. shows the beads that were measured, as well as lines indicating the directions of measurement.

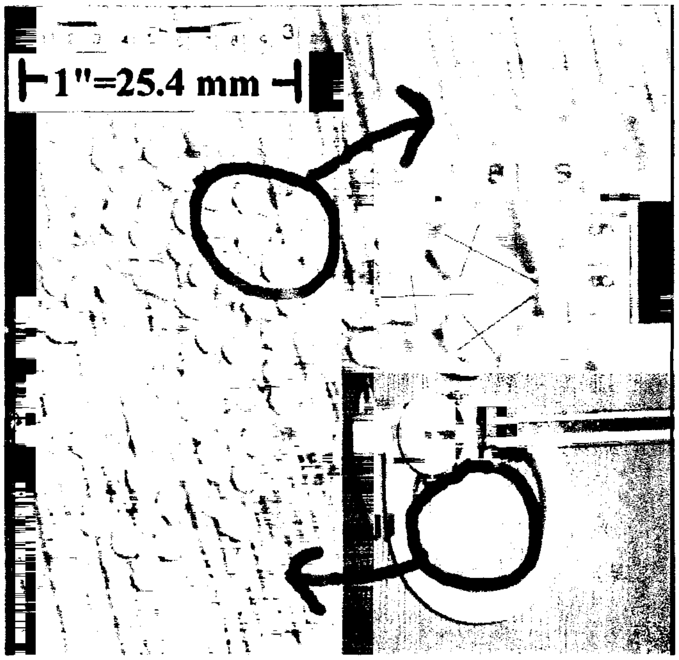


Figure 3.7. Measured Beads.

3.5. Reagents

Chitosan flakes (Med. Mol. Weight) [9012-76-4] were obtained from Aldrich. Glacial Acetic Acid (CH_3COOH) (99.7 % w/w) [64-19-7] was obtained from Fisher. Mercuric chloride ($HgCl_2$) [7487-94-7] of purity 99.5% was obtained from Aldrich. Sodium Hydroxide (NaOH) [1310-73-2] of purity 98.9% was obtained from Fisher. L-Cysteine ($HSCH_2CH(NH_2)CO_2H$) [52-90-4] of purity 97% was obtained from Aldrich. Zincon [62625-22-3] of 85% purity was obtained from Aldrich. Glutaric dialdehyde (glutaraldehyde) ($HCO(CH_2)_3CHO$) [111-30-8] 25% w/w was obtained from Aldrich. 4-(2-

hydroxethyl)-1-piperazinethanesulfonic acid (HEPES) [7365-45-9] 99% purity was obtained from Sigma. A 0.998 N nitric acid volumetric standard and a 0.1 N volumetric standard NaOH were obtained from Aldrich for the surface titration. All water used in the reagents and for rinsing the beads as well as the glassware was deionized with 18 MΩ resistivity using a Barnstead NanopureInfiinity system. Water used for preparation of titration reagents was cleansed of CO_2 by bubbling N_2 gas through the water.

Chapter 4

RESULTS

4.1. Adsorption Equilibrium Results

Experiments were conducted to determine the adsorption equilibrium of Hg onto the chitosan beads. In order to characterize the ability of the beads to remove Hg from solution, adsorption was studied at various pH values and initial Hg concentrations. Adsorption isotherms are presented below in Figure 4.1. Lines represent fitted Freundlich isotherms discussed in the next chapter. With the exception of Figure 4.3., all beads used in experiments were processed in a 2% cysteine solution unless otherwise marked.

Figure 4.2 shows the adsorption behavior as a function of pH. In order to optimize the synthesis of the beads, a set of experiments was conducted to study the Hg adsorption capacity of the beads as a function of the cysteine concentration of the grafting bath. The results of the experiment are shown below in Figure 4.3. No perceptible changes are observed at cysteine concentrations above 1%, but a 2% cysteine solution was used in the synthesis. This was done to economize the use of reagents while ensuring high uptake of Hg. The adsorption experiments for determining optimum cysteine concentration were allowed to proceed only for 48 hours, which is why adsorption levels are different from equilibrium values presented in the isotherms.

Figure 4.4 shows the effect of Cl^- concentration on Hg adsorption. Chloride binds Hg very strongly in solution, and could interfere with Hg adsorption onto the cysteine grafted chitosan beads. Once again, adsorption experiments were only conducted for 48 hours and this is reflected in differences between Figure 4.4. and Figure 4.1.

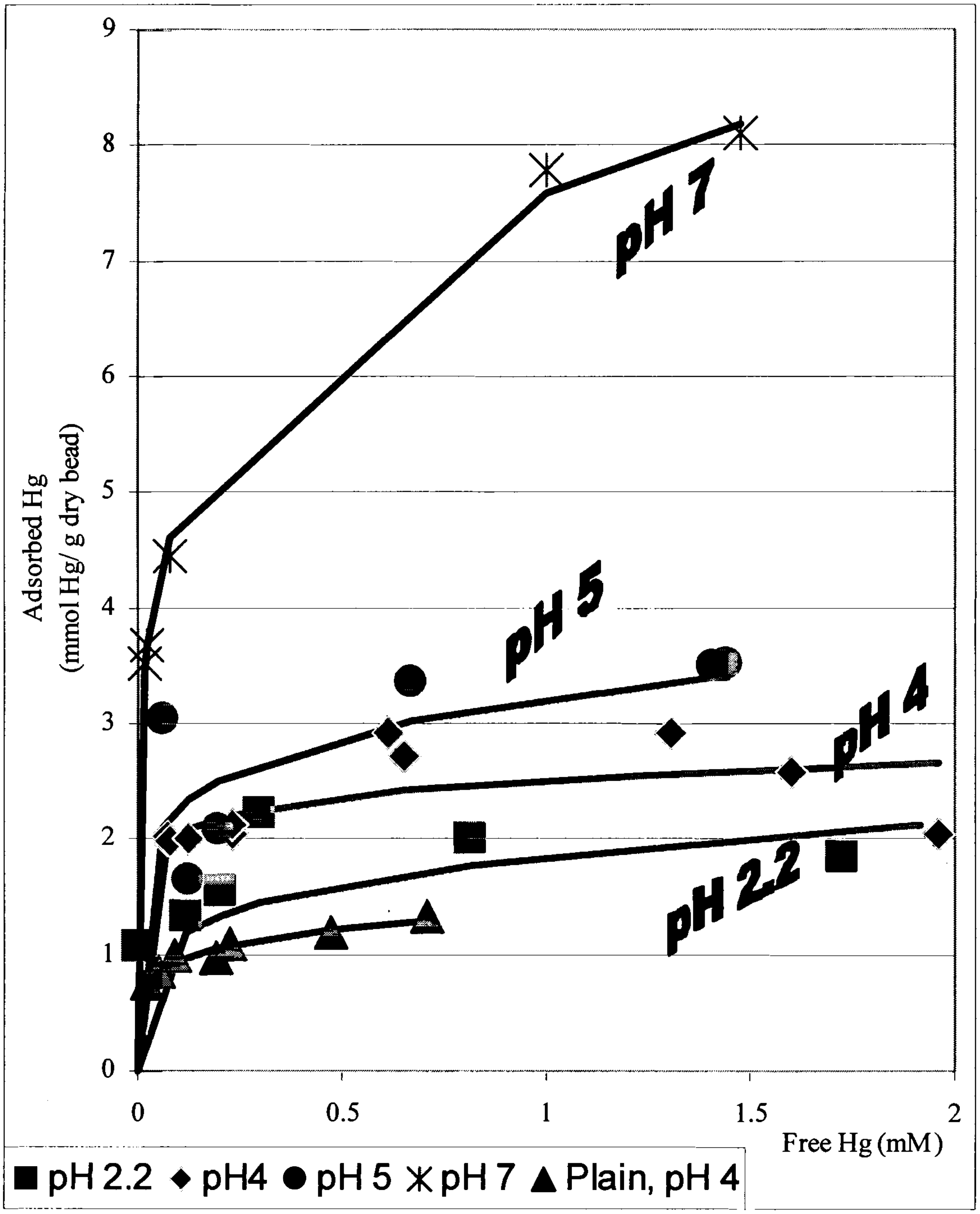


Figure 4.1. Adsorption Isotherms for Thiol-Grafted Chitosan Beads.

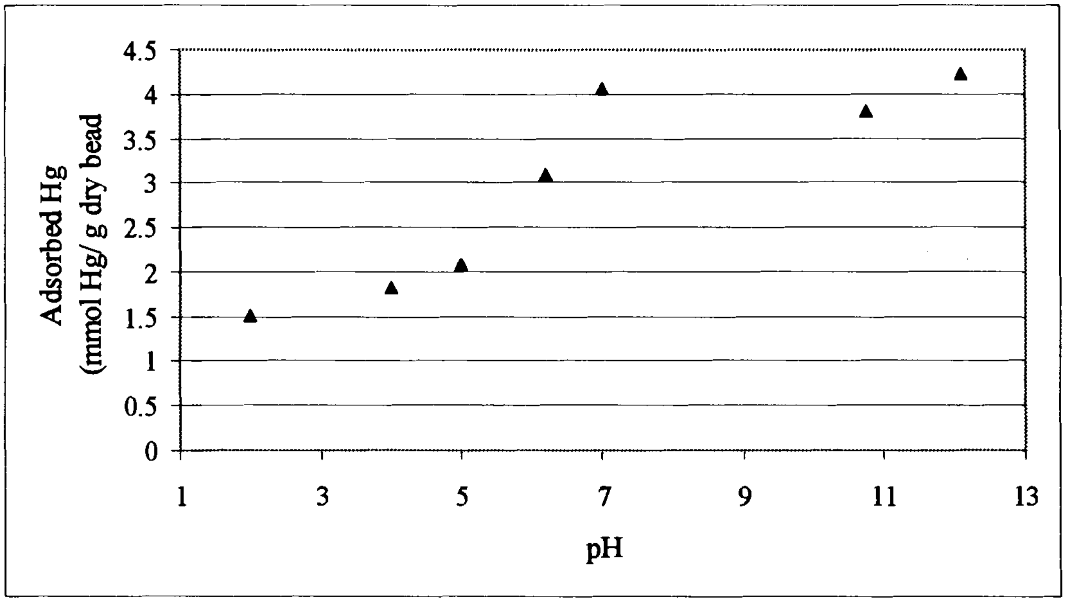


Figure 4.2. pH Edge. Approximately 0.01 g dry were used per 100 mL reactor. Initial [Hg] = 0.5 mM.

