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Craig Alcindor Ivan Bowe
University of South Florida

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Use of Silica-Supported Adsorbents, Modified Silica Gel, Modified Montmorillonite KSF and Magnetite in the Remediation of Selected Heavy Metals from Aqueous Media

by

Craig Alcindor Ivan Bowe

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of the requirements for the degree of
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Major Professor: Dean F. Martin, Distinguished Service Professor
Kirpal S. Bisht, Ph.D.
Abdul Malik, Ph.D.
Edward Turos, Ph.D.

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Dedication

I would like to dedicate this body of work to my mother, and to my grandmother, for their inspiration, love, and devotion. I wish to also thank them both for teaching the value of an education, a priceless facet of life that cannot be taken away. To my life teachers, through early and late adolescence, high school, college and graduate school, you have made a significant impact on my life and my development as an individual and as a scientist. To Drs. Marlene G. Katz, Ward W. Knockemus, Richard M. Pagni, and Fred M. Schell thank you for your inspirational thoughts, respect, wisdom and kindness that you have exemplified even in criticism. To the fellowship of loved ones, especially You, thank you for allowing me to share my passion with you and the sense of humor that not everyone is privy to. To my students, thank you for allowing me to share with you the beauty of our chemical universe and for including me in your own development as global citizens. The exploration of science not only improves our knowledge of the physical universe but it too illuminates our awareness of our perpetual ignorance of the physical universe keeping us humble and respectful of all that surrounds us and unites us. The rewards of failure and disappointment are indeed strength and wisdom. It is a fundamental truth that out of utter confusion comes deeper understanding. Thus, keep Hope alive and Peace perpetual. Always remember that all does not have to be well with our circumstances to be well with our souls. This journey demonstrates that with strength, confidence, dedication, perseverance and a foundation based upon truth, respect and love that all things are indeed possible.

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Use of Silica-Supported Absorbents, Modified Silica Gel, Modified Montmorillonite KSF and Magnetite in the Remediation of Selected Heavy Metals From Aqueous Media

Craig Alcindor Ivan Bowe

ABSTRACT

Pollution of the earth's water resources, including freshwater sources such as lakes and rivers, by heavy metals have been a detriment to the environment for as long as the industrial age of man. As these metallic pollutants accumulate in the supply of precious groundwater and drinking water the need for clean-up technologies to combat the increasing threat is becoming of more importance to government and industry alike. Previous work has established the possibility of using known chelating agents, such as LIX-54® supported on silica gel in the removal of selected heavy metal ions such as copper(II), nickel(II) , and cadmium(II) from standard aqueous solutions (Norris and coworkers, 1996). Remediation of heavy metals using coordinating agents such as dithiooxamides and aliphatic amines has also been an environmental cleanup technology that has proven to be effective in the uptake of selected heavy metals from aqueous media (Pooré and coworkers, 1996). The current study illustrates the effectiveness of using relatively inexpensive coordinating agents such as aliphatic amines and aliphatic thiols supported on silica gel and other solid supports to remove selected monovalent and divalent metals from aqueous standard solutions to achieve similar results. This study also reports the significance and results of an investigation involving the use of bifunctional compounds, such as 2-mercaptoethanol, to chemically attach and modify the silica gel, montmorillonite KSF, and magnetite, and subsequently be used in the uptake of selected heavy metals such as copper(II), cadmium(II), lead(II), nickel(II) and silver(I) ions.

Chapter One:

Potential Risks Involved in Having Heavy Metals in the Environment: Health and Economic Issues

Introduction

It is arguable (Hjeresen et. al., 2002) that the modern standards of living that most citizens in the industrialized world enjoy could not really exist without the support of the chemical industry and the chemicals that the industry produces to make life and living much easier.

Chemicals such as pharmaceuticals used in the treatment of ailments such as the common cold to more advance illnesses such as HIV/AIDS would not be possible without the expertise of dedicated scientists and an industry dedicated to serving the public need for better health and healthy living. Other products of the chemical industry include agrochemicals for our produce, semiconductors and electronics for our communications and recreational needs and basic consumer needs such as batteries and even cigarettes. The growth of the chemical industry is expected "to parallel the growth in human population" (Hjeresen et. al., 2002) and as a result the need for more products of this global commerce will be needed in the new global society. However, the need for more chemical products will in fact be an increasing hindrance as the amount of waste generated from the manufacture of these products increases in addition to the amount of potentially harmful substances and by-products are generated as well. Large chemical manufacturing companies have taken the initiative to curtail the production of waste that could potentially damage the environment by creating more environmentally friendly methods of production. In the production of an anticonvulsant drug chromium waste was generated as a product of the process (Hjeresen et. al., 2002). Such global chemical firms such as Dow Chemical and Mobil Technology have also taken more environmentally conscious or “Green Chemistry” approaches to the production of their products. The Pfizer group also took an environmentally friendly approach by limiting the amount of a titanium salt that was instrumental in the production of a drug commonly used in the treatment of depression, sertraline HCl. The implementation of new technologies that will limit the addition of hazardous waste to the earth’s environment and subsequent damage to the environment is needed not only for the survival of the environment but the survival of chemical industry as well. The removal of hazardous materials, such as heavy metals, that have been accumulating in the environment for decades is also a concern as some materials accumulate in the environment and the habitat of living organisms that are a vital part of the food chain. Thus, new legislation and regulations will become of paramount importance. The wood and textiles industry has taken an innovative approach to treating the wood products and have limited the use of a well-established carcinogenic mixture, chromate copper arsenate. Instead, a more environmentally friendly copper salt will be used to protect against pests and extend the longevity of the material being produced. In 1990, the U.S. Environmental Protection Agency investigated the amount of capital spent by U.S. based companies and determined that there was less than 5% of the companies investigated capital was used for pollution control and in the clean up of toxic chemicals. (Arora et. al., 1998)

With the success of using chelating agents and coordinating agents such as dithiooxamides and aliphatic monoamines in the removal of selected heavy metals from standard solutions it seems practical to again use monofunctional organic coordinating agents to accomplish identical goals of removal from a potential freshwater source in the environment. This is a practical application of environmental cleanup technologies that permit the concentration of harmful substances for storage and possible future treatment. The account presents the results of using straight-chain saturated alkyl amines, and mercaptans, adsorbed onto a solid surface, to effectively remediate copper(II), cadmium(II), nickel(II), silver(I) and lead(II) ions from prepared standard solutions of fixed concentration. The report also evaluates the use of chemically modified adsorbents using bifunctional binding agents such as 2-mercaptoethanol. The modified adsorbents will be used in the uptake of the before mentioned heavy metals to accomplish identical goals of removal and surpass the adsorbent materials in possibility and effectiveness. The solid supports utilized were chosen for availability and economic reasons in addition to their respective functionality. The choices made were prudent in that the goal was to create a new technology that did not do any further damage to the aquatic environment that the solid supports, both physically and chemically altered, were immersed in and subsequently removed. For this reason, commonplace chemical adsorbents such as silica gel, montmorillonite KSF and magnetite were the solids that would act as support bases for the binding agents used in the project. The goals of environmental cleanup at a far less economic burden would prove itself to be highly useful in industrialized and developing nations. This new emergent cleanup technology has a variety of uses in the environment and it is believed, can be duplicated on a macroscale for cleanup of most divalent and monovalent metals and their respective isotopes. Common and mostly benign metals such as copper and nickel were chosen to illustrate the utility of the method in addition to providing a basis for removal of metals contained within the same sub-groups on the periodic table. For example, the successful removal of cadmium holds promise for the removal of sub-group members zinc and mercury. Additionally, the removal of nickel holds a considerable amount of promise for the removal of both palladium and platinum, metals that are increasingly more important in the pharmaceutical industry as catalysts in the synthesis of compounds with medicinal applications (Suzuki, 1995; Moody, 2000). Increasingly as heavy metals become more prevalent in the synthesis of new pharmaceuticals or in the treatment of existing molecules, new and innovative methods will be needed to remove these undesirable by-products from the target compounds and subsequently from the environment.

Environmental cleanup is not as important as the medicinal compounds and the consumer need for products that make usage of heavy metals such as lead, which is in part the reason that current technologies are so expensive (Hjeresen, 2002, Arora, 1998). With the move toward environmentally friendlier technologies, the so-called “Green Chemistry”, it is becoming far more likely that past negligence can be remedied with cost effective remedies. Silica gel and aluminosilicate materials such as montmorillonite KSF are relatively common and have found prior use in a variety of chemical disciplines such as synthetic organic chemistry and chromatography. The advantage of utilizing these materials is fairly obvious, in familiarity and cost. Silica gel is probably the most commonly used adsorbent and is therefore moderately inexpensive and easy to find. montmorillonite KSF is another adsorbent that has found increasing usage in the laboratory, and as a result is a material that is appropriate to use as a solid support for metal binding agents. The compact structure (Greenwood, 1997) of both materials further supports the idea that these would make good supports for the selected binding agents studied. Also of paramount importance is the solubility in aqueous media; as both materials have very low solubility in aquatic environments at neutral pH (Greenwood, 1997). The presence of silicon bound hydroxyl functionalities, "silanols", at the surface of both silica gel and montmorillonite introduces chemical modification as a viable alternative to physical adsorption. Another type of material that would also prove to be a cost effective, commonplace, poorly soluble and ultimately useful material is magnetic iron oxide more commonly referred to as "magnetite". Unmodified magnetite is insoluble in neutral to acidic pH (Greenwood, 1997) but does not possess the free surface hydroxyl moieties that are prevalent with silica-based materials. However, it is indeed possible to modify the surface of the magnetite in order to utilize the material for cleanup purposes. Heavy metals have been added to the environment in a number of ways over the course of human history. In the pre-industrial past metals have been naturally added to the environment primarily from geologic weathering, and animal and human excretions (Garrett, 2000; Förstner, 1981). Industry has surpassed the amount of metals added to the environment by varying activity and quantity. Annually, metals are added to the environment as a by-product of industrial processing or from the limited usage of the products that the industry itself produces. Cars, electronic goods such as cell phones and computer monitors, cigarettes and transportation goods such as automobiles, aircrafts and locomotives are frequent sources of heavy metals such as nickel, cadmium, lead, zinc and copper (Förstner, 1981). Some of these metals have a history of being hazardous or have levels of toxicity that are of major concern to animals and human beings alike. The metal cadmium, is a well known toxic agent which became popularized in the late 1940's in Japanese villages creating a condition known as the "itai-itai" or ouch-ouch bone degenerative disease (Aoshima, 2003; Kasuya, 2000; Hutton, 1983). Lead, a metal that has found use throughout the ages is another toxic agent that been added and has accumulated not only in the environment, but also in the tissues of humans and wildlife alike. Lead poisoning has been known and well documented since the time of the early Greek civilizations to be a detriment to the health and well being of those afflicted with inflated levels (Forster, 1981; Greenwood, 1997). Silver, a common additive from the photographic industry, is another metal leached into the environment and has accumulated over the years as a toxic agent (Purcell, 1998). Copper, a well used element in industry and an essential element in some metallo-enzymes, has also raised some concern as elevated levels of it have been found in the environment either by being included in waste from industrial processes or by being a primary source of consumer materials added to the environment. These selected heavy elements originally removed from the Earth in benign form, as metallic ores, but added to the Earth's vital resources in ionic form and levels of toxicity to living organisms such as humans are of increasing concern across the globe.

Statement of the Problem:

The investigation of metal contaminants in aqueous media and the subsequent extraction of a selected group of metal cations have been explored in three important areas of research. These three areas explored deal with the interactive forces between the solid support and the binding agent or metal chelate.

The first deals with the interaction of adsorbent material and coordinating agent by means of ionic bonding or electrostatic attraction. Pooré (1996) reported the use of various chelating and coordinating agents supported on cationic and anionic exchange resins in the removal of selected heavy metals from aqueous media. Cationic exchange resins such as Dowex-50W were used as a support for chelating agents in the uptake of selected heavy metals such as silver(I), copper(II) and lead(II) ions. Anionic exchange resins such as Dowex 1-X10 were used as a solid support for an array of chelating agents in the uptake of selected heavy metals such as silver(I) and copper(II). This method was proven successful in the uptake of the selected heavy metals from aqueous media and provides an alternative method of extraction than currently used methods of cation uptake.

The second area of research involves the interaction between binding agent and adsorbent material by means of weakly bound forces such as dispersion forces and most recently hydrogen bonding forces of attraction. Norris and coworkers (1997) reported the use of well-known chelating agents supported onto silica gel in the effective removal of selected heavy metals such as nickel and cadmium. In this investigation well known chelating agents such as LIX54® and LIX860® were supported on silica gel. This loaded silica gel was used in the uptake of cadmium and nickel ions from aqueous media. Pooré and coworkers (1996, 1996) and Norris and coworkers (1995, 1996, 1997) both demonstrated that the use of monofunctional binding agents with a hydrophobic moiety was an effective metal chelate in the uptake of selected heavy metals from aqueous media. This hydrocarbon adsorption on silica (HAS) interaction termed the "corkscrew model" demonstrated the possibility of using monofunctional agents adsorbed onto the silica gel matrix and being effective in the removal of metal cations such as cadmium and nickel from aqueous media. Monofunctional amines were used in these studies involving mostly polarizable metallic ions. Sulfur analogs (Bowe et. al., 2002) of the monofunctional amines previously studied were chosen and found effective as alternative coordinate donors. In addition, monofunctional amines with longer hydrophobic tails (Bowe et. al., 2003) were used to investigate the effectiveness of using a wide array of monofunctional nitrogen donors to successfully uptake the metal cations under study.

The third area of research that was successfully used in the uptake of selected heavy metal cations involved covalent bonding where binding agent and solid support were actually chemically attached. This relatively new use for chemically modified adsorbents was proven not only to be a relatively cost effective method in its preparation and potential re-usage but additionally was proven to be highly effective alternative to the use of modified silica-based materials in the remediation of selected heavy metals. Further, the use of the modified material could be applied to areas of research that require selective uptake of cationic metal species when provided with media containing more than one metal cation.

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Chapter Two

Extraction of Heavy Metals By Amines Adsorbed Onto Silica Gel

Introduction

The concentration of heavy metals from dilute solutions is a technology that is arguably beneficial to the environment and a practical and economical approach to the problem of the removal of toxic substances from fresh water sources. The use of supported coordinating ligands offers a number of advantages for the removal of heavy metals including convenience and ease of separation (Pooré et. al., 1996; Soliman et. al., 1997; Mahmoud et. al., 1996; Beatty et. al., 1999). The use of silica gel supported amine derivatives such as ethylenediamine and phenylenediamine (Mahmoud et. al., 1996) has proven to be an alternate technology that favors the removal of heavy metals using this method as opposed to existing ion exchange resins commonly in use. Soliman (1997) reported the use of silica supported aliphatic di-, tri-, and tetramine Soliman (1997) illustrating the use of nitrogen donor atoms was an effective means of removing heavy metals such as copper(II) and nickel(II). The efficiency increased with the increasing number of nitrogen atoms within the ligand. The use of amines in the removal of heavy metals from aqueous media has been a growing technology that has proven to be an effective and also a reasonable simple means of remediation of heavy metals. The amino group is known to be a hard base and thus it is likely that bonding to certain metals such as the iron(III) ion and aluminum ion are favorable Pearson (1997). Presumably there should be the same affinity for certain metallic ions or cationic ions as well. The so-called "hard" acid cationic species such as calcium and magnesium ions would presumably be favored over the more polarizable or "soft" cations such as cesium and platinum. Since the affinity for the nitrogen donor exists there is a great possibility that the increase in nitrogen atoms to donate electrons to the metals in which it is in contact the greater the possibility for removal. The coordinating ligands, the amines, adhere to the surface of the silica gel and coordinate to the metal via a 4-coordinate model of binding (Figure 2-1).

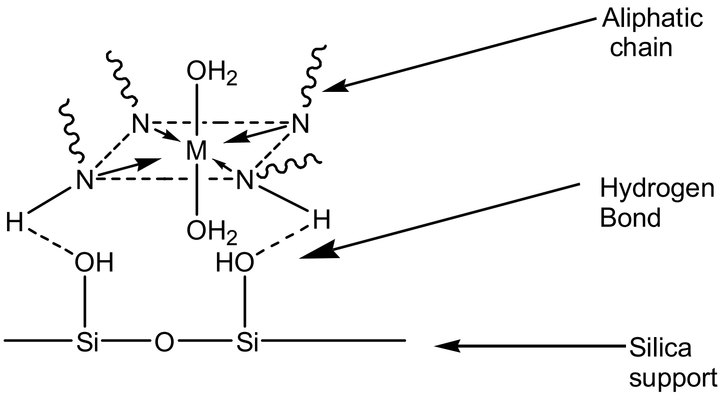

Figure 2-1 Proposed model of adsorption of amine onto silica gel by presence of hydrogen bonding.

Soliman and coworkers (1997) demonstrated the effectiveness of using multidentate nitrogen ligands such as diethylenetriamine (DETA), triethylenetetramine (TETA) with 3-chloropropyltrichloromethane modified silica gel in the removal of metals such as zinc(II), cadmium(II), cobalt(II), nickel(II) and lead(II) ions. The metal capacity demonstrated by the amine sorbents was noticeably different for each metal. In each case the extraction percent was increased with the increase in the number of amino groups. The pre-concentration of metals such as copper(II) ions was more effective for the polyamine adsorbents than for the mono and diamine groups. The maximum capacity for the amine adsorbents illustrated a particular trend, where the extraction percentage increased with increasing number of amino groupings for nickel(II) and other metals. Mahmoud and coworkers (1996) demonstrated the effectiveness of metal uptake with certain amine derivatives such as thiosemicarbazide, ethylenediamine and phenylenediamine. Silica-bound ion exchange resins containing carboxylic acid moieties were also used in the removal of heavy metals such as iron(III) and lead(II) ions. The metal ion uptake was also measured as a function of time and was found in each case study to increase with time. The prolonged exposure of the silica-bound agents increased the capacity of the silica adsorbents to pre-concentrate the metal cations studied. The effect of the pH was also studied to evaluate the capacity of the silica-bound adsorbents to uptake the metals. The investigation revealed that the amount of metal pre-concentrated by the silica reagent increased significantly with increasing pH. The plots indicated a curve that is similar to the titration curve of a weak acid. This indicates that the loss of a proton increases the capacity of the amine-binding agent to effectively bind to the metal being removed. The report revealed that it was also possible to remove the metal and recycle the binding agent quite successfully.

Additionally, an alternative approach using silica support was described (Pooré et. al., 1996) using a chelating agent with a long-chain hydrocarbon. Absorption of the chelator in silica was reported (Pooré et. al., 1996; Norris et. al., 1997; Benson et. al., 1992), and was presumably achieved by filling silica gel pores with a hydrophobic solvent, *n*-hexane, then adding the ligand with a hydrocarbon moiety. The subsequent removal of the solvent presumably led the hydrocarbon chain into the mostly hydrophilic pore to coil up like a "pig's tail" to minimize effects of hydrophobicity, caused by exposure to hydroxyl groups or silanols lining the inner pores of the silica gel matrix.

An alternative approach, however, was suggested by an IR spectroscopic study Zhandanov (1987) that indicated that surface hydroxyl groups, or silanols, are capable of hydrogen bonding, and thus, presumably, these surface silanol groups were capable of and were found to hydrogen bond with nitrogen-containing moieties. The use of a mono nitrogen species such as N, N'-diethylamine, to demonstrate the capacity of the silanol moiety to effectively make hydrogen bonds to the nitrogen donor was investigated.

Pooré and co-workers (1996) reported the success of using silica-supported mono-amines by this method of hydrocarbon chain adsorption, the incorporation of the amine into the silica gel matrix. These results were obtained for removal of nickel(II), copper(II) and lead(II) from aqueous solutions of known concentrations. The present study is concerned with the effectiveness of using longer primary amines of varying chain lengths loaded onto silica gel in removing selected aqueous heavy metals.

