USING MAGNETIC EXTRACTANTS FOR REMOVAL OF POLLUTANTS FROM WATER VIA MAGNETIC FILTRATION

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CHAPTER 1

GENERAL INTRODUCTION

1.1 Background and objective of the study

The major purpose of this study is to investigate the feasibility of synthesizing magnetic extractants for the remediation of water contaminated by hydrocarbons, radioactive materials, and heavy metals using magnetic filtration technology. Figure 1-1 is a cartoon that illustrates the concept of the magnetic extraction.

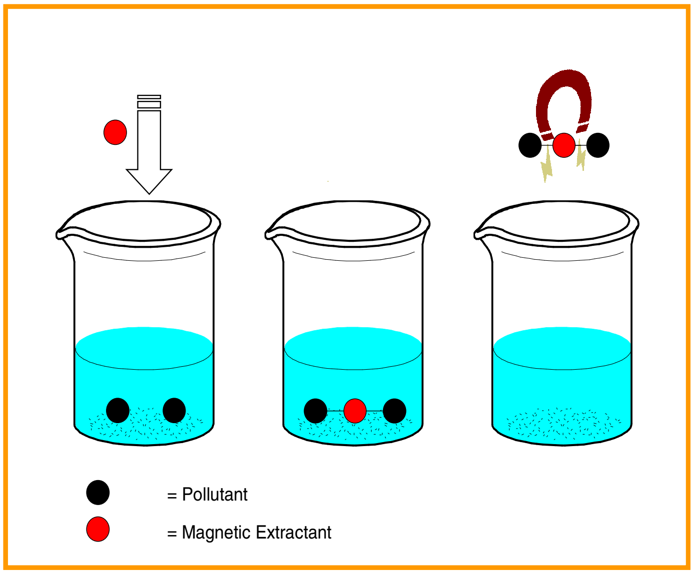

Figure1-1: Cartoon of magnetic extraction

Magnetic filtration can provide very rapid separation of magnetic pollutants from aqueous waste streams. Moreover, it does not pose safety and health problems to workers because of the ability to switch the magnetic filter on and off electronically.

To achieve this goal, a series of laboratory experiments were performed. Most of the environmental pollutants in the water are either non-magnetic or weakly magnetic. First of all, it is necessary for these pollutants to bind to the active site of the magnetic extractants to allow their separation via magnetic filtration. Iron and iron oxides as well as magnetite nanoparticles are used as effective sources of magnetism for the extractants. Their surfaces have been derivitized to provide suitable binding sites for pollutants by using a variety of functional groups. In order to accomplish the goal, the procedure for treating contaminated water follows these steps:

1- Adding magnetic extractant particles to contaminated water.
2- Mixing extractants and water to provide sufficient contact between the contaminants and extractants.
3- Removing magnetic extractants along with adsorbed contaminants from water via magnetic filtration.

1.2 Water Contamination

Almost all aspects of human life depend on water. The existence of humans and virtually all other living things is mainly dependent on water. Indeed, the importance of water to all life on the globe is unquestionably well known. In the next ten years, water will be the cause of conflicts in many areas of the world, and United Nations Secretary-General Kofi Annan said that "fierce competition for fresh water may well become a source of conflict and wars in the future,".[1] Therefore, countries with a shortage of water resources must manage what they have effectively. Three-quarters of the surface of the earth is covered by water, and it is continually recycled in the hydrological cycle of precipitation, infiltration, and evaporation.[2] In the water cycle, water can change states among liquid, vapor, and ice (see Figure 1-2).[3] Water can be on the surface of the earth such as in rivers, seas, and lakes, and it is identified as surface water. Another type of water is beneath the earth, and it is identified as ground-water.

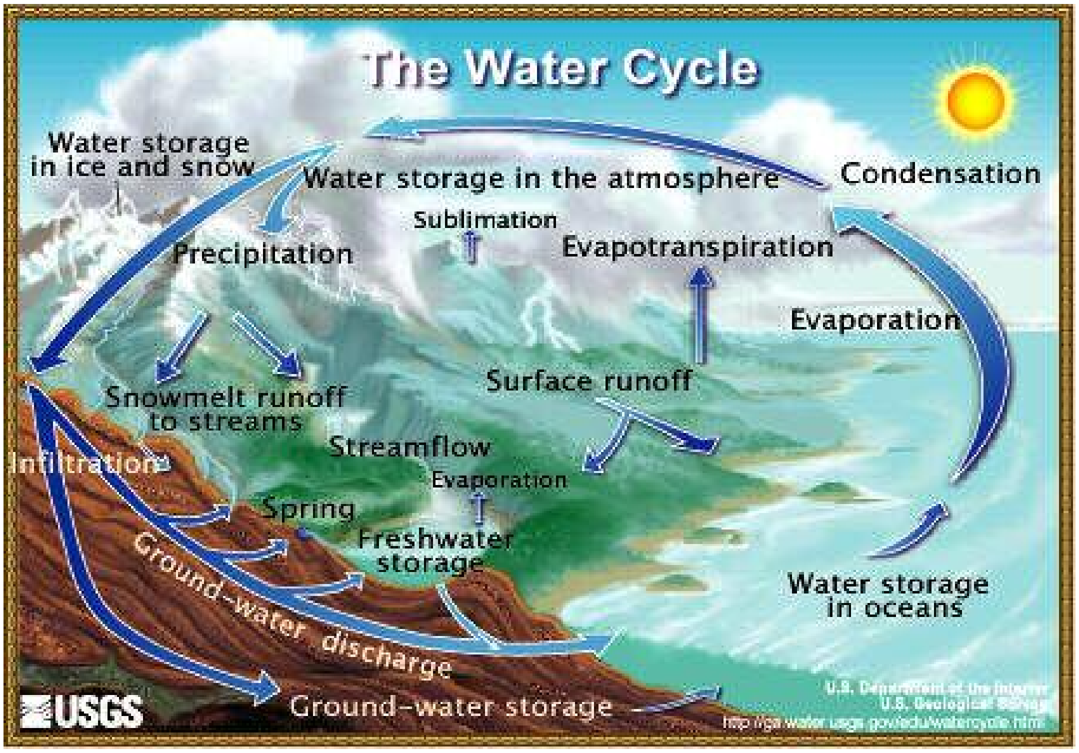

Figure 1-2: The water cycle (from reference 3)

The water composition (concentration of dissolved species and gases) depends on the chemistry of the geological formation through which it has passed since it usually moves slowly and equilibrates with the surrounding environment. The groundwater composition and depth of groundwater and surface water composition differ from place to place and, as a consequence, water quality is quite variable. Water contains many different pollutants that are either soluble or insoluble. The latter materials may easily be removed by many methods, such as filtration, but removing soluble materials requires more sophisticated methods. The aqua system can be contaminated by many things but in this thesis the major focus is on radioactive species, heavy metals, and organic compounds.

For more than a century, awareness has been growing about the dangers posed to human health and the environment by pollutant materials. Human health problems occur when contaminated water is used for drinking, irrigation, and other purposes. Using contaminated water for irrigation would affect plants and soil and eventually lead to human exposure when crops are ingested. Pollutants can be accumulated in the tissues of living organisms, leading to body burdens that pose potential risks of adverse health effects. These pollutants have serious health and environmental effects, which may include many things such as carcinogenicity, reproductive impairment, and developmenttal and immune system changes, and endocrine disruption. Consequently, contamination is the most important issue that gives rise to concerns on local, national, regional, and global scales.

Pollutants in water systems can be, in general, organic, inorganic, heavy metals, and radioactive species. The pollutants present in water can be suspended, dissolved, or colloidal materials. Environmental contamination of the aquatic environment by radioactive species is the most serious hazard, and yet other pollutants also present a significant hazard.[4] There are many sources that have an effect on water quality including industrial discharges, agricultural activities, human mistreatment of hazardous materials, and natural sources.

The United States Congress has passed two laws to protect water, namely the Clean Water Act, and the Safe Drinking Water Act. The former is aimed at protecting surface water and the latter to protection of groundwater and drinking water.[5] The United States Environmental Protection Agency (US. EPA) has listed almost all of pollutants and their maximum contaminant levels (MCLs) on a web page "www.epa.gov/safewater /mcl.html". Standards for roughly 90 contaminants in drinking water are established by the U.S. EPA. The pollutants are classified in groups: microbes, radionuclides, inorganic contaminants, synthetic organic contaminants, volatile organic contaminants, disinfectants, and disinfection byproducts.

The web page of the U.S. EPA states that in an overview of current total maximum daily load (TMDL) Program and Regulations that ˝over 40% of our assessed waters still do not meet the water quality standards states, territories, and authorized tribes have set for them. This amounts to over 20,000 individual river segments, lakes, and estuaries. These impaired waters include approximately 300,000 miles of rivers and shorelines and approximately 5 million acres of lakes -- polluted mostly by sediments, excess nutrients, and harmful microorganisms. An overwhelming majority of the population - 218 million - live within 10 miles of the impaired waters.˝.[6] If the situation in the US is like that, it is worse in the other countries. The importance of protecting our water resources can not be overstated. Some countries, like Saudi Arabia, lack water resources, especially surface water, and, therefore, depend on distilled water produced by desalinization seawater, and groundwater. Distilled water is not practical for irrigation or for industrial purposes due to its high cost, and the major cheaper source of fresh water for irrigation in countries such as Saudi Arabia is groundwater.

1.3 Introduction to Magnetism

The word *magnet* means a stone from Magnesia, a Greek city. Magnetism is generated from the movement of electric charges. Electrons have spins that generate magnetic fields.[7] Generally, all materials with unpaired electrons exhibit magnetism; however most of them display a negligible amount of magnetism.

Electrons govern the magnetic properties of matter by spinning and via the orbital motion of electrons. The spin is a quantum mechanical property and can have value of ±½. That means electron direction is up (+½) or down (-½).[8] No net magnetic field exists in an atom when its electrons form pairs with other electrons. Each electron in a pair spins in the opposite direction, and that cause their magnetic fields to cancel each other.[9] On the other hand, an atom that has unpaired electrons will have a net magnetic field. The flow of charge in a circular current loop also creates a magnetic field. Therefore, electrons circulating around the nucleus of an atom produce atomic current loops which create magnetic fields. However, the magnetic momentum that is created from orbital motion of electrons is very weak and can be neglected when compared with other factors. Any electron in an atom has a magnetic moment because of either its spin or its spin and orbital motion.

The magnetic moment of a material is the measure of the strength of the dipole. There are many magnetization terms required to understand this phenomenon. The magnetic induction or magnetic flux density (B) is related to magnetic field (H) as in the equation 1-1.[10]

$$\mathbf{B = \mu H} \qquad \mathbf{1\text{-}1}$$

In this equation μ is the magnetic permeability, and it has high values for materials that are easily magnetized. Placing a material in an applied magnetic field can induce a magnetic field that is the sum of applied field (H) and the magnetization M as in the equation 1-2.[11]

$$\mathbf{B = \mu H + \mu M} \qquad \mathbf{1\text{-}2}$$

The magnetization is the induced magnetic moment in the material per unit volume. The magnetism of weak magnetic materials is usually measured by magnetic susceptibility. That is the ratio between the magnetization and the applied field as in equation 1-3.[12]

$$\mathbf{\chi = M/ H} \qquad \mathbf{1\text{-}3}$$

Materials respond differently when placed within an external magnetic field depending on many factors such as atomic and molecular structure of the material and the net magnetic field associated with the atoms. The external magnetic field is typically applied by a permanent magnet or by an electromagnet. The materials can be classified by their response to the applied magnetic field into five types: diamagnetic, paramagnetic, ferromagnetic, antiferromagnetic, and ferrimagnetic.[8-12]

Diamagnetic materials have a very weak and negative susceptibility to magnetic fields and they are slightly repelled by an applied magnetic field. Furthermore, the material does not retain the magnetic properties when the external field is removed. Diamagnetism is observed in materials with all electrons paired giving a net spin of zero and, therefore, there is no permanent net magnetic moment per atom. Diamagnetic properties are generated from the orbital motion of electrons under the influence of an applied magnetic field which creates a small magnetic dipole within the atom that is opposite to the applied field. In fact, diamagnetic interactions increase with increasing atomic size. Most elements in the periodic table are diamagnetic.

All of the other types of magnetic behavior mainly depend on unpaired electrons in atomic shells of each atom. Paramagnetic materials are attracted by a magnetic field but do not become permanently magnetized. They have a small and positive susceptibility to magnetic fields. Paramagnetic properties are due to the presence of a number of unpaired electrons and from electron orbital motions caused by the external magnetic field. The paramagnetism requires that each atom have permanent dipole moments even without an applied field. These atomic dipoles do not interact with one another and are randomly oriented in the absence of an external field leading to zero net magnetic moment. Paramagnetic materials do not have long-range order. Paramagnetism and diamagnetism only exist with an applied magnetic field and also they do not retain permanent magnetization without an applied magnetic field.

Ferromagnetic materials can exhibit a spontaneous magnetization without application of an external magnetic field. In the material, microscopic regions with particular alignment of atomic magnetic dipoles are known as domains. If these domains are oriented parallel, this material has ferromagnetism. Ferromagnetism is responsible for the magnetic behavior encountered in everyday human life. In industry, the most important ferromagnetic elements are iron, cobalt, and nickel. On the other hand, if these domains are oriented antiparallel or unequal parallel and antiparallel, the materials are known as antiferromagne-tic and ferrimagnetic, respectively. The last three types of magnetism exhibit a long-range order at the atomic level that depends on temperature. Ferromagnetic and ferrimagnetic materials display paramagnetic behavior above a certain temperature, that is known as the Curie temperature (T_c), because of a thermal agitation. Also, antiferromagnetic materials possess paramagnetic behavior above the Néel temperature (T_N).

When a ferromagnetic material is placed in magnetic field, it will gain a large magnetization. Additionally, it will not relax back to zero magnetization after the applied field is removed. The magnetization of a material will trace out a loop that is known as a hysteresis loop. A hysteresis loop illustrates the relationship between the magnetic induction and the magnetizing force (applied magnetic field). The loop is often referred to as the B-H loop. When the applied magnetic field increases, the magnetic induction increases, following the line abc in the Figure 1-3. Consequently, all magnetic dipoles in the material are parallel with an applied field. That means the material reaches the saturation state, point c. When the applied field decreases until it reaches zero, the magnetization does not follow the same line abc. However, the material retains some magnetic induction that is called ˝remnant induction or magnetization˝ (RM). Indeed, the remnant magnetization requires a magnetic force to decrease to zero which is known as coercive force (CF).

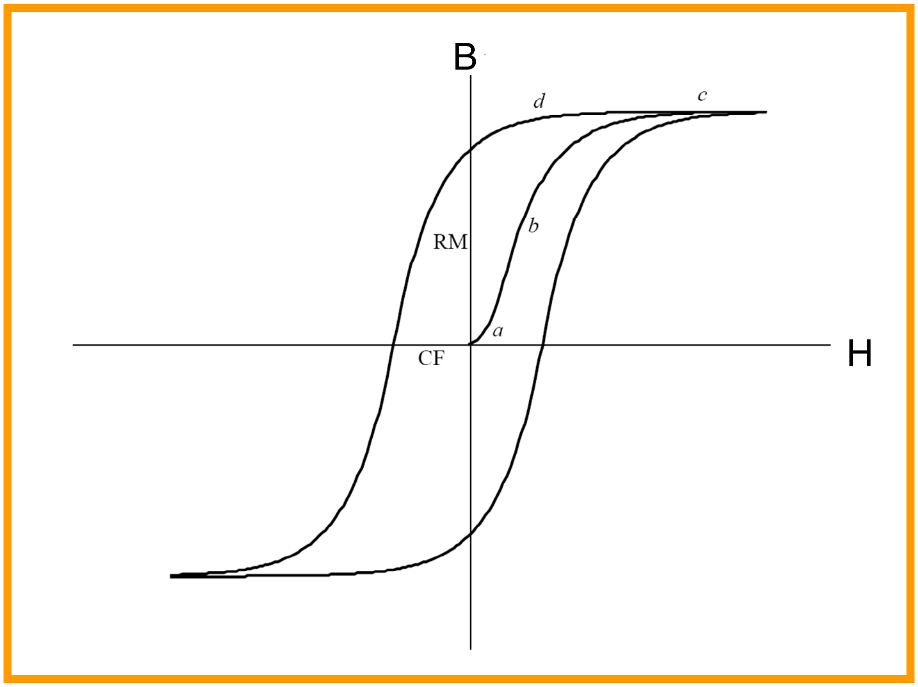

Figure 1-3: The hysteresis loop for ferromagnetic materials

Magnetic properties exhibit a size effect in which the magnetic materials act similarly to paramagnetic materials even at temperatures below the Curie or the Neel temperature. Nanometer scale magnetic particles captured the attention many researcher groups because of their numerous technological applications and their unique magnetic and chemical properties that differ from the bulk materials.[13,14] Magnetic nanoparticles describe particles with size scales from 1 to 100 nm. Superparamagnetism occurs when a ferromagnetic material is composed of very small nanoparticles. Each material has its own range of particle size at which it exhibits the superparamagnetic property.[15] For instance, the critical size of magnetite is less 25 nm.[16] Superparamagnetic materials will not have remnant magnetization when the applied field is removed. The number of domains in a particle decreases with decreasing particle size. At the critical particle size, the particle is a single domain, and it takes very little energy to change the direction of its magnetization that is known as crystalline anisotropy. Moreover, the magnetic induction saturation reaches maximum with lower applied magnetic fields compared with counterpart bulk materials, which results in a large coercive force and a low remnant magnetization.

1.4 Magnetic Filtration

Fundamentally, magnetic separation is a method to remove magnetic materials from non-magnetic materials. Magnetic separation has been developed as a recovery and pollution-control process for many environmental and industrial problems, including treatment of radioactive water,[17] waste water,[18] effluents from steel mills,[19] desulfurization of coal,[20] separation of mining ores and wastes,[21] clay processing,[22] purification of drinking water,[23] and filtration of cooling water in nuclear reactors.[24] Magnetic separation has been used since the nineteenth century but the development of high gradient matrix-type separators has greatly extended the range of applications of magnetic separation and magnetic filtration. There are a myriad of designs of magnetic separators that are capable of filtering out even weakly magnetic particles and there are also numerous methods for their application.[25]

Magnetic separators can be classified based on the strength of the magnetic field to categories of low- and high-intensity separators.[26] Magnetic separators that use magnetic gradient are always known as high gradient magnetic separation (HGMS) devices. HGMS depend on high magnetic field gradient being established inside the filter to capture the magnetic particles. It generally has a matrix of stainless steel wool (ferromagnetic materials) that is placed in a strong magnetic field (up to 20 kOe). When the magnetic field is turned on, a high field gradient is established and attracts very fine, even weakly magnetic particles. The captured particles may be easily washed out from the matrix, when the magnetic field is removed. The magnetic field can be generated by electromagnets or permanent magnets.