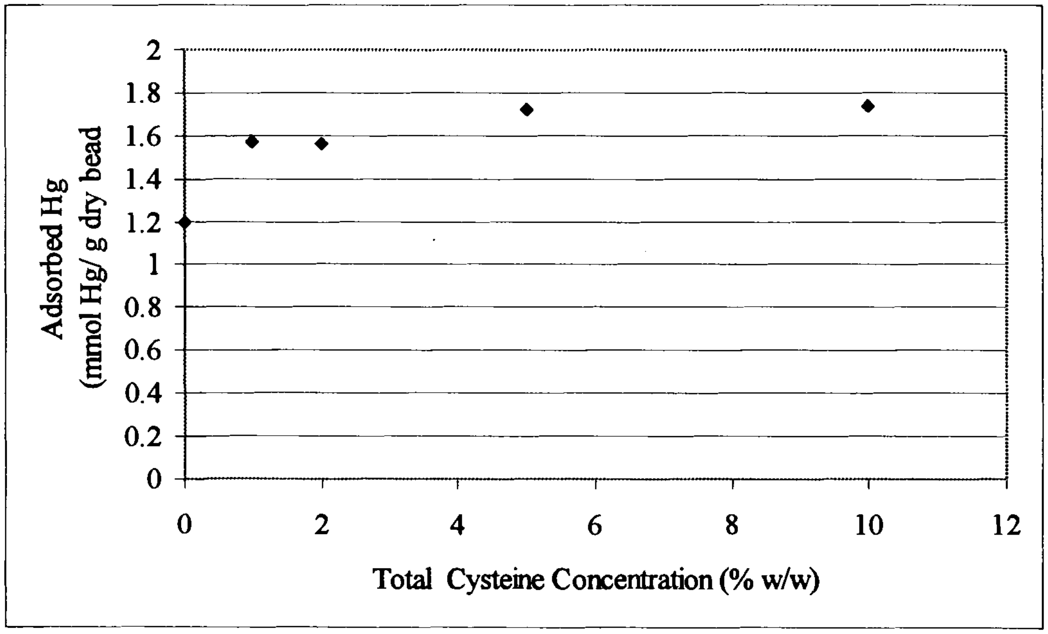


Figure 4.3. Effects of Cysteine Grafting Concentration on Hg Adsorption. pH 5, 150 RPM, Acetate Buffer, ~0.02 g dry bead/100 mL reactor, Initial [Hg] = 0.5 mM , Time = 48 hours.

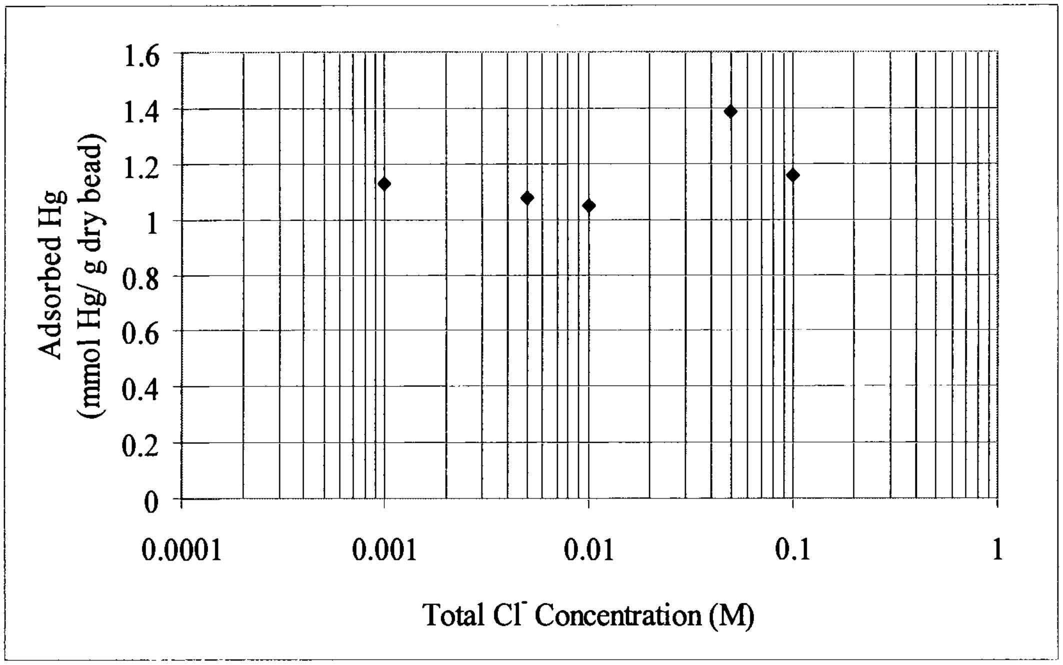


Figure 4.4. Effects of Cl^- on Hg Adsorption. pH 2.2, ~0.007 g dry bead/100 mL reactor, Time = 48 hours.

4.2. Kinetics

In addition to the equilibrium adsorption characteristics of the beads, it is important to characterize the rates at which adsorption occurs. In order to elucidate the characteristics that influence the adsorption rate, a series of kinetic experiments were conducted. As shown in Table 4.1, a wide range of agitation rates, pH values and initial Hg and adsorbent concentrations were investigated. The experimental results are presented in Figures 4.5-4.15. Lines are based on a square root of time fit discussed in the next chapter. All beads used in kinetics experiments were processed in a 2% cysteine solution.

<table>
<tr><td colspan="6">All experiments conducted at 25 C in 0.01 M KNO3. pH 4 and pH 5 reactors contained 0.01 M Acetate Buffer and pH 6.5 reactor contained 0.01 HEPES Buffer. Reactors contained 500 mL of solution.</td></tr>
<tr><th>Figure</th><th>pH</th><th>Initial [Hg] mM</th><th>Agitation Rate (cycle/min)</th><th>Wet Mass (g)</th><th>Approximate Dry Mass (g)</th></tr>
<tr><td>4.05</td><td>4</td><td>0.5</td><td>50</td><td>0.972</td><td>0.0972</td></tr>
<tr><td>4.06</td><td>5</td><td>0.5</td><td>50</td><td>0.983</td><td>0.0983</td></tr>
<tr><td>4.07</td><td>6.5</td><td>0.5</td><td>50</td><td>0.989</td><td>0.0989</td></tr>
<tr><td>4.08</td><td>4</td><td>0.5</td><td>75</td><td>0.979</td><td>0.0979</td></tr>
<tr><td>4.09</td><td>5</td><td>0.5</td><td>75</td><td>0.992</td><td>0.0992</td></tr>
<tr><td>4.10</td><td>4</td><td>0.25</td><td>150</td><td>0.48</td><td>0.048</td></tr>
<tr><td>4.11</td><td>4</td><td>0.5</td><td>150</td><td>0.95</td><td>0.095</td></tr>
<tr><td>4.12</td><td>4</td><td>1.25</td><td>150</td><td>2.05</td><td>0.205</td></tr>
<tr><td>4.13</td><td>4</td><td>2.5</td><td>150</td><td>3.59</td><td>0.359</td></tr>
<tr><td>4.14</td><td>4</td><td>0.5</td><td>200</td><td>0.976</td><td>0.0976</td></tr>
<tr><td>4.15</td><td>5</td><td>0.5</td><td>200</td><td>0.936</td><td>0.0936</td></tr>
</table>

Table 4.1. Summary of Kinetic Experiments.

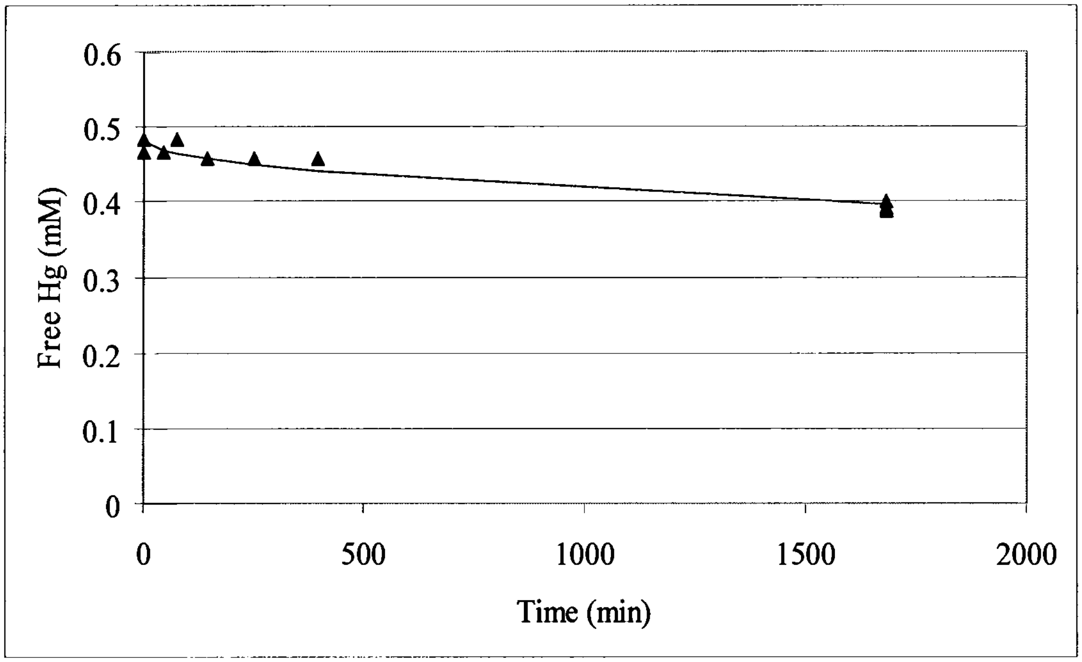


Figure 4.5. Kinetics plot for pH 4 at 50 rpm. 25 C, 0.01 M KNO_3, 0.01 M Acetate Buffer, and 0.972 g wet thiol-grafted chitosan beads.

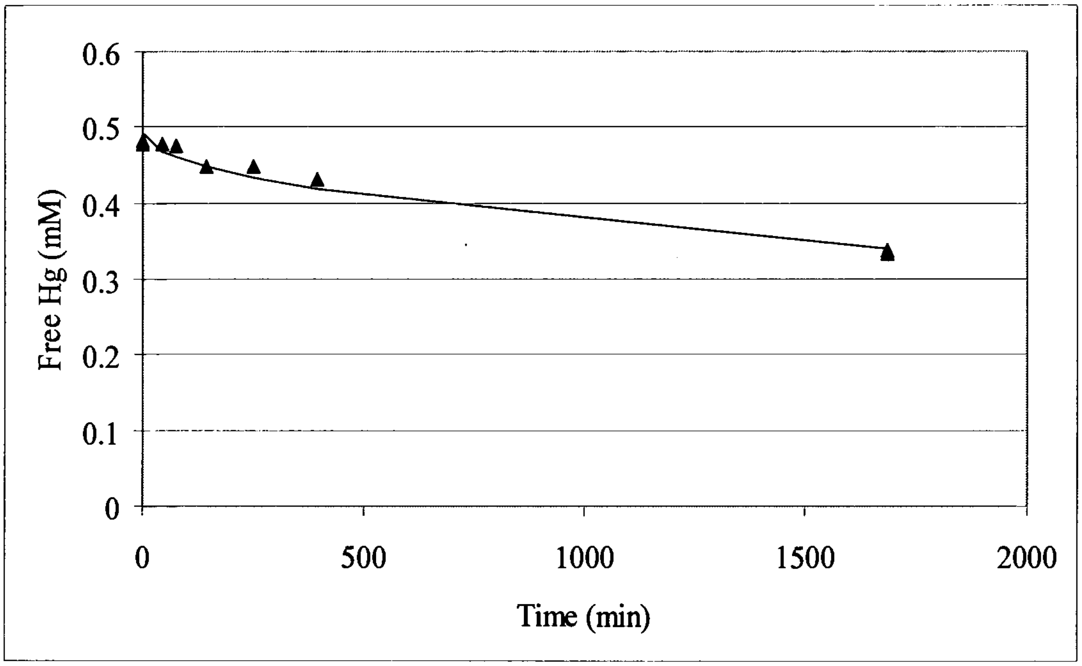


Figure 4.6. Kinetics plot for pH 5 at 50 rpm. 25 C, 0.01 M KNO_3, 0.01 M Acetate Buffer, and 0.983 g wet thiol-grafted chitosan beads.