With the success of using di, tri, tetra and polyfunctional amines as coordinating agents in the removal of heavy metals from standard solution, it is practical to use these reagents to accomplish identical goals of removal from a potential freshwater source in the environment. This report presents the results of using straight chain primary amines loaded onto silica gel to effectively remove copper(II), cadmium(II), nickel(II), silver(I) and lead(II) from standard aqueous solutions.

Experimental

Synthesis of Silica-Supported Amines

Amines were obtained from Aldrich Chemical and were used without further purification. A limited number of studies were done with *n*-hexadecylamine to establish the lower limit of effectiveness. A major limitation was the inability of this amine to be completely dissolved in *n*-hexane. The solubility of amines decreased with increasing chain length, due to the increased hydrophobicity of the amine ligand and the fixed volume of the hydrophobic solvent. Further, with the longer chain amines dissolution did not occur at ambient temperature and required the use of a heating source. Thus, most results were obtained with amines having fewer than 14 carbons.

Loading of silica gel

Activated silica gel (20 g) was treated with 40 mL of anhydrous *n*-hexane. Then a solution of 6.28 mmoles of the amine dissolved in 40 mL of anhydrous *n*-hexane was added to the silica gel mixture, and the solvent was evaporated under vacuum. The procedure worked well with all amines having 14 or fewer carbons. The silica-supported amine composites and metal cation supernatant were analyzed after completion of the experiment. The analyses were used to determine the amount of nitrogen donor present and the amount of metal extracted from the standards (Figure 2-2).

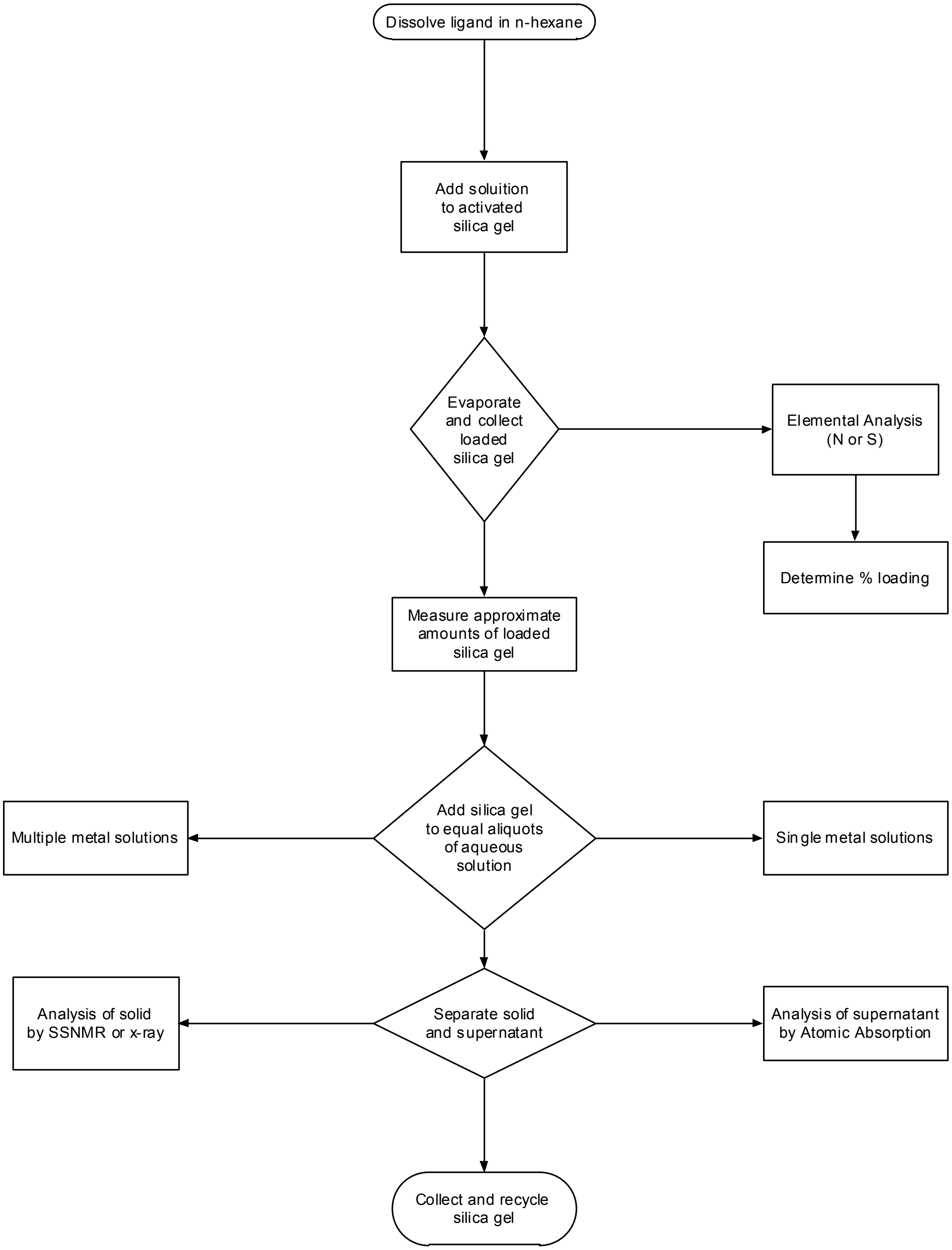

Figure 2-2: Scheme for loading and recycling silica gel.

Analyses

Metal analyses were obtained using a Varian SpectrAA 100 atomic absorption spectrometer coupled to a Mega computer and Hewlett Packard 520 C printer. Five standards, prepared by serial dilution, were used to determine the calibration plot. Typically, the concentrations were determined by the sensitivity range for a given metal, but typically standard solutions representing 0.5, 1.0, 5.0, 10.0 and 20.0 ppm were used to provide a calibration plot. The spectrometer determined the concentration of the given metal, the concentration of which did not exceed 20 ppm, by the calibration curve. Calibrations were performed each time an analysis was made, and a total of five samples were used to calibrate the instrument. The spectrometer performed an analysis on each sample in triplicate; each analysis (Table 2-1) represented the mean and standard deviation of five analyses corresponding to the five aliquot portions obtained. The standard solutions, prepared from a stock solution of the metal salt by serial dilution, remained unchanged with the exception of the silver and lead standards which were replaced every two weeks. The replacement of the standard solutions was necessary to limit the possibility of oxidation and subsequent increase of impurities.

Table 2-1 The removal of heavy metals (From 1.57 m*M* Solution) using amines supported on silica gel.

Metal	Coordinating Agent	Extraction,%*
Cu^{2+}	Butylamine**	98.5 ± 0.2
	Hexylamine	94.2 ± 1.3
	Octylamine	98.6 ± 0.5
	Decylamine	92.5 ± 1.0
	Hexadecylamine	34.0 ± 4.3
	Control	18.3 ± 5.1
Pb^{2+}	Butylamine**	98.5 ± 0.5
	Hexylamine	70.4 ± 3.6
	Octylamine	85.8 ± 1.1
	Decylamine	90.6 ± 1.2
	Hexadecylamine	NA
	Control	28.8 ± 14.2
Cd^{2+}	Hexylamine	87.7 ± 1.9
	Octylamine	88.0 ± 0.9
	Decylamine	92.5 ± 1.5
	Hexadecylamine	45.5 ± 4.9
	Control	13.2 ± 2.6

Table 2-1 (Continued)

Ag^+	Butylamine**	70.8 ±1.8
	Hexylamine	82.8 ± 3.3
	Octylamine	91.6 ± 0.5
	Decylamine	90.7 ± 0.4
	Hexadecylamine	NA
	Control	8.58 ± 3.3
Ni^{2+}	Butylamine**	88.1 ± 2.0
	Hexylamine	57.6 ± 5.9
	Octylamine	53.1 ± 2.0
	Decylamine	65.3 ± 1.9
	Hexadecylamine	NA
	Control	3.84 ± 1.8

* Sample size of five used for the batch experiments

** 3-12 mesh silica gel used with 0.03 *M* metal solutions. Sample size of three used for batch experiments)

Nitrogen analyses were performed by Constellation Technology Corporation, Largo, Florida. The elemental analysis was performed on two samples of silica-supported *n*-hexylamine that had been treated with a copper nitrate solution. Anal.: N, 0.46 % (preparation 1) , 0.52 % (preparation 2).

Removal studies

Solutions of 1.57 m*M* of lead(II) nitrate, cadmium(II) acetate, nickel(II) nitrate and copper(II) nitrate were prepared in 1.0-L volumetric flasks. Five 100- mL aliquots of stock solution were used. Ligand-treated silica gel (4.0g) was added to each metal solution, which seemed to be adequate removal based on the nitrogen analyses for two different preparations. The resulting mixtures were agitated at a rate of 200 rpm in a New Brunswick Scientific Company Model G76 gyrotory water bath ($25^{o}C$) shaker for two hours. Initially, rate studies were made of amounts removed as a function of time; most of the metals were removed within the first half hour, but the shaking was extended for a two- hour period to ensure maximum removal.

Samples were also prepared using samples of humic–colored lake water from Lettuce Lake, Fletcher Avenue, east of the University of South Florida. Water samples were returned to the lab, combined filtered through Whatman #1 filter paper, and treated with known amounts of divalent metal compounds. The removal studies were done the same way as for samples made in deionized water, except the standards were prepared in the same matrix. Samples were tested with *n*-hexylamine-silica composites (Table 2-2).

Table 2-2 The removal of heavy metals in Lettuce Lake water using n-hexylamine supported on silica gel

Metal	Binding Agent	Extraction,%*
Cu^{2+}	*n*-Hexylamine	95.4 ± 2.0
	Control	10.0 ± 6.0
Pb^{2+}	*n*-Hexylamine	68.6 ± 2.9
	Control	16.4 ± 7.4
Cd^{2+}	*n*-Hexylamine	47.6 ± 4.3
	Control	3.84 ± 2.1
Ag^{+}	*n*-Hexylamine	25.8 ± 8.6
	Control	8.58 ± 3.3
Ni^{2+}	*n*-Hexylamine	78.7 ± 5.6
	Control	29.0 ± 14.8

*Sample size of five used for the batch method.

The complete workup and format for loading the adsorbent material, its use and subsequent analysis of the supernatant is demonstrated in (Figure 2-2).

Results

The metal removal procedure is summarized (Equation 2-l), where SiO_2-Y-NH_2 is a representation of an amine-silica composite, and MX_2 is a divalent metal salt.

$$SiO_2 — Y — NH_2 \quad + \quad MX_2 \quad \longrightarrow \quad (SiO_2 — Y — NH_2)_n M^{+2} \quad + \quad 2X^- \qquad (2\text{-}1)$$

The nitrogen analysis of two samples indicates that there were approximately 7.51 mmoles and 6.65 mmoles of amine per gram of silica gel, and a 5:1 and 4:1 ratio respectively of supported ligand/metal ion ratio was used in our studies. The ratio of ligand/metal with the presence of a hydrophobic effect seems to indicate that these ligands occupy the same plane when coordinating to the metal (Figure 2-1).

Results (Table 2-1) indicate that it was possible to remove copper from solution using silica-supported amines with varying degrees of success. Removal of aqueous copper(II) nitrate using excess supported *n*-butylamine, *n*-hexylamine, *n*-octylamine, *n*-decylamine, and *n*-hexadecylamine provided an average removal of 98.5, 94.2, 98.6, 92.5 and 34.0%, respectively. With an excess of ligand, 4:1 ligand-metal mole ratio of silica-supported amine, the removal of copper ion from solution was achieved with significant success, e.g., up to 98.6 ± 0.5%.

Based on Student’s t-tests performed, there was no statistically significant difference in copper removal percentage among the shorter chain amines in attaining over 25% removal. When the chain length exceeded ten carbons, there was a statistically significant decrease in the amount of the metal removed by the supported agent. This result is attributed to the increase in the hydrophobicity and subsequent inhibition of the amine to effectively coordinate with the metal. (There is a practical chain length that can be accommodated by the silica pore size. Consequently, there is a possibility that the act of coordination may result in removal of the complex from the pore producing a suspension in solution.)

Additional results (Table 2-1) indicate a relatively greater uptake of aqueous cadmium ions using *n*-hexylamine, *n*-octylamine, *n*-decylamine, and *n*-hexadecylamine relative to other selected metal cations of equal concentration. The results obtained were 87.7, 88.0, 92.5 and 45.5% removal for six, eight, ten and sixteen carbon chains, respectively, from solution near a pH of 7 initially. Results indicate that again as the chain length increased the ability of the nitrogen atom to coordinate with the metal is decreased.

Removal of aqueous lead ions using silica-supported *n*-butylamine, *n*-hexylamine, *n*-octylamine, and *n*-decylamine, was similar to the results for aqueous copper and cadmium (Table 2-1). Distinctively, the percentage of metal removed was 98.5, 70.4, 85.8, and 90.6% for the four, six, eight, and ten carbon chains, respectively, from solution initially at a pH of 7. Results indicate that there was a lower degree of success achieved using ten carbons than there was using equal amounts of the shorter chain amines removed under identical conditions. These results indicate that ability to effectively coordinate to the metal by the ligand is maximized when the alkyl chain length is equal to ten carbons. Presumably a significant hydrophobic affect occurs when the chain length exceeds ten carbons, as seen for the copper and cadmium results.

For nickel ion solutions, the results obtained were 88.1, 57.6, 53.1, and 65.3% removal for the four, six, eight and ten carbon chains, respectively, from solution initially at a pH of 7 (Table 2-1). The acidity remained constant throughout the process as the surface silanol groups formed relatively stable hydrogen bonds to the surface. The surface acidity of the silanols groups, which are not much lower than a pK of 10, presumably are not strong enough proton donors to make electrostatic or ionic interactions with the binding ligands (Drago and Matwioff, 1968). Results here also indicate that, once the chain length is equal to ten carbons, a maximum amount of metal was removed under conditions identical to those used with the shorter-chain amines. These results indicate that the ability of an embodied ligand to effectively coordinate to the metal is dependent upon the distance of the coordinating atom, nitrogen, from the surface of the silica gel support and the hydrophobicity of the aliphatic chain.

Results were also obtained for treatment of metals in lake water from Lettuce Lake, a fresh water lake located east of the University of South Florida, Tampa campus. Results (Table 2-2) focused on using *n*-hexylamine-silica composites, and may be compared with the corresponding data in Table 2-1. Removal percentages of relatively lower quality, compared to water samples in the laboratory, were obtained for Lettuce Lake water; for lead, cadmium and silver; removal of nickel was somewhat of poorer quality, and removal of copper was statistically the same. Controls (Table 2-1 vs. Table 2-2) were similar. The amount of ligand adsorbed onto the silica support was measured as a function of the amount of metal removed, C_s, and the amount of metal that remained, C_{eq}, after the extraction was complete (Table 2-3, Figure 2-3). Isotherm Equation: $y = -0.9993x + 249.84$

Table 2-3 Sorption and equilibrium data in Lettuce Lake Water using n-hexylamine supported onto silica gel.

Concentration, ppm	C_s (sorption), microgram/gram	C_{eq} (Remaining), microgram/ gram
0.1 ppm	2.13	247.8
0.5 ppm	6.5	243.3
5.0 ppm	212	38
100 ppm	239	12

*Sample size of five for the composite material using the batch method.

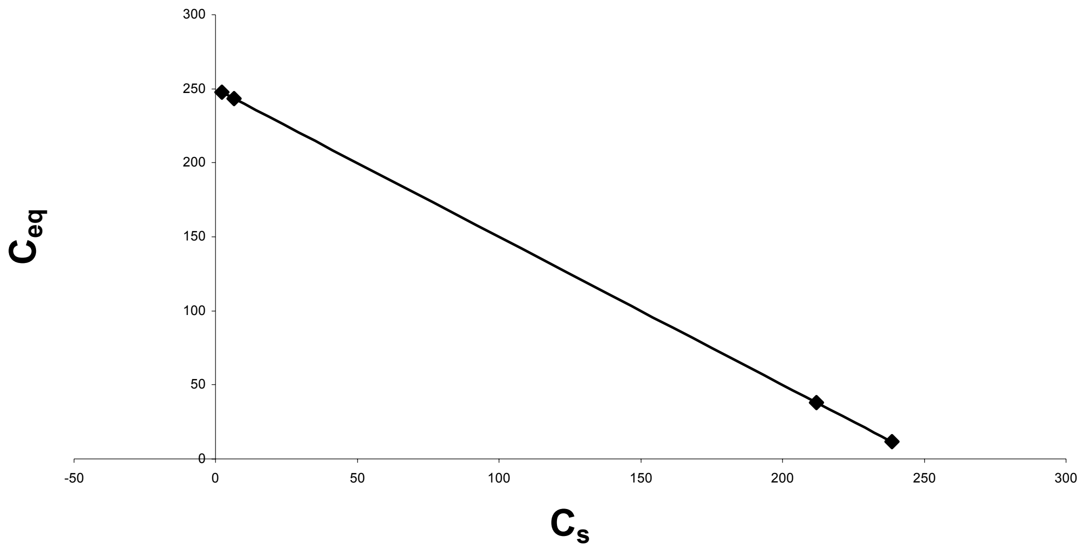

Figure 2-3 Plot of sorption and equilibrium data in Lettuce Lake Water using n-hexylamine supported on silica gel expressed as a function of concentration per gram.

Discussion

Use of silica-supported reagents affords a relatively inexpensive method for providing a convenient method of support of amines. And taking advantage of the hydrogen bonding of the alkyl amines in the silica pores affords an inexpensive method of loading the amines onto silica gel. The results indicate that a good degree of stability can be obtained, resulting in a favorable degree of removal of heavy metal ions from solution. The stability relationships of amines and heavy metals were summarized by Fernelius (1956), who noted that for a wide variety of chelating agents and bivalent metal ions, there was a fixed order of stabilities Mn<Fe<Co<Ni<Cu>Zn, the Irving-Williams Order. Martell and Calvin (1968) illustrated that for a wide variety of aliphatic amines used as chelating agents and bivalent metal ions, there was a fixed order of stabilities Ni<Cu>Cd. These ligands examined involved having nitrogen as the coordination donor, and some deviation from the Irving-Williams Order might be expected for multidentate ligands.

It is interesting to examine the amounts of metals removed. One might expect the maximum removals should be related to the relative chelating tendencies and might be expected to follow the extended order noted by Fernelius (1956), *viz*., Pd>Hg>UO_2 >Be>Cu>Ni>Co>Pb>Zn>Fe>Mn>Mg>Ca>Sr>Ba. For systems in deionized water, the metals and their maximum removals (in parentheses) were: Cu (98.6%), Cd (92.5%), Pb (90.6%), Ag (91.6%) and Ni (65.3%).

Conclusions

Heavy metal removal using amines supported on silica gel was achieved with a reliable degree of success. The removal effectiveness was independent of the type of metal used in the study. The validity of the proposed model, i.e. a hydrogen bonding model, was evident here as the efficiency increased with a maximum of ten carbons and a minimal hydrophobic effect by the aliphatic chain. This tendency was independent of the type of metal being studied. Use of silica-supported primary amines, utilizing hydrogen bonding, affords an inexpensive alternative and a convenient method of effective removal of selected heavy metal ions, and the application to other ligands should be considered.

Generally (with the exception of copper and nickel), removal of metals from humic-laden lake water was unsatisfactory. Clearly, the answer was not competitive chelation or copper would have been more notably affected, but it is evident that modifications of removal procedures must be devised for humic-laden waters to achieve greater success. The amount of metal extracted in the sample of lake water spiked with a known amount of copper(II) ion is a measure of the efficiency of the composite material itself. Table 2-3 and Figure 2-2 indicates that at varying concentrations that it is reasonable to presume that for a known amount of metal cation present that there is indeed an amount of silica-supported amine composite that can effectively remove the metal contaminant from the aqueous medium.