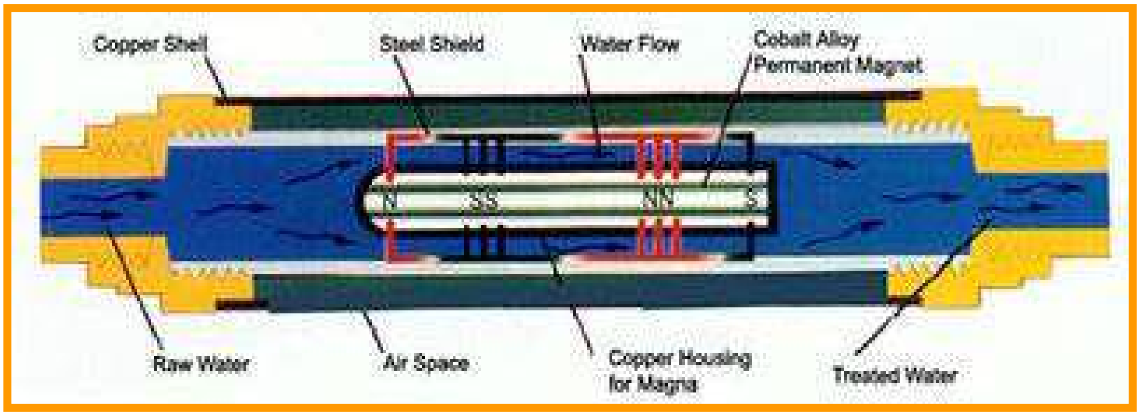

Figure 1-4: A design of a magnetic separator

Recently, HGMS has been applied in environmental processes for removal of non-polar organic,[27] dyes,[28] radioactive materials,[29] and heavy metals contaminants.[30] The technique utilizes magnetic particles bearing suitable functional groups for adsorption of pollutants. The two main components of magnetic filtration are magnetic particles that separate pollutants and the magnetic field used to separate them. The application of efficient magnetic filtration for decontamination and waste treatment operations is attractive because it can provide rapid removal of contaminants from aqueous waste streams. This coupled with the ability to switch the filter on and off electronically (avoiding any need for mechanical contact), allows the minimization of exposure of workers to harmful agents.

1.5 Iron and its Oxides

Iron is the fourth most abundant element in the earth's crust (4.6%), and the most common ores are magnetite and hematite.[31] It is the most used metal in daily life of humans. Generally, iron is classified as a heavy, malleable, ductile, magnetic silver-white transition metal. Iron is an excellent conductor of electricity and heat. The word iron originates from a Latin word ferrum and is symbol abbreviation is Fe. It can be found as oxides or carbonates as hematite (Fe_2O_3), magnetite (Fe_3O_4), and siderite ($FeCO_3$). [32]

The structure of iron is body cubic centered (bcc) at room temperature, and this phase is identified as α-iron. Moreover, it has three more allotropic (beta, gamma, and delta) depending on the temperature and pressure. It adopts a face- centered cubic at temper-atures above 910 °C and is identified as γ-iron. At about 1390 °C, iron is converted back to bcc and is identified as δ-iron. The most common oxidation state for iron is +2 and +3 while the highest oxidation state is +6 in $[FeO_4]^{2-}$ but it is very easily reduced. However, iron fails to have (+8) oxidation state which is its group oxidation state. Fe^{III} has five unpaired d electrons since Fe^{III} compounds are always high spin. Table 1-1 summarizes some properties of iron.[31]

Table 1-1

Some properties of iron

Property	
Atomic number	26
Number of naturally occurring isotopes	4
Atomic weight	55.845(2)
Electronic configuration	$[Ar]3d^4 4s^2$
Electronegativity	1.8
MP/°C	1535
BP/°C	2750
Metal radius (12-coordinate)/pm	126
Density (20 °C)/g cm^{-3}	7.874
Electrical resistivity (20 °C)/μohm cm	9.71

There are six iron oxides that are composed of Fe together with O where iron can be divalent, trivalent, or a mix of both.[31-33] Generally, oxygen ions form close packed arrays (cubic or hexagonal close packing) and iron ions occupy octahedral or tetrahedral sites. Iron in Fe_2O_3 has an oxidation state of three and has four modifications (α, γ, β, and ε-Fe_2O_3). Maghemite (γ-Fe_2O_3) can be found naturally in soils and it is a ferrimagnetic material. Both β and ε-Fe_2O_3 were synthesized in the laboratory and cannot be found nature. Wustite (FeO) has divalent iron, and is oxygen deficient in its structure. Magnetite (Fe_3O_4) has both divalent and trivalent iron. Iron oxides can vary quite notably in color, and this can be used as a tool for their identification and a purity check.

Magnetite and haematite (α-Fe_2O_3) will be used in this thesis and so more detailed will be given below.

Hematite, ferric oxide, can be found naturally as the mineral hematite in rocks and soils. The oxidation state is three, and hematite's formula is written as α-Fe_2O_3.[33] It has the corundum structure where the oxides ions form a hexagonal close packing (hcp) lattice and Fe^{III} ions occupy octahedral holes.[34] Two thirds of the holes are occupied with Fe^{III} ions and this arrangement produces pairs of $Fe(O)_6$ octahedra. In the structure, each octahedra shares edges with three other neighbors in the same plane and shares a face with another one from an adjacent plane. Hematite is ferromagnetic and its Curie temperature is 956 K.[35]

Magnetite can be found naturally as the mineral that is commonly known as lodestone and it is black and ferrimagnetic material.[31,33] It is also known as ferrous ferrate, magnetic oxide, and black oxide of iron. The oxidation state of magnetite is mixture of iron (II) and (III) since it has an inverse spinel structure $Fe^{II}Fe_2^{III}O_4$. Each unit of the crystal structure of magnetite consists of eight iron-II ions, sixteen iron-III ions, and thirty-two oxygen ions.[36] Oxygen atoms form a cubic close packed (ccp) lattice. Iron-II and half of the iron-III ions occupy octahedral holes, while the remaining half of iron-III ions occupies tetrahedral holes. At room temperature, the spins of the cations in the octahedral and tetrahedral holes are antiparallel, and the spin arrangement is written as $Fe^{III}\downarrow[Fe^{III}\uparrow Fe^{II}\uparrow]O_4$. Consequently, magnetite is ferrimagnetic, and its Curie temperature is 850 K.[36]

1.6 Silicon and Siloxane Agents

Silicon is extremely abundant in the earth's crust (about 20.5%). Silicon sits in the third row as a member of group 14 of the periodic table. Silicon atoms have three natural isotopic forms (^{28}Si, ^{29}Si, ^{30}Si), with ^{28}Si being the most abundant (92.18%).[31] The oxidation state of silicon is (+ 4). Tetrahedral coordination is the most common structure adopted by silicon compounds, but there are compounds that have penta- and hexa-coordinated silicon atoms.[37] Elemental silicon is a semiconductor and has a great affinity for oxygen. The Si-O bond has significant covalent character and has high stability.[38]

Silicon is always found in nature as an oxide and as silicates. The most abundant compound of silicon in the earth is silica. Common phases of silicon are quarts or cristoballite. Both phases consist of three-dimensional networks of SiO_4 tetrahedra.[39] Silicon is tetra-coordinated by oxygen to form SiO_4 tetrahedra. These tetrahedra act as building blocks to build up a polymeric structure by sharing one or more vertices of the SiO_4 tetrahedron. They have many structures, depending on how many SiO_4 tetrahedron vertices participate in the structure, such as chains, sheets, or isolated anions. [31]

Silica is often synthesized using a sol-gel process.[40] Sol-gel processes are generally described as preparation of a suspension of a solid in liquid, followed by densification of the solid and removal of the liquid. Conventionally, silica is prepared from tetraalkoxysilane [$(RO)_4Si$, where R= CH_3O or C_2H_5O].[41] The sol-gel process is described by two reactions, hydrolysis and condensation.[42-44] In the hydrolysis reaction, alkoxide groups are replaced by hydroxyl groups (formation of silanol groups Si-OH) as in Equation 1-1. Hydrolysis reactions are started by the addition of water to the reaction under acidic, basic, or natural conditions. Since silanes are not soluble in water, organic solvents are used.

$$\equiv\mathrm{Si{-}OR} + \mathrm{H_2O} \rightleftharpoons \equiv\mathrm{Si{-}OH} + \mathrm{ROH} \qquad \text{1-1}$$

Condensation reactions occur via two pathways to produce siloxane bonds as illustrated in equations 1-2 and 1-3. At this point, a silanol group can react with another silanol group or with alkoxide group to produce siloxane bonds and expel water or alcohol molecules, respectively. As the number of siloxane bonds increases, the siloxane can aggregate to form a network.

$$\equiv\mathrm{Si{-}OH} + \equiv\mathrm{Si{-}OH} \rightleftharpoons \equiv\mathrm{Si{-}O{-}Si}\equiv + \mathrm{H_2O} \qquad \text{1-2}$$

$$\equiv\mathrm{Si{-}OH} + \equiv\mathrm{Si{-}OR} \rightleftharpoons \equiv\mathrm{Si{-}O{-}Si}\equiv + \mathrm{ROH} \qquad \text{1-3}$$

Silicones (or siloxanes) are defined to be materials that contain a silicon-oxygen bond, in addition to an organic group or hydrogen. Silicones play a significant role in heterogonous catalysis,[45] nanotechnology,[46] and photoimaging.[47] They have great thermal and chemical stability because of the strength of the Si-C bond and the disiloxy (Si-O-Si) linkages. Polymerization of siloxanes leads to important polymeric materials (polysiloxanes) that have been commercially available since early 1940s. The repeat unit of polysiloxanes contains silicon, oxygen, and two organic groups or two hydrogen atoms (see Figure 1-5).[48]

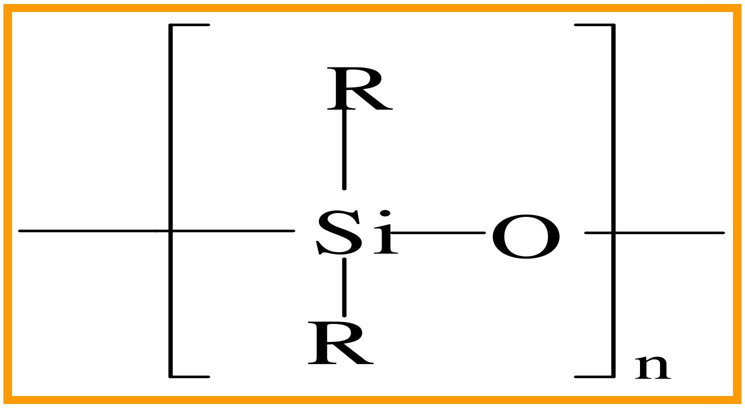

Figure 1-5. Polysiloxane repeat unit

The general formula of a silsesquioxane is $(RSiO_{3/2})_{2n}$, where R= hydrogen or any organic group.[49] Scott's group was first to describe the first organosilsesquioxane in 1946.[50] Since that time many research groups have reported syntheses of a vast number of organosilsesquioxanes. Silsesquioxanes have three subclasses: the first one is a functional silsesquioxane that has one or more functional groups such as amino, epoxy, mercapto, and vinyl.[51] The next class is a nonfunctional silsesquioxane that do not have functional groups. In these materials all silicon atoms are usually bonded to alkyl or aryl groups. The last one is a bridged polysilsesquioxane that has an organic fragment as an integral component of its three-dimensional network. Generally, silsesquioxanes are formed with cross-linked Si-O bonds and their structures can be random, ladder, cage, or partial cage as illustrated (Figure 1-6).[51]

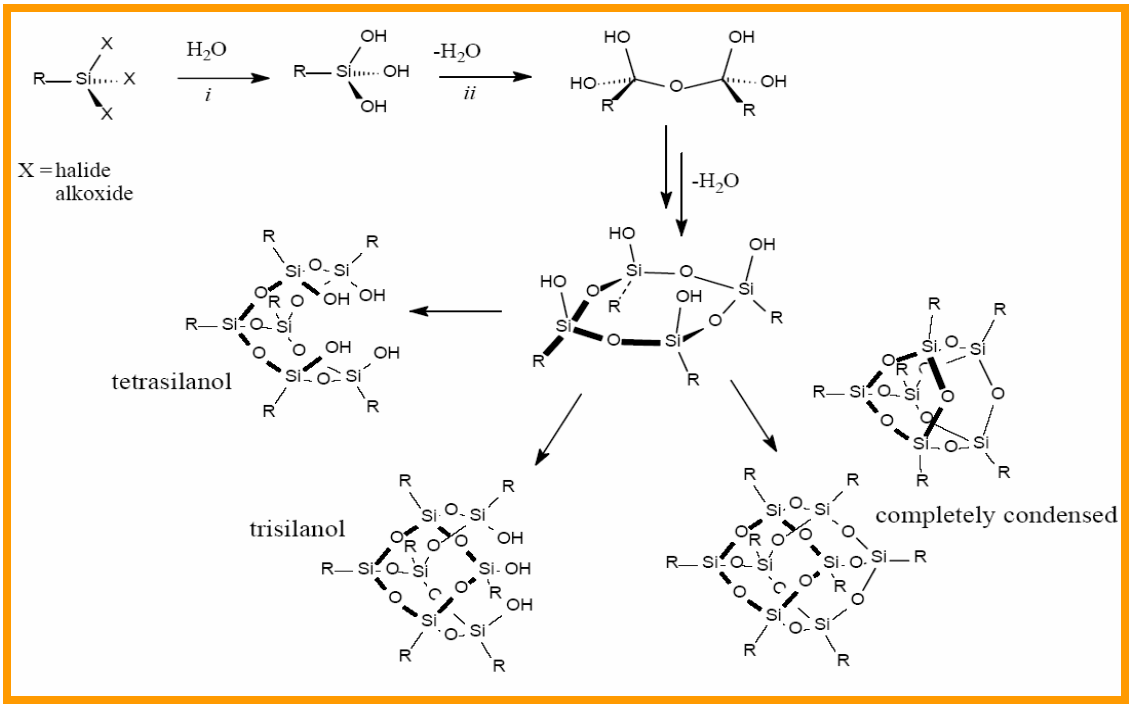

Figure 1-6 Silsesquioxane syntheses and types.

The preparation of silsisquioxanes depends on the sol-gel process and leads to completely condensed and incompletely condensed (silanol groups). Generally, silsesquioxane synthesis consists of a multi-step hydrolysis condensation reaction of the corresponding trifunctional organosilicon $RSiCl_3$ or $RSi(OR)_3$ (Scheme 1-3).[51] Such steps lead to completely condensed and incompletely condensed (silanol groups). The first step (i) is hydrolysis of a precursor with water, and the second step (ii) is a condensation of the result from first step. The second step determines the size and type of the product.

Using silsesquioxanes as a ligand for transition-metal and main group elements leads to metallasilsesquioxanes.[45] The Feher group was first group to synthesize metallasilsesquioxanes in 1986.[46] Since than, many research groups have reported the synthesis of numerous metallasilsesquioxane complexes. Ormosils differ from silsesquioxanes that every second silicon atom is substituted by organic group and the general formula is $(RSi_{1.75}O_3)_n$. The word ormosil is originated from organically modified silica.

1.7 Scope of the Dissertation

In this thesis, magnetic extractants will be synthesized by functionalization of the surface of magnetic substrates with different siloxane and silane reagents. This thesis consists of five chapters. The first chapter presents the aim of the study, and a general introduction to some related fundamental subjects to the study. The next three chapters focus on synthesis of the extractants and their applications for removal of pollutants from water. The final chapter will conclude the study and the future work.

The second chapter will focus on the syntheses of many extractants based on iron, hematite, and magnetite. These extractants will aim for removing hydrocarbons and other organics from water so that their surfaces have hydrophobic character. Magnetite nanoparticles will be synthesized and used as a source of magnetism in the third and fourth chapter. Magnetite particles are functionalized by different functional groups such as amine and thiol groups. Further, their ability is tested for the removal of radioactive species and heavy metals from water. Removal of uranium species from aqueous solution is performed in the third chapter. The fourth chapter focuses on the removal of copper and mercury.

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CHAPTER 2

Removal of Hydrocarbons Pollutants from Water by Using Magnetic Filtration

2.1 Introduction

This chapter discusses the development of magnetic extractants for use in removing hydrocarbons and other organics from water. Pollution with this species since all countries, particularly industrialized ones, uses mainly crude oil and coal to meet their tremendous requirements for energy. Also, vast tons of organic chemicals are produced annually. All of these are stored or transported from one place to another by pipelines or tankers and can contaminate water systems due to leakage of pipelines and storage tanks, spills, improper transportation and disposal, as well as other ways. Sudden oil spills happen on a daily basis throughout the world. Contamination of water by hydrocarbons can originate from various sources. Hydrocarbons and their derivatives are found throughout nature and hydrocarbon pollutants can be formed by biological degradation of organic substances.[1] Contamination of water by organics is a widespread problem, especially in industrial and agriculture sites.[2] In addition, organic pollutants are persistent in subsurface water and groundwater, and they can migrate from one place to another.

The term hydrocarbon represents any compound that is composed entirely of carbon and hydrogen. Hydrocarbon compounds are a branch of organic chemistry, and they are the parent of other organic compounds. They are classified as either open-chain or cyclic, and both of these groups are also sub-divided into saturated and unsaturated compounds. Carbon atoms in saturated hydrocarbons have the maximum number of bonded hydrogen atoms. On the other hand, unsaturated compounds have a deficiency in the required number of hydrogen atoms compared to the number of carbon atoms. Open-chain compounds are composed of one or more carbon atoms, and the carbon atoms are joined to each other by covalent bonds. The chain may have one or more side branches. Cyclic hydrocarbons are made up of three or more carbon atoms that form one or more closed rings. The stability of hydrocarbons is due mainly to the inertness of C-C and C-H bonds.

Open-chain compounds are divided according to their chemical structure into three main groups. Firstly, the alkane group, also called the paraffin group, is considered saturated since all bonds between carbon atoms are single bonds. In this group, the compounds are somewhat unreactive, and the lighter compounds are gases, the intermediate molecular weight compounds are liquids, and the heavier compounds are semi-solids or solids. The alkene, or olefin family, contains unsaturation in which there is at least one double bond between two carbon atoms. Alkene compounds are more reactive than alkanes. The physical appearances of this family range from gases to liquids to solids with increasing number of carbon atoms. Last of all, the alkyne family is chemically a very active system and has a triple bond between two carbon atoms.