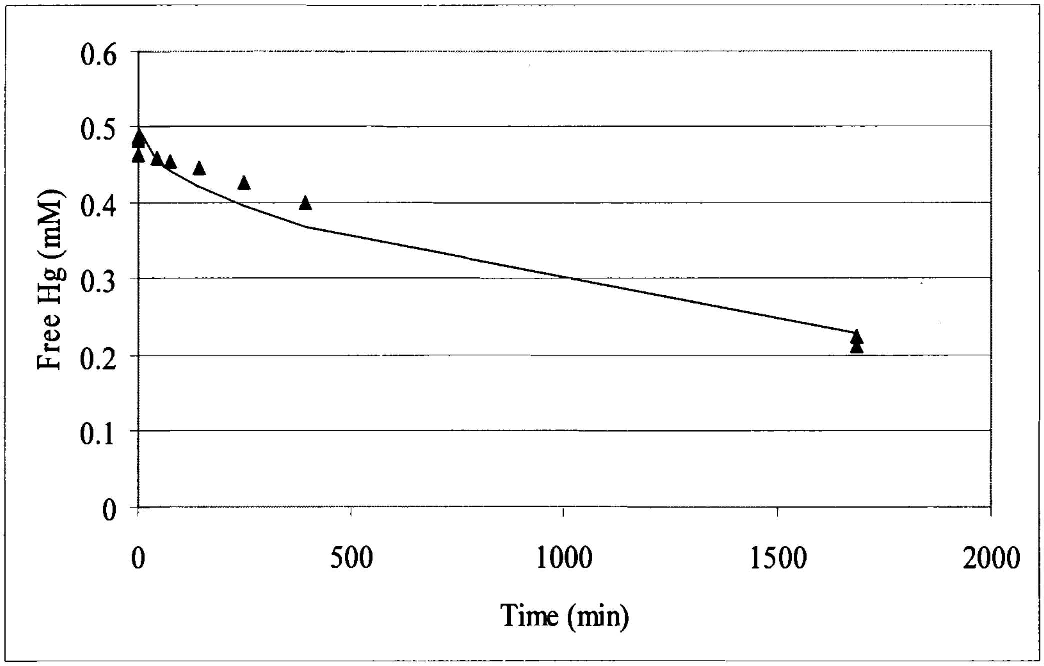


Figure 4.7. Kinetics plot for pH 6.5 at 50 rpm. 25 C, 0.01 M KNO_3, 0.01 M HEPES Buffer, and 0.989 g wet thiol-grafted chitosan beads.

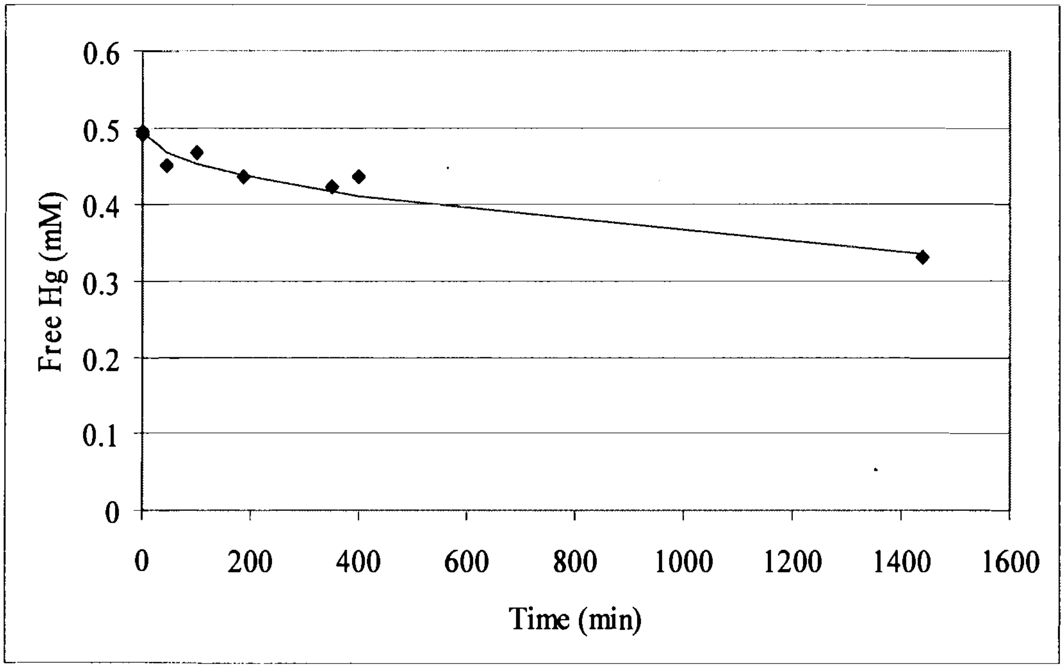


Figure 4.8. Kinetics plot for pH 4 at 75 rpm. 25 C, 0.01 M KNO_3, 0.01 M Acetate Buffer, and 0.979 g wet thiol-grafted chitosan beads.

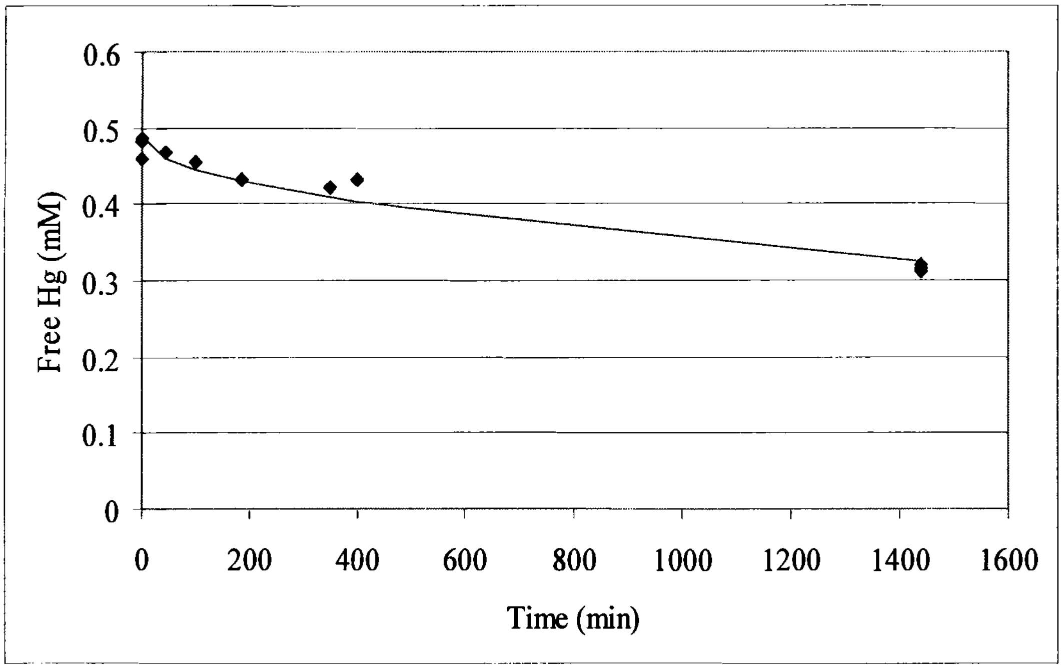


Figure 4.9. Kinetics plot for pH 5 at 75 rpm. 25 C, 0.01 M KNO_3, 0.01 M Acetate Buffer, and 0.992 g wet thiol-grafted chitosan beads.

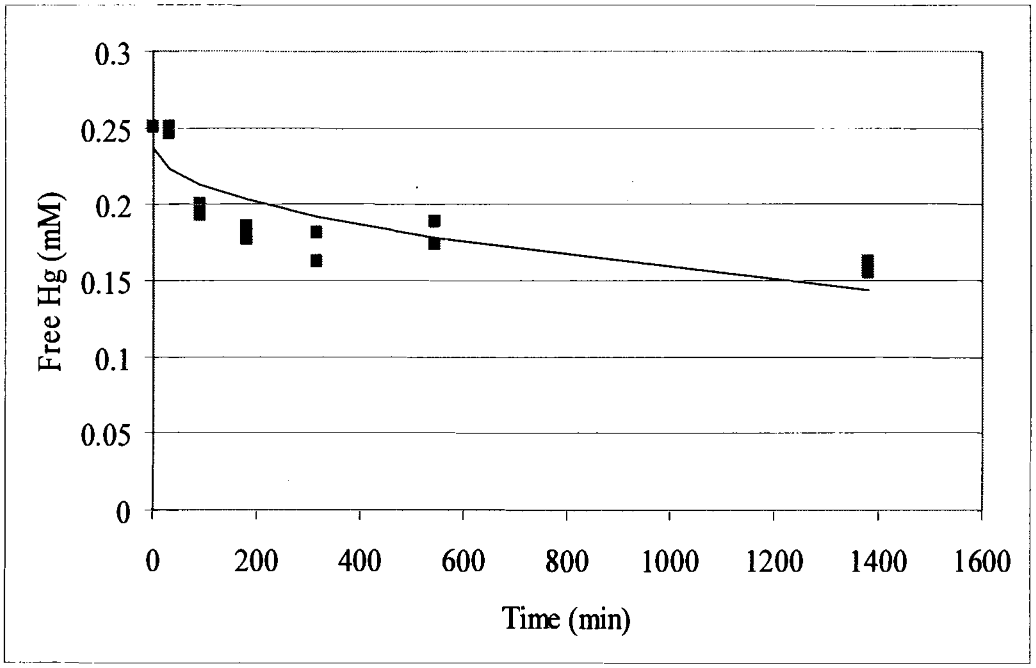


Figure 4.10. Kinetics plot for pH 4 at 150 rpm. 25 C, 0.01 M KNO_3, 0.01 M Acetate Buffer, and 0.48 g wet thiol-grafted chitosan beads.