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Chapter Three

Heavy Metal Removal By Mercaptans Adsorbed Onto Silica Gel By a Corkscrew Mechanism

Introduction

Previous work in the area of environmental cleanup technologies and the remediation of selected heavy metals has established the efficiency of using chelating agents supported on silica gel. In another related study, chelating agents, supported on silica gel, were used in the removal heavy metal ions such as cadmium, and copper(II). The role of silica gel in heavy metal extraction has been used in the removal of various metal ions from aqueous media. It has been illustrated (Norris and coworkers, 1995, 1996, 1997) that silica gel can be used in the removal of metals such as copper(II) from solution. In separate studies by Pooré and coworkers (1996) and Norris and coworkers (1995, 1996, 1997), silica gel has been used as a support for chelating and coordinating agents in the removal of heavy metals from standard aqueous solutions. It has also been reported that the silica gel alone is an effective tool in the removal of metal ions from solution (Norris et. al. 1997). Results have proven that the pores embedded throughout the silica gel matrix can effectively remove ions such as copper from solution. This hydrocarbon adsorption on silica gel (HAS) has been demonstrated to be an effective alternative in loading the hydrocarbon moieties onto the silica gel matrix. This so-called corkscrew mechanism (Figure 3-1 a,b) as demonstrated by saturated aliphatic mercaptans has been reported to be an effective tool and viable alternative in the removal of toxic metallic ions from aqueous media. The silica pores are lined with the hydrophilic silanol groups and the slightly hydrophobic siloxane groups. These hydrophobic pores make it easier for the hydrophobic aliphatic chains to be adsorbed with the loss of the non-polar solvent, *n*-hexane. The free energy here may also present a good argument for the legitimacy of the corkscrew mechanism. It has been well documented that the interaction between unlike or dissimilar solvents, such as oil and water, is slightly exothermic Lowry (1987). This means that the enthalpy change is negative. The negative enthalpy and the negative change in entropy contribute to the favorable free energy change. These are competing factors but the end result provides support for the argument that the corkscrew mechanism is indeed plausible. The same logic can be applied with the hydrophilic or polar silica gel and the non-polar and hydrophobic aliphatic chain of the hydrocarbon being adsorbed into the pores of the silica gel. The entropy change with the loss of the non-polar solvent is negative as the freedom of motion is decreased with the adsorption takes place. Secondly, the same logic that we apply to the interaction between two dissimilar solvents can be applied here. The logic being that the interaction between the aliphatic chain of the coordinating agent and the hydrophilic pores of the silica gel is exothermic, providing a negative enthalpy. The negative change in both enthalpy and entropy lead to a favorable change in free energy. Thus, we can conclude that the corkscrew model is a viable alternative to loading hydrocarbons onto silica gel.

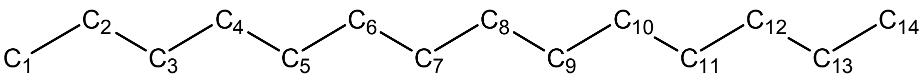

Figure 3-1a: Ligand Immersed In Favourable Hydrophobic Environment

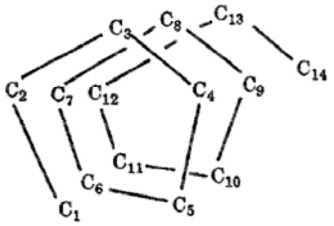

Figure 3-1b: Ligand Immersed In Non-Favourable Hydrophilic Environment; Corkscrew Mechanism

Conversely, one can also presume that there is some interaction between the surface silanol groups of the silica gel support and the sulfhydryl groups of the mercaptan (Figure 3-2). These sulfhydryl groupings would provide weak hydrogen bonds which would make the interactions possible and a point of exploration. High energy x-ray photoelectron spectroscopy was attempted to elucidate the nature of the interaction between the silica gel support and the alkane-thiols but the results were proven inconclusive.

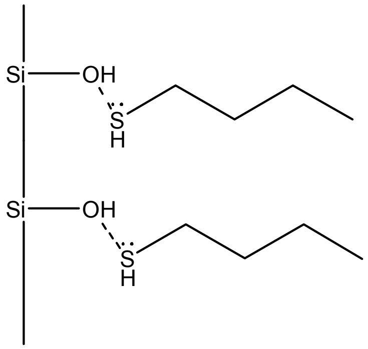

Figure 3-2: Weakly Bound Interraction Between Surface Silanol Groups of Silica Support and Sulfhydryl Groups of Mercaptan Moiety

Other investigations have illustrated that the use of polymer-based resins in the removal of selected heavy metals such as nickel(II), copper(II) and cobalt(II) by the batch method. The research indicated that the variety of silica-polymer composites used were relatively effective in the removal of the three heavy metals used. As noted previously (Norris and coworkers, 1997), removal of heavy metals has attracted considerable interest for several applications, including improved analyses (through concentration of metals), economy, remediation, and general concern for eliminating toxic substances from environmental samples or preventing their introduction to the environment. Obviously, concentration of metals from dilute aqueous samples would be economically sound for disposal purposes.

Supported coordinating agents offer several advantages for metal-ion removal. The method should provide favorable equilibria for removal, together with the co-advantages of convenience and ease of separation. Supported coordinating agents afford the possibility of design of ligands for specific applications, both in the selection of the ligands to be used for given types of metals (calcophiles, with an affinity for sulfur, or lithophiles with an affinity for oxygen donors, etc). And a variety of supports are available.

Supports have included several polymeric systems. Polystyrene impregnated with ß-diphenylglyoxime was a selective reagent for palladium Warshawsky (1974). Krause and Patchornik (1979) described several examples of polymeric reagents. Ion-exchange resins were used as supports for those chelating agents that can be derivatized or converted to ions (Lee et. al., 1976; Lee et. al., 1978; Norris et. al., 1995; Norris et. al., 1996). Attachment of the ligand to the substrate through derivatization is effective, of course, but it means an additional step and an additional cost.

An alternative, economical approach using silica support was described (Norris, et. al. 1997; Node et. al., 2001; Benson et. al., 1992) using a ligand with a long-chain hydrocarbon. The method consisted in filling silica gel pores with *n*-hexane that the hydrocarbon moiety would be soluble in and would presumably exist in a stretched configuration. Removing the *n*-hexane by evaporation, presumably led to the hydrocarbon chain in the pore to coil upon itself to minimize effects of hydrophobicity, caused by exposed hydroxyl groups lining the pores. London forces would favor a corkscrew configuration with perhaps two-three turns per chain of 12 carbons (*cf.*10). The coil would cause the hydrocarbon moiety to be wedged into the pores.

Previous studies indicated the success of the method. Benson and Martin (1992) observed that *n*-dodecylbenzoylacetone was loaded onto silica gel and removed 99.9% of available aqueous copper in a single-pass method. Subsequent studies indicated that sorption could account for considerable fraction of the removal of copper, depending on the pH using LIX® 54 (*n*-dodecylbenzoylacetone), oleoylacetone, or *n*-dodecylsalicyldoximine (Norris and coworkers, 1997). Similar results were obtained for removal of cadmium from aqueous solutions. *N, N*' –didodecyldithiooxamide supported on silica gel was effective in removing aqueous copper (99.1 ± 0.3%), nickel (70.7 ± 0.1.7%), and silver (83.5 ± 0.7%) near neutral pH (Pooré and coworkers, 1996).

The present study is concerned with the effectiveness of mercaptans of varying chain lengths loaded onto silica gel in removing selected aqueous heavy metals. With the success of using chelating agents in the removal of heavy metals from solution, it seems practical to use organic coordinating agents to accomplish identical goals of removal from a potential freshwater source in the environment. This report presents the results of using straight chain mercaptans loaded onto silica gel to effectively remove cadmium(II), copper(II), lead(II), and nickel(II) ions from standard aqueous solutions.

Mercaptans have been prepared by the addition reaction between hydrogen sulfide and a variety of vinylic aliphatic compounds. Reid (1958). On the surface of solid supports such as silica gel, clays such as attapulgite and montmorillonite (Fuller's Earth) and silica-alumina the synthesis of mercaptans using this method has been quite successful. It is therefore, reasonable to presume that due to the possibility of preparing the mercaptans on the surface of the silica gel that it would be plausible for the silica gel to act as a solid support for aliphatic moieties like saturated amines and thiols. Mercaptans have also been prepared via the reaction between alcohols, sulfuric acid and sodium hydrosulfide. (Reid et. al., 1958; Noller et. al., 1951) This reaction becomes important in regards to the synthesis and use of bifunctional compounds.

Experimental

Synthesis of Silica-Supported Coordinating Agents

Mercaptans were obtained from Aldrich Chemical and were used without further purification. A limited number of studies were done with hexylmercaptan to establish the lower limit of effectiveness. A major limitation was the notable odor associated with the compound, even using a modern hood, and use of this compound was curtailed by popular demand. The aroma of thiols - research into the pungent nature of the thiol functional groups has been investigated in Japan. The studies involved the examination of the odor from aliphatic and aromatic methyl esters. The investigation began with the demethylation of aliphatic and aromatic methyl esters. A series of thiols were investigated and the intensity of the smell of each thiol was determined using a rating scale. It was determined that the odor itself of longer chain aliphatic mercaptans was indeed "odor-less" in comparison to other mercaptans studied. Node (2001)

Loading of silica gel

Activated silica gel (20 g, 28-200 mesh; Aldrich) was suspended in 40 mL of anhydrous n-hexane. Then a solution of 1.57 mmoles of the mercaptan dissolved in 40 mL of anhydrous n-hexane was added to the silica gel suspension, and the solvent was evaporated under vacuum. The identical protocol that was employed in Chapter Two respective to the preparation of the silica composite material, analysis of the composite and supernatant were employed with the silica-supported thiols.

Analyses

Metal analyses were obtained using a Varian SpectrAA 100 atomic absorption spectrometer coupled to a Mega computer and Hewlett Packard 520C printer. Five standards (1, 2, 5, 10, 20 ppm for Cd, Cu, Ni; and 1,2,4,6,8 ppm for Pb), prepared by serial dilution, were used to determine the calibration plot. The spectrometer determined the concentration of the given metal, the concentration of which did not exceed 20 ppm, by the calibration curve**.** Calibrations were performed each time an analysis was made, and a total of five samples were used to calibrate the instrument. Detection limits for the metals listed in Table 3-1 were 0.025 (Cu), 0.018 (Ni), 0.019 (Pb), and 0.028 (Cd) ppm. Detection limits for the metals listed in Table 3-2 were 0.13 (Cu), 0.06 (Ni), 0.13 (Pb), and 0.05 (Cd) ppm.

Table 3-1. Removal of selected divalent metal ions (1.57*mM*) using thiols supported on silica gel at pH=7*.

Divalent Metal	Coordinating Agent	Extraction, %
Cu^{2+}	Hexanethiol	28.0 ± 7.9
	Dodecanethiol	53.0 ± 7.7
	Hexadecanethiol	80.7 ± 7.4
	Octadecanethiol	37.3 ± 3.9
	Control	18.3 ± 5.1
Ni^{2+}		
	Dodecanethiol	76.9 ± 0.8
	Hexadecanethiol	67.0 ± 1.9
	Octadecanethiol	76.3 ± 0.6
	Control	3.84 ± 1.8
Pb^{2+}	Hexanethiol	43.8 ± 14.7
	Dodecanethiol	63.9 ± 1.8
	Hexadecanethiol	67.0 ± 1.5
	Octadecanethiol	65.6 ± 2.7
	Control	20.3 ± 1.3
Cd^{2+}	Hexanethiol	94.6 ± 3.6
	Dodecanethiol	86.2 ± 2.3
	Hexadecanethiol	89.7 ± 2.4
	Octadecanethiol	82.8 ± 2.3

Table 3-1 (Continued)

	Control	13.2 ± 2.6
Ag^+	Hexanethiol	91.6 ± 0.3
	Octanethiol	91.9 ± 0.4
	Dodecanethiol	90.9 ± 0.8
	Hexadecanethiol	85.8 ± 2.4
	Octadecanethiol	83.3 ± 1.0
	Control	8.6 ± 3.3

*Sample size of five used for the batch method

Sulfur analyses were performed by Constellation Technology Corporation, Largo, Florida. The elemental analysis was performed on a sample of silica-supported mercaptan, 1-hexadecanethiol, which had been treated with a copper sulfate solution. Anal.: S, 0.755% .

Saturated, straight chain mercaptans were attached to silica gel and used as coordinating agents for removal of cadmium(II), copper(II), lead(II), and nickel(II) ions from standard solutions. It is believed that the mercaptans become wedged in the silica pores, but are available for reaction. Four thiols were used, viz., 1-hexanethiol, 1-dodecanethiol,1- hexadecanethiol, and 1-octadecanethiol. Standard solutrions of metals (1.57 mM) were stirred with the supported mercaptans for two hours, and at 25°C, and the sample supernatants were analyzed using atomic absorption spectrometry. At pH =

8, the percent removal was 99 (Cd), 91.5 (Cu), 80.8 (Pb), and 97 (Ni). It was possible to acidify the metal-containing solids, and regenerate the supported chelating agents.

Removal studies

Solutions of 1.57 m*M* (about 100 ppm) of cadmium(II) acetate, copper(II) nitrate, lead(II) nitrate, and nickel(II) nitrate were prepared in 1.0-L volumetric flasks. Five 100- mL aliquots of stock solution were used. Silica-supported ligand (4.0g) was added to each metal solution, and the resulting mixture was agitated in a New Brunswick Scientific Company Model G76 gyrotory water bath shaker at 25° C for a period of two hours. [Previous studies (Norris, 1995) had demonstrated that most removal by supported chelating agents occurred within the first hour.]

Results

The metal removal procedure is summarized (Equation 3-l), where SiO_2-Y-SH is a representation of a silica-loaded mercaptan, and MX_2 is a divalent metal salt.

$$2\ SiO_2\text{-Y-SH} + MX_2 \leftrightarrow (SiO_2\text{–Y- S})_2M + 2\ HX \qquad [3\text{-}1]$$

The sulfur analysis indicates that there was approximately 0.235 mmoles of mercaptan per gram of silica gel., and a 6:1 ratio of supported ligand/metal ion ratio was used.

Results (Table 3-1) indicate that it was possible to remove copper from solution using silica- supported mercaptans with varying degrees of success. Removal of aqueous copper(II) nitrate using equimolar supported 1-hexanethiol, 1-dodecanethiol, 1-hexadecanethiol and 1-octadecanethiol provided an average removal of 28.0, 53.0, 80.9 and 37.3%, respectively. With an initial equimolar, 1:1, ligand-metal mole ratio of silica-supported mercaptan, the removal of copper ion from solution was achieved with significant success.

Based on the Student's t-tests performed, there was no statistically significant difference in copper removal percentage among the shorter chain mercaptans in attaining over 25% removal. When the chain length exceeded ten carbons, there was a significant increase in the amount of the metal removed by the supported agent. This result is attributed to the corkscrew model (Benson and coworkers, 1992) in which the hydrophobic chain extends from the surface of the silica gel base, which permits coordination between the sulfur atom and the metal.

Additional results (Table 3-1) indicate better removal of aqueous cadmium ions using 1-hexanethiol, 1-dodecanethiol, 1-hexadecanethiol, and 1-octadecanethiol. The results obtained were 94.6, 86.2, 89.7 and 65.5% removal for the six, twelve, sixteen and eighteen carbon chains, respectively, from solution initially at a pH of 7. Results indicate that despite the chain length there was relatively an equal amount of metal removed under identical conditions, with the exception of the last mercaptan.

Removal of aqueous lead ions using supported 1-hexanethiol, 1-dodecanethiol, 1-hexadecanethiol, and 1-octadecanethiol was similar to the results for aqueous copper (Table 3-1). Specifically, we obtained 43.8, 63.9, 62.1 and 65.6% removal for the six, twelve, sixteen and eighteen carbon chains, respectively, from solution initially at a pH of 7. Results indicate that once the chain length exceeded ten carbons that there was essentially an equal amount of metal removed under identical conditions. These results indicate that ability to effectively coordinate to the metal by the ligand is dependent upon the distance of the coordinating atom, sulfur, from the surface of the silica gel support.

For nickel(II) ion solutions, the results obtained were 43.8, 76.9, 67.0 and 76.3% removal for the six, twelve, sixteen and eighteen carbon chains, respectively, from solution initially at a pH of 7 (Table 3-1). Results indicate that once the chain length exceeded ten carbons that a relatively an equal amount of metal was removed under identical conditions. These results again suggest the ability to effectively coordinate to the metal by the ligand is dependent upon the distance of the coordinating atom, sulfur, from the surface of the silica gel support. The results with 1-hexanethiol, though limited, reveal a ligand that was less effective than the longer chain mercaptans. This may be ascribed to differences in the proximity of the coordinating sulfur to the surface of the silica support.

Control values, obtained with silica gel treated with the hydrophobic solvent, n-hexane, showed ability to remove metals, the amount of removal depending upon the metal and the pH used (see Tables 3-1 and 3-2).

Use of silica-supported reagents, using a corkscrew mechanism, affords a relatively inexpensive method for providing a convenient method of support. Apparently a good degree of stability can be obtained: We were also able to regenerate a sample of silica-supported ligand a by sequential acid and base washes. This process is made possible by the reversible process as a result of coordination by the sulfur atom (Equation 3-1). With this treatment, 72.6% of the silica-supported ligand gel was recovered, then dried and re-used; there was no significant difference in the percent removal of copper being removed (initial, 80.7% removed vs, 82.8% for regenerated material. The amount of protons available from the sulfhydryl groupings was made evaluated using a basic titration with dilute sodium hydroxide. The initial titration curve (Figure 3-1) is characteristic of the titration of a strong base and weak acid. The second titration curve (Figure 3-3) illustrates that the presence of the sulfhydryl groups in the presence of a metal cation such as copper is characteristic of a strong base and a diprotic acid. This permits the conclusion that the sulfhydryl moiety is indeed available near the surface of the solid support.

The utility and effectiveness of the silica-supported thiol composite was evaluated using what was termed as the percent recovery. This method of determination of the amount of metal cation present was calculated to determine if the amount of cation adsorbed onto the composite was accounted for and in agreement with the amount of metal cation that was initially used in the investigation. The results (Table 3-3) indicate that the amount of metal cation was indeed accounted for based on the amount of composite material used and the amount of cadmium(II) cation used in the aqueous medium. The percent recovery was evaluated by taking into account the difference between the concentration of the stock solution and the individual supernatant solutions from the analytical trials. This difference was used in each calculation with the difference of the first trial and the stock solution. The quotient of these two values was determined and the result multiplied by 100 to determine the percentage. In each instance the amount of recovered metal cation was near or exceeded 90% indicating a good deal of return from the amount of metal present at the onset of the experiment.

Discussion

Fernelius (1956) noted that for a wide variety of chelating agents and bivalent metal ions, there was a fixed order of stabilities Mn<Fe <Co<Ni<Cu>Zn, the Irving-Williams Order. Fernelius (1956) also noted that the available data justified including other metals in a series of relative stabilities or coordinating tendencies: Pd>Hg>UO_2 >Be >Cu >Ni> Co> Pb> Zn> Cd> Fe> Mn> Mg> Ca> Sr> Ba. Generally, the ligands examined involved oxygen or nitrogen types, and some deviation might be expected for ligands with sulfur donors. The presence of the sulfhydryl groups within the silica gel matrix was investigated by means of a basic titration using dilute sodium hydroxide. The titration experiments were performed in two sets of work, titration of the silica-supported thiol and titration of the silica-supported thiol in the presence of the metal cation copper(II). The result of the initial titration is characteristic of a titration curve of a strong base weak acid. (Figure 3-3) The second titration performed under similar conditions in the presence of copper(II) ion is characteristic of a strong base weak diprotic acid (Figure 3-4). This titration study indicates that there are free sulfhydryl groupings available at the surface of the silica gel composite that are exposed and available for coordination to the metal cation. The titration further demonstrates that there exists an equilibrium characteristic of a weak acid salt.