Cyclic hydrocarbons can be saturated or unsaturated compounds. The saturated cyclic hydrocarbons are called cycloalkanes, and they are more reactive than their open-chain counterparts. The previously mention hydrocarbons (alkanes, alkenes, alkynes, and cycloalkanes) are called aliphatic hydrocarbons. The most well-known family of unsaturated cyclic hydrocarbons is the aromatics that have special stability and properties because of a closed loop of electrons. Thus, a molecule with $2n + 2$ delocalized π electrons is considerably stabilized.[3] Aromatic compounds are the second most abundant class of organic compounds on earth. The most well-known aromatic is benzene, C_6H_6, which has six π electrons. Indeed, the benzene ring is recognized as the back-bone of the family of aromatic compounds. Aromatics containing several rings are called polycyclic aromatic hydrocarbons (PAHs).

Hydrocarbon pollutants can be a mixture of aliphatic and aromatic hydrocarbon compounds. They may be classified based on their origin to being petrogenic, pyrolytic, and biogenic. This means that they can be from petroleum inputs, partial combustion of fuels and burning of grass, or biosynthesis by marine and earthly organisms, respectively. These contaminants can be present in water as a non-aqueous phase liquid (NAPL) or as dissolved contaminants. Most of the contaminants originate from crude oil, and they are known as total petroleum hydrocarbons (TPH). TPH is a complex mixture of aliphatic and aromatic hydrocarbons that are divided into fractions that have similar chemical properties.[4] TPH composition varies in the environment, and its toxicity will depend on the composition. Furthermore, TPH compositions in the aqueous environment continuously change because of weathering due to physical, chemical, and biological processes such as volatilization, dissolution in water, and biodegradation.[5] The definition of dissolved organic carbon (DOC) is that which will pass through a membrane with pores of 0.45 μm size. DOC has a concentration in the range of 0.1- 115 mg l^{-1}.[6]

The most threatening hydrocarbons to an aquifer are BTEX and PAHs. BTEX refers to the monocyclic compounds benzene, toluene, ethylbenzene, and xylene. Generally, organic contaminations can be classified to two groups: i) volatile organic compounds (VOCs) and ii) semivolatile organic compounds (SVOCs). The definition of VOCs by the U.S. Environmental Protection Agency (EPA) is any organic compound with vapor pressure over 0.01 kPa at 25 °C and includes alkyl, aromatic, and halogenated hydrocarbons. On the other hand, SVOCs include larger hydrocarbon molecules such as pesticides. In the United State, a study of volatile organic compounds (VOCs) shows that the U.S. Environmental Protection Agency drinking water criteria is exceeded in 6.4% of 2,948 sampled wells.[7]

The potential threat of hydrocarbons in the environment towards human health is well documented. The hazard varies from one location to another and depends on the composition of the pollutant. Some hazards to humans will be briefly mentioned. Hydrocarbons are capable of inducing cancer in human and animals. Benzene can cause leukemia, and vinyl chloride causes liver sarcomas. Most hydrocarbons are considered carcinogenic or probable carcinogens to humans, due to their potent carcinogenicity in animals. Moreover, they can have adverse effects on the nervous system. For instance, hexane and trichloroethylene can harm the peripheral nervous system. Furthermore, hydrocarbon materials may be harmful to skin, they can be cardiovascular toxicants, and they may affect male and female reproductive systems.

Numerous methods (physical, chemical, and biological) have been proposed for the decontamination of polluted water and many research groups still search for improved remediation processes. These methods include biological treatment and physical-chemical treatments such as air stripping, chemical oxidation, and using granular activated carbon.[8] Each method has advantages and some drawbacks. For example, in the biological treatment, microorganisms are used to remove organics where organic contaminants can be biodegraded aerobically[9] or anaerobically.[10] Indeed, this method is widely used in industrial wastewater treatment. However, the biological treatment is sensitive to environmental conditions (temperature, pH, and concentration of organics). Conditions have to be optimal otherwise the procedure will be slow. Moreover, not all organic compounds can be easily biodegraded.[11]

Chemical oxidation of contaminated water is a well-known technology that converts organic contaminants to carbon dioxide and water or to non-hazardous or less toxic materials.[12] Oxidizing agents, such as ozone, potassium permanganate, chlorine, and hydrogen peroxide are used to oxidize organic contaminants.[13] Although, it is a powerful process, it still needs refinement. Any reducing agents used to treat water can react with oxidizing agents. Consequently, larger quantities of oxidizing agents are required. Furthermore, more toxic compounds may be produced if chlorine and/or ozone are used as the oxidizing agent.[14] Wet air oxidation is a useful process for removal of organic materials from wastewater streams. Oxidizing agents, such as oxygen, nitric acid, or ammonium nitrate can convert the contaminated water with organics to carbon dioxide.[15] Unless there are excesses of organics that are able to be oxidized, the NO_x byproduct may affect the efficiency of the processes.[16]

Research is in progress to find facile methods to remediate contaminated water. Air stripping technology is used to remove volatile organic compounds from water by increasing the surface area of the contaminated water exposed to air.[8] It is simply a technique of passing air through contaminated water which enhances the mass transfer of volatile contaminants from water to the air. Nonvolatile organic compounds can not be easily removed efficiently. Another problem with this method is the volatile contaminants will pollute the air. Activated carbon can be used to adsorb the volatile pollutants but this is costly.[17]

Sorption is a physical process by which the pollutants are physically adsorbed onto the surface of an adsorbent. Activated carbon is the most widely used adsorbent material and is available in both powder and granular form. Commonly, granular activated carbon (GAC) is used as an adsorbent for removal of organic compounds from groundwater and industrial waste streams. There is still a need to effectively recover pure water from contaminated water by a system that is economical to operate, requires little equipment, has no harmful impact on the environment, and does not pose safety and health problems to workers.

Magnetic separation has been demonstrated to be useful for separation of hydrocarbons or oil from water and minerals. An example is in coal beneficiation using magnetic fluids that are composed of magnetic particles, a suspending agent, and a carrier solvent that selectively wets the contaminant particles (oxide minerals in the case of coal).[18] One method for removing oils from water is to mix magnetite so that the oil is absorbed onto the surface of the magnetic powder.[19] However, an extremely large amount of magnetite was used [ratio of 40 Fe_3O_4:1 oil (fatty acid) by weight] and the magnetic filtration reduced the oil from 500 ppm to 2 ppm. This method is not applicable for the removal of normal hydrocarbons from water. For example, when the same approach was applied to a 3000 ppm B-heavy oil in a water emulsion, the final concentration of oil was only reduced to 57 ppm.[20]

This thesis addresses methods to synthesize appropriate magnetic extractants to eliminate hydrocarbons from water via magnetic filtration. All hydrocarbon pollutants are well known non-magnetic substances. Therefore magnetic extractants as filtering aids must be developed that can bind contaminants and allow their magnetic separation. Several different materials were used to coat iron, magnetite, or hematite to enhance their absorption of hydrocarbons.

2.2 Experimental

All reagents were ACS reagent grade and were used without further purification. Iron, magnetite and hematite were employed. Silane reagents, such as octadecyltrimethoxysilane, tetramethoxysilane, and 3-glycidoxypropyltrimethoxysilane, were used. Also, two different polydimethylsiloxane (PDMS) oils were used, namely a low viscosity (10 centistokes material) and a moderate viscosity material (1000 centistokes). Other reagents were used such as 1-hexadecylamine. Figure 2-1 illustrates the siloxane reagents and other reagents used in the research.

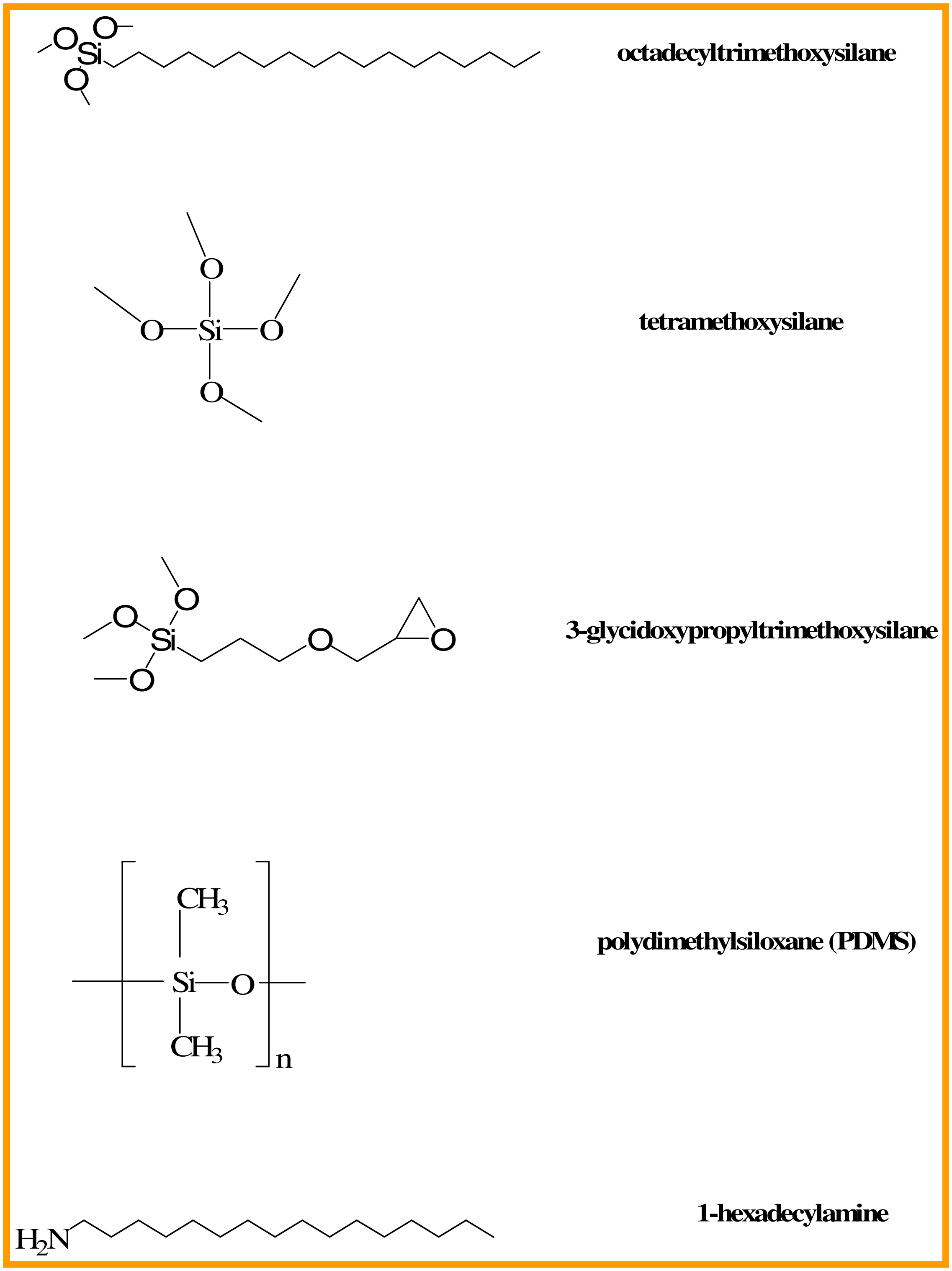


Figure 2-1: Reagent structures

For dye removal, Congo Red and Bromothymol Blue dyes were used [see Figure 2-2 for their structures]. Water was purified by reverse osmosis and deionization. Toluene, xylene, and decane were HPLC grade and were used as received.

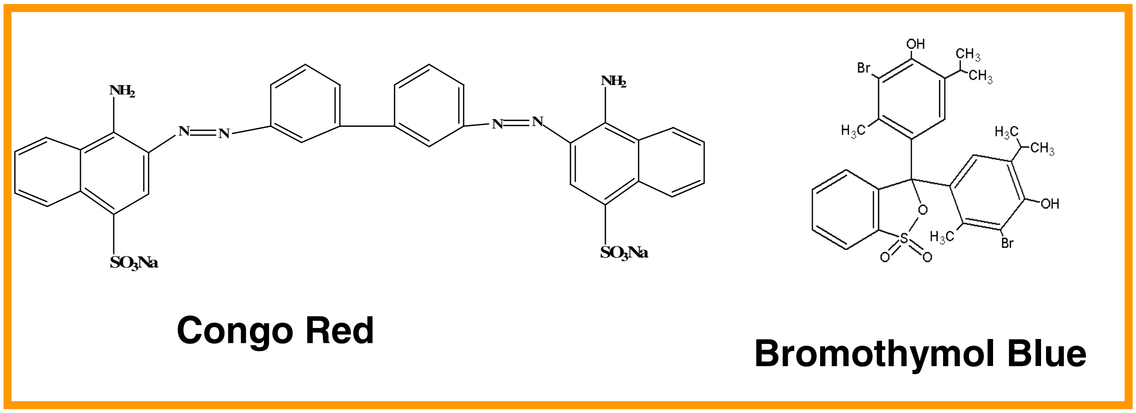


Figure 2-2: Structure of dyes

Fourier Transform Infrared (FT-IR) spectra were recorded at room temperature in the region of 4000-400 cm^{-1}. IR spectra were collected by diffuse reflectance of a ground powder diluted with potassium bromide on a Nicolet Magna-IR 750 spectrometer. The surface areas were measured with a Quantachrom Nova 1200 surface area analyzer, via a nitrogen adsorption isotherm, using the Brunauer- Emmett- Teller (BET) method, and six points in the range of 0.05 to 0.30 P/P_o. Magnetic filtration was performed using glass pipets packed loosely with steel wool (# 00 fine grade) and taped to the side of an electromagnet. The latter magnet was a 24 V extended-reach-electromagnet with a 170 pound pull and dimensions of 3″ x 1″x 1.4″. The electromagnet was powered by a 30 watt direct current power supply. Gas chromatograph/mass spectroscopic analysis (GC/MS) for decane was performed on a Hewlett Packard G 1800A instrument equipped with 30 m x 0.25 mm HP5 column (crosslinked 5% PhMe silicone). The temperature program used was an initial hold of 2 min at 35 °C, a ramp of 5 °C/min to 170 °C, and a final hold of 5 min. The helium flow rate was 1 ml/min and the injection port was set at 250 °C. The mass spectrometer was used in the selective ion monitoring mode with the parent ion of the decane (m/e = 142 a.m.u.) being observed. UV-visible spectroscopy was performed on an HP 8453 UV-visible spectrometer using a quartz cell with a 10 mm path length. Thermogravimetric analyses were performed using a Seiko EXSTAR 6000 TG/DTA 6200 instrument. The temperature was ramped from 25 °C to 700°C at a rate of 5 °C/min under a 50 ml/min flow of dry air. The sizes of oil droplets in emulsions were measured by dynamic light scattering on a Malvern HPPS dynamic light scattering instrument.

2.3 Preparation of Extractants

Preparation of Octadecylsilsesquioxane - Coated Iron, Magnetite, and Hematite

Iron powder (30 g) was treated with water (17.0 g) in order to introduce hydroxyl groups, and was then dried at room temperature. This iron was then mixed with a solution of octadecyltrimethoxysilane (1.0 g) in toluene (20 g) overnight. Afterwards, the derivativized powder was isolated by filtration, washed extensively with toluene to remove unattached molecules, and dried in vacuo.

The preparation of octadecylsilsesquioxane coated magnetite was performed using the same procedure as for iron but without the pretreatment with water.

The preparation of octadecylsilsesquioxane coated hematite was preformed by mixing hematite powder (30 g) with a solution of octadecyltrimethoxysilane (1.0 g) in toluene (20 g) at 100 °C overnight. The derivative powders were isolated by filtration, washed extensively with toluene, and dried in vacuo.

Preparation of Silica - Coated Iron, Magnetite, and Hematite

Iron (saturated with water), magnetite, and hematite powders (30 g) were treated with a solution of tetramethoxysilane (1.0 g) in toluene (20-25 g) at 100 °C overnight. Afterwards, the derivativized powders were isolated by filtration, washed extensively with toluene, and dried in vacuo.

Preparation of 3-Glycidoxylpropylsilsesquioxane - Coated Iron, Magnetite, and Hematite

Iron (saturated with water), magnetite, and hematite powders (30 g) were added to a solution of 3-glycidoxypropyltrimethoxysilane (1.0 g) in toluene (20-25 g) and the resulting mixture was heated at 100 °C overnight. The derivative powders were washed extensively with toluene in a Soxhlet rextractor and were then dried in a vacuum at room temperature.

Preparation of 3-Glycidoxylpropylsilsesquioxane Modified - Coated Magnetite

Magnetite powder (30 g) was placed in a hybridization tube along with a solution of 3-glycidoxypropyltrimethoxysilane (2.0 g) in xylene (50 g). The mixture was heated to 100 °C for 24 hours while rotating in a hybridization oven. The derivativized powder was isolated by filtration, washed extensively with xylene, and dried in vacuo. The material (26.42 g) was treated with a solution of 1-hexadecylamine (2 g) in xylene (50 g) in a hybridization tube. The mixture was then heated to 100 °C for 6 hours while rotating in a hybridization oven and was then isolated by filtration, washed extensively with xylene, and dried in vacuo.

Preparation of Polydimethylsiloxane / Iron, Magnetite, or Hematite Composites

Equal weights (4g of each) of a low viscosity PDMS (PDMS-10) or a moderate viscosity PDMS (PDMS-1000) were stirred with iron, magnetite, or hematite powders. The resulting mixture was heated at 280 °C for an hour. Afterwards, the material was washed with toluene in a Soxhlet extractor to remove any unattached PDMS and was then dried in a vacuum oven at room temperature.

2.4 Testing of Magnetic Extractants

Testing of Magnetic Extractants for Hydrocarbons Removal from Aqueous Solution

A suspension of approximately 500 - 700 ppm decane was prepared by stirring the required amount of decane with 250 g of water overnight. GC/MS analysis was used to determine the actual concentration of decane. The testing of the ability of the extractants to adsorb decane was performed by mixing 20 g of decane stock suspension with 0.5 g of extractant for two hours. After filtration, 6 g of the filtrate was extracted by 1 g of hexane and vigorous shaking for 5 minutes. Finally, the hexane layer was analyzed for decane by GC/MS.

Testing of Magnetic Extractants for Dye Removal from Aqueous Solution

30 ppm solutions of Congo Red and Bromothymol Blue dye were prepared by mixing the required amount of dye with 100 ml of water. The pH of the Bromothymol Blue solution was adjusted to 4.0. The testing of extractant ability was performed by mixing 7 g of dye solution with 0.2 g of extractant for two hours. After magnetic filtration, the resulting solution was analyzed for residual dye by UV/Visible spectroscopy. Dye concentrations were calculated using a calibration curve constructed from serial dilutions of the dye over the range of interest.