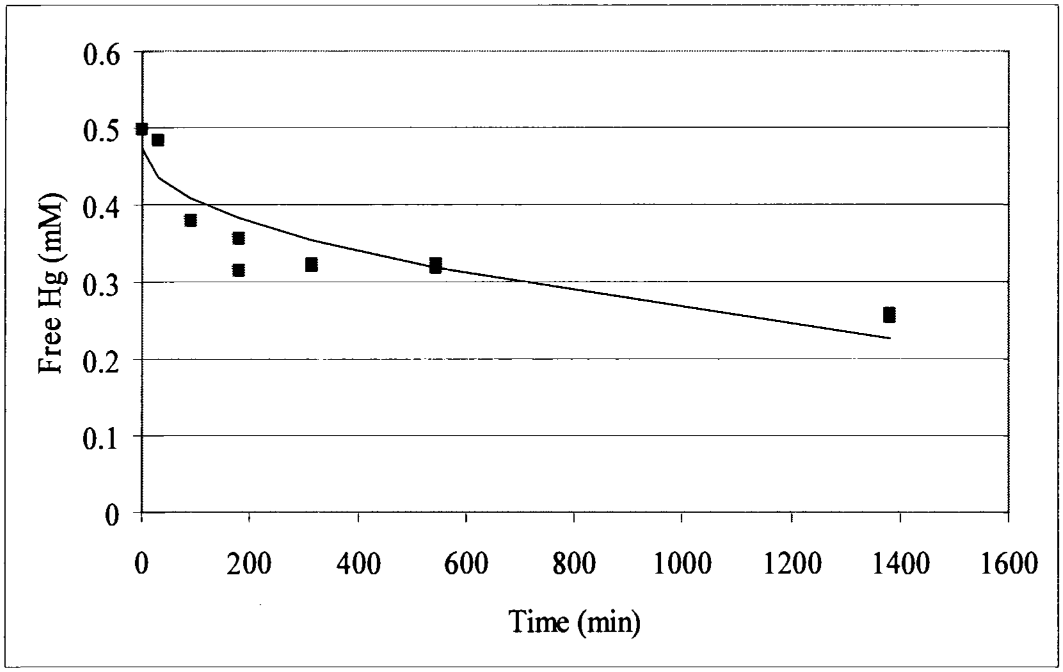


Figure 4.11. Kinetics plot for pH 4 at 150 rpm. 25 C, 0.01 M KNO_3, 0.01 M Acetate Buffer, and 0.95 g wet thiol-grafted chitosan beads.

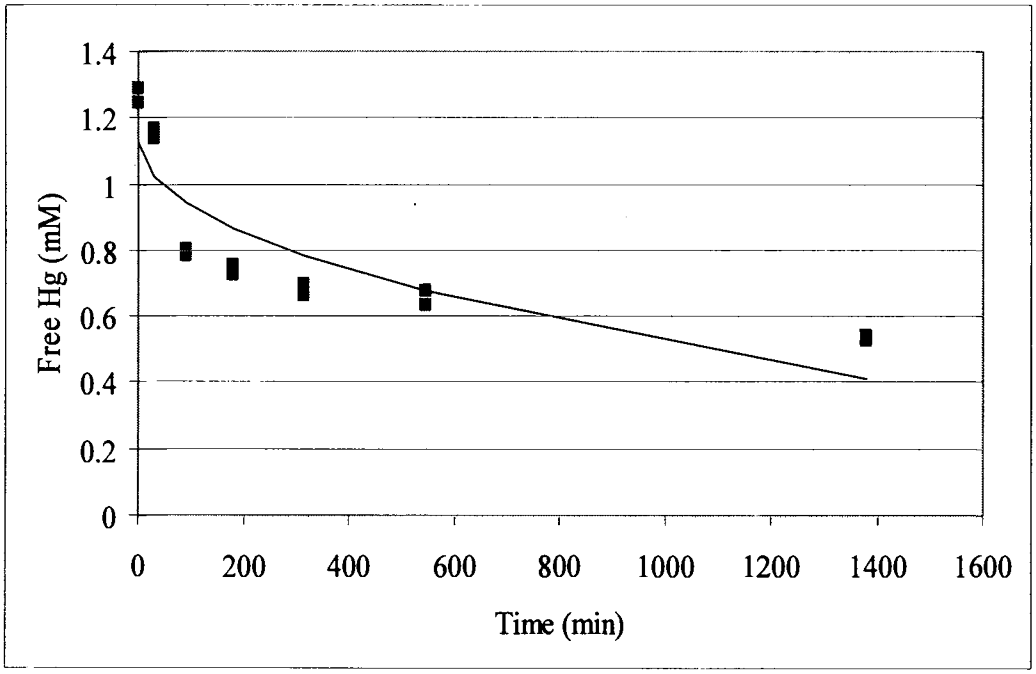


Figure 4.12. Kinetics plot for pH 4 at 150 rpm.25 C, 0.01 M KNO_3, 0.01 M Acetate Buffer, and 2.05 g wet thiol-grafted chitosan beads.

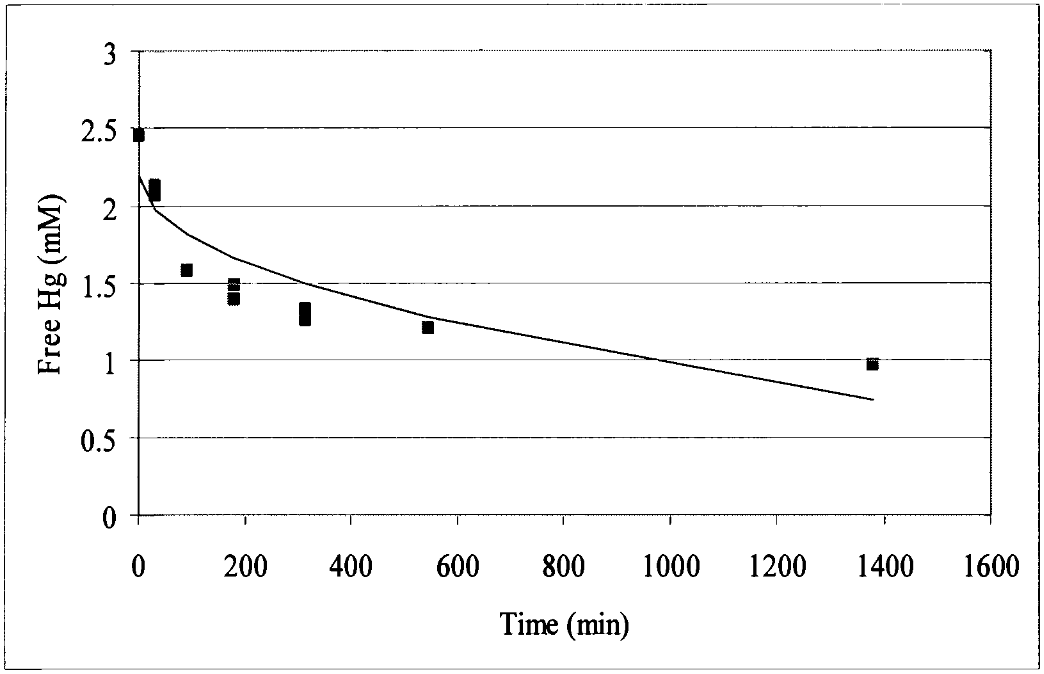


Figure 4.13. Kinetics plot for pH 4 at 150 rpm. 25 C, 0.01 M KNO_3, 0.01 M Acetate Buffer, and 3.59 g wet thiol-grafted chitosan beads.

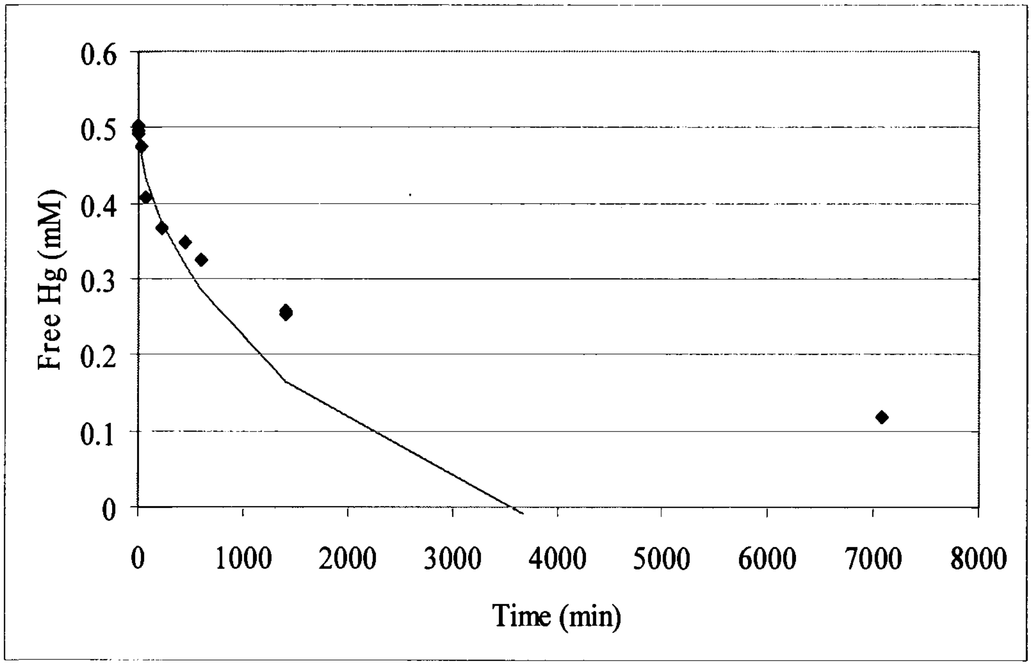


Figure 4.14. Kinetics plot for pH 4 at 200 rpm. 25 C, 0.01 M KNO_3, 0.01 M Acetate Buffer, 0.976 g wet thiol-grafted chitosan beads.