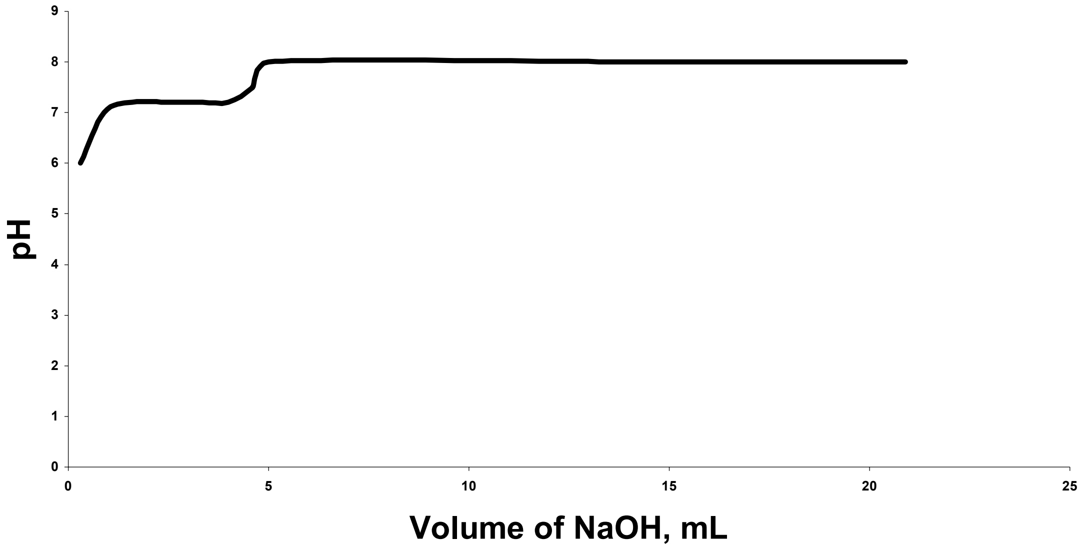

Figure 3-3 Plot of the titration of dilute sodium hydroxide and silica-supported thiol in the absence of selected divalent copper ions.

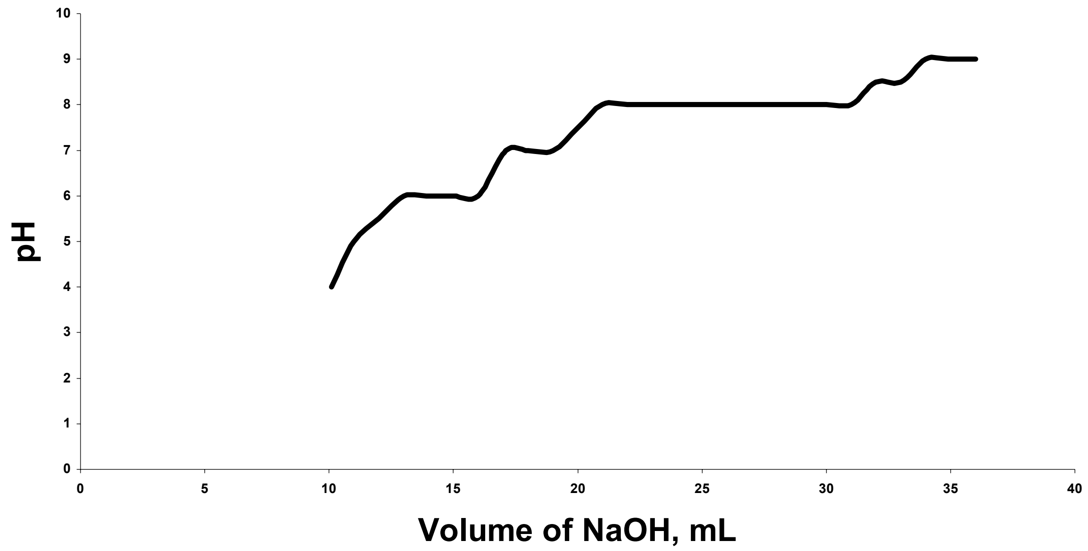

Figure 3-4 Plot of the titration of dilute sodium hydroxide and silica-supported thiol in the presence of selected divalent metal ion.

It is interesting to examine the amounts of metals removed, which represent an equilibrium situation inasmuch as there was no effort to "force" the reaction by adding base (See Equation 3-1) to shift the equilibrium. Thus the maximum removals should be related to the relative chelating tendencies and might be expected to follow the extended order. The metals and their maximum removals (in parentheses) were: Cu (80.9%), Ni (76.3%), Pb (65.6%) and Cd (89.7%). Of the four (arranged in the extended order above), cadmium was the exception, which at first glance may not be surprising because it is a calcophile and favors coordination with sulfur donors, though actually all four of the metals presently examined are calcophiles.

The effect of pH has been investigated previously, on silica gel silanol moieties to determine the relative stability of the material itself (Stumm and Morgan, 1970). The effect of pH was verified using *n*-dodecanethiol, and the effect of adjusting the pH from 7 to 8 is noted (Table 3-2) to determine the quantitative removal was obtained (except for lead). This is encouraging, but requires cautious interpretation: cadmium can be removed quantitatively using silica gel and adjusting the pH. For example, the % removal after two hours shaking (control) was 13.2 ± 2.6 at pH 7, but 78.2 ± 1.5 at pH 8.

Table 3-2 Removal of selected divalent metal ions (1.57 *mM*) using *n*- dodecanethiol supported on silica gel; effect of pH*

Metal ion	% Removal (Extraction, %)	% Removal (Extraction, %)
	pH = 7	pH = 8
Cu	53.0 ± 7.7	91.5 ± 1.1
Control	18.3 ± 5.1	35.4 ± 0.5
Ni	76.9 ± 0.8	97.0 ± 0.0
Control	3.84 ± 1.8	4.45 ± 2.2
Pb	63.9 ± 1.8	80.8 ±3.0
Control	20.3 ± 1.3	28.8 ± 14.2
Cd	86.2 ± 2.3	99.3 ± 0.0
Control	13.2 ± 2.6	78.5 ± 1.5

*Sample size of five used for the batch method

Table 3-3 Percent recovery of silica-supported mercaptan composite material and cadmium(II) ion present in 1.57 mM solution.

Binding Agent	Percent Recovery	Trial
1-hexanethiol	100	1
	96.8	2
	104.2	3
	94.5	4
	101.0	5
1-dodecanethiol	100.0	1
	105.8	2
	104.6	3
	101.8	4
	99.9	5
1-hexadecanethiol	100.0	1
	96.6	2
	93.4	3
	94.8	4
	98.1	5

Table 3-3 (Continued)

1-octadecanethiol	100.0	1
	110.2	2
	102.8	3
	113.4	4
	116.5	5

*Sample size of five used for the batch method.

Conclusions

Heavy metal removal using silica-supported thiol was achieved with a varying degree of success. The removal effectiveness varied with respect to the type of metal cation used in the study. The use of a “soft” base, the alkane-thiol, presumably attributed to the effectiveness of the metal extracted. The metal cations selected, silver, cadmium, lead, copper and nickel are all part of a class of elements known to favor sulfur coordination. Secondly, the amount of polarizability exhibited by each metal cation is an additional factor that increases the possibility of coordination to the polarizable sulfur donor. This fact explains the trend that was exhibited by the cations selected. The proposed model, the corkscrew model, for hydrocarbon chain absorption was evident here as the efficiency increased with increase in chain length of the mercaptan. This tendency was independent of the type of metal being studied. Adjusting the pH to 8 led to quantitative removal for copper, nickel, and cadmium ions, and 80% removal for lead (still an improvement over the results for pH 7). Use of higher pH would probably lead to degradation of the silica. Use of silica-supported mercaptans, using a corkscrew mechanism, affords a relatively inexpensive method for providing a convenient method of effective removal of selected heavy metal ions and the application to other ligands should be considered.

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Chapter Four

Heavy Metal Remediation Using Chemically Modified Silica Gel With 2-Mercaptoethanol

Introduction

The removal of selected heavy metals has attracted considerable interest for several applications, including improved analyses (through concentration of metals), economy, remediation, and general concern for eliminating toxic substances from environmental samples or preventing their introduction to the environment. Concentration of heavy metals from dilute aqueous samples would be economically sound for disposal purposes and another useful environmental cleanup technology.

Supported coordinating agents offer several advantages for metal-ion removal from aqueous standard solutions. The use of solid supports such as silica gel has proven to be a reasonably cost effective and efficient means of using coordinating agents embedded within the pores of the solid support or used to modify the solid support itself. The method of using non-covalently modified agents should provide favorable equilibria for removal, together with the co-advantages of convenience and ease of separation.

Supported coordinating agents afford the possibility of design of ligands for specific applications, both in the selection of the ligands to be used for given types of metals (chalcophiles, with an affinity for sulfur, or lithophiles with an affinity for oxygen donors, etc). A variety of supports are available commercially at a reasonable cost to the researcher.

Supports have included several polymeric systems. Polystyrene impregnated with ß-diphenylglyoxime was a selective reagent for palladium Warshawsky (1974). Krause and Patchornik (1979) and described several examples of polymeric reagents. Treated foam was used as a support for chelating agents (Lee et. al., 1978). Ion-exchange resins were used as supports for those chelating agents that can be derivatized or converted to ions (Lee et. al., 1978; Norris and coworkers, 1995; Norris and coworkers, 1996). Chemical attachment of a ligand to the substrate through derivatization is relatively more effective, of course, as Soliman (1997) has demonstrated using 3-chloropropyltrimethoxysilane as a means of attaching polyamines to the silica gel support. Such derivatization it means an additional step at an additional cost. On a macroscale, researchers at a Colorado based chemical firm, Metre-General, Inc., have devised a composite material called Octilog® which utilizes a silica-based polymeric material with amino functionalities. This material is currently being used in the uptake of selective heavy metals on an industrial scale. An alternative, seemingly more economical approach using silica support was described (Pooré and coworkers, 1996; Martell and Calvin, 1952; Fernelius, 1956) using a ligand with a long-chain hydrocarbon. The method consisted in filling silica gel pores with hexane that the hydrocarbon moiety would be soluble in and would presumably exist in a stretched configuration. Removing the hexane by evaporation, presumably led to the hydrocarbon chain in the pore to coil upon itself to minimize effects of hydrophobicity, caused by exposed hydroxyl groups lining the pores. London forces would favor a corkscrew configuration with perhaps two-three turns per chain of 12 carbons (*cf.*11). The coil would cause the hydrocarbon moiety to be wedged into the pores.

Previous studies indicated the success of the method. Benson and Martin (1992) observed that *n*-dodecylbenzoylacetone was loaded onto silica gel and removed 99.9% of available aqueous copper in a single-pass method. Subsequent studies indicated that sorption could account for a considerable fraction of the removal of copper, depending on the pH using LIX® 54 (*n*-dodecylbenzoylacetone), oleoylacetone, or *n*-dodecylsalicyldoximine (Norris, 1997). Similar results were obtained for removal of cadmium from aqueous solutions. *N, N’* –didodecyldithiooxamide supported on silica gel was effective in removing aqueous copper (99.1 ± 0.3%), nickel (70.7 ± 0.1.7%), and silver (83.5 ± 0.7%) near neutral pH (Fernelius, 1956).

Our previous studies were concerned with the effectiveness of mercaptans of varying chain lengths loaded onto silica gel in removing aqueous heavy metals, using normal mercaptans with chain lengths from six to eighteen carbons. Under optimal conditions, essentially quantitative removal was achieved for Cd, and about 80% removal for Cu, Pb, Ni (Krause and Patchornik, 1979). The present study looks at an alternative approach of attaching a mercaptan containing moiety: condensation of silica gel with 2-mercaptoethanol.

Secondly, the use of bifunctional compounds such as mercaptoalcohols is another viable alternative to the conventional methods of heavy metal removal. Silica gel has been shown to react with certain organic moieties Legrand (1998) and it is conceivable for a mercaptoalcohols to react with the silanol groups based upon the functionality. The use of 2-mercaptoethanol for the purpose of modifying the silica gel solid support was the choice of modification agent in order to bind the hydroxyfunctionality to the solid support and to expose the sulfhydryl grouping above the surface to bind to the metal cation.

Previous work in the emergent field of environmental cleanup technologies has established the possibility of using known chelating and coordinating agents supported on silica gel in the removal of heavy metals such as lead, silver, copper and nickel from standard aqueous solutions. Silica gel is currently being used as a solid support for various straight chain mono- and bifunctional compounds such as amines, thiols (mercaptans), mercaptoalochols and aminoalcohols. The current study reports the results of an investigation involving the use of a saturated, straight chain mercaptalcohol covalently attached to the silica gel support. As a coordinating agent, this bifunctional compound with be used in the uptake of copper(II), cadmium(II), nickel(II), silver(I) and lead(II) from standard aqueous solutions. The mercaptoalcohol used in the study was 2-mercaptoethanol.

Experimental

Synthesis of chemically modified silica gel using 2-mercaptoethanol

The substrate, 2-mercaptoethanol, was obtained from Fisher Scientific and was used without further purification. The activated silica gel solid support (28, 200 mesh, 20 g) was treated with 50 mL of toluene dried with 2 g of anhydrous sodium sulfate. The mixture was transferred to a 500 mL flat bottom flask that was fitted with a Dean-Stark trap and a condenser Williamson (1999). Then, the Dean-Stark trap was filled with toluene, a solution of approximately 0.1 mole of 2-mercaptoethanol dissolved in 50 mL of anhydrous toluene was added to the silica gel mixture, and the reaction mixture was agitated under reflux, 120 ^{o}C, on a magnetic stirrer hot plate for two hours. Upon cooling the solid was separated by filtration, dried under vacuum, and used for analyses.

Removal Studies

Solutions of 1.57 *mM* of lead(II) nitrate, cadmium(II) acetate, and copper(II) nitrate were prepared in 1.0-L volumetric flasks. Five 100- mL aliquots of stock solution were analyzed using an excess of 2-mercaptoethanol-silica gel composite (4 g.) which was added to each metal solution, and the resulting mixture was agitated in a New Brunswick Scientific Company Model G76 gyrotory water bath shaker for a period of two hours (200 rpm).

Relative acidity studies

A solution of 1.57 mM of copper(II) nitrate was prepared in a 1.0 L volumetric flask. A single 20 g sample of the modified silica gel composite was added to a 250 mL Erlenmeyer flask that contained a magnetic stir bar. To the contents of the flask, an aliquot of the copper(II) solution equal to 100 mL, was added to the flask, the contents stirred, and the pH was monitored using a Orion pH meter model 420A until constant pH was measured. In a separate experiment, 100 mL of deionized water was added to a 250 mL Erlenmeyer flask, with a magnetic stirring bar and containing a 20 g sample of the modified silica gel composite. The pH was also measured using an Orion pH meter until constant pH was maintained (Table 4-1).

Analyses

Metal analyses were obtained using a Varian SpectrAA 100 atomic absorption spectrometer coupled to a Mega computer and Hewlett Packard 520C printer. Five standards, prepared by serial dilution, were used to determine the calibration plot. The spectrometer determined the concentration of the given metal, the concentration of which did not exceed 10 ppm, by the calibration curve**.** Calibrations were performed each time an analysis was made, and a total of five samples were used to calibrate the instrument.

Results

The reaction of 2-mercaptoethanol and the silica gel solid support can be summarized (Equation 4-1), where A is a representation of silica gel-ligand composite. The reaction is performed under acidic conditions using concentrated sulfuric acid.

$$SiO_2 + HOCH_2CH_2SH \longrightarrow \underset{A}{SiO_2\text{-}CH_2CH_2SH} + H_2O \qquad (4\text{-}1)$$

The metal removal procedure is summarized (Equation 4-2),

$$\underset{A}{2\,SiO_2\text{-}CH_2CH_2SH} + MX_2 \rightleftharpoons \underset{B}{(SiO_2\text{-}CH_2CH_2S)_2M^+} + 2HX \qquad (4\text{-}2)$$

The present study looks at an alternative approach of attaching a mercaptan: condensation of silica gel with 2-mercaptoethanol. The reaction of 2-mercaptoethanol and silica gel can be summarized (Equation 4-1), where A is a representation of silica gel-ligand composite. The mechanism pathway itself can be described in much the same manner as the combination of functionalized alcohols can also be described (Figure 4-2). The acid catalyzed process is analogous to the combination of two alcohol moieties to produce an ether-like product. The loss of water as a by-product of the synthesis is expected. The metal removal procedure is summarized (Equation 4-2), where B is a representation of the metal-containing product composite.

Compound B is a representation of the metal-containing product. An experiment was performed to determine the validity of the proposed reaction pathway. The experiment involved utilizing the composite material in two aqueous sources, deionized water and a solution containing a known amount of copper(II) ion. The results, Table 4-1, indicate that the amount of protons lost as an effect of the coordination between the sulfhydryl moiety and the metal cation is almost quantitative to the amount of metal cation at the onset of the experiment. From the sulfur elemental analysis that was performed, it was determined that the expected amount of protons released from the silica composite material is equivalent to 23.5 mmoles. The results also indicate that the weakly acidic sulfhydryl moiety was indeed free and the loss of the proton there is characteristic of a weak mono-protic acid. Using the final pH of the solution in the experiment which involved the copper(II) solution the amount of protons lost was determined to be equivalent to 2.51 mmoles. The elemental analysis done on a sample of the modified silica gel composite material determined that there were 23.5 mmoles of sulfhydryl groupings available for coordination with the metal cation per gram of sample. The initial concentration of the copper(II) solution, 1.57 mM indicates that there was an excess of composite sulfhydryl moieties and subsequently protons available for successful uptake of the metal cation. Further, with the amount of copper removed (Table 4-2) it is reasonable to presume that a quantitative amount of the metal cation can be removed by the amount of chelating agent present in each sample of composite material.

Table 4-1. Measurement of pH of 2-mercaptoethanol chemically modified silica gel composite and a copper(II) Ion (1.57*mM*).

Aqueous Media	Time Elapsed, mins.	Measured pH
Control (DI Water)	0.0	6.7
	1.0	6.4
	5.0	5.4
	10.0	5.1
	20.0	4.1
	30.0	4.1
Copper (1.57 mM)	0.0	6.6
	1.0	5.4
	5.0	4.1
	10.0	3.1
	20.0	2.6
	30.0	2.6

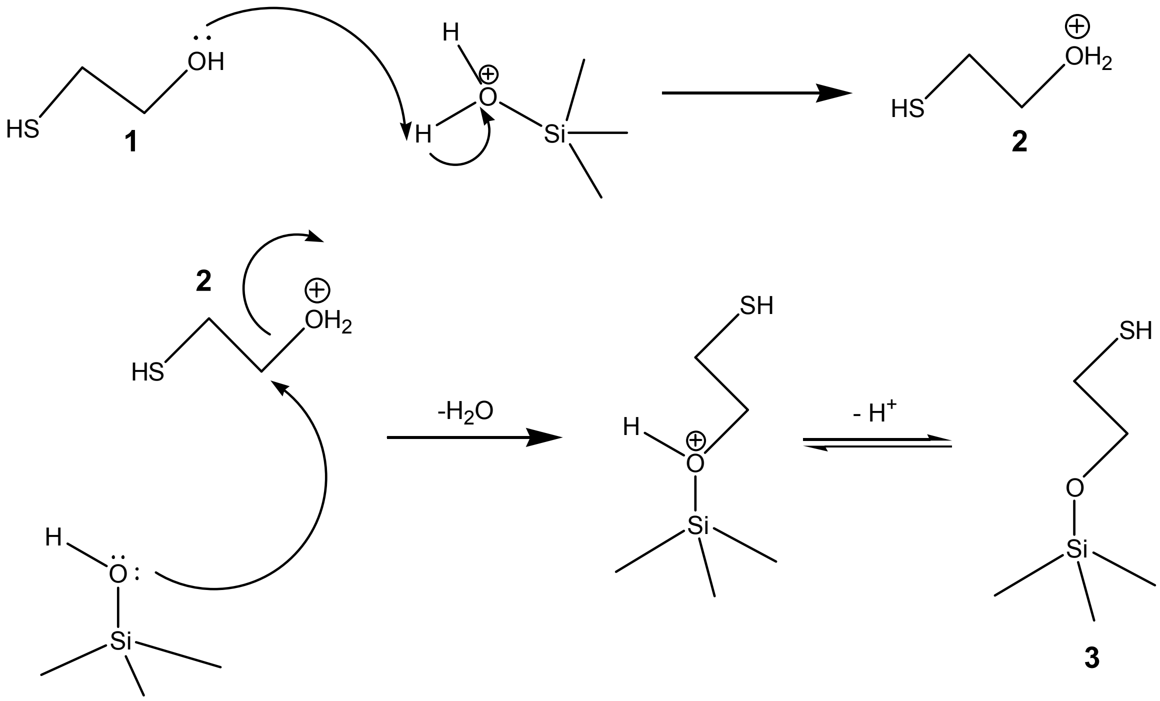

Figure 4-1. The proposed mechanism of reaction between the 2-mercaptoethanol substrate and the silica gel solid support (Williamson, 1999).