2.5 Results and Discussion

The main goal for this part of the study was to separate hydrocarbons and other organic compounds from contaminated water via magnetic filtration. Various magnetic extractants with a Varity of functional groups were synthesized by using siloxane polymers and organosilane reagents. The materials that were used as the magnetic core were iron, hematite and magnetite. Two methods were used to graft the hydrocarbons binding sites on the metal surface. In the case of organosilanes, the grafting was accomplished by mixing the reagent with iron or iron oxides at low temperature. Thermal treatment was used in the case of siloxane polymers. Using a temperature at which siloxane chains undergo scission / recombination reactions via radical processes. Reaction of the radicals with the oxide surface lead to binding of the PDMS to the magnetic core.

Several different organosilane reagents were explored to introduce diverse groups such as octadecyl, methoxy, and glycidoxylpropyl groups. Silane reagents introduce reactive sites onto the surface of iron and iron oxides that act as binding sites for hydrocarbon contaminants. It is reported that silane reagents are able to link covalently to a silanol-covered surface.[21] In general, organosilane reagents were condensed with each other and with surface hydroxyl groups on the metal surface. Iron and iron oxides were mixed with a toluene solution of organosilane in an anhydrous system at low temperature. This reaction led to composite materials that consisted of two components. The first was the iron, magnetite, or hematite that offered magnetic properties to composite materials. The second phase was a layer of polymerized silsesquioxane that coated the metal particles. Figure 2-3 illustrates the reaction between the iron or iron oxides and the alkylalkoxysilane reagents.

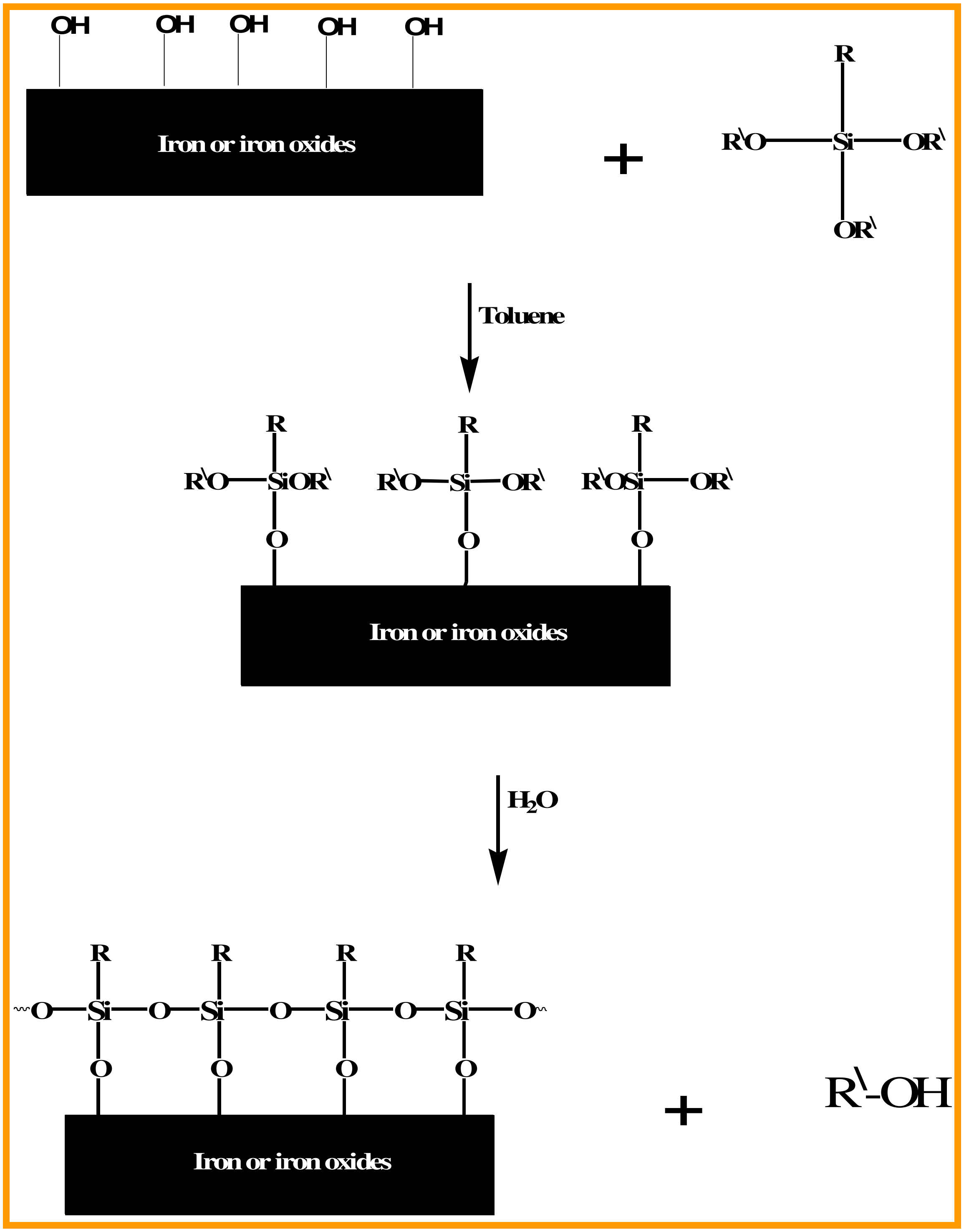


Figure 2-3: Cartoon exemplifying the reaction between the reagents and the metal

In this case, alkoxy groups on the organosilane reagents react with hydroxyl groups on the metal surface liberating alcohol (R\OH) molecules. Subsequently, the silane molecules react with water and cross-link with each others by a siloxane bonds (Si-O-Si) that form a network of siloxanes. Since the alkyl groups (R) are not hydrolyzed they become grafted to the metal surface via the siloxane network. Therefore, the surfaces of the metal particles are coated with a monolayer of silsesquioxane of the general formal $(RSiO_{1.5})_X$. Lower temperatures and non-aqueous solvents decrease the hydrolysis and condensations of the alkylalkoxysilanes in solution.

In this procedure, water was not used for the hydrolysis of alkylalkoxysilane reagents, and the reaction is sealed from moisture to prevent the extensive cross-linking. Indeed, alkylalkoxysilane molecules are very sensitive to water. As soon as they are exposed to moisture, they will begin to hydrolyze and condense. The hydrolysis of the silane reagents depends on the ability of the silane to adsorb water from surrounded atmosphere during preparation since the synthesis was not performed under an inert gas. Before use, iron metal powder was stirred in oxygenated water to induced formation of a thin film hydroxylated oxide (FeOOH) on its surface and thus provides the means for the silane reagents to attach to iron at low temperature.

Octadecyltrimethoxysilane (OTMS) has the octadecyl group ($-C_{18}H_{37}$) and three methoxy groups bound to the silicon center atom. The methoxy groups can readily condense with the surface hydroxyl groups on the iron or iron oxides surface subsequent exposure to humidity in the air leads to further hydrolysis and condensation of the remaining methoxy groups. This condensation leads to an octadecylsilsesquioxane coating on the particle surfaces. Thus, the extractant surface has pendant octadecyl groups that facilitate removal of hydrocarbons from water. The infrared spectra of octadecylsilsesquioxane/iron, magnetite or hematite show strong peaks around 2918 cm^{-1}

and 2850 cm^{-1} and between 1528-1467 cm^{-1}. That are due to the $–CH_2$ and $–CH_3$ groups of the octadecyl chains. Two peaks at 1029 cm^{-1} and 1150 cm^{-1} distinguish the Si-O bond stretches.

Another reagent that was used is tetramethoxysilane (TMS) which can react with surface hydroxyls to replace the protons with trimethoxysilyl groups. Further hydrolysis upon expose to humidity in air is expected to lead to complete hydrolysis of methoxy groups to form mainly silica since methoxy groups are highly reactive groups toward hydrolysis and condensation. Usually TMS is a good candidate for use in preparation of silica. However, the silica formed in such a manner is expected to maintain a small amount of hydroxyl and methoxy residues.

The IR spectra of silica/iron, hematite, or magnetite extractants show a strong Si-O peak around 1100 cm^{-1} that is more intense than that observed for other extractants. Thermogravimetric analyses of these extractants shows no weight loss that can be indicative of the elimination of organic groups. For example, the thermogravimetric analysis trace of silica/hematite, shown in Figure 2-4, shows almost no major changes in weight over the range from 25 °C to 600 °C.

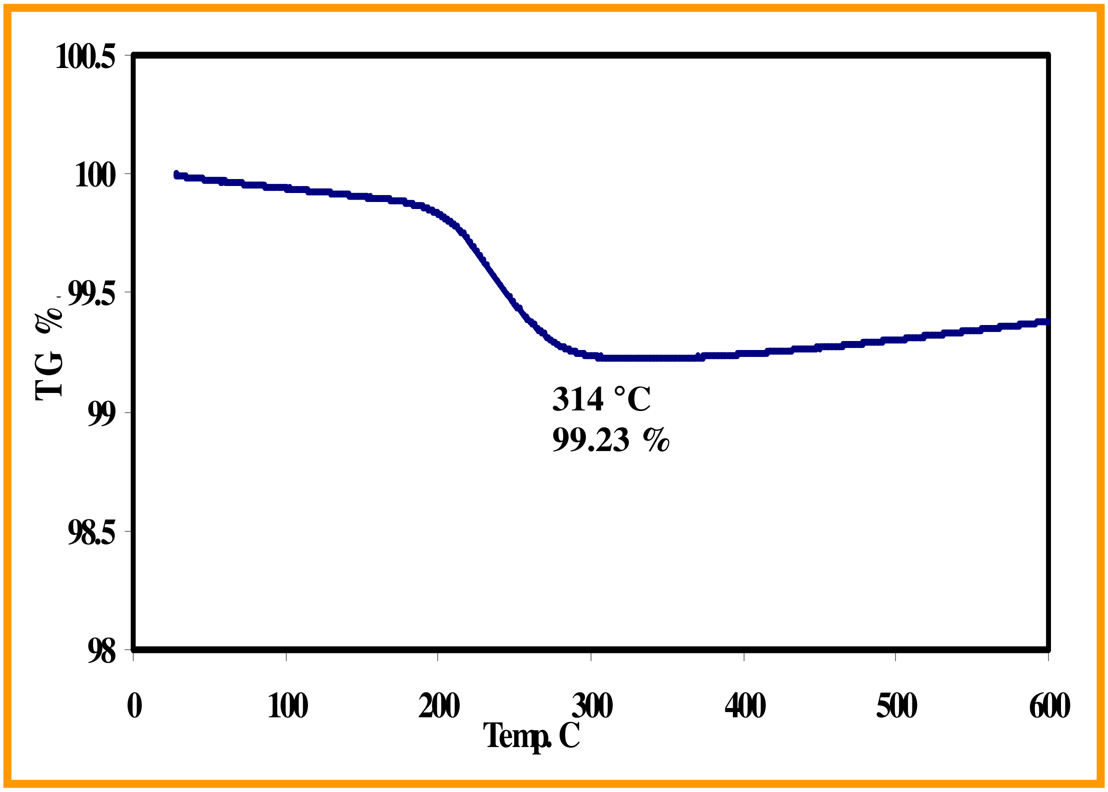
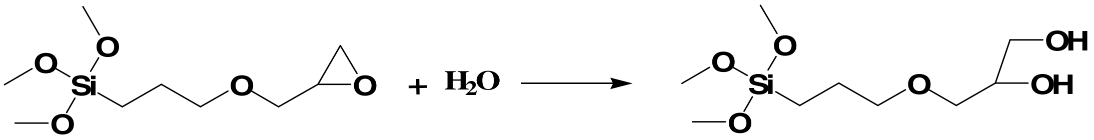


Figure 2-4: Thermogravimetric analysis trace of silica/hematite

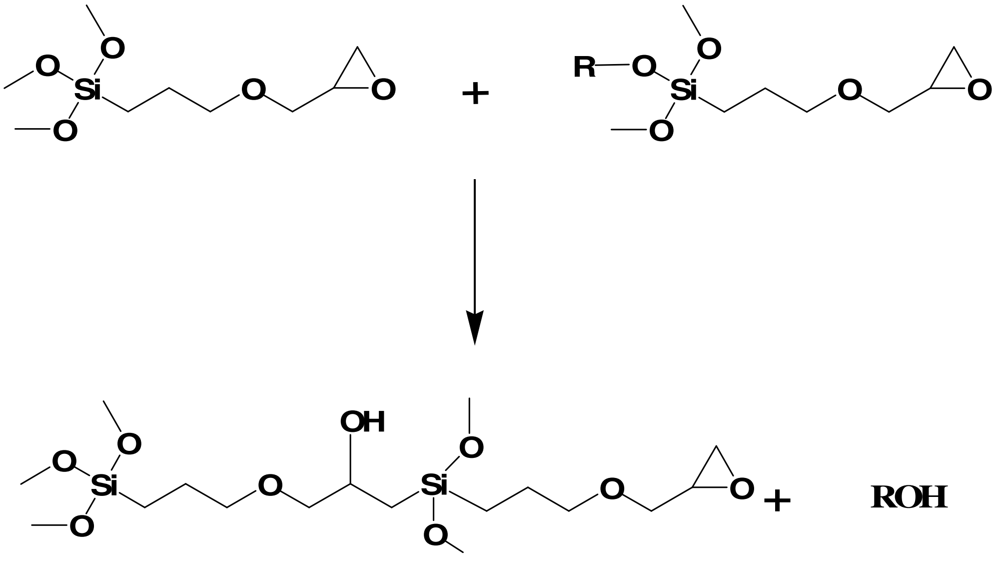
Slight weight loss of 0.77 % is likely due to dehydroxylation of silyl groups. This indicates that the material is composed of namely silica and hematite. That TGA data indicate that the surface of iron and iron oxides that coated by using TMS are mostly coated by silica that sustain a tiny number of hydroxyl and methoxy residues, and the reaction resulted in almost complete condensation.

In 3-glycidoxypropyltrimethoxysilane reagent (GTMS), three methoxy groups are bound to the silicon center atom besides the glycidoxypropyl group. GTMS is reported to be a good coupling agent for immobilization of biomolecules.[22] In the same way, methoxy groups condense and lead to a monolayer of silsesquioxane coated iron or iron oxides that are predicted to be $[(C_6H_{11}O_2)SiO_{1.5}]_X$. The glycidoxypropyl group has an epoxide ring that undergoes ring opening in water to produce a diol (two hydroxyl groups) as in equation 2-1.



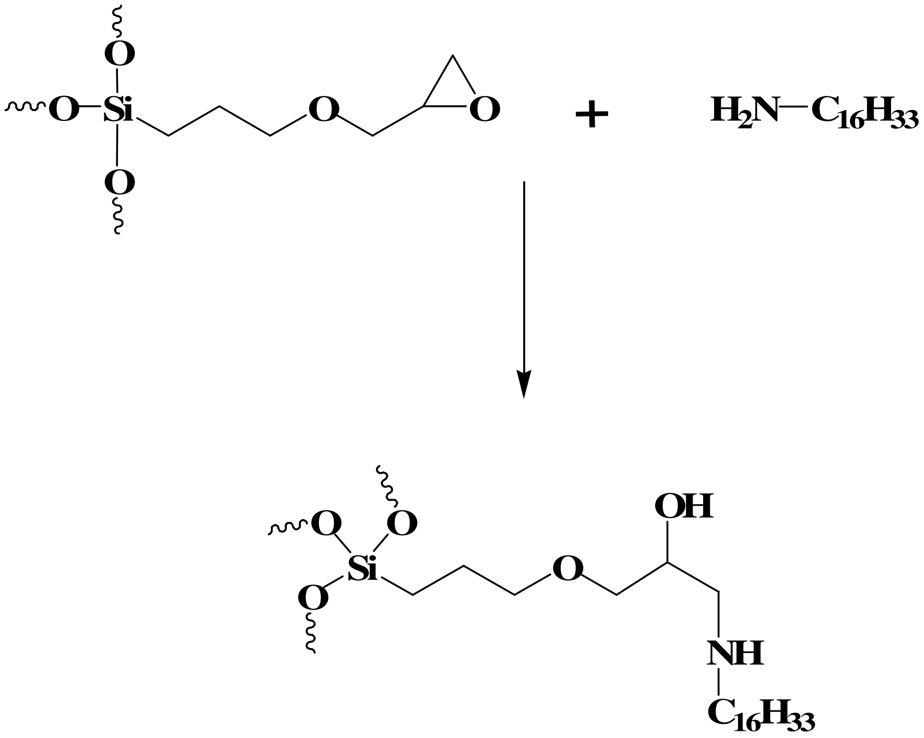
2-1

Therefore, the reaction system has to be tightly sealed from moisture or unwanted reactions can take place that may affect the R group in the GTMS molecule such as polymerization.[24] Transesterification can occur between two GTMS molecules as shown in Equation 2-2.[23] It is believed that the intermediate is a ring-opened diol.



2-2

A modified 3-Glycidoxylpropylsilsesquioxane /magnetite extractant was prepared by taking advantage of the epoxide ring in GTMS molecules to attach a large hydrophobic aliphatic group (hexadecyl group, $C_{16}H_{33}$). The epoxide ring is reactive toward nucleophiles such as amines, alcohols, and acids. Thus, reaction with 1-hexadecylamine results in attach of the epoxide ring by the amine group and attachment of an octadecyl group to the magnetite particle. Equation 2-3 illustrates the reaction.

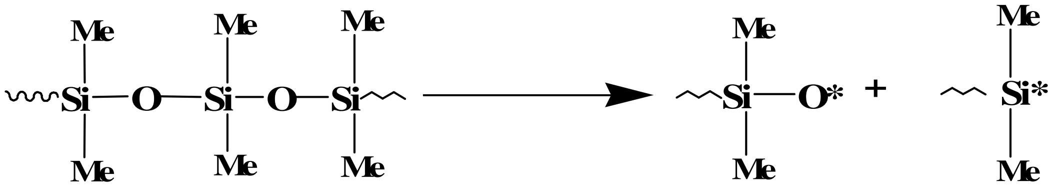


3-2

The second method used for preparation of magnetic extractants was generation of composites of PDMS with iron or iron oxides by a thermally-induced radical process. Polydimethylsiloxane (PDMS) fluids have linear chains of formula $[-SiMe_2O-]_n$ where n varies from 3 to 10,000 repeating units. PDMS used in this investigation has an average molecular weights of 1,000 g/mole and chain length approximately 15 units long. The second PDMS used in this investigate was a 1000 cSt oil that has an average molecular weight of 28,000 g/mole and an average chain length of 378 siloxanes.