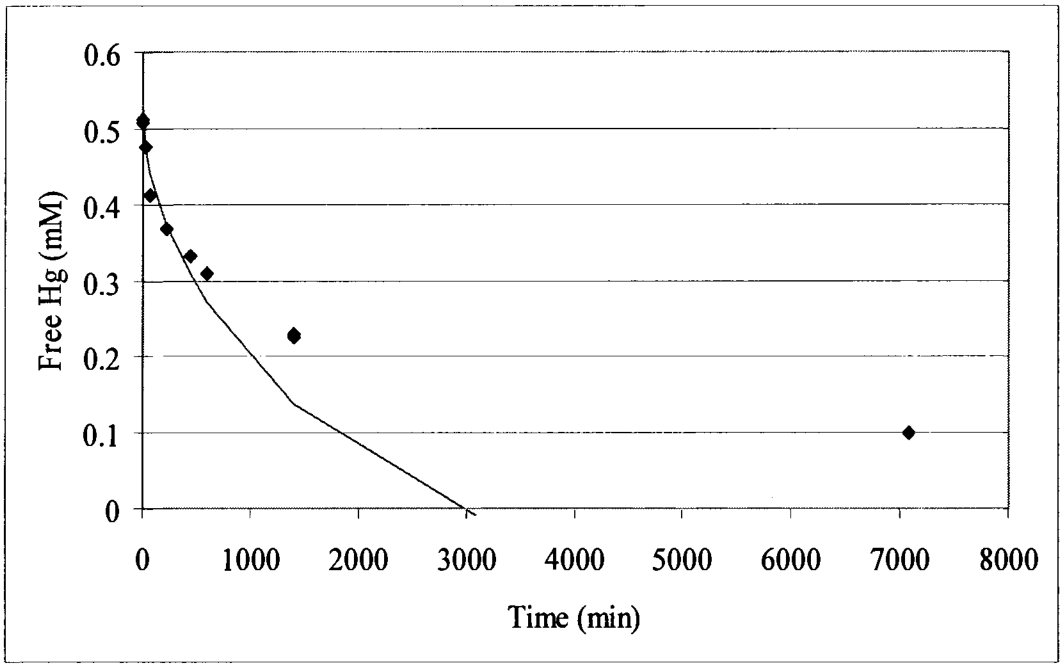


Figure 4.15. Kinetics plot for pH 5 at 200 rpm. 25 C, 0.01 M KNO_3, 0.01 M Acetate Buffer, and 0.936 g wet thiol-grafted chitosan beads.

4.3. Physical Data

In addition to the chemical properties, it is desirable to know those physical characteristics of the beads that influence pore diffusion and adsorption of the solutes. This information is useful in formulating transport models, and also helps to give some indication of the performance of the beads. Table 4.2 shows the measured physical properties of the beads.

Properties of Cysteine Modified Chitosan Beads				
Average Bead Diameter	2.8	+/-	0.5	mm
Average Bead Length	4.4	+/-	1.2	mm
Nominal Spherical Bead Diameter	3.2	+/-	0.9	mm
Porosity	0.9	+/-	0.05	
Specific Gravity	2	+/-	0.1	
BET Surface Area *	96.8			m^2/g
BJH Surface Area *	98.7			m^2/g
Pore Volume (single point) *	0.32			cm^3/g
Pore Volume (BJH) *	0.26			cm^3/g
BET Average Pore Diameter *	132			Angstroms
BJH Average Pore Diameter *	107			Angstroms
Total S **	4.98			% w/w

Table 4.2. Physical Properties of Thiol-Grafted Chitosan Beads, * from MicroMeritics, ** from Huffman Labs.

Chapter 5

DISCUSSION

5.1. Adsorption Isotherms

Experimental data by itself is of little value when attempting to solve problems. In order to be of use outside of the arena of laboratory reactors, the data must be fit to a model based on sound scientific principles, which allows for extrapolation and interpolation. Care must be taken to choose a model that is relevant from a physiochemical point of view, and approximates the observed behaviors reasonably well. If sufficiently useful for predicting behavior, an empirical curve fit may prove to be an excellent tool without the added complexity of theoretical rigor. There are two fairly simple models that are often used to approximate adsorption behavior, the Freundlich and Langmuir isotherms.[118] A third model, the linear adsorption isotherm, often used in adsorption and transport modeling is a special case of the Freundlich isotherm. The Freundlich isotherm is simpler of the two and is represented by the equation 5.1.

$$C_s = m * C_w{}^n \quad (5.1)$$

Where C_s is the adsorbed solute concentration

C_w is the solute concentration in the aqueous phase

m is a constant representing the partitioning between phases, and

n is a measure of the nonlinearity of the adsorption relationship.

The Langmuir isotherm is represented by equation 5.2.

$$C_S = \frac{q * K_{ads} * C_w}{1 + K_{ads} * C_w} \quad (5.2)$$

Where

q represents the number of available binding sites, and

K_{ads} is the equilibrium adsorption constant.

The Freundlich isotherm allows for infinite adsorption, while the Langmuir model is appropriate for the case where there is a single type of binding sites with relatively constant bond energy. The Freundlich model is also appropriate for cases where there is multilayer adsorption, or adsorption takes place onto sites with different binding energies as long as the maximum adsorption capacity has not been reached.

The equilibrium adsorption data presented in section 4.1 were modeled using the Freundlich isotherm. The solid lines presented in Figure 4.1 are the fitted Freundlich isotherms. The fitted values are shown below in Table 5.1.

Freundlich Parameters			
	pH	m	n
Plain Beads	4	1.37	0.1574
Cysteine Beads	2.2	1.85	0.2074
	4	2.51	0.0862
	5	3.22	0.1534
	7	7.59	0.1946

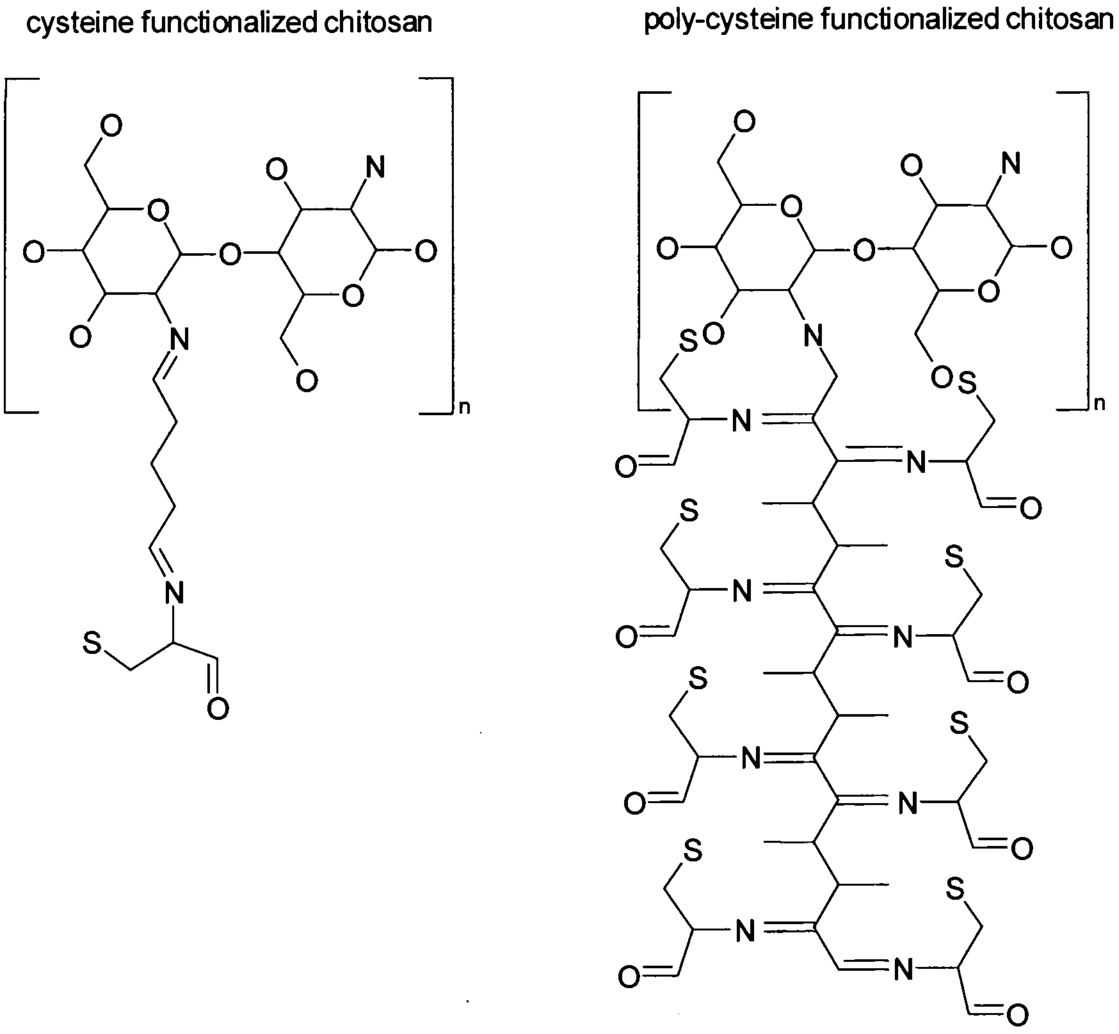
Table 5.1. Freundlich Isotherm Values.

Table 5.2 is a collection of experimental equilibrium adsorption data for metal adsorbents from literature. This table is not exhaustive and is primarily composed of references that include the adsorption isotherms. The molar adsorption capacity of the beads from this work compare favorably with those published by others.

Kawamura's[119] polyfunctionalized chitosan beads outperform this work in terms of adsorption capacity, with a capacity of 10.5 mmol/g dry. This is most likely due to the use of a polyaminated compound to enhance adsorption. Examples of grafted monomeric and polymeric cysteine onto chitosan are shown in Figure 5.1.

Some Metal Adsorbents, NR = not reported

Investigator	Adsorbent	Metal(s)	pH	Capacity (mmole/g)
Kawamura et al., Wat. Sci. Tech., 1997	Polyaminated Chitosan Beads	Hg	NR	~10.5
This Work	Cysteine-Grafted Crosslinked Chitosan Beads	Hg	7	~8
Guibal et al., 1998	0.95 mm crosslinked chitosan beads	V	3	7.9
Guibal et al., 2000	crosslinked chitosan beads	Mo	4	~ 7
Rorrer and Hsien, 1993	1 mm, 3 mm crosslinked chitosan beads with magnetite	Cd	6.5	~4.6 , ~1.7
Pacific Northwest National Lab, 2002	Thiol SAMMS	Cu, Pb, Cd, Hg, Ag	NR	0.59, 0.63, 0.86, 3.17, 4.08
Sing and Yu, 1998	Phanerochaete Chrysosporium Mycelia	Cu	6	~3.9
Blair et al., 1980	chitosan flakes	Cu	NR	~ 3
Ohga et al., 1987	(Chloromethyl)oxirane Crosslinked Cd-Complexed Chitosan	Cu,Hg	5	1.4, 2.6
Brown et al., 2000	Mercaptopropyl-functionalized silica mesostructures	Hg	NR	~2.3
Inoue et al., 1993	Copper crosslinked chitosan powder	Pt,Pd	NR	~1.6, ~2.1
Evans et al., in press	chitosan flakes	Cd	8	~ 2
Guibal et al., 1995	microcrystalline chitosan flakes	U	6	~1.5
Guibal et al., 1999	2.6 mm crosslinked chitosan beads	Pt	2	~1.4
An et al., 2001	Crab Shell Flakes	Cu,Cr,Pb,Cd	5	~1,~1,~1.5 ,~2
An et al., 2001	Dowex Cation Exchange Resin	Cu,Cr,Pb,Cd	5	~1,~1,~1.2, ~1.1
Coughlin et al., 1990	1-10 mm partially deacetylated shellfish waste flakes	Cr, Ni, Cu	NR	~0.3, ~0.6, ~1.6
Navarro et al., 1999	Functionalized cellulose	Co , Zn, Cu	6	~ 0.3, ~0-.4, ~1
Jha et al., 1988	chitosan flakes	Cd	6.5	~ 0.5
Navarro et al., 1999	Functionalized cellulose	Co , Cu	2.5	~ 0.2 - ~0.4
Ngah and Liang, 1999	chitosan flakes	Au	4	~0.16
Bassi et al., 2000	chitosan flakes	Pb,Cd,Cu, Zn	6-7	~0.06, ~0.09, ~0.2,~ 0.35
Gutierrez et al., 1999	Poly-l-aspartate grafted glass beads	Ce, Eu, La	7	~0.007, ~0.007, ~0.007



cysteine functionalized chitosan

poly-cysteine functionalized chitosan

Figure 5.1. Comparison of Monomeric Functionalization and Polyfunctionalization.