Results (Table 4-2) indicate that it was possible to remove more than 90% of three heavy metals from aqueous solutions using silica-ligand composites with a removal of aqueous copper(II) nitrate using excess 2-mercaptoethanol provided an average removal of 92.1%. With an excess of silica-bonded 2-mercaptoethanol, the removal of copper ion from solution was achieved with significant success. Removal of lead from aqueous lead(II) nitrate using 2-mercaptoethanol provided an average removal of 91.2%. Removal of cadmium from aqueous cadmium acetate provided an average removal of 92.8%. Based on the student t-test performed, there was no statistically significant difference in the removal percentage among the divalent metals studied using equal amount of 2-mercaptoethanol.

As noted previously (Norris and coworkers, 1997), removal of heavy metals has attracted considerable interest for several applications, including improved analyses (through concentration of metals), economy, remediation, and general concern for eliminating toxic substances from environmental samples or preventing their introduction to the environment. Obviously, concentration of metals from dilute aqueous samples would be economically sound for disposal purposes.

Supported coordinating agents offer several advantages for metal-ion removal. The method should provide favorable equilibria for removal, together with the co-advantages of convenience and ease of separation. Supported coordinating agents afford the possibility of design of ligands for specific applications, both in the selection of the ligands to be used for given types of metals (calcophiles, with an affinity for sulfur, or lithophiles with an affinity for oxygen donors, etc). And a variety of supports are available.

Supports have included several polymeric systems. Polystyrene impregnated with ß-diphenylglyoxime was a selective reagent for palladium Warshawsky (1974). Krause and Patchornik (1979) described several examples of polymeric reagents. Treated foam was sued as a support for chelating agents (Lee and coworkers, 1976). Ion-exchange resins were used as supports for those chelating agents that can be derivatized or converted to ions (Lee and coworkers, 1978; Norris and coworkers, 1995; Norris and coworkers, 1996). Attachment of the ligand to the substrate through derivatization is effective, of course, as Soliman and coworkers (1997) has demonstrated using 3-

chloropropyltrimethoxysilane as a means of attaching polyamines to silica gel (Beatty et. al., 1999). Such derivatization it means an additional step at an additional cost.

An alternative, economical approach using silica support was described (Norris et. al., 1994; Martell and Calvin, 1952; Fernelius, 1956) using a ligand with a long-chain hydrocarbon. The method consisted in filling silica gel pores with hexane that the hydrocarbon moiety would be soluble in and would presumably exist in a stretched configuration. Removing the *n*-hexane by evaporation, presumably led to the hydrocarbon chain in the pore to coil upon itself to minimize effects of hydrophobicity, caused by exposed hydroxyl groups lining the pores. London forces would favor a corkscrew configuration with perhaps two-three turns per chain of 12 carbons (*cf.*11). The coil would cause the hydrocarbon moiety to be wedged into the pores.

Previous studies indicated the success of the method. Benson and Martin (1992) observed that *n*-dodecylbenzoylacetone was loaded onto silica gel and removed 99.9% of available aqueous copper in a single-pass method. Subsequent studies indicated that sorption could account for considerable fraction of the removal of copper, depending on the pH using LIX® 54 (*n*-dodecylbenzoylacetone), oleoylacetone, or *n*-dodecylsalicyldoximine Norris (1997). Similar results were obtained for removal of cadmium from aqueous solutions. *N, N*' –didodecyldithiooxamide supported on silica gel was effective in removing aqueous copper (99.1 ± 0.3%), nickel (70.7 ± 0.1.7%), and silver (83.5 ± 0.7%) near neutral pH Shriver (1956).

Our previous studies were concerned with the effectiveness of mercaptans of varying chain lengths loaded onto silica gel in removing aqueous heavy metals, using normal mercaptans with chain lengths from six to 18 carbons. Under optimal conditions, essentially quantitative removal was achieved for Cd, and about 80% removal for Cu, Pb, Ni (Bowe et. al., 2002).

Results (Table 4-1) indicate that it was possible to remove more than 90% of three heavy metals from aqueous solutions using silica-ligand composites with a removal of aqueous copper(II) nitrate using excess 2-mercaptoethanol provided an average removal of 92.1%. With an excess of silica-supported 2-mercaptoethanol, the removal of copper ion from solution was achieved with significant success. Removal of lead from aqueous lead(II) nitrate using 2-mercaptoethanol provided an average removal of 91.2%. Removal of cadmium from aqueous cadmium acetate provided an average removal of 92.8%. Based on the student's t-tests performed, there was no statistically significant difference in the removal percentage among the divalent metals studied using equal amount of 2-mercaptoethanol.

Table 4-2. Removal of selected divalent metal ions (1.57*mM*) using 2-mercaptoethanol chemically modified silica gel at pH=7*.

Divalent Metal	Binding Agent	Extraction, %
Cu^{2+}	2-Mercaptoethanol	92.1 ± 1.2
	Control	18.3 ± 5.1
Ni^{2+}	2-Mercaptoethanol	91.9 ± 1.3
	Control	3.84 ± 1.8
Pb^{2+}	2-Mercaptoethanol	91.2 ± 0.3
	Control	28.8 ± 14.2
Cd^{2+}	2-Mercaptoethanol	92.8 ± 0.5
	Control	13.2 ± 2.6
Ag^{+}	2-Mercaptoethanol	90.2 ± 1.9
	Control	8.6 ± 3.3

*Where sample size is equal to five for batch method

Discussion

The solid support has been modified using the condensation reactions between the support itself and silane-based materials with amino containing functionalities Soliman (1997). Condensation reactions of solid supports and the organic substrate ligand has found a degree of success with siloxy-containing moieties such as (triethoxysilyl)propylamine Kates (2000). These processes were used to attach funtionalities to the solid support for subsequent use in organic synthesis. The use of condensation reactions could be adapted for use as an environmental cleanup technology. The condensation process can be made more efficient by employing the azeotropic distillation process commonly used in the preparation of esters in synthetic organic chemistry. The use of the Dean-Stark apparatus facilitates the collection of the water by-product in addition to permitting the researcher to monitor the progress of the reaction by measurement of the loss of this product of the synthesis. The Dean-Stark apparatus has been used in a variety of condensation reactions involving organic compounds and solid supports. The esterification reaction between aliphatic alcohols and carboxylic acids, Williamson (1999), where water is lost as a by-product, is a notable and common example of the use of the Dean-Stark apparatus as part of a synthetic protocol. Silica surfaces slightly acidic, with pK_a of about 10, (Lee et. al., 1978), and can thus facilitate reactions that involve acid catalysis. It was reasonable to surmise that the silica gel support can facilitate a acid catalyzed condensation reaction between the solid support and a bifunctional compound such as a 2-mercaptoethanol, Scheme 4-1. Further, with the constant removal of water (See Equation 4-1) the otherwise reversible reaction is driven to completion, and we can expect a high yield of composite product.

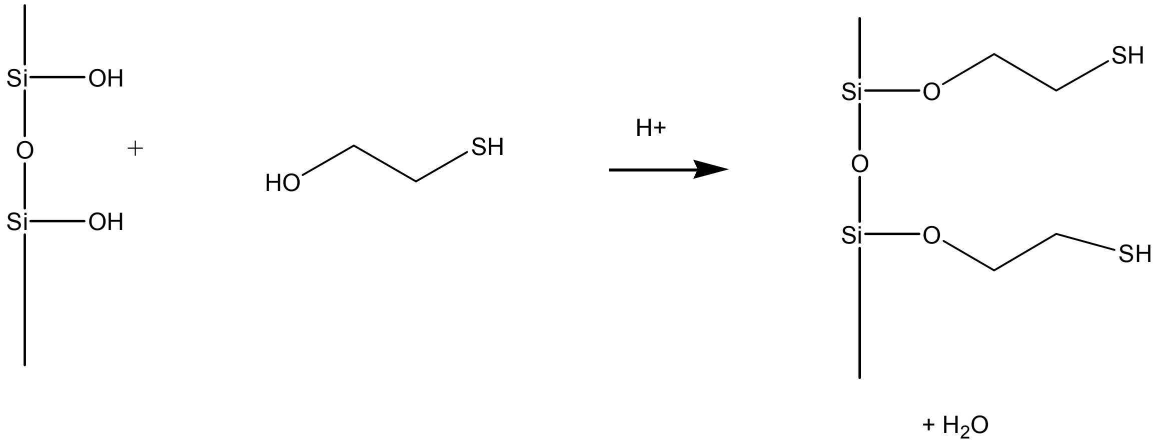

Figure 4-2 The synthesis of modified silica gel using 2-mercaptoethanol with a Dean-Stark trap apparatus.

Removal of selected heavy metals has been of concern for a significant time in our experience with these elements. Fernelius noted (1956) that for polydentate ligands such as chelating agents, that for bivalent metal ions, there was a fixed order of stabilities Mn<Fe <Co<Ni<Cu>Zn, the Irving-Williams Order. Fernelius (1956) also noted that the available data justified including other metals in a series of relative stabilities or coordinating tendencies:

Pd>Hg>UO_2>Be>Cu>Ni>Co>Pb>Zn>Cd>Fe>Mn>Mg>Ca>Sr>Ba. Generally, the ligands examined involved oxygen or nitrogen types, and some deviation might be expected for ligands with sulfur donors.

It is worthy of note that the examination of removing selected heavy metals, that represent an equilibrium (See Equation 4-2) that there was no effort to "force" the reaction by adding base (See Equation 4-1) to shift the equilibrium. Instead, we depended upon the availability one of the counter-ions, acetate or nitrate, a weak base to assist the shift of the equilibrium. Thus, the maximum removals should be related to the relative chelating tendencies and might be expected to follow the extended order. The metals and their maximum extractions (in parentheses) were: Cu (92.1%), Pb (91.2%) and Cd (92.8%). Presumably enhanced removal percentages could be obtained using added base, although this would add to the cost for an actual process. Of the three metals examined, cadmium proved to be the most successfully removed, which is perhaps to be expected from the extended order. Cadmium is also a chalcophile and coordination with sulfur donors should be favored (Norris, 1996).

Using 2-mercaptoethanol attached to silica gel, >90% of the copper (92.1 ± 1.2%), lead (91.2 ± 0.3%), or nickel (91.9 ± 1.3%) ions could be removed from dilute aqueous solutions. The controls, using unmodified silica gel, removed varying amounts of metal cations ranging from 4-18%.

Use of silica-supported bifunctional alcohols, using a Dean-Stark trap, affords a relatively inexpensive method for providing convenient method of effective removal of selected heavy metal ions and the application to other ligands should be considered. An alternative, typically used is derivatization by a silicon reagent, e.g. 3-

chloropropyltrimethoxysilane (Fernelius, 1956), which requires the use of an additional reagent, which adds to the cost of the process, and introduces the need for disposal of product. The process used here, produces innocuous water, and the amount gives a measure of the extent of the reaction. In our hands, the conversion was typically quantitative.

Presumably the nature of the ligand could be varied and multidentate ligands would be used provided one end was an alcohol and the other terminus was not a moiety that would condense with silica gel. We also presume that a potential ligand of the type HO–Y-Z could be used provided the donor moiety has certain characteristics. For example, the acidity of Z must be greater than that of silica gel, or suitable blocking agents must be available to prevent condensation at the wrong end. The scope of the reaction is being explored.

Conclusions

The use of the acid catalyzed condensation reaction of the solid support and the bifunctional substrate containing a hydroxyl moiety is indeed a plausible and was demonstrated to be an effective approach to the chemical modification of the silica gel solid support. It was also demonstrated from the relative acidity studies that the sulfhydryl group was indeed available for basic titration and coordination to the metal cation when the modified solid support was combined with a solution containing a metal cation. Additionally, the reaction between the modified composite material and the metal cation follows a well-known pattern for combination of the thiol-containing moiety and the metal cation. The use of this viable material for the use in the remediation of selected heavy metals is a technology that will indeed advance the field of environmental cleanup technologies. The hydroxyl functionality promotes the use and future usage of a wide array of solid supports and silica based materials. The use of substrates such as the mercapto-alcohols, permits the attachment of materials that were not originally prepared in this manner and at a reasonably competitive cost.

Recognition

Competing financial interests: The author notes that a patent disclosure has been submitted by the University of South Florida.

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Chapter Five

Extraction of Heavy Metals Using Modified Montmorillonite KSF and Modified Magnetite, Polyethylene Glycol and D-Lactose Adsorbent Materials

Introduction

The problem of removing toxic substances from fresh water sources is alleviated by the concentration of substance such as heavy metals from aqueous solutions. This environmental cleanup technology is a beneficial resource in the cleanup of the aquatic environment that is both practical and economical. The use of montmorillonite as a nutritional-based matrix for alfalfa plants proved successful in the removal of toxic metals such as cadmium(II) and zinc(II) from aqueous media. These studies were done at different acidity contents and each proved to be beneficial in the removal of the previously stated metal ions. The investigation concluded that phytoremediation utilizing montmorillonite-based soils was a viable means of removing heavy metals by competing rhizofiltration and ion exchange processes (Peralta-Videa et. al., 2002).

Related investigations in the removal of heavy metals from aqueous sources illustrate the effectiveness of using montmorillonite as an ion exchange substance. The study, completed over a period of weeks, culminated in the conclusion that montmorillonite was a proficient ion exchange material even with the interaction of humic substances (Lothenbach, 1997, 1999). The use of humic substances, humic and fulvic acids had been used with the montmorillonite adsorbent to remove heavy metals from a natural aqueous system. This combination was used quite successfully in the removal of high concentrations of lead, cadmium and copper ions (Liu and Gonzalez, 1999). Montmorillonite clays have been used as well in the extraction of lead and cadmium from aqueous solution. The clay material was treated with acidic and basic washes that improved the ion exchange capacity of the clay sorbent. The results were reported as being very good with more success being observed with the lead ion than the cadmium ion Barbier (2000).

The application of using clay sorbents in the removal of heavy metals was attempted in wastewater treatment. The use of acid-treated montmorillonite facilitated the removal of the heavy metals zinc, copper, and nickel from wastewater Vengris (2001). Research has also investigated the use of montmorillonite that was impregnated with organic-based ligands. The use of di-(2-ethylhexyl)phosphoric acid (DEHPA) as a binding ligand was tested with aqueous media. These studies concluded that the use of the binding agent, DEHPA, impregnated within the layers of clay sorbents such as montmorillonite, had high chemical sorption and fast kinetics in the uptake of heavy metals such as copper(II) ions (Cox, 2001). Also, the use of sodium dodecylsulfate (SDS) as a binding ligand was tested with standard solutions. These studies were performed as a function of relative acidity and concluded that the sorption of metal ions copper(II) and zinc(II) increased as a function of increasing pH (Lin and Juang, 2002).

Experimental

Reagents Used --- Calcium sulfate (anhydrous), 2-mercaptoethanol, and concentrated sulfuric acid were obtained from Fisher Scientific and were used without any further purification. Toluene (optima grade, Aldrich Chemical) was used without further purification as the solvent for the synthesis of modified adsorbent material that was dried over anhydrous calcium sulfate.

Synthesis of modified montmorillonite KSF agents --- Montmorillonite KSF (20 g, Aldrich Chemical) was treated with 50 mL of toluene that was pre-treated with anhydrous calcium sulfate. Then, 11.7 g (0.15 moles) of 2-mercaptoethanol dissolved in 50 mL of anhydrous toluene was added to the clay–toluene suspension, and four drops of concentrated sulfuric acid were added as a catalyst to facilitate the condensation reaction between the adsorbent and the bifunctional binding agent. The resulting mixture was refluxed for a period of two hours utilizing a Dean-Stark apparatus fitted with a Barrett trap to collect the water by-product. After the reaction was driven to completion, with elimination of 1.8 mL of water, the mixture was allowed to cool to room temperature and the solvent was removed by reduced pressure evaporation using a rotatory evaporator. A separate control experiment using the clay adsorbent suspended in toluene with sulfuric acid catalyst was completed producing 0.5 mL of water during the two-hour reflux period.

Synthesis of modified polyethylene glycol and silica gel supports --- Polyethylene glycol 600 (36 g, 0.06 moles, Fisher Scientific) was treated with 6 g (0.06 moles) of triethylamine and 100 mL of toluene that was pre-treated with anhydrous calcium sulfate. In a separate experiment, a mixture of triethylamine and adipoyl chloride was prepared using a solution of 4 g (0.04 moles) of triethylamine in 100 mL of dry toluene at a flow rate of 3 mL/minute under anhydrous conditions to which 7.6 g (0.04 moles) of adipoyl chloride in 100 mL of dry toluene at 12 °C with stirring, the result being a hydrochloride complex. The two mixtures, the polyethylene glycol and the hydrochloride complex, were combined and heated to reflux for a period of 1.5 hrs. The mixture was extracted in quadruplicate with 80% sodium chloride. The solvent toluene was evaporated under vacuum and the crude material was washed in triplicate with petroleum ether and subsequently recrystallized with anhydrous methanol.

Synthesis of modified D-Lactose agents --- D-Lactose (20 g, Sigma Chemical) was treated with 50 mL of toluene that was pre-treated with anhydrous calcium sulfate. Then, 11.7 g (0.15 moles) of 2-mercaptoethanol dissolved in 50 mL of anhydrous toluene was added to the sugar–toluene suspension, and four drops of concentrated sulfuric acid were added as a catalyst to facilitate the condensation reaction between the adsorbent and the bifunctional binding agent. The resulting mixture was refluxed for a period of two hours utilizing a Dean-Stark apparatus fitted with a Barrett trap to collect the water by-product.

After the reaction was driven to completion, with elimination of 5.0 mL of water, the mixture was allowed to cool to room temperature and the solvent was removed by reduced pressure evaporation using a rotatory evaporator. A separate control experiment using the oligosaccharide adsorbent suspended in toluene with sulfuric acid catalyst was completed producing 1.9 mL of water during the two-hour reflux period.

Synthesis of modified Chromosorb W --- Chromosorb W (5.0 g, Sigma Chemical) was treated with 50 mL of toluene that was pre-treated with anhydrous calcium sulfate. Then, 11.7 g (0.15 moles) of 2-mercaptoethanol dissolved in 50 mL of anhydrous toluene was added to the sugar–toluene suspension, and four drops of concentrated sulfuric acid were added as a catalyst to facilitate the condensation reaction between the adsorbent and the bifunctional binding agent. The resulting mixture was refluxed for a period of two hours utilizing a Dean-Stark apparatus fitted with a Barrett trap to collect the water by-product. After the reaction was driven to completion, with elimination of 2.0 mL of water, the mixture was allowed to cool to room temperature and the solvent was removed by reduced pressure evaporation using a rotatory evaporator. A separate control experiment using the carbohydrate adsorbent suspended in toluene with sulfuric acid catalyst was completed producing 0.5 mL of water during the two-hour reflux period.