The synthesis procedure involved impregnating iron or iron oxide particles with PDMS, followed by a thermal treatment at 280 °C. This leads to cross-linking and attachment of the PDMS polymer to the surface of the magnetic substrates. This procedure was adapted from work of the Soares group where composite materials of PDMS with iron (III) and aluminum oxide and calcium carbonate where prepared.[25] PDMS coatings were targeted because it was previously reported that PDMS is a good sorbant for phenanthrene.[26]

The PDMS was activated by being heated at 280 °C in the presence of air. That led to siloxane chain opening which produced reactive Si—and O—terminal groups [see Equation 2-4]. These radicals subsequently reacted with hydroxyl groups on the metal surface. The active groups also cross-link with each other forming branches and larger chains. The low viscosity PDMS [10 centistokes] yielded homogenous, thinly-coated powders while the moderate viscosity PDMS [1000 centistokes] generated a rubbery composite. The latter extractant has a thicker PDMS coating than the former due to the larger molecular weight of the starting materials.



$$\sim\underset{\mathrm{Me}}{\overset{\mathrm{Me}}{\mathrm{Si}}}-\mathrm{O}-\underset{\mathrm{Me}}{\overset{\mathrm{Me}}{\mathrm{Si}}}-\mathrm{O}-\underset{\mathrm{Me}}{\overset{\mathrm{Me}}{\mathrm{Si}}}\sim \longrightarrow \sim\underset{\mathrm{Me}}{\overset{\mathrm{Me}}{\mathrm{Si}}}-\mathrm{O}^{*} + \sim\underset{\mathrm{Me}}{\overset{\mathrm{Me}}{\mathrm{Si}}}{}^{*} \qquad \textbf{2-4}$$

The infrared spectra confirmed the coating PDMS on the surface of iron and iron oxides. For instance, the IR spectra of the composites that were coated by moderate viscosity PDMS show absorption band sat about 2960 cm^{-1} and 1260 cm^{-1}that can be assigned to CH_3 and Si-C stretches, respectively. Also, two peaks at about 1100 cm^{-1} and 1050 cm^{-1} distinguish the Si-O bond stretches.

The thermogravimetric analyses studies show high thermal stability of the synthesized extractants coated by PDMS with the degradation step of the PDMS coating starting at 350 °C. For instance, in Figure 2-4, the thermogravimetric analyses trace of PDMS-1000/hematite, shows two noticeable weight loss regions. The first weight loss region occurs between 25 °C and 195 °C and was a small transition, which the second region occurred above 350 °C and was the main, large transition. The small transition can be assigned the loss of water and / or hydroxyl species. The main transition started at 350 °C and was clearly assigned to the loss of methyl groups [about 5.9% of the weight] due to oxidation. The final residual weight of 94.0% at 552 °C can be assigned to hematite coated by silica, SiO_x.

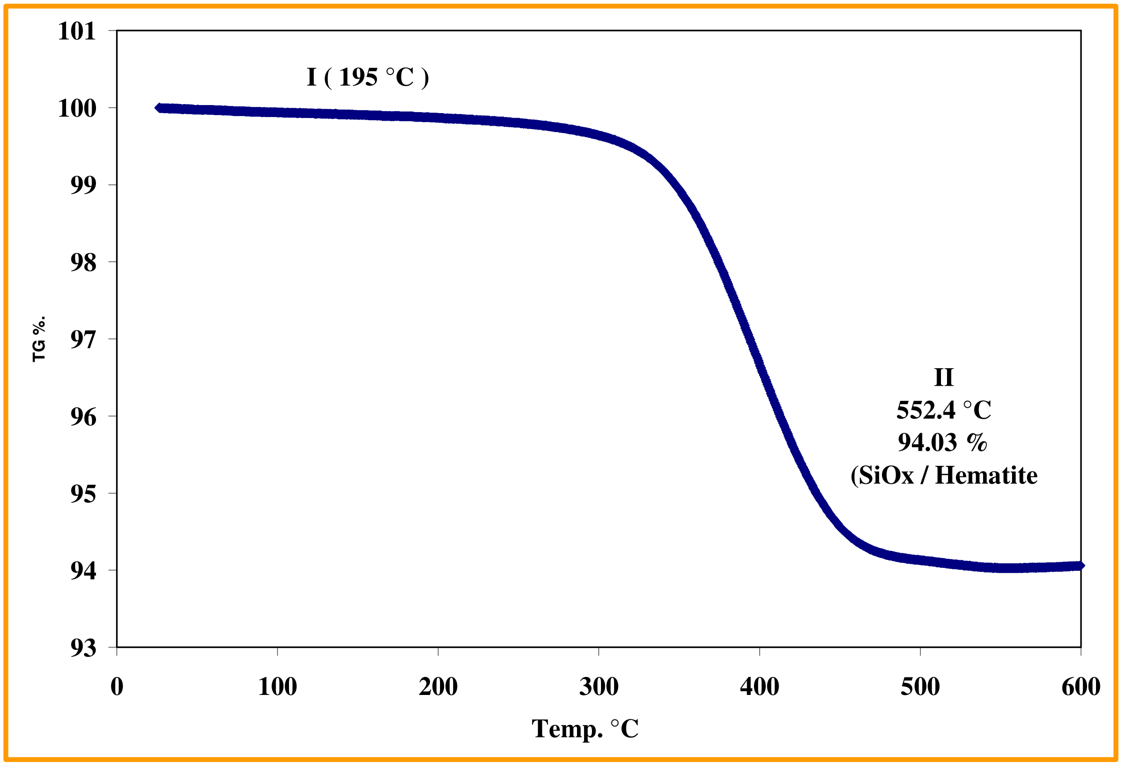


Figure 2-5: Thermogravimetric analysis trace of PDMS-1000/hematite

The thermogravimetric analysis studies of magnetic extractants coated with PDMS were conducted at 800 °C and the results are listed in Table 2-1. The percentage of PDMS coating was estimated based on the repeat unit of PDMS $[SiO(CH_3)_2]_n$. The amount of coating increases with the increasing viscosity of PDMS. The ability of the substrate to be coated decreases in this sequence iron, magnetite, and hematite. This likely reflects the amount of reduce ion {Fe(0) or Fe(II) } available to initiate radical reactions that graft the siloxane to the substrate.

Table 2-1

Result from the thermogravimetric analysis studies of magnetic extractants coated with PDMS.

Extractant	%Weight lost	% coating of PDMS
PDMS-10/Iron	5.96	14.7
PDMS-10/magnetite	4.14	10.2
PDMS-10/Hematite	2.33	5.7
PDMS-1000/Iron	13.68	33.8
PDMS-1000/magnetite	7.40	18.3
PDMS-1000/Hematite	5.78	14.3

Testing of Magnetic Extractants for Hydrocarbons Removal from Aqueous Solution

The testing of the extractants for removal of hydrocarbons was performed using a suspension of approximately 600 ppm decane. Decane was selected as a representative for hydrocarbons. In general, hydrocarbons are not soluble in water as the golden rule of solubility states “like dissolve like”. Water is a polar solvent, and hydrocarbons are non-polar solutes. However, hydrocarbon compounds do have finite solubilities although they may be very low. The definition of solubility is the maximum amount of solute that can dissolve in certain amount of solvent at a certain temperature. From the definition, the amounts of solute that exceed the solubility will make a separate phase in the mixture. As an example, the solubility of decane is 52 ± 4.3 ppb or μg/l which means only about 52 μg of decane dissolves in a liter of water.[27] Additional decane might be expected form a separated non-aqueous phase and this phase will float above the aqueous phase due to decane density. However, decane readily forms stable emulsions in water leading to conflicting reports of its water solubility.

To challenge the synthesized extractants, an oil/water dispersion process was used to prepare a suspension of decane to test the ability for removal of decane from water.[28, 29] In this investigation a concentration of decane was chosen that provided both dissolved and homogenously dispersed decane. Using this mixture allowed the assessment of the magnetic extractants to remove dissolved hydrocarbons and break oil and water emulsions. The decane stock suspension was prepared in a sealed vessel by stirring the required amount of decane with 250 g of water overnight. The resulting mixture was clear and did not have two separate phases [see Figure 2-6]. The decane mixture was stored sealed in a refrigerator.

Figure 2-6: Photograph of the decane stock solution

Standard solutions of decane in hexane were prepared and were analyzed for decane by GC/MS. These standards were used to determine the decane concentration in samples by calculation of the response factors from peak areas in the GC/MS spectra. The actual concentration of the decane stock solution was determined by extraction of 6 g of the solution with 1 g of hexane. The hexane layer was than analyzed for decane by GC/MS. The decane stock solution was not stable indefinitely and had to be freshly prepared. Decane droplets slowly aggregate and form a separate floating phase of decane on the water surface. The droplet size and the size distribution were estimated by using dynamic light scattering (DLS). Figure 2-7 shows the DLS results on the decane solution after stirring overnight. Droplets averaged 7.03 µm and the polydispersity index (PDI) was 0.763. High PDI indicated a wide polydispersity which meant the solution contained droplets with widely different sizes of diameters.

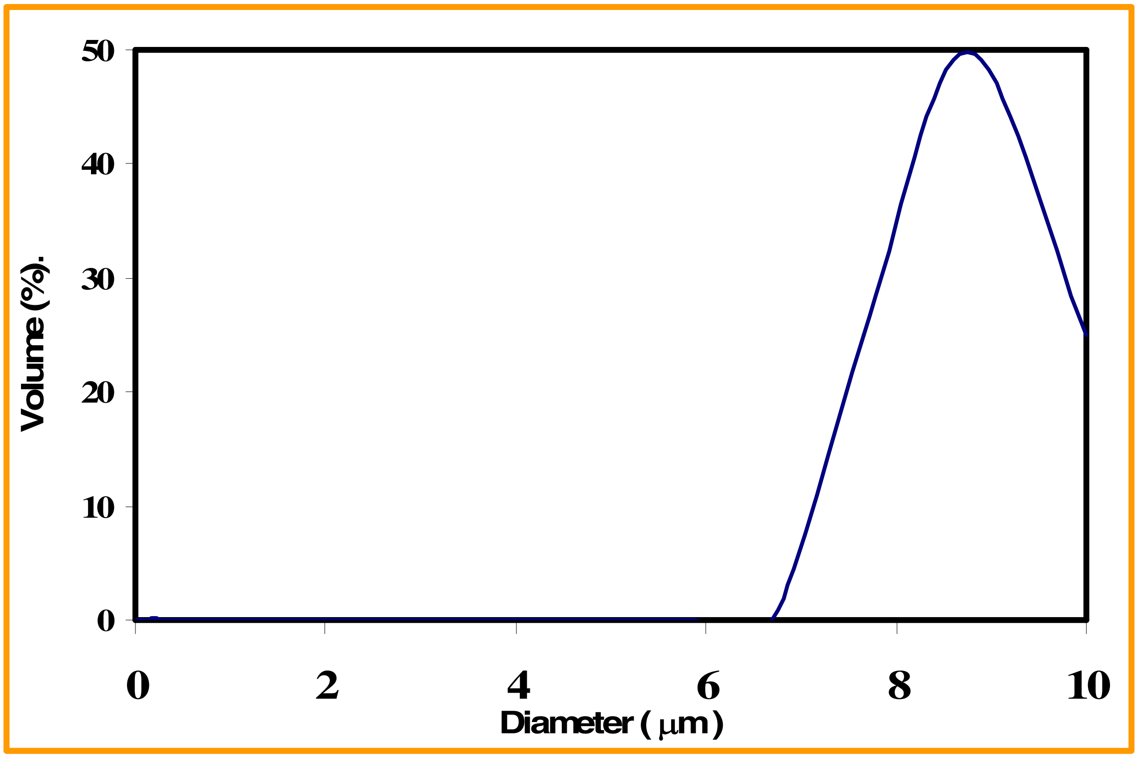


Figure 2-7: Droplet size distribution of the decane stock solution

The ability of extractants to remove of decane from water was tested by mixing a sample of 20 g of decane solution with 0.5 g of extractant for two hours in roller mill. After filtration, 6 g of filtrate was extracted by 1 g of hexane and the hexane layer was analyzed for decane by GC/MS. The ratio of extractant to decane solution was kept low (1:40 times), and the contact time between extractant and decane solution was maintained at two hours. Moreover, fresh stock solutions were prepared weekly as were standard solutions of decane in hexane. All glassware used was a carefully cleaned and washed with dichloromethane to ensure no interference from other hydrocarbons. Table 2-2 summarizes the results for testing ability of the synthesized extractants that synthesized by using silane reagents.

Table 2-2

Results from treatment of aqueous mixtures of decane with magnetic extractants

Extractant	Final Concentration (ppb)	% decane removal	SSA (m^2/g)
Octadecylsilsesquioxane/Iron	3322	99.53	0.39
Octadecylsilsesquioxane/magnetite	1037	99.85	2.01
Octadecylsilsesquioxane/ hematite	0*	100	1.72
Silica /iron	0*	100	0.33
Silica /magnetite	3350	99.54	1.18
Silica/ hematite	684	99.91	12.08
3-Glycidoxylpropylsilsesquioxane/iron	233	99.97	0.54
3-Glycidoxylpropylsilsesquioxane/Magnetite	0*	100	2.92
3-Glycidoxylpropylsilsesquioxane/ Hematite	338	99.95	8.20
3-Glycidoxylpropylsilsesquioxane modified/ Magnetite	0*	100	5.31

* Below detection limit (1 ppb)

The majority of the extractants have hydrophobic surfaces that have affinity for non-polar molecules such as hydrocarbons. These surfaces include long organic chains, polymethylsiloxane chains and silica. Decane molecules preferentially partition out of the aqueous phase onto the surface of the extractant. Once decane molecules were absorbed, they are tightly bound to the extractant surface. Although higher alkanes are less soluble in water, it can be predicted that they will partition even better. Interestingly, the silica-derivitized particles performed well suggesting that the silica surface is more attractive to decane than water.

All extractants demonstrated excellent performance and reduced the concentration of decane to the parts per billon level. Not only did some of the extractants remove all of the suspended decane, but they also removed the majority of the dissolved decane as well, i.e. those that have more than 99.98% decane removed [see Table 2-1]. Indeed, some extractants showed a powerful ability to extract and removed the decane bellow the1 ppb detection limit of the GC/MS.

Extractants coated with PDMS demonstrated even better performance compared to the other extractants (see Table 2-2). Unexpectedly, other extractants with higher surface area and long hydrophobic chains such as octadecylsilsesquioxane/iron and silica/hematite performed less effectively. Extractants coated with PDMS may have a more hydrophobic character than other extractants because they do not have any polar groups in their structure. The other extractants derived from silanes may have hydroxyl or alkoxy groups that formed during condensation process. This suggested that enhancing the hydrophobic nature of the extractants is more effective for hydrocarbon removal than enhancing the organophilic nature of the extractants. The same conclusion was reported by the Watson group using mathematical and experimental data.[30] They suggested that PDMS membrane mobility is decreased by enhancing the organophilic nature of PDMS due to the permeate-polymer interactions and the interchain interactions. Another group reported the same conclusion when they used PDMS membrane for removal of VOCs from water.[31] A further difference between the two methods of coating may also be due to the thicker PDMS coating which provides more capacity for adsorption of hydrocarbons. By comparison Table 2-1 and Table 2-3, the ability of extractants coated with PDMS obviously increases with the increasing of coating of the siloxane.

Table 2-3

Results from treatment of aqueous mixture of decane with magnetic extractants coated with PDMS

Extractant	Final Concentration (ppb)	% decane removal	SSA (m^2/g)
PDMS-10/Iron	34.6	99.99	0.48
PDMS-10/magnetite	187.5	99.97	4.20
PDMS-10/Hematite	261.4	99.96	6.40
PDMS-1000/Iron	7.8	99.99	1.54
PDMS-1000/magnetite	255.7	99.96	2.10
PDMS-1000/Hematite	0*	100	3.44

* Below detection limit (1 ppb)

The surface area of the extractant does not play a major role in the effectiveness the various extractants. For example comparisons between extractants coated by tetramethoxysilane confirmed this speculation. The silica/iron extractant's surface area was 0.33 m^2/g and it reduced the decane concentration to less than 0.001 ppm. Although, silica/hematite and silica/magnetite have higher surface areas, they did not reduce the concentration of decane to less than 1 pbb. It is possible that the substrate influences the nature of the silica coating that is formed which subsequently affects the physisorption of decane. At this time, these changes are poorly understood. Future work in which the composition and surface properties of the silica coating are determined may shell light on the differing abilities to adsorb decane.

Testing of some Magnetic Extractants for Dye Removal from Aqueous Solution

Several of the extractants based on magnetite were tested for their ability to uptake large hydrocarbon molecules such as dyes from water. PDMS-10, PDMS-1000, and octadecylsilsesquioxane/magnetite were specifically used in this test. Two different dyes were chosen namely Congo Red and Bromothymol Blue. The former is an anionic brownish-red powder, $C_{32}H_{22}N_6Na_2O_6S_2$. Bromothymol Blue, $C_{27}H_{28}Br_2O_3S$, in its sulfone form is neutral, and it gives as yellow solution. Figure 2-2 [page 33] illustrates structures of both dyes. The Bromothymol Blue acts as acid or base, depending on the pH of the solution. In pH below 6, the solution is yellow and the sulfone form is neutral. At pH greater than 6, the solution is blue, and the dye is in its anionic form.

Two separated aqueous solutions of both dyes were prepared with a concentration of 30 ppm. The pH of the Bromothymol Blue solution was adjusted to 4.0 to maintain it in a neutral form [yellow]. Dye concentrations were calculated by using UV/Visible spectroscopy to measure absorptions and by comparing them to a calibration curve from standard dye solutions over the concentration range of interest. The procedure to test extractant ability involved shaking 7 g of dye solution with 0.2 g of extractant for two minutes. The resulting mixture was than filtered by magnetic filtration, and the filtrate was analyzed for dye concentration by UV/Visible spectroscopy. The wavelengths used for the absorption measurements were at the maximum visible light absorption (λ_{max}) for

Congo Red and Bromothymol Blue, that are at 497 and 420 nm, respectively. The results of investigation are summarized in Table 2-4.

Table 2-4

Results from treatment of aqueous solution of dye (30 ppm) with magnetic extractant

Extractant	Congo Red(ppm)	BromothymolBlue (ppm)
Octadecylsilsesquioxane/magnetite	25.8	26.6
PDMS-10/magnetite	25.8	9.70
PDMS-1000/magnetite	29.4	21.0
Uncoated magnetite	4.8	22.3

All extractants are coated with non-polar coating and showed poor adsorption capacity for anionic Congo Red dye from water. On the other hand, uncoated magnetite showed very good performance due to its naturally positively charged surface. However, uncoated magnetite performed poorly in a test for removal of the neutral dye Bromothymol Blue from water. Magnetite coated by low viscosity PDMS demonstrated the best performance compared with other extractants. Indeed, PDMS-10/magnetite extractant can be used to selectively adsorb the neutral dye from an aqueous solution that has a mixture of an ionic and neutral dye. PDMS-1000 and octadecylsilsesquioxane/magnetite extractants show reduced performance compared with PDMS-10/magnetite to adsorb Bromothymol Blue. This might be due to the surface area of PDMS-10/magnetite extractant being double that of the other extractants [see Table 2-1]. In general, these results show the capability of using magnetic filtration to remove organics from water.