Although the use of polyfunctional groups may restrict access to the smallest of pores, the addition of many more adsorption sites to the same molecular footprint on the polymer chain helps to overcome the stoichiometric limitations imposed by the free sites on the polymer. Polyfunctional groups that bind to themselves at any point during synthesis should be avoided, since this would decrease the amount of available sorption sites and the accessibility of the remaining sites.

5.2. Adsorption Kinetics

The process of metals adsorbing onto chitosan beads as well as other porous sorbents can be represented by four steps: 1) transport from the bulk solution to the boundary layer, 2) diffusion across the boundary layer, 3) diffusion through the pores and 4) adsorption onto the surface of the beads.[140] Adsorption onto a surface is usually quite fast compared to the transport of ions.[141] The remaining steps of the process are illustrated in Figure 5.2.

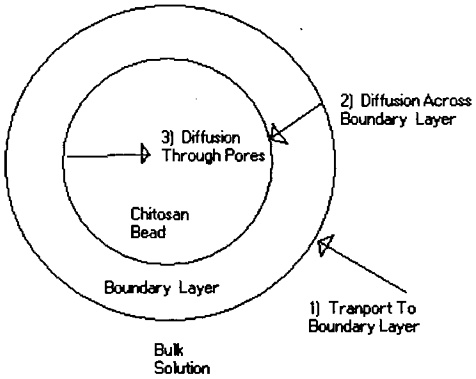


Figure 5.2. Rate Limiting Steps for Adsorption.

5.2.1. Bulk Transport

Diffusive transport in the bulk solution for a given solute is controlled by the chemical gradients in the solution, as described by Fick's laws of diffusion.[142] In order to facilitate transport it is important to keep gradients at interfaces as large as possible. This can be accomplished by mixing a solution to ensure that the concentration at the interface is close to the average bulk concentration.

5.2.2. Boundary Layer Diffusion

In addition to reducing spatial concentration gradients, mixing will affect the thickness of the boundary layer. Lower mixing rates result in thicker boundary layers.[143] Diffusion occurs faster across a thinner layer. This is usually shown in a one-film model of mass transfer to be a first order relationship.[144] However, it has been assumed that pore diffusion is an important step in the adsorption of Hg onto cysteine modified chitosan beads, and a model dependent upon the square root of time has been chosen. This choice is based upon the work of McKay and is suitable for processes that can be modeled as diffusion into a sphere of infinite radius.[145] Diffusion in a semi-infinite domain can be described using a differential equation with a solution based upon the square root of time. McKay also suggests that the extent of the boundary layer resistance can be found by extrapolating the square root of time vs. adsorbed concentration curve to obtain an intercept on the time axis. In Figure 5.3, the kinetic data have been plotted against the square root of time. It should be noted that the higher mixing rate data (150 & 200 RPM) have been combined and the linear fit through the data has been forced through the origin. By extrapolating to the time axis it can be seen that the intercept for 50 RPM is ~9.9 $\text{min}^{0.5}$, and the intercept for 75 RPM is ~1.6 $\text{min}^{0.5}$.

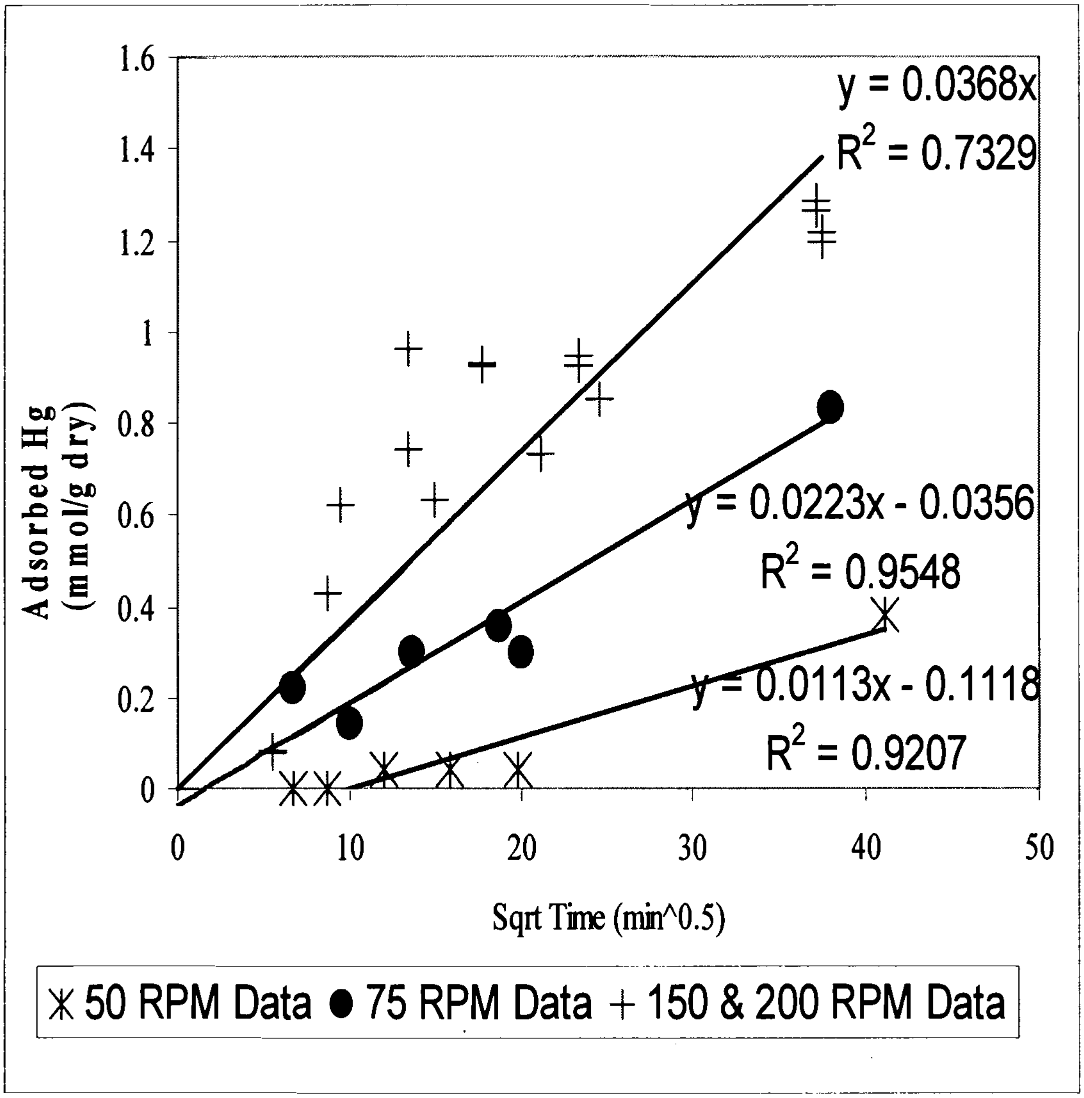


Figure 5.3. Adsorbed Hg vs Square Root of Time.

5.2.3. Pore Diffusion

Once past the boundary layer, an ion diffuses through the pore structure until it approaches surface adsorption site and adsorbs. The kinetic model in this work is based upon the square root of time and is shown here in two different forms. Equation 5.3, which is representative of the lines shown in Figures 4.5-4.15, is based upon the aqueous concentration of Hg.

$$C = C_o - kt^{0.5} \quad (5.3)$$

where C is the solute concentration at any point in time (in mM),

C_o is the initial solute concentration (mM)

k is a coefficient with units mM/ $\text{min}^{0.5}$.

t is time in minutes.

Values for k are listed in Table 5.3.

This model provides a good fit for the kinetic data at 50, 75 and 150 RPM for the duration of the experiment, suggesting that the assumption of solute diffusion within a sphere of infinite radius as an important step is reasonable (Figs. 4.5-4.13). This model, however, does not provide a reasonable fit to the adsorption data at 200 RPM data, especially at times greater than 1000 min (Figs. 4.14 and 4.15). For the case of adsorption at 200 RPM, where experiments are carried out more than 7000 min, deviation between the model fit and the experimental data suggests that the assumption of infinite sphere is unreasonable at times greater 1000 min.

The square root of time vs. concentration relationship may also be normalized in terms of adsorbed mass of solute with respect to mass of solid and represented as equation 5.4. This equation uses a coefficient of *k'* with units of mmole Hg/(g bead $\text{min}^{0.5}$). It is important to note that only the time intercept in the model is reflective of boundary layer effects.

$$\text{Hg}_{ads} = k' t^{0.5} \quad (5.4)$$

Where Hg_{ads} is the adsorbed concentration of Hg in mmole/g dry bead,

k' is a mass transfer coefficient with units of mmole / (g $\text{min}^{0.5}$))

Values for k' can be found in Table 5.3. The straight lines in Figure 5.3 suggest that the adsorption process is controlled by diffusion through a porous system, similar to that observed by Guibal et al[146] and McKay et al.[147].

The poor fit illustrated by the straight line in Figure 5.3 for higher RPM as well as the deviation of the model from the data evident in Figures 4.10-4.15 suggests that the kinetic process can not be described as simple pore diffusion with an infinite domain. In order for such a model to work, the metal concentration at the center of the bead must be 0. This is only true for the time period in which the model and the data match. Logically, the time for which the assumption holds true is related to the overall mass transfer rate. Faster transfer translates into faster deviation from the model. Had the slower RPM experiments been performed for a longer period of time, then deviation from the model would have eventually become apparent.