Synthesis of modified magnetite --- Magnetite (20.0 g, Aldrich Chemical) was chemically modified in two successive steps. The first modification of the material involved treatment with dilute sodium hydroxide, 1.0 N, for a period of 8 hrs at a temperature of 60 °C. The collected “hydrated” magnetite was filtered by gravity filtration and dried to constant weight in a 60 °C oven. The collected dried magnetite was transferred to a round bottom flask and treated with 50 mL of toluene that was pre-treated with anhydrous calcium sulfate. Then, 11.7 g (0.15 moles) of 2-mercaptoethanol dissolved in 50 mL of anhydrous toluene was added to the magnetite–toluene suspension, and four drops of concentrated sulfuric acid were added as a catalyst to facilitate the condensation reaction between the adsorbent and the bifunctional binding agent. The resulting mixture was refluxed for a period of two hours utilizing a Dean-Stark apparatus fitted with a Barrett trap to collect the water by-product. After the reaction was reached, with elimination of 6.5 mL of water, the mixture was allowed to cool to room temperature and the solvent was removed by reduced pressure evaporation using a rotory evaporator. A separate control experiment using the magnetite adsorbent suspended in toluene with sulfuric acid catalyst was completed producing 0.5 mL of water during the two-hour reflux period.

Analyses

Metal analyses were obtained using a Varian SpectrAA 100 atomic absorption spectrometer coupled to a Mega computer and Hewlett Packard 520C printer. Five standards, prepared by serial dilution, 0.5 ppm, 1.0 ppm, 2.0 ppm, 5.0 ppm and 10.0 ppm, were used to determine the calibration plot. The spectrometer determined the concentration of the given metal cation, which did not exceed 20 ppm, by the calibration curve. Calibrations were performed each time an analysis was completed, and a total of five standards were used to calibrate the instrument.

Sulfur analyses were performed by Constellation Technology Corporation, Largo, Florida. The elemental analysis was performed on a sample of modified montmorillonite KSF prepared as described above. Each analysis was performed in duplicate. Anal.: S, 22.1%.

Metal-removal studies

Aqueous solutions (1.57 m*M*) of lead(II) nitrate, cadmium(II) acetate, nickel(II) nitrate, silver(I) nitrate and copper(II) nitrate were prepared in 1.0-L volumetric flasks. Five 100-mL aliquots of stock solution were used. Modified montmorillonite KSF (4.0g) was added to each metal solution, and the resulting mixtures were agitated at a rate of 200 rpm in a New Brunswick Scientific Company Model G76 gyrotory water bath (25°C) shaker for two hours. This is a period of time that has proven to be sufficient for quantitative removal in previous studies (Norris, 1997).

Results

(Montmorillonite KSF)----- The metal removal procedure is summarized (Equation 5-l), where Clay–OCH_2CH_2-SH is a representation of a mercaptoethanol-montmorillonite composite and MX_2 is a divalent metal salt . The amount of water eliminated suggests condensation of 5 mmoles of 2-mercaptoethanol per gram of montmorillonite KSF, and a considerable excess of composite was used in our studies with initial pH of the large excess of composite constituted a driving force, as did the loss of a proton (Equation 5-1) that permits driving the reaction to completion by using alkali. [It should also be possible by using acid to reverse the process in order to recycle the composite.]

$$\text{Clay–OCH}_2\text{CH}_2\text{-SH} + \text{MX}_2 \rightarrow \text{Clay–OCH}_2\text{CH}_2\text{-S M}^+ \text{X}^- + \text{H}^+ \qquad (5\text{-}1)$$

Results (Table 5-1) indicated that it was possible to remove the selected metal ions from aqueous solutions using the modified montmorillonite with a varying degree of success. For example, removal of three metals was considered success, *viz.*, cadmium, 97.7 ± 0.5%; silver, 90.2 ± 1.9%; and copper, 85.2 ± 2.3%. On the other hand, two metals were less successfully removed, *viz.*, lead, 55.8 ± 13.8 and nickel, 30.7 ± 6.4%.

Table 5-1. The removal of heavy metals using modified montmorillonite KSF from 1.57 m*M* solution.*

Metal	Sample	Extraction,%
Cu^{2+}	Composite	85.2 ± 2.3
	Control	10.0 ± 6.0
Pb^{2+}	Composite	55.8 ± 13.8
	Control	19.9 ± 4.5
Cd^{2+}	Composite	97.7 ± 0.5
	Control	3.84 ± 2.1
Ag^{+}	Composite	90.2 ± 1.9
	Control	9.72 ± 4.7
Ni^{2+}	Composite	30.7 ± 6.4
	Control	6.18 ± 1.0

*Where sample size is equal to five for the batch method

Magnetite----- The metal removal procedure is summarized (Equation 5-2), where Fe_2O_3–OCH_2CH_2-SH is a representation of a mercaptoethanol-magnetite composite and MX_2 is a divalent metal salt . The amount of water eliminated suggests condensation of 5 mmoles of 2-mercaptoethanol per gram of hydrated magnetite, and a considerable excess of composite was used in our studies with initial neutral pH and the large excess of composite constituted a driving force, as did the loss of a proton (Equation 5-2) that permits driving the reaction to completion by using alkali.

$$Fe_2O_3\text{–}OCH_2CH_2SH + MX_2 \rightarrow Fe_2O_3\text{–}OCH_2CH_2SM^+ + X^- + H^+ \quad (5\text{-}2)$$

Results (Table 5-2) indicated that it was possible to remove the selected heavy metal ions from aqueous solutions using the modified hydrated magnetite with a varying degree of success. For example, removal of three metals was considered acceptable, cadmium, 24.6 ± 23.7%; lead, 16.8 ± 10.8%; and copper, 16.2 ± 2.3%.

(D-Lactose)----- The metal removal procedure is summarized (Equation 5-3), where Sugar–OCH_2CH_2-SH is a representation of a mercaptoethanol-sugar composite and MX_2 is a divalent metal salt . The amount of water eliminated suggests condensation of 14 mmoles of 2-mercaptoethanol per gram of sugar-based material, and a considerable excess of composite was used in our studies with initial neutral pH and the large excess of composite constituted a driving force, as did the loss of a proton (Equation 5-3) that permits driving the reaction to completion by using alkali.

$$\text{Sugar–OCH}_2\text{CH}_2\text{-SH} + \text{MX}_2 \rightarrow \text{Sugar–OCH}_2\text{CH}_2\text{-S M}^+\ \text{X}^- + \text{H}^+ \qquad (5\text{-}3)$$

Results (Chromosorb W)----- The metal removal procedure is summarized (Equation 5-4), where Chromosorb–OCH_2CH_2-SH is a representation of a mercaptoethanol-silica composite and MX_2 is a divalent metal salt . The amount of water eliminated suggests condensation of 14 mmoles of 2-mercaptoethanol per gram of silica-based material, and a considerable excess of composite was used in our studies with initial neutral pH and the large excess of composite constituted a driving force, as did the loss of a proton (Equation 5-4) that permits driving the reaction to completion by using alkali.

$$\text{Chromosorb–OCH}_2\text{CH}_2\text{-SH} + \text{MX}_2 \rightarrow \text{Chromosorb–OCH}_2\text{CH}_2\text{-S M}^+\ \text{X}^- + \text{H}^+ \qquad (5\text{-}4)$$

Discussion

(Montmorillonite KSF) --- Use of modified montmorillonite KSF reagents potentially affords a relatively inexpensive and convenient method for using solid-based materials in the remediation of heavy metals. Clays, related to montmorillonite KSF, seem to be relatively less expensive than silica, which is a commonly used solid support. In addition, this clay is more stable over a wider range of pH (up to 11). Although silica gel is stable under acidic conditions and showed very little loss when placed in very acidic and basic media, it has the disadvantage of becoming more soluble at pH 10 or greater

(Stumm and Morgan, 1996). In addition, the method of attachment of the β-oxyethylmercapto moiety should be both inexpensive and an example of green chemistry (provided the toluene is recycled). Making the best usage of the reversible reaction between the sulfhydryl moiety and binding metal permits us the opportunity to presumably recycle the material and concentrate the metal being removed from the aquatic source.

The results indicate that a favorable equilibrium (Equation 5-1) can be obtained, resulting in a favorable degree of removal of heavy metal ions from solution without the aid of basic material to drive the reaction to completion. Adjustment of pH (Equation 5-1) would be a driving force, but it would also constitute an additional cost, and it seemed worthwhile to see if significant removal would occur without such adjustment. Unfortunately, the results were successful for some, but not all metals, as indicated by the results in Table 5-1. All five metals are Group B–type metals, for which S-atom coordination is favored over O-atom donors. All metals fall into a group called calcogenides, indicating the tendency to be found in nature associated with sulfur.

The stability relationships that apply to various coordinating agents, including amines, and heavy metals were summarized by Fernelius (1956), who noted that for a wide variety of chelating agents and bivalent metal ions, there was a fixed order of stabilities Mn<Fe<Co<Ni<Cu>Zn, the so-called Irving-Williams Order. Martell and Calvin (1952) illustrated that for a wide variety of aliphatic amines used as chelating agents and bivalent metal ions, there was a fixed order of stabilities Ni<Cu>Cd. The same logic can be applied to ligands that are sulfur-based. These examined ligands involved having sulfur as the coordination donor, and some deviation from the Irving-Williams Order might be expected for unidentate ligands with S-donor atoms.

It is interesting to examine the amounts of metals removed. One might expect that the maximum removals should be related to the relative chelating tendencies and might be expected to follow the extended order noted by Fernelius (1956), *viz*., Pd>Hg>UO_2>Be>Cu>Ni>Co>Pb>Zn>Fe>Mn>Mg>Ca>Sr>Ba. For systems in deionized water, the metals and their maximum removals (in parentheses) were: Cu (85.2%), Cd (97.7%), Pb (55.8%), Ag (90.2 %) and Ni (30.7%).

On the other hand, the results may be better understood in terms of a HASB (Hard acid, soft base) concept (Pearson, 1997). The results are feasible due to the fact that the donor atom and metals selected are considered to be moderately "soft" and very polarizable (Pearson, 1997), and the favorable removal of cadmium, silver, and copper is consistent with the interaction of a soft base and a soft acid (borderline for Cu^{+2}) versus a soft base and a borderline metal (lead and nickel).

The coordinating moiety, β-oxyethylmercaptan, could function as a chelating agent, but there is no evidence concerning this possibility. It is possible to compare the removal values for this composite versus those composites obtained by using mercaptans absorbed on silica gel (Bowe et. al., 2002). For the latter substrates, there was no possibility of chelation. These results do not indicate a notable difference in removal. The maximum removal (Bowe et. al., 2002) for copper ion was 80.7 ± 7.4 (vs 85.2 ± 2.3 for copper, Table 5-1). A similar trend was observed for cadmium (94.6 ± 3.6, Bowe and coworkers, 2002 vs 97.7 ± 0.5, Table 5-1) and, in fact, better removal percentages were obtained by Bowe and co-workers (2002) for supported alkyl mercaptans for lead (65.8 ± 2.1) and nickel (76.9 ± 0.8) than are reported for the two metals in Table 5-1.

Thus, while one might not expect a great enhancement of coordination with β-oxyethylmercaptan versus an alkyl mercaptan, nevertheless the results do not support the trend expected for behaviour as a chelating agent, and one may suspect that steric factors were in play in the present study.

Conclusions

Heavy metal removal using modified montmorillonite KSF was achieved with a reliable degree of success. The removal effectiveness was independent of the type of metal used in the study. The same efficiency is presumably not specific to the valence of the metal, nor its size. The validity of the proposed model (summarized in Equation 5-1) was evident here as the relative pH decreased which is indicative of the increase in the concentration of protons. Further consideration of the reaction (Equation 5-1) indicates that the product of reaction with metal ions and the composite could subsequently be treated with acid to regenerate the adsorbent material for subsequent extraction studies. The success of regeneration was achieved previously with silica-supported mercaptans (Bowe et. al., 2002). This tendency is presumably independent of the type of metal being studied. Use of modified montmorillonite using 2-mercaptoethanol affords a relatively inexpensive, convenient and effective method for removing selected heavy metal ions, and the application to other ligands and solid-support materials should be considered.

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Chapter Six

Comparisons Between Batch and Column Methods of Metal Remediation and Selective Ion Removal Studies

Introduction

Previous work has established the possibility of utilizing known supported silica reagents in the removal of metals designated as toxic or hazardous in some way. Similarly, heavy metal removal utilizing modified silica gel, modified clays such as montmorillonite, and modified magnetite have been explored as a viable alternative to methods currently in use. These studies revealed the utility of these materials in the removal of heavy metals such as lead, silver, copper and cadmium from aqueous media. Silica gel, has been used as a solid support for various coordinating agents such as alkane thiols and chelating agents such as LIX 54® and LIX 860® in the removal of heavy metals from standard solutions (Norris et. al. 1997). The solid support has also been modified using the azeotropic distillation process to condense 2-mercaptoethanol with the silica based material. The resulting product as a coordinating agent was used to remove copper(II), cadmium(II), silver(I), nickel(II) and lead(II) ions from standard aqueous solutions. Without adjusting the pH, the percent removal observed was better than 90% of the metal ions investigated. A further aspect of this investigation will test the selectivity of the binding agent, 2-mercaptoethanol, to remove solutions of more than a single metal ion. Application to freshwater sources has been imagined from the potential usage of this material at local contaminated waste sites such as Delaney Creek, Florida (Gallardo-Williams et. al., 2002). The concentration of heavy metals from dilute solutions is a technology that is not only beneficial to the environment but a practical and economical approach to the problem of removal of toxic substances from fresh water sources. The use of silica gel supported with various chelating agents (Norris et. al., 1995) and coordinating binding ligands such as alkanethiols (Bowe et. al., 2002) has proven to be successful in the removal of toxic metals such as cadmium(II) and zinc(II) from aqueous media (Ritchie et. al., 2001).

The application of using clay sorbents in the removal of heavy metals was attempted in wastewater treatment. The use of acid treated montmorillonite facilitated the removal of the heavy metals zinc, copper, and nickel from wastewater (Vengris, 2001). Research has also investigated the use of montmorillonite that was impregnated with organic-based ligands. The use of di-(2-ethylhexyl)phosphoric acid (DEHPA) as a binding ligand was tested with aqueous media. These studies concluded that the use of the binding agent, DEHPA, impregnated within the layers of clay sorbents like montmorillonite, had high chemical sorption and fast kinetics in the uptake of heavy metals such as copper(II) ions Lothenbach (1997). Also, the use of sodiumdodoecylsulfate (SDS) as a binding ligand was tested with standard solutions. These extraction studies were performed as a function of relative acidity and it was concluded that the sorption of metal ions copper(II) and zinc(II) increased as a function of increasing pH units. The study also determined that these metal ions extracted, copper, zinc and nickel had an order of uptake or selectivity that favored the uptake or removal of copper. The actual order of uptake was determined to be Cu > Ni > Zn ions. Conversely, when the same sorbent material was run using a column method the opposite trend of cation uptake occurred Vengris (2001). Most of the investigations reported have been performed on a microscale to prove effectiveness in and improve on the technology. However, the environment does not have microscale problems to improve upon. Thus, an investigation to simulate "real-world" conditions was needed to elucidate whether the technology proven effective in the laboratory is a good candidate for possible macroscale conditions. Thus, the use of the technology by using a column method was another focus of this work.

Experimental

The procedure described in Chapter 4 was followed in this investigation as well. 2-mercaptoethanol, calcium sulfate and concentrated sulfuric acid were obtained from Fisher Scientific and was used without further purification. Toluene, optima grade, was used as the solvent for the synthesis of the modified silica gel and was made anhydrous by utilizing calcium sulfate as a drying agent. The toluene and silica gel, 28-200 mesh was used without any further modification to the adsorbent.

Silica gel (20 g) was treated with 50 mL of toluene that was pre-treated with anhydrous calcium sulfate. Then a solution of 11.1 grams (0.15 moles) of the 2-mercaptoethanol was dissolved in 50 mL of anhydrous toluene that was added to the silica adsorbent mixture, and four drops of concentrated sulfuric acid was added as a catalyst. The resulting mixture was refluxed for a period of two hours utilizing a Dean Stark trap apparatus to collect the water by-product. After the reaction was driven to completion the mixture was allowed to cool to room temperature and the solvent was removed by rotatory evaporation.

Analyses

Metal analyses were obtained using a Varian SpectrAA 100 atomic absorption spectrometer coupled to a Mega computer and Hewlett Packard 520C printer. Five standards, prepared by serial dilution, 0.5 ppm, 1.0 ppm, 2.0 ppm, 5.0 ppm and 10.0 ppm, were used to determine the calibration plot. The spectrometer determined the concentration of the given metal, the concentration of which did not exceed 20 ppm, by the calibration curve. Calibrations were performed each time an analysis was made, and a total of five samples were used to calibrate the instrument.

Sulfur analyses were performed by Constellation Technology Corporation, Largo, Florida. The elemental analysis was performed on two samples of modified silica gel that had been treated produced in toluene as a solvent. Anal.: S, 15.1%

Removal studies: batch method

Solutions of 1.57 mM of lead(II) nitrate, cadmium(II) acetate, nickel(II) nitrate and copper(II) nitrate were prepared in 1.0-L volumetric flasks. Five 100-mL aliquots of stock solution were used. Modified silica gel (4.0g) was added to each metal solution, and the resulting mixtures were agitated at a rate of 200 rpm in a New Brunswick Scientific Company Model G76 gyrotory water bath (25°C) shaker for two hours.

Removal studies: column method

Solutions of 1.57 mM of lead(II) nitrate, cadmium(II) acetate, nickel(II) nitrate and copper(II) nitrate were prepared in 1.0-L volumetric flasks. One 100-mL aliquot of stock solution was used. Modified silica gel (20.0g) was added to a column of 12.0 inches x 1.5 inch diameter dimensions. Each metal solution, 100 mL volume capacity, and the resulting mixtures were added to a prepared column (using deionized water) at a temperature of 25°C until the supply of the solution had been exhausted. The eluting solution was passed through the column at a rate of 5 mL per minute. This rate of elution was used in each experiment for each of the metal cations investigated. The filtrate was collected and analyzed by atomic absorption spectrometry.

Regeneration of the columns was an aspect of this project that needs some further exploration.

Results

The metal removal procedure is summarized (Equation 6-l), where SiO_2-CH_2CH_2-SH is a representation of a mercaptoethanol-silica composite, and MX_2 is a divalent metal salt .

$$SiO_2\text{-}CH_2CH_2\text{-}SH + MX_2 \rightarrow SiO_2\text{–}CH_2CH_2\text{-}SM^+ + 2H^+ \qquad (6\text{-}1)$$

The sulfur analysis of a single sample indicates that there was approximately 9.66 mmoles of 2-mercaptoethanol per gram of silica gel, and 6:1 ratio respectively of modified silica ligand/metal ion ratio was used in our studies. The ratio of ligand/metal with the presence of two hydroxyl groups on the surface of the silica gel presumably indicates that these ligands are attached in a certain manner (See Chapter 4, Figure 4-2).

After the attachment to the silica surface, it is presumed that the chelation of the ligand and the metal ion follows a well-established formula for thiolated compounds and the metal being removed (Figure 6-2). The loss of a proton, Equation 6-1, is an important aspect that permits us to drive the reaction to completion by using a basic additive and to possibly reverse the process in order to recycle the binding material.

Results (Table 6-1) indicate that it was possible to remove the selected metal ions from solution using the column or batch method. Removal of aqueous copper(II) nitrate using excess modified silica gel, provided an average removal of 85.2%. With an excess of ligand, 6:1 ligand-metal mole ratio of 2-mercaptoethanol modified silica gel, the removal of copper ion from solution was achieved with significant success, e.g., up to 85.2 ± 2.3%

Table 6-1 Removal of selected divalent metal ions by the batch method (1.57*mM*) using 2-mercaptoethanol chemically modified silica gel at pH=7*.