Moreover, the results show that selective magnetic extractants can be synthesized for different aqueous contaminants.

2.6 Conclusions

Novel composite materials were synthesized that can act as single-component magnetic filtration aids. The results show that the magnetic extractants are effective for removing decane and, by extrapolation, other hydrocarbons from water. Magnetic filtrations using the synthesized magnetic extractants, was found to have significant potential for separation of hydrocarbons from water. These magnetic extractants can be used to break an emulsion by removing oil from aqueous emulsions. The ability of several extractants based on magnetite has been tested for removal of dyes from water via magnetic filtration. Such ability indicates promise for selective separation of dyes from aqueous solutions.

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CHAPTER 3

Removal of Radioactive Materials Pollutants (Uranium) from Water Using Magnetic Filtration

3.1 Introduction

This chapter focuses on the development of magnetic extractants for removal of radionuclides specifically uranium from water. Contamination of the aquatic environment by radioactive species is a serious hazard. Recent statistics showed that 90 percent of groundwater in the United States is contaminated by radioactive materials.[1] Humans can be exposed to radiation by inhalation, ingestion, and direct exposure. Human health problems occur when polluted water is used for drinking, irrigation, and other purposes. Using radioactively-polluted water for irrigation would affect plants and soil and eventually lead to human exposure when crops are ingested. Radioactive species could concentrate in various parts of the human body such as in the lungs, liver, and bones.

Radioactive species have short-term effects on living organisms and long-term effects on genetics, which may have fatal consequences for later generations. Water may be contaminated by many radioactive sources. In the third world countries, the most important sources of radioactivity are ores that are found in underground layers. Leaching of radioactive species from such ores can contaminate groundwater. Delving deeper into the ground to obtain water increases the probability of reaching strata containing radioactive compounds. Improper handling of radioactive materials or wastes may also contaminate the environment.

Radioactivity is the property of some atoms whereby they give off energy as particles or waves that is called ″ionizing radiation″. The atoms that make up the radioactive materials are the source of radiation. The emitted radiation is energy that travels in the form of waves or high speed particles that can be alpha or beta particles and gamma rays. The most common naturally-occurring radionuclides are ^{234}U, ^{238}U, ^{228}Th, ^{230}Th, ^{232}Th, ^{226}Ra, ^{228}Ra, and ^{222}Rn.[2] Uranium and thorium are long-lived radioactive elements that are the usual sources of radioactivity in natural waters. These elements decay to other radionuclides, which in turn decay to others until they reach stable lead isotopes. The hazards of radioactive contamination to the environment and human health depend on the nature and concentration of the radioactive pollutant, and the extent of the spread of contamination.

Uranium is one of the heaviest, densest, and most hazardous elements in nature and is the most common radioactive contaminant in water. Natural uranium is relatively abundant in rocks, soils, and water. It has an atomic number of 92 and an atomic mass of 238.03 g/mole. Natural uranium consists of three isotopes: uranium-238, uranium-235, and uranium-234 with abundances of 99.27 %, 0.72 %, and 0.0055 %, respectively. Uranium undergoes radioactive decay by emission of an alpha particles accompanied by weak gamma radiation. People typically are exposed to radioactivity from uranium primarily through food and water because alpha particles that are released by uranium cannot penetrate the skin.

World Health Organization (WHO), stated that the tolerable daily intake of uranium is 0.6 μg/kg of body weight per day.[3] The average daily intake of uranium from food ranges from 0.07 to 1.1 micrograms per day. The radioactivity of uranium is secondary to uranium's effect on human health since uranium also acts as a heavy metal. Moreover, the radioactivity of uranium plays an important role in environmental problems because of its long half- live. Uranium may exist in water in three oxidation states, namely (U(IV), U(V), and U(VI), and the most stable uranium species is U(VI) as the uranyl ions UO_2^{2+}. Uranium (VI) cations readily form soluble complexes with anions or neutral species that are found in water such as sulfate, carbonate, and phosphate.[4] Consequently, uranium can migrate easily with water and contaminate other areas.

Uranium is mainly used in nuclear power plants as fuel and for military purposes. In the United States, there are more than 100 nuclear power plants. Natural uranium has to undergo enrichment for use in nuclear reactors or weapons. Thus, the amount of the uranium-235 has to be increased from its original natural abundance, and the resulting material is called ″enriched uranium″. On the other hand, uranium is called ″depleted uranium″ when the amount of the uranium-235 has decreased from its original natural abundance. Both enriched and depleted uranium have the same chemical properties, but differ in radioactivity. Depleted uranium is the byproduct of the enrichment process.

In the Simpsonville-Greenville, South Carolina, thirty-one drinking water wells were contaminated by high amounts of uranium(30 – 9900 μg/L).[5] This significantly exceeds the U.S. Environmental Protection Agency's (EPA) proposed maximum contaminant level (MCL) of 30 μg/L in drinking water. Naturally occurring uranium in surface water and ground water can exceed the MCL. Uranium risk increases when it is ingested in food or water and enters the human system. Nevertheless, 99 % of the uranium ingested leaves the human body. The remaining uranium is absorbed and carried through the bloodstream and concentrates in specific locations in the body, particularly the bones, where it will remain for years. This absorbed uranium leads to many fatal health problems such as the risk of cancer of the bone, liver, certain blood diseases, and kidney damage.

In order to decontaminate radioactively contaminated water, several methods have been proposed that include physical, chemical, and biological technologies. These methods include aerobic and anaerobic biological purification, electrolysis, membrane filtration, distillation, and ion exchange. Each method has advantages and some drawbacks. For example, in the process of distillation the foam formed during evaporation can transport radioactive substances together with the exhaust air.[6] Many research groups still search for facile methods to remediate radioactive contaminated groundwater. Poon[7] suggested using an electroflotation device, which involved using a platinum-clad niobium anode and a stainless steel screen as the cathode. However, the proposed method only removed Zn, Pb, and Cu/CN from polluted groundwater samples.

Gu et al.[8] used zerovalent iron to remove U(VI) from contaminated groundwater in which U(VI) was reduced to U(IV) that was subsequently adsorbed on the iron surface. Further study is needed for optimization of the process because U(IV) can be reoxidized by oxygen and, thereby, desorbed from the iron surface. Another group used titanium oxide since it has a strong affinity for uranium.[9] However, It has a low uptake capacity since it has low surface active site density.[10]

Activated carbon has been used for removal of U(VI) from water since it can be considered to be the most effective and economic process.[11] However activated carbon can not be transported easily without being crushed. There is still a need to effectively recover pure water from radioactively contaminated water by a system that is economical to operate, requires little equipment, has no harmful impact on the environment, and does not pose safety and health problems to workers. Extraction of radioactive or heavy metals by selective complexation with ligand groups is currently being pursued as a promising method for purification of drinking, and irrigation water.[12] This thesis addresses methods to synthesize appropriate magnetic extractants which eliminate radioactive uranium from water.

3.2 Experimental

All reagents were ACS reagent grade and were used without further purification. Water was purified by reverse osmosis and deionization. Toluene was HPLC grade and was used as received. Sodium hydroxide and ammonium hydroxide were also used. Iron(II) chloride tetrahydrate and iron(III) chloride hexahydrate were employed. [1-(2-aminoethyl)-3-aminopropyl]trimethoxysilane, mercaptopropyltrimethoxysilane and 2-vinylpyridine were used to coat magnetite nanoparticles and Figure 3-1 illustrates them.

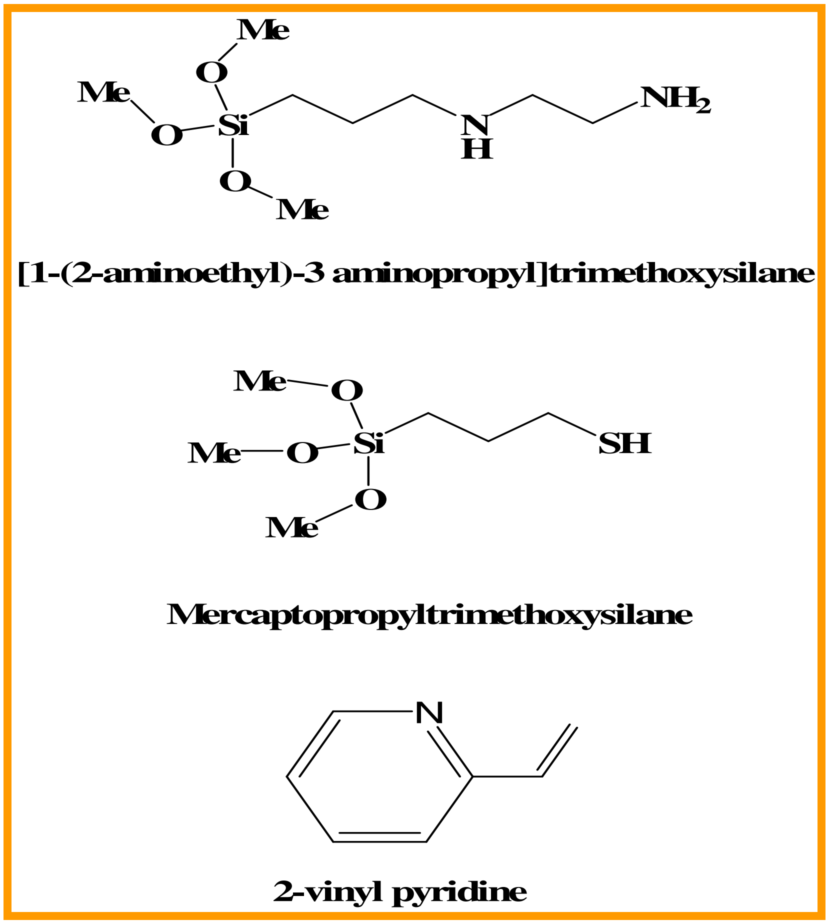


Figure 3-1: Reagent structure

Magnetic filtration was performed using glass pipets packed loosely with steel wool (# 00 fine grade) and taped to the side of an electromagnet. The latter magnet was a 24 V, extended-reach-electromagnet with a 170 pound pull and with dimensions of 3″ x 1″x 1.4″. The electromagnet was powered by a 30 watt direct current power supply. UV-visible spectroscopy was used to assess uranium concentration and spectra were recorded on an HP 8453 UV-visible spectroscopy using a quartz cell with a 10 mm path length. The X- ray powder diffraction (XRD) patterns were recorded on a Bruker AXS D8 Advance diffractomer using copper K_α radiation. The crystalline phases were identified by comparison with data from the International Centre for Diffraction Data (ICDD).

Magnetic extractants were characterized by several methods. Fourier Transform Infrared (FT-IR) spectra were recorded at room temperature in the region of 4000-400 cm^{-1}. They were collected by diffuse reflectance of a ground powder diluted with potassium bromide on a Nicolet Magna-IR 750 spectrometer. The surface areas were measured with a Quantachrom Nova 1200 surface area analyzer, via a nitrogen adsorption isotherm, using the Brunauer- Emmett- Teller (BET) multilayer nitrogen adsorption method, and six points in the range of 0.05 to 0.30 P/P. Thermogravimetric analyses were performed using a Seiko EXSTAR 6000 TG/DTA 6200 instrument. The temperature was ramped from 25 °C to 700 °C at a rate of 5 °C/min under a 50 ml/min flow of dry air. The sizes of particles were measure by using the dynamic light scattering with a Malvern HPPS dynamic light scattering instrument. In addition, both Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM) were used. TEM images were obtained by a JEOL 2000-FX intermediate voltage (200,000 eV) electron microscope with magnification of 50x to 1,000,000 x. The samples were prepared by placing a drop of solution on a carbon-coated Cu grid and allowing the drop to dry in air. The SEM photographs were recorded using a JEOL 6400.

3.3 Preparation of Magnetite Nanoparticles

Magnetite nanoparticles were prepared by mixing and stirring two equivalents of iron(II) chloride tetrahydrate with three equivalents of iron(III) chloride hexahydrate at room temperature. The mixture was treated by adding 100 ml of 28% ammonium hydroxide. Immediately, the color of the solution turned from orange to black.[13] Magnetite nanoparticles precipitated and were washed three times with 5% NH_4OH solution using the magnetic decantation method. IR (KBr, cm^{-1}): 3401 (m, br), 1607 (s), 1398 (s), 1296 (m), 1295 (w), 1135 (w), 1078 (m), 971 (w), 584 (s,br).

3.4 Preparation of Extractants

Preparation of 1-(2-aminoethyl)-3-aminopropyl silsesquioxane coated magnetite nanoparticles

Magnetite nanoparticles (3.0 g) were treated with a solution of [1-(2-aminoethyl)-3-aminopropyl]trimethoxysilane (2.0 g) in toluene (30 ml). The reaction mixture was allowed to stir by using a mechanical stirrer at 80 $^{\circ}$C for 24 hours. Afterwards, the material was isolated by filtration, washed extensively with toluene, and dried in an oven at 65 $^{\circ}$C. The material is designated as AEAPS-MN and was obtained in a yield of 3.63 g. IR (KBr, cm^{-1}): 3474 (w), 3297 (w), 2223 (w), 2083 (w), 1790 (m, br), 1669 (m), 1587 (m), 1449 (m), 1357 (w), 1201 (m), 1117 (s), 1027 (s), 776 (m), 579 (m), 445 (s).

Immobilization of Pyridine onto AEAPS-MN

Exactly 1.5 g of AEAPS-MN material was mechanically stirred in a solution of 2-vinyl- pyridine (1.0 g) in toluene (20 ml) at 80 °C overnight. The material was isolated by filtration, washed extensively with toluene to remove any unattached 2-vinylpyridine, and was then dried in an oven at 65 °C. The yield of the product was1.46 g and this material will be referred to as PyAEAPS-MN. IR (KBr, cm^{-1}): 3309 (w), 2945 (w), 2886 (w), 2709 (m), 2364 (m), 1802 (w), 1664 (s), 1600 (m), 1449 (s), 1352 (s) 1207 (m) 1147 (s), 1022 (w), 893 (w), 785 (m), 693 (w), 598 (m).

Preparation of 1-(2-Aminoethyl)-3-aminopropylsilsesquioxane (Prepolymer)

[1-(2-Aminoethyl)-3-aminopropyl]trimethoxysilane (10 g) was treated with 2.34 g of sodium hydroxide aqueous solution (0.31 M) in a 50 ml round bottomed flask. The reaction mixture was allowed to stir at 60 °C for 3 hours, followed by stirring at 80 °C for 12 hours. The product was diluted by ethanol to produce two coating solutions 10 wt % and 20 wt %. They were designated AEAPS-10 and AEAPS-20, respectively.

Preparation of Silica Coated Magnetite Nanoparticles

Exactly 7g of AEAPS-10 or AEAPS-20 was stirred with 7 g of magnetite nanoparticles, and the resulting mixture was heated at 280 °C for 12 h. Afterwards, the material was extracted with toluene for 3 h at 80 °C, washed extensively with water, and dried at 70 °C for 3 h. Prepared materials from 10% and 20% AEAPS coating solutions were designated as MNAS-10, and MNAS-20, and the reaction yielded 6.09 g, and 6.38 g, respectively. IR for MNAS-10 (KBr, cm^{-1}): 3552 (s), 3320 (s), 1623 (s), 1150 (m), 1077 (s), 640 (m), 578 (m). IR for MNAS-20 (KBr, cm^{-1}): 3349 (s, br), 3073 (m), 2906 (w), 1615 (s), 1372 (w), 1146 (m), 1074 (s), 692 (m), 640 (s) 563 (m).

Preparation of Mercaptopropylsilsesquioxane (Prepolymer)

Mercaptopropyltrimethoxysilane (19.6 g) was treated with 0.01 g of 30% aqueous hydrochloric acid (~ 0.078 mmol) in a 50 ml round bottomed flask. Then the mixture was hydrolyzed by dropwise addition of water (5.4 g). The reaction mixture was allowed to stir at room temperature for 2 hours followed by stirring at 60 °C for 12 h. The product was diluted by ethanol to produce 20 wt % of the final product that was designated TPS-20.

Preparation of Thiol-Functionalized Ormosil Coated Magnetite Nanoparticles

TPS-20 (4 g) was stirred with 4 g of magnetite nanoparticles, and the resulting mixture was heated at 280 °C for 12 h. Afterwards, the material was extracted with toluene for 3 h at 80 °C, washed extensively with water, and dried at 70 °C for 3 h. The yield of the product was 3.58 g and this material will be referred to as MNST-20. IR for MNTS-20 (KBr, cm^{-1}): 3588 (w), 3496 (w), 3059 (m), 2622 (w), 2381 (w), 2194 (w, br), 1664 (w, sh), 1443 (s), 1368 (s), 1244 (w), 1186 (w), 1069 (m), 953 (w), 704 (m), 645 (w), 572 (m).

3.5 Testing of Magnetic Extractant for Uranium Removal from Water

A range of different concentrations of stock solutions of UO_2^{2+} (0.03 M – 0.06M) were prepared and treated with the synthesized magnetic extractant. The mixtures were stirred for two hours and then filtered via magnetic filtration. UV visible spectroscopy was used to measure the concentration of UO_2^{2+} in the permeate solution (the equilibrium concentration). The Langmuir isotherm equation was applied to calculate the adsorption capacity of the magnetic extractants.

3.6 Results and Discussion

The main objective of this investigation was to extract uranyl ions from contaminated water via magnetic filtration. Magnetite nanoparticles were used as the source of magnetism in the synthesized extractants. Nanoscale extractants have been used due to their small size that results in very high surface areas which tremendously accelerates reactions with contaminants. The small size also contributes to more complete reactions and higher sorption capacity. Nanoparticles can also exhibit higher chemical reactivity due to unusual crystal shapes, lattice order, and surface morphology and chemistry. Therefore, nanoparticles can serve as excellent sorbants for toxic species. Yet another property of magnetite nanoparticles that can be exploited for separation and environmental applications is the superparamagnetism of magnetic nanoparticles. For this application supermagnetic magnetite particles would be useful since the nanoparticles have strong attraction to a magnetic field, but there would not be problems with remnant magnetization. For example, they will not clump and stick together in the absence of a magnetic field.