The lack of dependence of the uptake rate on mixing rate indicates that at mixing rates greater than 150 RPM, pore diffusion is the rate-limiting step. The dependence of the uptake rate on mixing rates below 150 RPM, together with its square root of time dependence however, indicates that both boundary layer-resistance and pore diffusion control the uptake rate. At mixing rates significantly lower than 50 RPM, boundary layer resistance would be expected to control the uptake rate, as manifested by a first-order dependence of uptake rate on time.

Figure	k (mM/min^0.5)	k' (mmole/(g * min^0.5))
4.05	0.0021	0.0108
4.06	0.0037	0.0188
4.07	0.0060	0.0303
4.08	0.0042	0.0215
4.09	0.0043	0.0217
4.10	0.0025	0.0260
4.11	0.0066	0.0347
4.12	0.0193	0.0471
4.13	0.0391	0.0545
4.14	0.0093	0.0476
4.15	0.0105	0.0561

Table 5.3. Mass Transfer Coeffcients.

5.2.4. Effect of Size on Uptake Rate

Although only beads of uniform size were studied in this work, it is useful to examine the effect of size on adsorption rates. This also allows for comparison of uptake rates with Guibal's study of the adsorption of Mo and V on chitosan.[148] As seen below in Figure 5.4, smaller beads tend to have faster uptake rates. Although the differences between the metals makes it difficult to directly compare the uptake rates, it appears as if the beads synthesized here perform comparably to Guibal's beads. Lines for Figure 5.4 have been generated using *k*' values from Table 5.2, or are obtained from Guibal's work.[149]

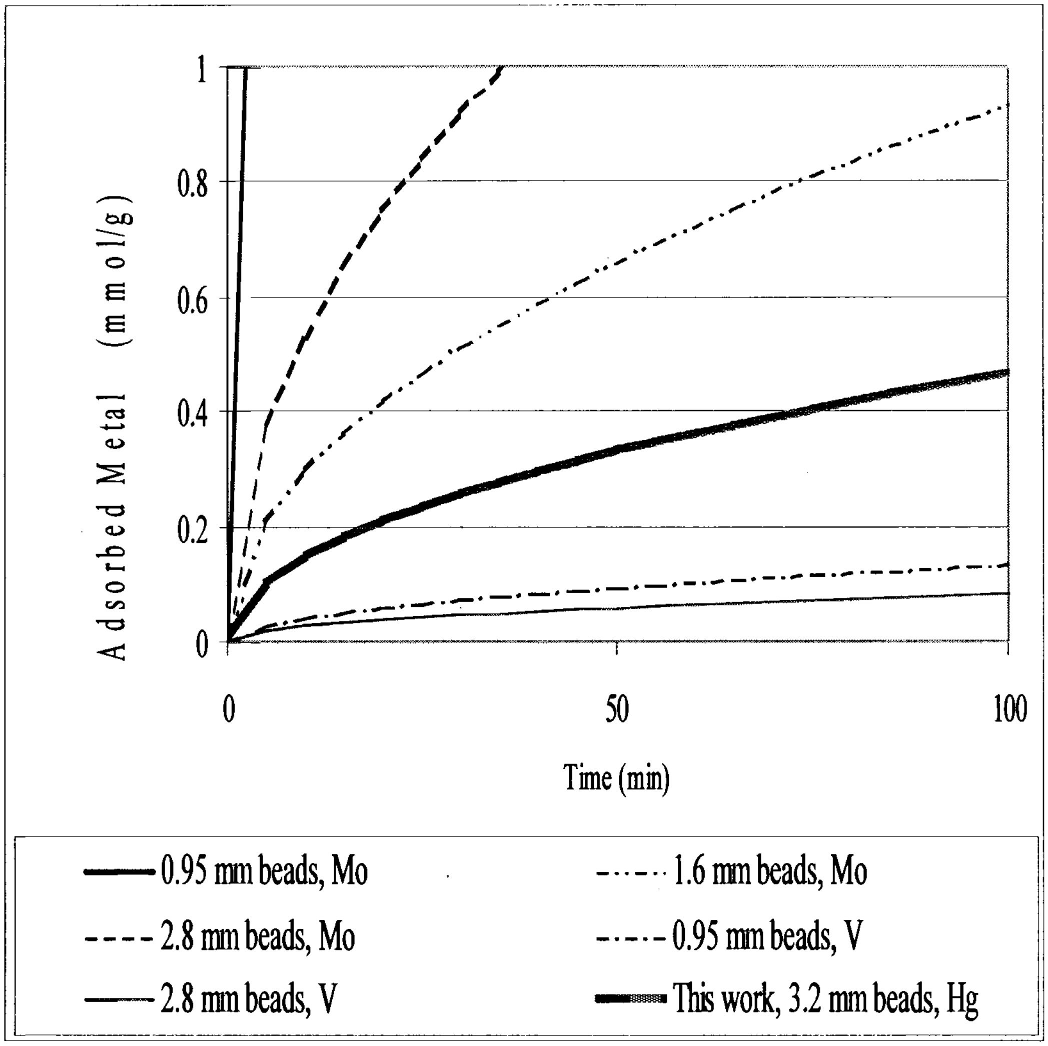


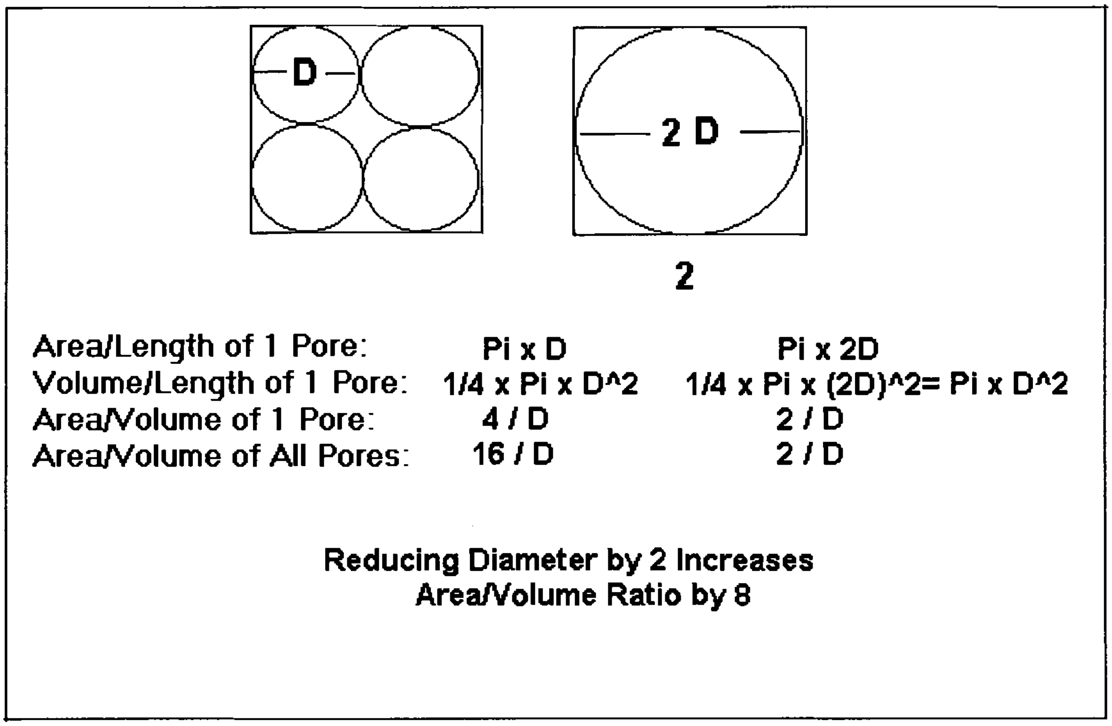
Figure 5.4. Comparison of Adsorption Rate With Guibal's[150] Different Sized Chitosan Beads. ~ 1 mM metal, 150 RPM.

5.3. Recommendations for Optimization

The beads synthesized in this work are effective adsorbents for Hg, but more could be done in order to improve them. Major areas of improvement towards which future research should be conducted include increasing the available total surface area for sorption, increasing the rate at which adsorption occurs, increasing the number of available adsorption sites and reducing the hazards of producing the beads.

5.3.1. Surface Area Optimization

Total surface area in a microporous system is controlled by the surface area of the internal pores. The area of the pores is determined by the geometry of the pores as well as their number and size distribution. Smaller pores have a higher surface area to volume ratio than do large pores. More pores can also be packed into the same volume. This is illustrated in Figure 5.5.



Area/Length of 1 Pore:	Pi x D	Pi x 2D
Volume/Length of 1 Pore:	1/4 x Pi x D^2	1/4 x Pi x (2D)^2= Pi x D^2
Area/Volume of 1 Pore:	4 / D	2 / D
Area/Volume of All Pores:	16 / D	2 / D

Reducing Diameter by 2 Increases
Area/Volume Ratio by 8

Figure 5.5. Effect of Diameter on Area.

Several modifications could be implemented in order to increase the available surface area of chitosan beads. Unlike crab shells, which exhibit the same surface area per unit weight regardless of particle diameter[151], chitosan beads do have different surface areas per unit weight when cast at different diameters.[152] The pore structure of cast chitosan beads is determined by the forces acting upon the bead at the time of gelling. These can be broken into external compressive osmotic forces and internal electrostatic repulsion.[153] If the compressive forces are visualized as analogous to hydrostatic pressure it becomes clear that smaller beads will have less compressive forces acting upon them. For solutions composed of similarly sized chitosan polymers the internal forces will remain fairly constant. In order to optimize the effects of repulsive electrostatic forces it is important to try to reduce the size of the chitosan beads. This could be done through improved equipment similar to the spinneret described by Rorrer.[154] It is possible that the use of a surfactant could also reduce the size of the beads through a decrease in viscosity.

5.3.2. Optimization of Factors Affecting Kinetics

Small pores offer increased surface area, but take longer for ions to diffuse into. Larger pores are more accessible, but have less surface area. Clearly a balance must be found between accessibility and surface area. Size is also an important consideration in the kinetics of adsorption because it controls the distance over which diffusion must occur. Smaller beads will equilibrate faster than larger beads of the same pore geometry, simply because of the smaller average diffusion paths in the former beads.

Two possible strategies for controlling the size of pores include the use of different sized cross-linking agents and the inclusion of poregens such as silica gels. Glutaraldehyde, used in this study, is a relatively small molecule with only a 3 carbon chain. If a longer chain, perhaps 10 or 30, could be used with aldehyde functional groups on the end, it could perhaps be used to cross-link the chitosan and form a structure with larger pores. Glutaraldehyde could later be added to the bead to serve as attachment sites of the thiol-containing molecules.

A poregen such as silica gel could be included in the dissolved chitosan solution and then removed later in the NaOH bath. Silica gels are available in many different sizes, and could be mixed in proportions designed to optimize pore size distribution.