Divalent Metal	Binding Agent	Extraction, %
Cu^{2+}	2-Mercaptoethanol	92.1 ± 1.2
	Control	18.3 ± 5.1
Ni^{2+}	2-Mercaptoethanol	91.9 ± 1.3
	Control	3.84 ± 1.8
Pb^{2+}	2-Mercaptoethanol	91.2 ± 0.3
	Control	28.8 ± 14.2
Cd^{2+}	2-Mercaptoethanol	92.8 ± 0.5
	Control	13.2 ± 2.6
Ag^{+}	2-Mercaptoethanol	90.2 ± 1.9
	Control	8.6 ± 3.3

*Where sample size is equal to five for the batch method

Based on Student's t-tests performed, there was no statistically significant difference between the removal percentages of the metals studied.

Additional results (Table 6-1) indicate better removal of aqueous cadmium ions. The results obtained were 97.7% removal for the modified absorbent material. Results indicate that again the ability of the sulfur atom to coordinate with the metal.

Removal of aqueous lead ions using modified silica gel, was similar to the results for aqueous copper and cadmium (Table 6-1). Distinctively, the percentage of metal removed was 55.8%, from solution initially at a pH of 7. These results indicate that the ability to coordinate to the metal by the ligand. For nickel ion solutions, the results obtained were 30.7% removal, from solution initially at a pH of 7 (Table 6-1). These results indicate that the ability of a chemically attached ligand to effectively coordinate to the metal is dependent upon the distance of the coordinating atom, sulfur, from the surface of the silica gel material.

The remediation of metal cations has been previously demonstrated using a solution that contained just a single cation of interest. The selective ion removal involving more than a single cation in a mixed cation solution is an aspect of the project that has proven to be both interesting and effective. The cations selected were all divalent but of varying ionic radii. The results (Table 6-2) from the comparison of copper(II) and lead(II) ions indicated a definite preference for the copper(II) cation a preference of 98:2 removal ratio between the two cations. The comparison of copper and nickel ions (Table 6-2) also indicate a preference of the copper cation by the modified silica gel composite. Copper and cadmium ions were the third mixed cation medium and it was demonstrated that the cadmium ion was the preferred cation by the modified silica composite material (Table 6-2).

Table 6-2 The removal of heavy metals using β-ethoxymercaptan modified silica gel from 1.57 m*M* solution using batch method.*

Metal(% Extraction)	Metal(%Extraction)	Metal(%Extraction)	Metal(%Extraction)
Cu^{2+} (Modified)	Pb^{+2} (Modified)	Cu^{+2}(Control)	Pb^{+2}(Control)
98.2 ± 1.2	1.82 ± 1.1		8.39 ± 5.0
Cu^{2+} (Modified)	Cd^{2+}(Modified)	Cu^{+2}(Control)	Cd^{+2}(Control)
68.6 ± 5.1	94.8 ± 3.5	12.5 ± 5.3	6.36 ± 4.4
Cu^{2+} (Modified)	Ni^{2+} (Modified)	Cu^{+2} (Control)	Ni^{+2}(Control)
97.8 ± 0.1	33.1 ± 18.0	10.2 ± 5.4	3.96 ± 3.7

*Where sample size is equal to five for the batch method

The sequential removal of the selected cations was evaluated using a column of dimensions equal to 1.5 inch x 12 inches x 2 inch diameter. These conditions were used to emulate actual conditions out in the field or on macroscale. The removal of each metal was followed by a sequential wash with dilute acid. The results (Table 6-3) indicate that there was a loss of nickel, silver and copper that was similar in effectiveness as with the using the modified composite material using the more conventional batch method. The uptake of lead and cadmium ions (Table 6-3) were far less than in the reported batch method indicating that there may have been some loss of the active part of the binding composite.

Table 6-3 The removal of heavy metals in chronological order using β-ethoxymercaptan modified silica gel from 1.57 m*M* solution using column method.*

Metal(% Extraction) Batch	Metal(%Extraction) Column	Metal(%Extraction) Batch	Metal(%Extraction) Column
Cu^{2+}	Cu^{+2}	Cu^{+2}(Control)	Cu^{+2}(Control)
92.1 ± 1.2	87.9	18.3 ± 5.1	34.9
Cd^{2+}	Cd^{2+}	Cd^{+2}(Control)	Cd^{+2}(Control)
92.8 ± 0.3	64.9	13.2 ± 2.6	
Pb^{2+}	Pb^{2+}	Pb^{+2} (Control)	Pb^{+2}(Control)
91.2 ± 0.3	15.3	28.8 ± 14.2	
Ni^{2+}	Ni^{2+}	Ni^{+2}(Control)	Ni^{+2}(Control)
91.9 ± 1.3	84.7	3.84 ± 1.8	
Ag^{+}	Ag^{+}	Ag^{+}(Control)	Ag^{+}(Control)
90.2 ± 1.9	84.4	8.6 ± 2.3	

*Where sample size is equal to five for batch method

Discussion

The results in Table 6-2 from the use of the composite material to selectively bind to one metal cation as opposed to another indicates that the technology can be applied to solutions that have a multiple cation medium. The preference for a metal cation based primarily on the relative polarizability (Pearson, 1997) of the cation can be an effective tool in the design of appropriate environmental cleanup technologies. Selective ion removal holds a lot of promise for wastewater treatment facilities in which it is necessary to target a single cationic species for removal over more benign and relatively less toxic non-indigenous chemicals.

The results (Table 6-3) indicate that the column used was presumably exhausted at the instance that the fifth metal ion (lead) was subjected to the process. Secondly, the column itself was regenerated after each of the trials indicated, and the washing with dilute nitric acid after the elution with each metal ion solution was indeed sufficient to remove some of the binding agent itself embedded with the composite. This may have attributed to the decrease in effectiveness of the composite material as the sequence was continued.

Use of modified silica gel as an environmental cleanup technology affords a relatively inexpensive alternative method for providing a convenient means of using solid-based materials in the remediation of heavy metals. Making the best usage of the reversible reaction between the sulfhydryl moiety and binding metal permits us the opportunity to presumably recycle the material and concentrate the metal being removed from the aquatic source. The choice of a sulfur-based composite was instrumental in the determination of the effectiveness of the environmental cleanup technology to selectively remove or target cations of equal valence but different size and polarizability. The results in Table 6-2 indicate that a good degree of stability can be maintained even with the presence of more than a single metal cation. The resulting effectiveness is in a favorable degree persists without the aid of basic material to drive the reaction to completion.

It is noteworthy to examine the amounts of metals removed and compare the uptake to the Irving-Williams Order for binding effectiveness. The use of this logic to selective ion removal investigations indicate that in the comparison of copper and nickel the order of selectivity was indeed expected. The order of selectivity was indeed also maintained in the comparison between lead and copper. The expectation of the maximum amount of metal cations should be related to the relative chelating tendencies and might be expected to follow the extended order noted by Fernelius (1956), *viz.*, Pd>Hg>UO_2 >Be>Cu>Ni>Co>Pb>Zn>Fe>Mn>Mg>Ca>Sr>Ba.

Conclusions

The ion selective removal using modified silica gel was achieved with a reliable degree of success. The removal effectiveness demonstrated that the uptake of a single cation when compared with another cation of equal valence was indeed dependent upon the relative polarizability of the cation and did follow a known order of chelation. The same relative efficiency in the uptake of the metal cations was evaluated using a column extraction and it was determined that there was a similar degree of effectiveness in washing the column pre-loaded with the composite material as having the mixed cation/composite in a gyrotorary shaker. The validity of the proposed model demonstrated in Chapter 4, Figure 4-2, was applicable here, as the relative acidity (the pH value) decreased which is indicative of the increase in the concentration of protons. As it follows from Table 4-2, the loss of the protons from the composite material indicates that the presence of the metal cation does in fact increase the capacity for the sulfhydryl moiety to lose the single acidic proton. Further, equation 6-1, (Palacious et. al., 2001) demonstrates that the coordination of the ligand-based material and the metal ion under study, illustrates that the binding of the metal cation would indeed release a proton and can subsequently be treated with acidic medium to restore the adsorbent material for subsequent extraction studies. This tendency is presumably independent of the type of metal being studied. The use of the modified silica gel using 2-mercaptoethanol, affords a relatively inexpensive environmental cleanup technology for affording a convenient method of selective ion removal of multi-cationic metallic solutions, and the application to other ligands and solid-support materials should indeed be considered. The application of this cleanup technology also has use when utilizing a column as a method of removal of metals from aqueous media. The objective here is that the technology can be used on a much larger and become more portable in order to meet the increasing needs of industrialized and developing populations.

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Chapter Seven

Selected Reactions on the Surface of Silica, Alumina and Aluminosilicates Using Condensation of Bifunctional Compounds and Solid Support

Introduction

Previous work has established the possibility of utilizing known chelating agents, and coordinating agents supported on silica gel, and ion exchange resins reagents (Norris et. al., 1997). These supported reagents were used successfully in the removal of metals designated as toxic or hazardous to wildlife and humans alike. Similarly, heavy metal removal utilizing modified reagents such as silica gel, modified clays such as montmorillonite KSF, modified magnetite, modified polyols and chemically modified carbohydrates such as D-Lactose have been explored as a viable alternative to methods currently in use. These studies revealed the utility of these materials in the removal of toxic heavy metals such as lead, silver, copper and cadmium from aqueous media. Silica gel, has been used as a solid support for various coordinating agents such as alkane thiols and chelating agents such as LIX 54 ® and LIX 860 ® in the removal of heavy metals from standard solutions Norris (1997). The solid support has also been modified using the condensation reactions between the support itself and silane-based materials with amino functionalities (Ali et. al., 2001). Further, the condensation of the solid support and the organic ligand has found a degree of success with siloxy-containing moieties such as (triethoxysilyl)propylamine (Figure 7-1. Kates et. al., 2000).

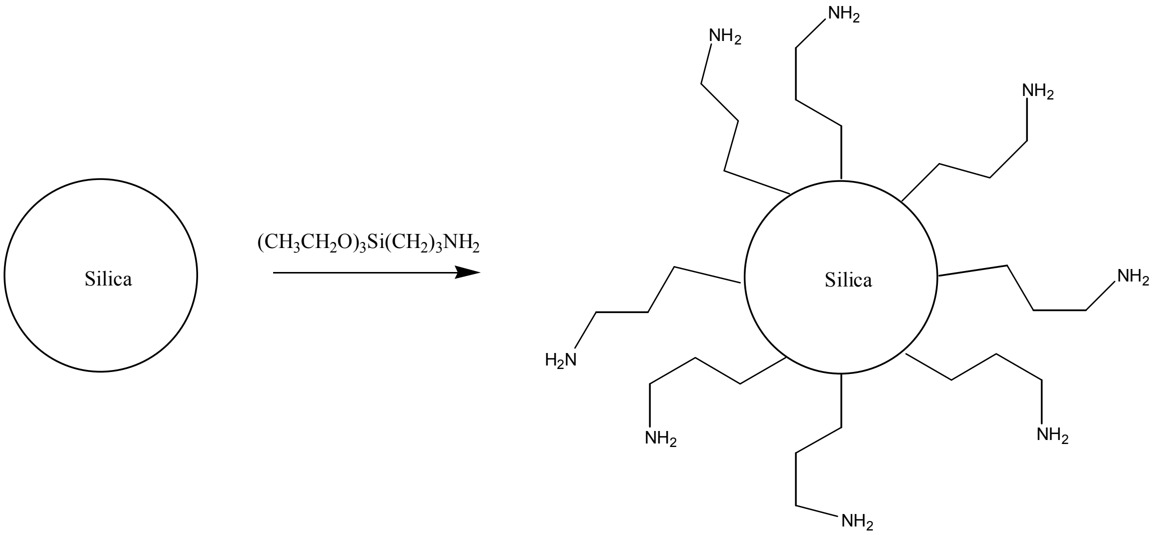

Figure 7-1 Synthesis of silica based organic moieties using silica gel and ethyoxy-amino silated compounds.

These processes were used to attach funtionalities to the solid support for subsequent use in synthesis and could be adapted for use in the field of environmental cleanup technology. The condensation process can be made more efficient by utilsing the azeotropic distillation process commonly used in the preparation of esters in synthetic organic chemistry. The use of the Dean-Stark apparatus facilitates the collection of the water by-product in addition to permitting the researcher to monitor the progress of the reaction by measurement of the loss of this product of the synthesis. The condensation process described in previous work addresses the use of this technique to condense the bifunctional agent, 2-mercaptoethanol with the silica based solid support (Figure 7-1).

The resulting product was used as a coordinating agent to uptake copper(II), cadmium(II), silver(I), nickel(II) and lead(II) ions from standard aqueous solutions. Without adjusting the initial pH, the percent removal observed was better than 90% of the metal ions investigated. A further aspect of this investigation evaluated the use of other solid supports containing the hydroxyl functionality such as polyethylene glycol, D-lactose, hydrated magnetite and montmorillonite KSF. These supports were subjected to the condensation process and the effectiveness of the process itself and the subsequent use of the adsorbent materials were examined. The condensation of bifunctional agents and solid supports has been described and has led to an entirely new and exciting field of synthetic chemistry. Condensation reactions are simple and are effective in utilizing bifunctional compounds that can successfully react with a solid based material with loss of a small molecule such as water (Ali et. al., 2001; Navarro et. al., 1997; Ono et. al., 1997). This is a technology that is not only proven to be beneficial to the synthetic chemist but to the environmental researcher as well. The technique has proven to be a practical, relatively safe and economical approach to the problem of uptake of organic and inorganic toxic substances from fresh water sources.

The application of using clay sorbents in the removal of heavy metals was attempted in wastewater treatment. The use of acid treated montmorillonite facilitated the removal of the heavy metals zinc, copper, and nickel from wastewater (Vengris et. al., 2001). Research has also investigated the use of montmorillonite that was impregnated with organic-based ligands. The use of di-(2-ethylhexyl)phosphoric acid (DEHPA) as a binding ligand was tested with aqueous media. These studies concluded that the use of the binding agent, DEHPA, impregnated within the layers of clay sorbents like montmorillonite KSF, had high chemical sorption and fast kinetics in the uptake of heavy metals such as copper(II) ions (Lothenbach et. al., 1997). Also, the use of sodiumdodoecylsulfate (SDS) as a binding ligand was tested with standard solutions. These studies were performed as a function of relative acidity and concluded that the sorption of metal ions copper(II) and zinc(II) increased as a function of increasing pH units (Vengris et. al., 2001). Most of the investigations reported have been performed on a microscale to prove effectiveness in and improve on the technology. However, the environment does not have microscale problems to improve upon. Thus, an investigation to simulate “real-world” conditions was needed to elucidate whether the technology proven effective in the laboratory is a good candidate for possible macroscale conditions.

Experimental

Materials and methods

Synthesis of modified silica gel using 2-Mercaptoethanol

2-mercaptoethanol, calcium sulfate and concentrated sulfuric acid were obtained from Fisher Scientific and was used without further purification. Toluene, optima grade, was used as the solvent for the synthesis of the modified silica gel and was made anhydrous by utilizing calcium sulfate as a drying agent. The toluene and silica gel, 28-200 mesh, was used without any further modification to the adsorbent.

Silica gel (28-200 mesh, 20 g) was treated with 50 mL of toluene that was pre-treated with anhydrous calcium sulfate. Then a solution of 11.1 grams (0.15 moles) of the 2-mercaptoethanol was dissolved in 50 mL of anhydrous toluene that was added to the silica adsorbent mixture, and four drops of concentrated sulfuric acid was added as a catalyst. The resulting mixture was refluxed for a period of two hours utilizing a Dean-Stark trap apparatus to collect the water by-product. After the reaction was driven to completion the mixture was allowed to cool to room temperature and the solvent was removed by rotatory evaporation.

Analyses

Metal analyses were obtained using a Varian SpectrAA 100 atomic absorption spectrometer coupled to a Mega computer and Hewlett Packard 520C series printer. Five standards, prepared by serial dilution, 0.5 ppm, 1.0 ppm, 2.0 ppm, 5.0 ppm and 10.0 ppm, were used to determine the calibration plot. The spectrometer determined the concentration of the given metal, the concentration of which did not exceed 20 ppm, by the calibration curve**.** Calibrations were performed each time an analysis was made, and a total of five samples were used to calibrate the instrument. Sulfur analyses were performed by Constellation Technology Corporation, Largo, Florida. The elemental analysis was performed on two samples of modified silica gel that had been treated produced in toluene as a solvent. Anal.: S, 15.1%

Removal studies: batch method

Solutions of 1.57 mM of lead(II) nitrate, cadmium(II) acetate, nickel(II) nitrate and copper(II) nitrate were prepared in 1.0-L volumetric flasks. Five 100-mL aliquots of stock solution were used. Modified silica gel (4.0g) was added to each metal solution, and the resulting mixtures were agitated at a rate of 200 rpm in a New Brunswick Scientific Company Model G76 gyrotory water bath (25°C) shaker for two hours.

Results

The metal removal procedure is summarized (Equation 7-l), where $SiO_2\text{-}CH_2CH_2\text{-}SH$ is a representation of the silica gel composite material, containing the thiol-containing moiety combining with a metal cation with loss of protons. Table 4-1, Chapter 4, indicates that the number of protons released as a result of combining the sulfur impregnated composite and a metal cation such as copper(II) demonstrates that there is a correlation between the number of protons released as a product of coordination and the number of available sulfhydryl groups within the silica based composite.

$$SiO_2\text{-}CH_2CH_2\text{-}SH + MX_2 \quad = \quad (SiO_2\text{–}CH_2CH_2\text{-}S)_2M \; + \; 2H^+ \qquad (7\text{-}1)$$

Discussion

The use of silica as a solid support is viable and promotes a wide array of applications. The surface silanol functionality that is present with the silica gel material permits the reaction between this functionality and other substrates much the same way that aliphatic alcohols react with substrate materials. The condensation of an alcohol containing moiety and another alcohol containing functionality is commonplace in synthetic organic chemistry. Our previous work in addition to work that is being done and already completed in the field of synthetic organic chemistry makes use of the hydroxyl functionality in the condensation of the solid support and another functional group. Silanol and aluminol groups, the silicon and aluminum analogs of the carbon-based alcohol, are able to condense with other functional groups in much the same way that the alcohol does in basic organic synthesis. This makes the chemical modification of the solid support much less synthetically complicated. The use of bifunctional agents such as mercaptoalcohols, provides a much more cost effective approach to the chemical modification of the silica gel support than the more commonplace and relatively expensive silyl-complex compounds (Figure 7-2).

$$\mathrm{Si{-}OH} + \mathrm{Si{-}OH} \longrightarrow \mathrm{Si{-}O{-}Si} + \mathrm{H_2O}$$

$$\mathrm{Si{-}OH} + \mathrm{Si{-}OR} \longrightarrow \mathrm{Si{-}O{-}Si} + \mathrm{ROH}$$

Figure 7-2 Condensation reactions using silica gel and organic-based silica materials.

Conclusions

The use of the condensation reaction of the solid support and the bifunctional substrate containing a hydroxyl moiety is a plausible and demonstrated to be an effective approach to the chemical modification of the silica gel support. Further, the use of solid supports containing an aluminol and silanol grouping, such as montmorillonite KSF is too a viable material for chemical modification and subsequent use in the remediation of heavy metals. The hydroxyl functionality promotes the use and future usage of a wide array of solid supports such as oligosaccharides, metallic oxides such as magnetite, and various clays and silica based materials. The use of substrates such as mercapto-alcohols and amino-alcohols, which also contain a hydroxyl functionality, permits the attachment of materials that were not originally prepared for the purpose of using the product composite as an environmental cleanup technology. The attachment of a bifunctional agent to a solid support also has promising synthetic applications that permit the further modification of the material by activation of the terminal end of the modified support.