There are several methods for the synthesis of magnetite nanoparticles.[14] For instance, Sarel's group reported that reacting ferrous sulphate with bispyridoxylidene hydrazine phthalazine for 10 minutes at pH 7 yielded nanocrystalline magnetite.[15] Recently, another group reported in a patent the reduction of goethite (α-FeOOH) to produce controlled size and shaped magnetite nanoparticles.[16] The co-precipitation method was selected to prepare magnetite nanoparticles, because it was reported that magnetite nanoparticles prepared by this method have extensive hydroxyl groups on their surface.[17] Magnetite nanoparticles were prepared by the chemical co-precipitation of Fe(II) and Fe(III) salts by treatment with aqueous ammonium hydroxide as described in Reimers procedure and illustrated in the equation 3-1.[13]

$$\mathbf{2Fe(II) + 3Fe(III) \xrightarrow[pH=9]{NH_4OH} Fe_3O_4\downarrow} \tag{3-1}$$

Figure 3-2 illustrates the X-ray diffraction pattern of the crude product produced by this method. The broad reflections in this pattern match that of magnetite in the ICDD database which the sharper were identified as being due to the ammonium chloride (NH_4Cl) by-product. Washing with water removed the latter imparity. The crystallite size of the magnetite was estimated to 3.3 nm using Warren-Averbach method. The surface area of magnetite nanoparticles is 56.79 m^2/g.

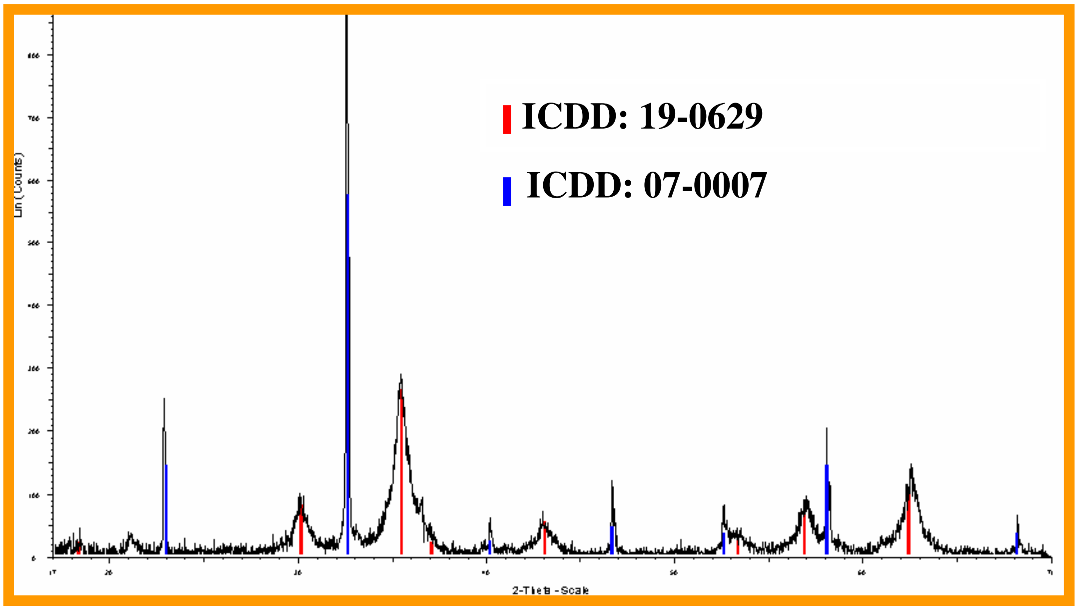


Figure 3-2: XRD pattern of magnetite nanoparticles

The surface of the magnetite nanoparticles can be functionalized with various groups by treatment with a reactive silane. It is well known from the literature review that silane reagents are able to link covalently to a hydroxyloted surface.[18] The magnetite particles have extensive hydroxyl groups on the surface due to their mode of synthesis and thus can be easily coupled with silane reagents by the formation of Fe-O-Si covalent bonds. [1-(2-aminoethyl)-3 amino-propyl]trimethoxysilane (AEAPS) was one of the reagents used to coat the magnetite nanoparticles. AEAPS has a center silicon atom that is attached to three methoxy groups and a 1-(2-aminoethyl)-3 aminopropyl group, and AEAPS is known as diamine silane. AEAPS has also been chosen because it has a terminal primary amine. From the literature, primary amines are known as excellent ligands for metal ions. Therefore, amine groups can act as adsorbents for radioactive metals in contaminated water.[19]

Magnetite particles were refluxed with a toluene solution of AEAPS. The H_2O : diamine silane molar ratio was kept very low. The hydrolysis depends on the ability of the silane to adsorb water from the surrounding atmosphere during preparation since the synthesis was not performed under an inert gas. In this case, hydroxyl groups on the surface of magnetite particles were reacted with AEAPS molecules with methoxy groups (leaving group) on the AEAPS molecules. Alcohol (ROH) molecules were liberated. The Si-O-Fe bonds covalently form instantly, and the silane molecules react with water and cross-link with each other via a siloxane bond (Si-O-Si) formation. An insoluble cross-linking network structure of siloxanes was formed. Whether the grafted silicon atom is bound via one, two, or three Fe-O bonds depends on the availability of the hydroxyl groups on the surface of the magnetite nanoparticles. Since the alkyl groups are not hydrolyzed, they become grafted to the metal surface via a siloxane network. Therefore, the surfaces of the metal particles are coated with a film of silsesquioxane of the general formal ([1-(2-aminoethyl)-3-aminopropyl]$SiO_{1.5})_X$. Figure 3-3 illustrates this reaction and the material was designated as AEAPS-MN.

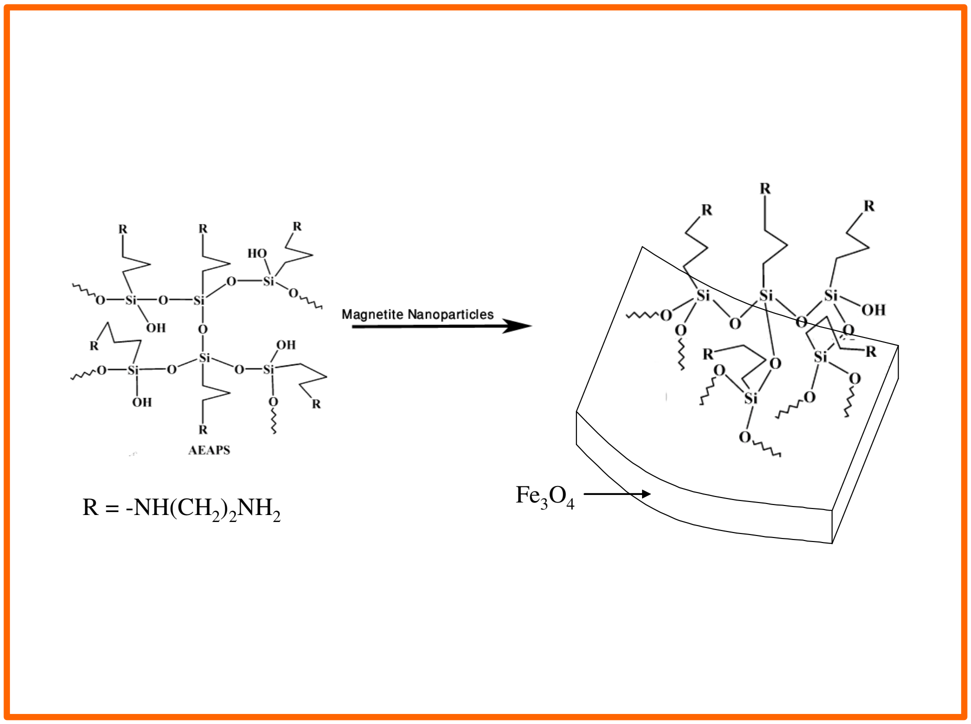


Figure 3-3: Cartoon exemplifying the reaction between AEAPS and the magnetite nanoparticles

Indeed, using lower temperatures and non-aqueous solvents decreased the hydrolysis of AEAPS molecules and hindered condensations between each other. Consequently, the 1-(2-aminoethyl)-3 aminopropyl groups are grafted to the metal surface via a siloxane network. This reaction led to composite materials that consisted of two phases. The inner phase was magnetite nanoparticles that produce the desired magnetic properties in composite materials. The outer phase was a monolayer of polymerized silsesquioxane that coated the particles. The outer coating provided amino groups as reactive sites for the binding of uranium ions.

The surface morphology of the particles can not be definitely identified since NMR spectroscopy is not helpful in this situation due to magnetism of the magnetite.

On the other hand, other techniques can give a clear picture of the synthesized magnetic extractant. The XRD pattern (Figure 3-4) indicates that the crystal structure of the nanoparticles can be identified as magnetite. Moreover, the crystallite size of the AEAPS-MN particles was calculated to be 6.7 nm using the Warren-Averbach method. The XRD pattern shows that the magnetite nanoparticles are free of ammonium chloride (a reaction by-product). No additional steps are needed to purify the synthesized nanoparticles.

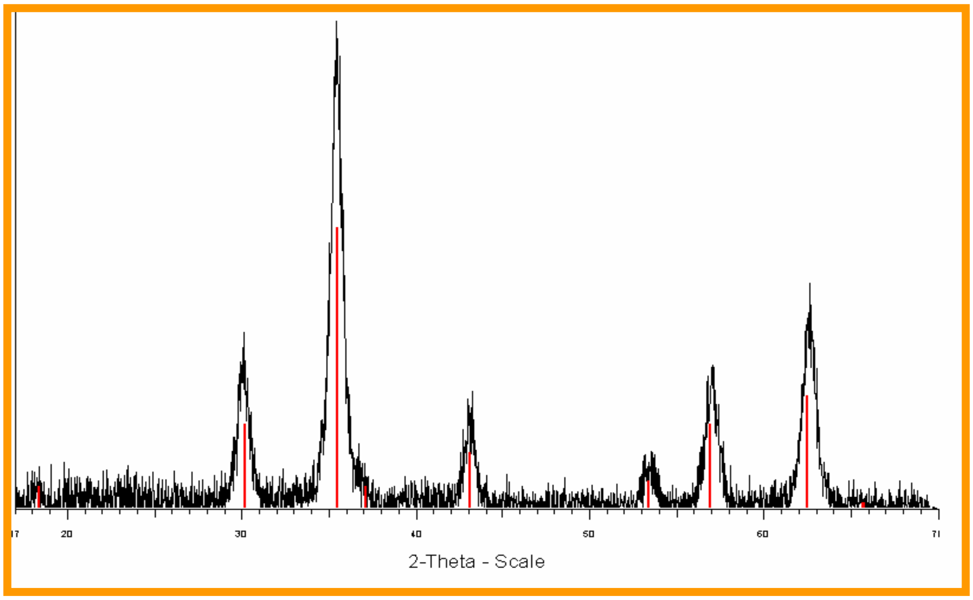
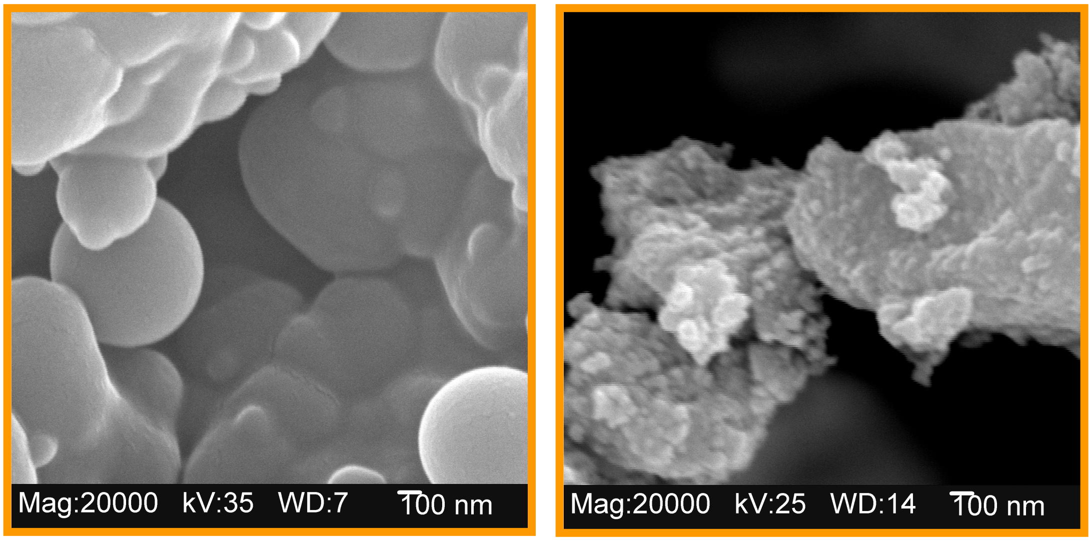


Figure 3-4: XRD pattern of the AEAPS-MN particles. Vertical bars represent the ICDD pattern for magnetite (# 19-0629)

An IR spectrum of AEAPS-MN shows strong absorption bands that appear at roughly 1623 cm^{-1} and 1070 cm^{-1} that are due to the NH_2 group vibration and the Si-O stretching vibration, respectively. This confirmed that the particles were successfully coated. SEM images of the coated and uncoated magnetite nanoparticles are shown in Figure 3-5. These images indicate that the magnetite particles are almost homogeneously coated. The images show some aggregation of the magnetite particles but less than that of the uncoated magnetite nanoparticles. Furthermore, the images show that the coated magnetite particles have spherical shape with less aggregation. Grafting diamine silane to the surface of the magnetite nanoparticles resulted in a remarkable decrease in the specific surface area of the magnetite nanoparticles (from 56.8 m^2/g to 1.5 m^2/g). The likely cause of the surface area decrease arising from grafting AEAPS molecules to the nanoparticle surfaces is that the aminosilane blocks the framework channels.



AEAPS-MN Magnetite Nanoparticles

Figure 3-5: SEM images of AEAPS-MN and magnetite particles

The thermogravimetric investigation of AEAPS-MN presented in Figure 3-6 shows a gradual decrease of weight starting at approximately 50 °C. Weight loss continues upto 700 °C, and ceases beyond this point. Definitely, the region up to 150

°C can be assigned to water molecules and hydroxyl groups. Next, the organic groups decompose until the magnetite particles are just coated by silica with no additional organic groups. At 700 °C, the particles had lost approximately 38% of their weight. All the TGA experiments in this research were preformed under nitrogen to minimize the mass increase due to any magnetite oxidation.

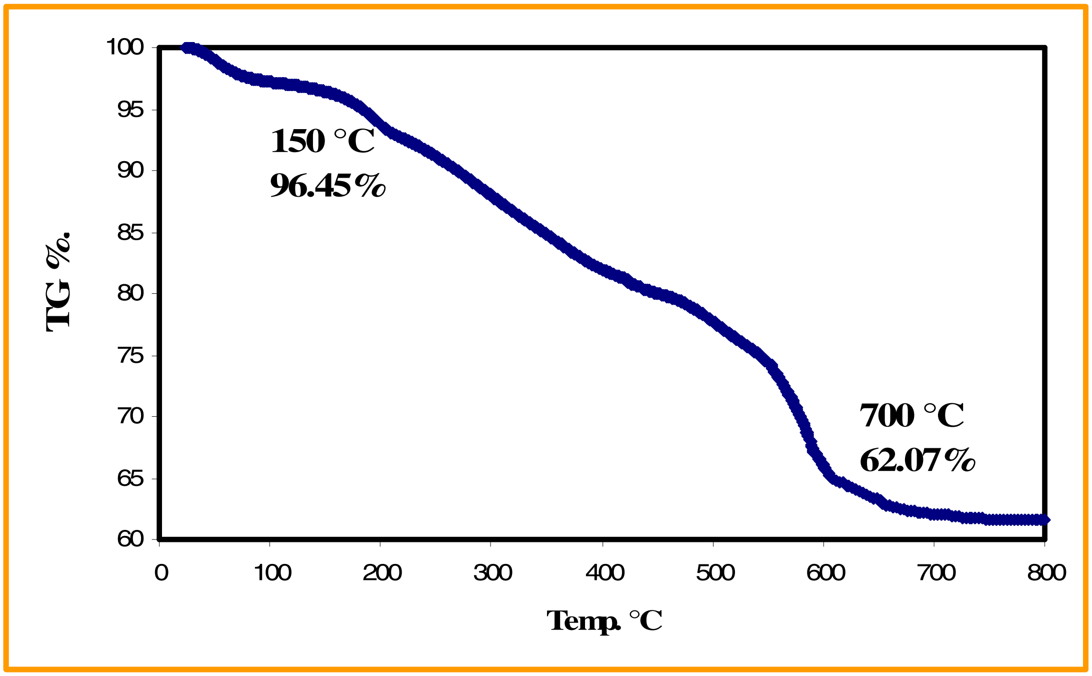
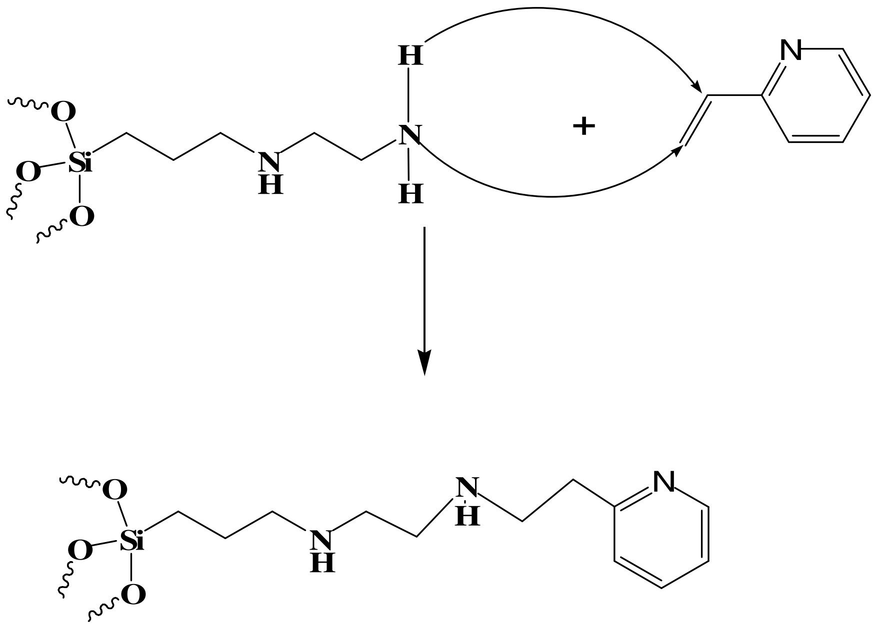


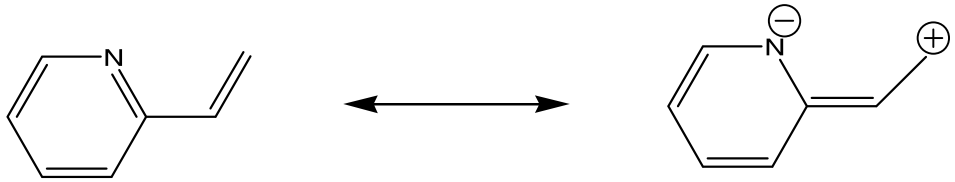
Figure 3-6: TGA pattern of AEAPS-MN

The AEAPS-MN extractant was successfully functionalized with a pyridine group. The immobilization of the pyridine group on AEAPS-MN particles was achieved by mixing AEAPS-MN with 2-vinylpyridine as in equation 3-2. This reaction is known as a Michael addition reaction.