5.3.3. Adsorption Site Optimization

Adsorption capacity could be increased through the addition of more functional groups or compounds that have higher affinities for Hg than those found on cysteine. Molecules with multiple adsorption sites, such as polycysteine, could be grafted onto the beads in order to greatly increase their adsorption capacity. This is conceptually illustrated above in Figure 5.1.

5.3.4. Risk Mitigation

The first set of risks associated with the production of chitosan beads are associated with the harvesting of the raw materials and conversion into chitosan. Utilization of fungal chitosan and chitin, which might be grown in reactors, would reduce the risks associated with the harvesting of sea creatures as well as lessen the need for the harsh chemical treatments illustrated in Table 2.1. Fungal biomass has been studied in the adsorption of copper.[155]

The risks encountered in the dissolution of chitosan and casting of the beads were due largely to the small scale of the production process. Properly designed industrial facilities could easily compensate for the hazards posed by high speed mixing and exposed hypodermic needles. The chemicals and concentrations involved (4% Acetic Acid, 0.5 M NaOH) were fairly benign, although some thought would be required to operate a very large gelling bath.

Cross-linking represents the area in which the most improvement can be made. Cross-linking agents are fairly reactive, as suggested by their function of binding polymer chains and other molecules together. Many of them are also quite toxic, including the glutaraldehyde used in this work. Future research should be directed at finding nontoxic agents that can effectively perform the tasks of a cross-linking agent (providing chemical and physical stability, increasing surface area, providing attachment mechanisms).

5.4. Micrographs of Chitosan Beads

Cysteine-grafted chitosan beads are highly porous and possess a total surface area as high as ~100 m^2/g. These factors combine to make a complex internal geometry. Micrographs of freeze dried beads were taken with an IntelPlay QX3 Digital Microscope and are presented below in Figures 5.6. -5.10..

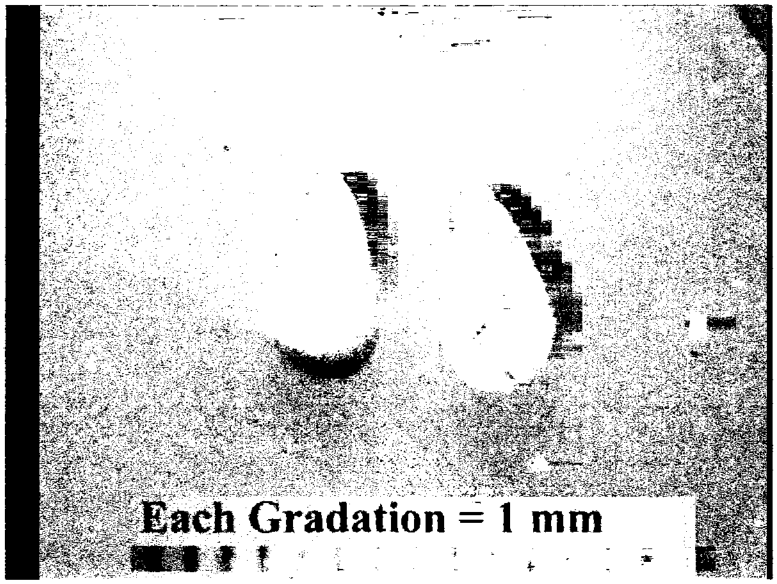


Figure 5.6. Split Chitosan Bead at 10X Magnification.

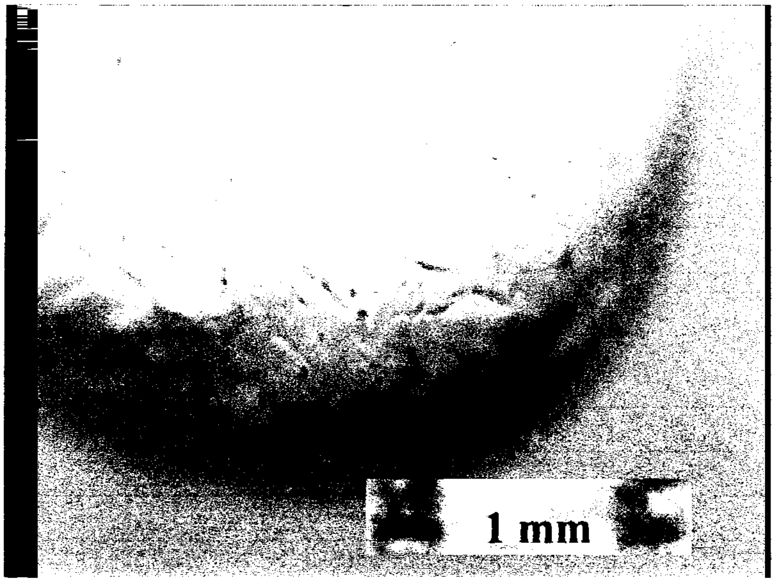


Figure 5.7. Exterior of Chitosan Bead at 60 X Magnification.

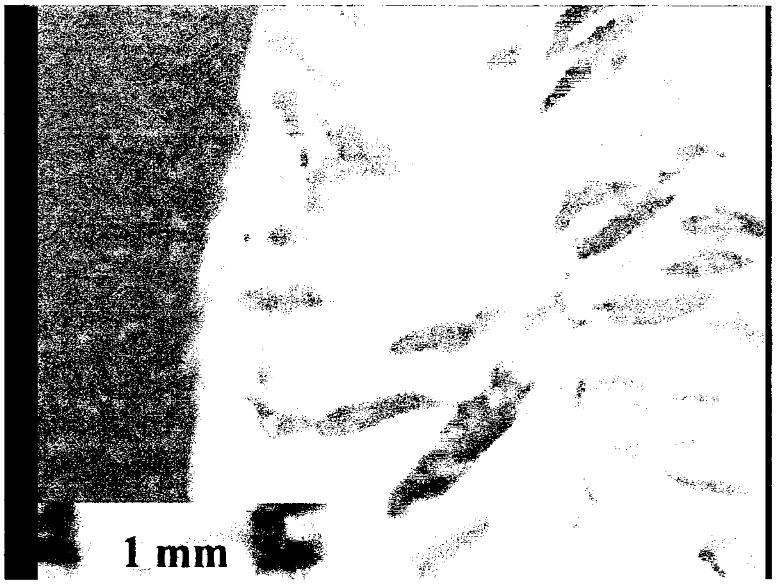


Figure 5.8. Interior of Chitosan Bead at 60 X Magnification.

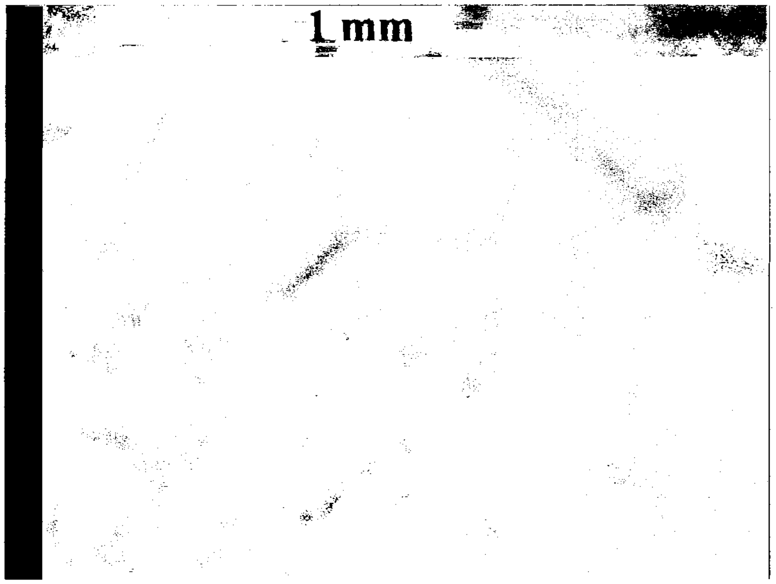


Figure 5.9. Exterior of Chitosan Bead at 200 X Magnification.

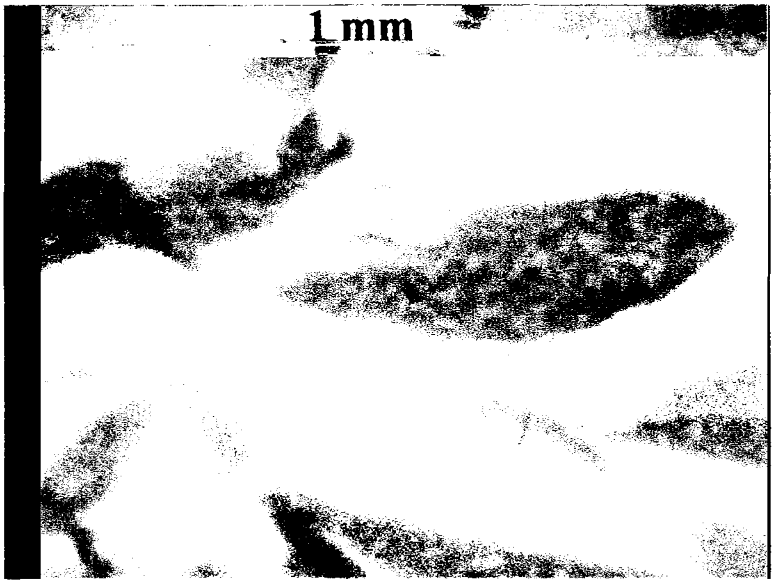


Figure 5.10. Interior of Chitosan Bead at 200 X Magnification.

5.5. Other Applications for Chitosan Beads

The beads synthesized here are intended for use in treating waste streams and preventing or reducing pollution. However, there are other applications which may be worth pursuing. Properly functionalized chitosan beads could be used to remove metals of interest from the environment, either through direct processing of environmental fluids such as ocean water, or through the treatment of injected and recovered acid streams.

Mining the oceans has long been a pipe dream due to the enormous energy costs associated with removing the vast quantities of water, as well as interference from other dissolved species. Adsorbents that are selective for specific metals and tolerant of high ionic strengths could be used to remove metals from this plentiful resource.

Metals are often removed from the ore that contains them by piling crushed ore on a tarp or other fluid recovery system and then applying an acidic solution to the ore. The metal-rich acid is then collected and processed for the metal. The exposure of ores to the oxidizing atmosphere creates unwanted byproducts, and open-air dispersal of acid can result in acid landing in undesired locations and consequent damage to the environment. Injecting acid into the ground helps to prevent the acid from becoming airborne, reduces the chances for oxidation and also avoids unsightly pit mines. In addition to mining metal rich ores, a perhaps overlooked source for metals is landfills. Electronic instruments are full of precious metals, and landfills are full of electronic instruments. Acid mining and subsequent adsorptive recovery of metals from landfills could represent an economical and environmentally sound method of metal (re)acquisition. Properly functionalized chitosan beads could be used to obtain metals from landfills using acid mining.

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