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Chapter Eight

Overview, Conclusions, Summary

Overview

The scope of this project examined the utility of using modified and physisorbed composite materials in the remediation of heavy metals from aqueous media. We examined the use of a variety of materials to ascertain the effectiveness of not only the materials itself but the ligands that were used as coordinating donors. The versatility of the adsorbents used, silica gel and montmorillonite KSF clay, provides the basis for a project that can not only find promise in industrial processes and waste management facilities but can also find use in underdeveloped countries that are affected by the presence of heavy metals in the aquatic environment. The range of binding agents which have been used to chemically modify the surface of the clay and silica gel materials provides valuable insight into what types of ligands or coordinating donors are best suited for a specific type of adsorbent. The wide array of binding agents used in the amine and mercaptan projects and the relatively low economic cost therein further supports the idea that this technology can be successfully transferred between borders and can also be used in a macroscale environment such as a waste treatment facility. The use of chemically modified adsorbents, silica gel, montmorillonite, magnetite, D-lactose, and polyethylene glycol provide an extraordinary opportunity to provide and environmental cleanup technology which is effective and relatively inexpensive to the manufacture. The use of the modified composites illustrates that at higher concentration levels used in the laboratory that the composites were able to successfully uptake the metal cations selected with no further detriment to the environment than the change in the relative acidity of the aqueous medium. That result can be circumvented by using composite material that was buffered with a solution containing relatively benign anionic counter-ion; such as an acetate buffer. The use of the modified silica gel composite was tested on an eluting column, to emulate industrial conditions and macroscale applications. It was determined that the technology does in fact work without the aid of an external force, that comes from constant agitation of the composite-metal ion mixture. Finally, the use of the chemically modified silica gel composite in the determination of cationic selectivity was investigated. From this investigation there is presumably selectivity involved in having sulfur as the coordinating donor in the silica composite material.

Conclusions

The use of the various composite materials in the uptake of selected heavy metals provides a solid foundation for further investigation in academic and industrial research. We can conclude that whether the solid support is chemically altered or unmodified, the binding agents being held to the support by hydrogen bonding, London dispersion forces or chemical attachment these composites demonstrated a high degree of effectiveness and the technology is very reliable. It has also been demonstrated that the technology itself can be used in the two most common methods, batch and by use of a column. This fact further supports the belief that this is a viable technology that has wide ranging applications not only in industrialized society but also in societies that are affected by pollutants of this type and wide ranging magnitude. Third, the technology has demonstrated that it’s use and effectiveness can also find use in the event that there are multiple metal cations in a polluted source. Selective ion removal is an application that is more applicable to the existing problem and we have demonstrated that the use of chemically modified silica gel is sufficient to selectively target or bind efficiently to a single metal cation over another. We can surmise that the technology here is not only relatively inexpensive but is also highly efficient in the uptake of the selected metal cations.

Summary

The use of the various composite materials in the uptake of selected heavy metals provides not only a solid foundation for further investigation in academic and industrial research but also a promising future for the concentration of selected heavy metals from aqueous media.

The physical adsorption of selected monofunctional binding agents provides a proven basis for the concentration of heavy metals such as cadmium and nickel. Physical adsorption on selected ion exchange materials, such as Dowex X-10, was used with various monofunctional and polyfunctional coordinating agents, such as dithiooxamides, and has proven to be a viable technology. Secondly, the adsorption of coordinating agents on silica-based materials has proven also to be a viable technology utilizing monofunctional aliphatic ligands such as alkane-thiols and dithiooxamides. These binding agents were used successfully in the uptake of selected heavy metals by weak adhering forces such as London dispersion forces. The effectiveness of using aliphatic thiols were tested at higher levels of relative basicity to not only elucidate the reaction pathway but to evaluate the effectiveness of using the silica-supported thiol composite at higher levels of basicity. It was determined that the material could support the higher levels and the effectiveness of the composite to uptake the metal cations increased with increasing value of pH. Selected multidentate binding ligands, such as LIX 54 ® a well-known chelating agent, was supported onto silica gel and used in the uptake of selected heavy metals such as nickel and cadmium. The effectiveness of the material itself was tested at varying levels of relative basicity and it was determined that the binding agent and support were effective at higher levels of basicity.

Physical adsorption using stronger intermolecular attraction such as hydrogen bonding was successfully completed using straight chain aliphatic amines. Studies have proven that silica-based solid supports can be used to effectively bind to nitrogen donors such as alkyl amines and in addition this composite material can be used to remove heavy metals with varying polarizability.

The chemical modification of the selected solid supports, D-lactose, silica gel, magnetite, montmorillonite KSF, polyethylene glycol and chromosorb W permitted the use of and provided a basis for using hydroxyl containing supports and moieties as substrates for simple condensation reactions. The collection of the water by-product not only provided proof that the reaction was indeed plausible, and at the same time provided a viable means for chemically altering the solid support for use in the uptake of the metal cations investigated. We concluded that whether the solid support is chemically altered silica gel or montmorillonite clay, the selected binding agents, 2-mercaptoethanol and 2-aminoethanol, were indeed good economic and synthetic choices for use as substrates. The use of the sulfur analog proved to be more effective as a coordinating donor than the nitrogen analog in part because of polarizability and the fact that the metal cations selected have a higher affinity for sulfur than the nitrogen counterpart. The fact that the reaction between the sulfhydryl moiety and the metal cation is reversible and can be manipulated by basic addition adds promise to an existing and proven successful method of metal cation remediation. The technology itself was demonstrated to be effective in the two most commonly used methods, batch and by use of an eluting column. This fact further supports the contention that this is a very viable and important technology that has wide ranging scientific and consumer applications. Third, the technology has demonstrated that it's use and effectiveness can also find use in the event that there are multiple metal cations in a polluted source. Selective ion removal is an application that is more applicable to the existing problem and we have demonstrated that the use of chemically modified silica gel is sufficient to selectively target or bind efficiently to a single metal cation over another. We can surmise that the environmental cleanup technology here is not only relatively inexpensive but is also highly efficient in the uptake of the selected metal cations. There are limitations if the technology is applied on a wider scale but environmental cleanup technologies are an emergent field in environmental studies and the future of using modified and supported adsorbents are indeed promising.

Appendices

Appendix A:Data Tables

List 1: Base constants for straight chain alkyl amines

IUPAC name [of compound]	Base Constant
methylamine	4.27×10^{-4}
ethylamine	5.01×10^{-4}
propylamine	3.98×10^{-4}
butylamine	5.89×10^{-4}
pentylamine	4.27×10^{-4}
hexylamine	3.63×10^{-4}
heptylamine	4.68×10^{-4}
octylamine	4.47×10^{-4}
nonylamine	4.37×10^{-4}
decylamine	4.37×10^{-4}
undecylamine	4.27×10^{-4}
dodecylamine	4.27×10^{-4}
tridecylamine	4.27×10^{-4}
tetradecylamine	4.17×10^{-4}
pentadecylamine	4.07×10^{-4}
hexadecylamine	4.27×10^{-4}
octadecylamine	3.98×10^{-4}

Appendix A(Continued)

List 2: Formulas of Selected Amines and Mercaptans

IUPAC name of compound	Formula
n-butylamine	$CH_3(CH_2)_3NH_2$
n-hexylamine	$CH_3(CH_2)_5NH_2$
n-octylamine	$CH_3(CH_2)_7NH_2$
n-decylamine	$CH_3(CH_2)_9NH_2$
n-dodecylamine	$CH_3(CH_2)_{11}NH_2$
n-hexadecylamine	$CH_3(CH_2)_{15}NH_2$
1-hexanethiol	$CH_3(CH_2)_5SH$
1-octanethiol	$CH_3(CH_2)_7SH$
1-dodecanethiol	$CH_3(CH_2)_{11}SH$
1-hexadecanethiol	$CH_3(CH_2)_{15}SH$
1-octadecanethiol	$CH_3(CH_2)_{17}SH$

Table 1: Extraction of copper using n-hexylamine

Sample [of silica composite]	%Extraction
1	96.2
2	92.9
3	92.9
4	93.6
5	95.2
Average	94.2
Standard Deviation	1.3
RSD, %	1.4

Appendix A (Continued)

Table 2: Extraction of copper using n-octylamine

Sample [of composite]	%Extraction
1	98.2
2	98.9
3	99.0
4	99.1
5	97.9
Average	98.6
Standard Deviation	0.5
RSD, %	0.5

Appendix A (Continued)

Table 3: Extraction of copper using n-decylamine

Sample [of composite]	%Extraction
1	93.6
2	91.0
3	92.8
4	92.9
5	92.4
Average	92.5
Standard Deviation	1.0
RSD, %	1.0

Appendix A (Continued)

Table 4: Extraction of copper using n-hexadecylamine

Sample [of composite]	%Extraction
1	38.8
2	38.9
3	31.2
4	33.4
5	27.9
Average	34.0
Standard Deviation	4.8
RSD, %	14.1

Table 5: Extraction of cadmium using n-hexylamine

Sample [of silica composite]	%Extraction
1	84.8
2	88.0
3	89.1
4	87.0
5	89.5
Average	87.7
Standard Deviation	1.9
RSD, %	2.1

Appendix A (Continued)

Table 6: Extraction of cadmium using n-octylamine

Sample [of composite]	%Extraction
1	89.5
2	87.7
3	87.3
4	87.8
5	87.5
Average	88.0
Standard Deviation	0.9
RSD, %	1.0

Table 7: Extraction of cadmium using n-decylamine

Sample [of composite]	%Extraction
1	91.2
2	93.6
3	90.8
4	94.2
5	92.8
Average	92.5
Standard Deviation	1.5
RSD, %	1.6

Table 8: Extraction of cadmium using n-hexadecylamine

Sample [of composite]	%Extraction
1	51.5
2	46.4
3	42.4
4	39.0
5	48.1
Average	45.5
Standard Deviation	4.9
RSD, %	10.7

Table 9: Extraction of lead using n-hexylamine

Sample [of silica composite]	%Extraction
1	64.9
2	70.2
3	68.4
4	74.1
5	74.5
Average	70.4
Standard Deviation	3.6
RSD, %	5.1

Table 10: Extraction of lead using n-octylamine

Sample [of composite]	%Extraction
1	86.9
2	85.5
3	86.2
4	86.2
5	84.1
Average	85.8
Standard Deviation	1.1
RSD, %	1.2

Table 11: Extraction of lead using n-decylamine

Sample [of composite]	%Extraction
1	89.7
2	91.0
3	91.7
4	91.7
5	89.0
Average	90.6
Standard Deviation	1.2
RSD, %	1.3

Appendix A (Continued)

Table 12: Extraction of nickel using n-hexylamine

Sample [of silica composite]	%Extraction
1	54.3
2	56.0
3	54.0
4	54.4
5	69.3
Average	57.6
Standard Deviation	5.9
RSD, %	10.2

Appendix A (Continued)

Table 13: Extraction of nickel using n-octylamine

Sample [of composite]	%Extraction
1	49.5
2	53.5
3	52.9
4	54.1
5	55.5
Average	53.1
Standard Deviation	2.0
RSD, %	3.8

Appendix A (Continued)

Table 14: Extraction of nickel using n-decylamine

Sample [of composite]	%Extraction
1	62.9
2	65.8
3	64.7
4	64.9
5	68.1
Average	65.3
Standard Deviation	1.9
RSD, %	2.9

Table 14: Extraction of silver using n-hexylamine

Sample [of silica composite]	%Extraction
1	85.7
2	84.6
3	84.9
4	77.8
5	81.0
Average	82.8
Standard Deviation	3.3
RSD, %	4.0

Table 15: Extraction of silver using n-octylamine

Sample [of composite]	%Extraction
1	90.9
2	91.5
3	92.2
4	91.8
5	91.7
Average	91.6
Standard Deviation	0.5
RSD, %	0.5

Appendix A (Continued)

Table 16: Extraction of silver using n-decylamine

Sample [of composite]	%Extraction
1	90.4
2	90.5
3	91.3
4	90.8
5	90.5
Average	90.7
Standard Deviation	0.4
RSD, %	0.4

Table 17: Extraction of copper using 1-hexanethiol

Sample [of silica composite]	%Extraction
1	27.4
2	43.3
3	21.5
4	22.8
5	24.9
Average	28.0
Standard Deviation	7.9
RSD, %	28.3

Table 18: Extraction of copper using dodecanethiol

Sample [of composite]	%Extraction
1	37.9
2	57.9
3	57.3
4	54.0
5	57.9
Average	53.0
Standard Deviation	7.7
RSD, %	14.5

Table 19: Extraction of copper using 1-hexadecanethiol

Sample [of composite]	%Extraction
1	75.9
2	88.9
3	87.0
4	74.3
5	73.7
Average	80.9
Standard Deviation	7.4
RSD, %	9.1

Table 20: Extraction of copper using 1-octadecanethiol

Sample [of composite]	%Extraction
1	34.7
2	43.2
3	38.5
4	
5	33.0
Average	37.3
Standard Deviation	3.9
RSD, %	10.5

Table 21: Extraction of cadmium using 1-hexanethiol

Sample [of silica composite]	%Extraction
1	95.2
2	92.2
3	99.3
4	89.9
5	96.2
Average	94.6
Standard Deviation	3.6
RSD, %	3.8

Table 22: Extraction of cadmium using 1-dodecanethiol

Sample [of composite]	%Extraction
1	84.2
2	89.1
3	88.1
4	85.7
5	84.1
Average	86.2
Standard Deviation	2.3
RSD, %	2.6

Table 23: Extraction of cadmium using 1-hexadecanethiol

Sample [of composite]	%Extraction
1	92.9
2	89.7
3	86.8
4	88.1
5	91.2
Average	89.7
Standard Deviation	2.4
RSD, %	2.7

Table 24: Extraction of cadmium using 1-octadecanethiol

Sample [of composite]	%Extraction
1	60.6
2	65.5
3	66.0
4	67.0
5	68.5
Average	65.5
Standard Deviation	3.0
RSD, %	4.5

Table 25: Extraction of lead using 1-hexanethiol

Sample [of silica composite]	%Extraction
1	65.8
2	43.6
3	46.2
4	25.6
5	37.6
Average	43.8
Standard Deviation	14.7
RSD, %	33.5

Table 26: Extraction of lead using 1-dodecanethiol

Sample [of composite]	%Extraction
1	65.4
2	64.7
3	64.1
4	64.8
5	60.3
Average	63.9
Standard Deviation	1.8
RSD, %	2.9

Table 27: Extraction of lead using 1-hexadecanethiol

Sample [of composite]	%Extraction
1	64.0
2	63.5
3	60.8
4	60.3
5	61.7
Average	62.1
Standard Deviation	1.5
RSD, %	2.4

Table 28: Extraction of lead using 1-octadecanethiol

Sample [of composite]	%Extraction
1	66.4
2	64.4
3	68.3
4	67.9
5	60.9
Average	65.6
Standard Deviation	2.7
RSD, %	4.1

Table 29: Extraction of nickel using 1-dodecanethiol

Sample [of silica composite]	%Extraction
1	77.2
2	76.5
3	76.2
4	77.8
5	76.9
Average	76.9
Standard Deviation	0.6
RSD, %	0.8

Table 30: Extraction of nickel using 1-hexadecanethiol

Sample [of composite]	%Extraction
1	76.7
2	76.0
3	75.8
4	75.9
5	77.1
Average	76.3
Standard Deviation	0.6
RSD, %	0.7

Table 31: Extraction of silver using 1-hexanethiol

Sample [of silica composite]	%Extraction
1	91.5
2	91.5
3	91.3
4	92.2
5	91.5
Average	91.6
Standard Deviation	0.3
RSD, %	0.4

Table 32: Extraction of silver using 1-octanethiol

Sample [of composite]	%Extraction
1	92.5
2	91.5
3	91.6
4	91.8
5	92.3
Average	91.9
Standard Deviation	0.4
RSD, %	0.5

Appendix A (Continued)

Table 33: Extraction of silver using 1-dodecanethiol

Sample [of composite]	%Extraction
1	91.7
2	89.9
3	91.0
4	90.3
5	91.7
Average	90.9
Standard Deviation	0.8
RSD, %	0.9

Table 34: Extraction of silver using 1-hexadecanethiol

Sample [of silica composite]	%Extraction
1	85.0
2	88.4
3	82.1
4	86.3
5	87.1
Average	85.8
Standard Deviation	2.4
RSD, %	2.8

Table 35: Extraction of silver using 1-octadecanethiol

Sample [of composite]	%Extraction
1	82.5
2	83.2
3	82.2
4	84.1
5	84.5
Average	83.3
Standard Deviation	1.0
RSD, %	1.2

Table 36: Extraction of silver using 2-mercaptoethanol modified silica gel

Sample [of silica composite]	%Extraction
1	93.1
2	91.1
3	89.4
4	88.1
5	89.3
Average	90.2
Standard Deviation	1.9
RSD, %	2.2

Table 37: Extraction of copper using 2-mercaptoethanol modified silica gel.

Sample [of composite]	%Extraction
1	94.4
2	91.8
3	91.9
4	91.1
5	91.5
Average	92.1
Standard Deviation	1.2
RSD, %	1.3

Table 38: Extraction of lead using 2-mercaptoethanol

Sample [of composite]	%Extraction
1	91.7
2	89.9
3	91.0
4	90.3
5	91.7
Average	90.9
Standard Deviation	0.8
RSD, %	0.9

Table 39: Extraction of nickel using 2-mercaptoethanol modified silica gel.

Sample [of silica composite]	%Extraction
1	31.6
2	30.7
3	35.5
4	35.9
5	20.0
Average	30.7
Standard Deviation	6.4
RSD, %	20.9

Table 40: Extraction of silver using 2-mercaptoethanol modified silica gel

Sample [of silica composite]	%Extraction
1	58.8
2	54.6
3	56.8
4	53.6
5	59.0
Average	56.6
Standard Deviation	2.4
RSD, %	4.3

Table 41: Extraction of copper using 2-mercaptoethanol montmorillonite KSF.

Sample [of composite]	%Extraction
1	85.8
2	89.8
3	85.1
4	90.8
5	89.7
Average	88.2
Standard Deviation	2.3
RSD, %	2.6

Table 42: Extraction of lead using 2-mercaptoethanol modified montmorillonite KSF

Sample [of composite]	%Extraction
1	46.3
2	55.5
3	62.0
4	75.3
5	39.8
Average	55.8
Standard Deviation	13.8
RSD, %	24.8

Table 43: Extraction of nickel using 2-mercaptoethanol modified montmorillonite KSF.

Sample [of silica composite]	%Extraction
1	31.6
2	30.7
3	35.5
4	35.9
5	20.0
Average	30.7
Standard Deviation	6.4
RSD, %	20.9

Table 44: Extraction of cadmium using 2-mercaptoethanol modified montmorillonite KSF with the absence of acid catalyzation.

Sample [of silica composite]	%Extraction
1	21.5
2	24.0
3	24.3
4	18.6
5	9.37
Average	19.6
Standard Deviation	6.1
RSD, %	31.4

Table 45: Extraction of cadmium using 2-mercaptoethanol modified montmorillonite KSF.

Sample [of silica composite]	%Extraction
1	96.9
2	98.1
3	98.1
4	97.8
5	97.7
Average	97.7
Standard Deviation	0.5
RSD, %	0.5

Table 46: Extraction of selected heavy metals using 2-mercaptoethanol modified silica gel on a column.

Divalent Metal Cation [of silica composite]	%Extraction
Cu^{+2}	87.9
Cd^{+2}	64.9
Pb^{+2}	15.3
Ni^{+2}	84.7
Ag^{+}	84.4

About the Author

Craig Bowe was born and raised in the beautiful Commonwealth of The Bahamas. He received an education at St. Paul's Methodist College in Freeport, Grand Bahama, where he learned high school chemistry from Mrs. Deidre Murtagh. He enrolled at Huntingdon College located in Montgomery, Alabama, where under the guidance of Dr. Marlene Katz and Dr. Ward Knockemus, he received a bachelor's in Chemistry. He was a technician in the public analyst laboratory, a high school Mathematics teacher, volunteer at the local library and a member of the Bahamas National Trust. He enrolled at the University of South Florida in 1998 to pursue a Ph.D. in Chemistry.

At USF, he was an active volunteer with the AMP program, at UCH hospital and with the Florida 2012 committee. In addition to being the graduate representative for the Chemistry Safety Committee he is co-author on at least three publications in reputable science journals.