3-2

The terminal amine of silsesquioxane attacked the electron-deficient terminal carbon atom of the vinyl group of 2-vinylpyridine.[20] The vinyl group is more exposed to attack by nucleophilic reagents because the resonance interaction with the pyridine ring extends to the double bond as in equation 3-3. Therefore, the terminal amine group of AEAPS-MN with the lone pair on the nitrogen is a nucleophile that attaches to the vinyl group on the pyridine ring.



3-3

The success of the reaction was determined by comparison of the IR spectra of AEAPS-MN and PyAEAPS-MN as shown in Figure 3-7. The spectra illustrate that AEAPS-MN materials have undergone changes when reacted with 2-

vinylpyridine and obviously show evidence of immobilization of the pyridine group on AEAPS-MN particles by the appearance of peaks at 1470 and 1365 cm^{-1} that can be attributed to the vibration of C=N and C=C in the pyridine ring, respectively.[21] The strong peak at 2730 cm^{-1} may be attributed to the C-H stretching vibration of the pyridine ring. These FTIR spectra not only confirm that the magnetite particles have successfully been coated but also prove that organic groups survive this reaction.

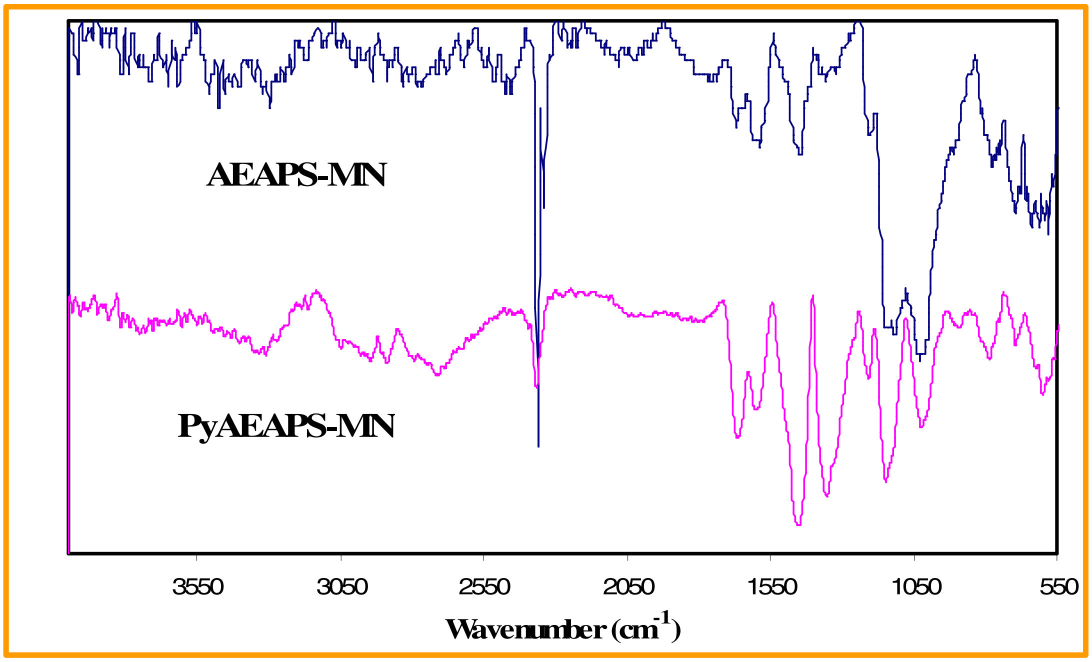


Figure 3-7: IR spectra of AEAPS-MN and PyAEAPS-MN

Both extractants give very stable suspensions when stirred with distilled water. The suspended particles start to settle down at a pH lower than neutral. The suspended particles provide an opportunity to determine the size and extent of aggregation of the particles. Particle size can be assessed by Dynamic Light Scattering (DLS). Figure 3-8 shows the particle size of both extractants using DLS, and the data in the graphs express size distribution by intensity. PyAEAPS-MN particles have an average size of 56.3 nm and polydispersity index of 0.146. On the other hand, AEAPS-MN particles have an average size of 72.1 nm and a polydispersity index of 0.220.

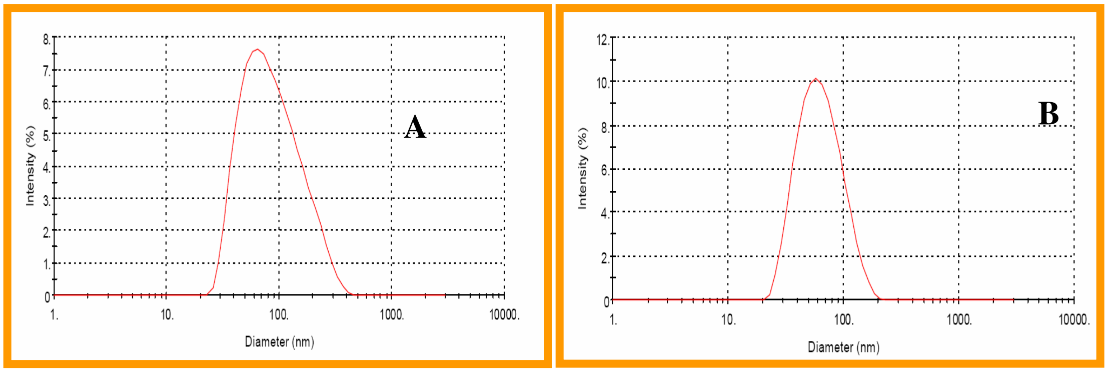


Figure 3-8: DLS graphs of the A (AEAPS-MN) and B (PyAEAPS-MN)

Immobilization of pyridine on the surface of magnetite particle reduces the surface energy of the particles. Consequently, PyAEAPS-MN aggregated less than the other material. Moreover, DLS results show that PyAEAPS-MN have a smaller size (they differ by almost 16 nm) and also have a narrow distribution. TEM images for PyAEAPS-MN indicate a particle size range from 10-20 nm in Figure 3-9. Those particles are expected to exhibit superparamagnetism because of their size being less than 25 nm. It has been reported that magnetite particles less than the critical particle size (25 nm) will exhibit superparamagnetism.[22] Moreover, the images show that particles have a spherical shape as the SEM images indicate for AEAPS-MN particles in figure 3-3. TEM images also indicate the extent of aggregation for PyAEAPS-MN particles.

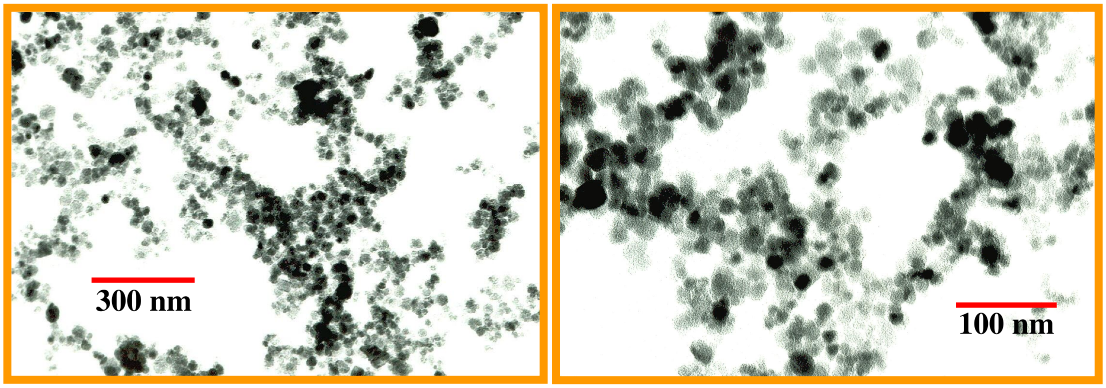


Figure 3-9: TEM images of the PyAEAPS-MN

A different procedure was used to coat magnetite nanoparticles by the same reagent (AEAPS) with the aim of generating an extractant with a high specific surface area. First, the prepolymer was prepared by hydrolysis and condensation (sol-gel process) of a silane reagent in the presence of sodium hydroxide as a base catalyst as in Figure 3-10. 1-(2-aminoethyl)-3aminopropylsilsesquioxane produced (AEAPS) is a sticky oil with the general formal is [1-(2-aminoethyl)-3 aminopropyl $SiO_{1.5}]_X$, and it is insoluble in water. Methoxy groups were hydrolyzed to free methanol molecules and were replaced by hydroxyl groups (forming silanol). Consequently, the silanol groups condensed with each other or with silanol from another molecule to liberate water molecules and forms siloxane bonds as linkers. The product was diluted with ethanol to produce two coating solutions of 10 wt % and 20 wt % PAEAPS that were designated AEAPS-10 and AEAPS-20, respectively.

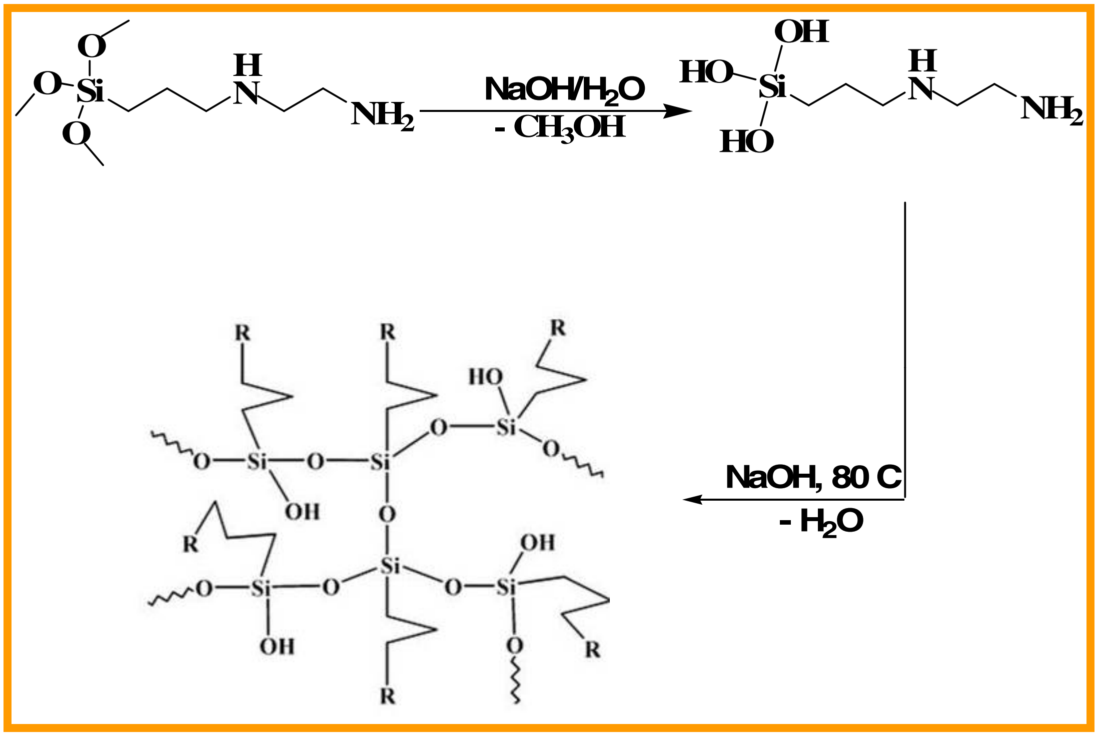


Figure 3-10: Cartoon exemplifying the preparation of AEAPS

Afterward, the coating solution was mixed with magnetite particles and heated to 280 °C. This high temperature induces the prepolymer to interact with hydroxyl groups on the magnetite surface. Figure 3-11 illustrates the interaction between AEAPS and magnetite nanoparticles. The magnetic extractants Prepared from 10% and 20% PAEAPS coating solutions were designated as MNAS-10 and MNAS-20, respectively, even though the 1-(2-aminoethyl)-3aminopropyl groups were decomposed during the coating process because of the high temperature. The magnetite particles were coated by amorphous silica and were expected to maintain a small amount of hydroxyl and organic group residues. The coating method has two stages depending on the temperature. Up to 100 °C, the prepolymer interacted with surface hydroxyl groups. Between 100 °C and 280 °C, the organic groups were decomposed, and physically adsorbed molecules (such as water and methanol) were released. At this stage, the decomposed organic groups formed pores in the siloxane network that were occupied by water and methanol molecules along with sodium ions. Sodium ions help prevent pore shrinkage upon evaporation of the water and methanol since complete evaporation occurs between approximately 100 °C and 280 °C.

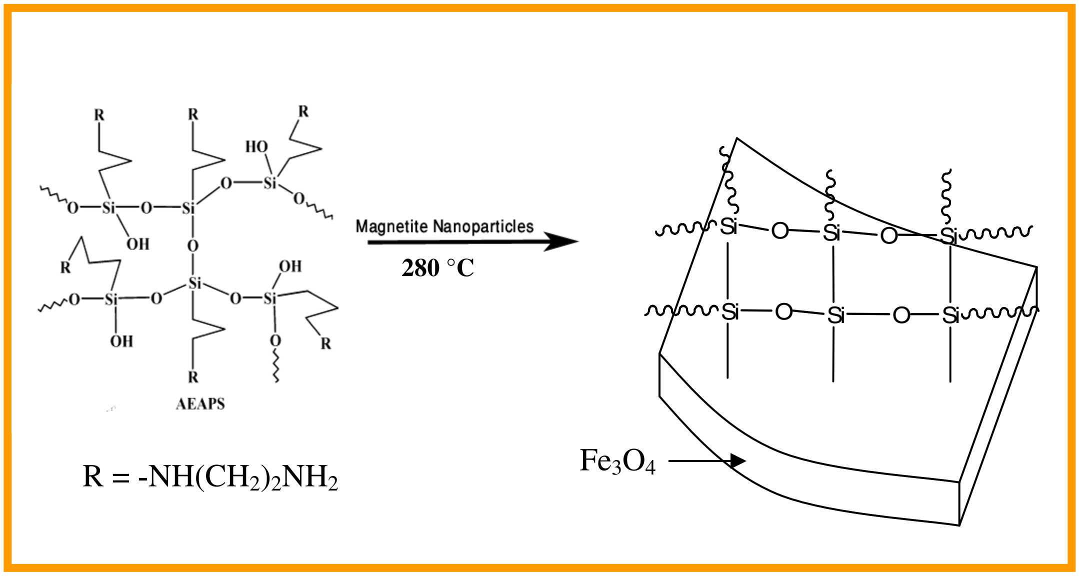


Figure 3-11: Cartoon exemplifying the reaction between the coating solution and the magnetite nanoparticles

The MNAS-10 and MNAS-20 extractants have high specific area compared with previous synthesized extractants, 59.2 and 51.4 m^2/g, respectively. The common reagents (tetramethoxy or tetraethoxysilane) to prepare silica were not used, instead of organo-silanes were used. Organic groups of silane molecules usually form pores when decomposed, and the sodium ions might play a roll to maintain the shape of pores (template). Sodium cations are captured inside the silicate network which has an opposite charge. By comparing the specific surface area of MNAS-10 and MNAS-20, only a difference of 7.7 m^2/g was realized. This indicated there are other than only the silsesquioxane concentration in the coating solutions influence the surface area. Since MNAS-10 was prepared from a solution which the silsesquioxane concentration was 50% of the other one.

SEM images of the MNAS-20 indicate that the magnetite particles are homogeneously coated (Figure 3-12). The images show some aggregation of the particles but this is less than aggregation of the uncoated magnetite nanoparticles. The particles terminated by an amine or pyridine have less aggregation than particles coated by silica because they have greater repulsive force between the particles. Moreover, The MNAS-10 and MNAS-20 particles do not suspend easily in water.

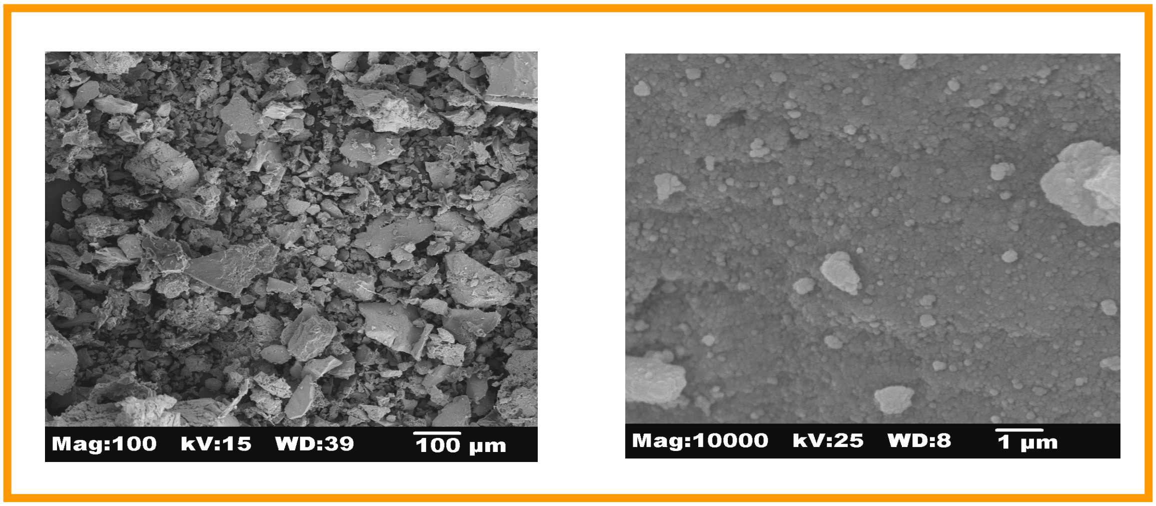


Figure 3-12: The SEM images of MNAS-20

The thermogravimetric analysis trace of MNAS-20 shows two noticeable weight loss regions in Figure 3-13. The first weight loss region is at 193 °C, and the second region is at 450 °C. The first transition can be assigned to the loss of water molecules that were physically bound within the siloxane network and the dehydration of hydroxyl groups [about 3.5% of the weight]. The other transition started from 193 °C to 450 °C, which corresponded to a loss of about 6.3% of the weight. This transition can be indication of a large concentration of chemisorbed hydroxyl groups on the surface of the pores. The transition could also result from loss of organic groups and the interior water and methanol molecules. Beyond 450 °C, only slight changes in weight occur. The final residual weight of 89.60% at 800 °C can be assigned to magnetite particles coated by silica, SiO_x.

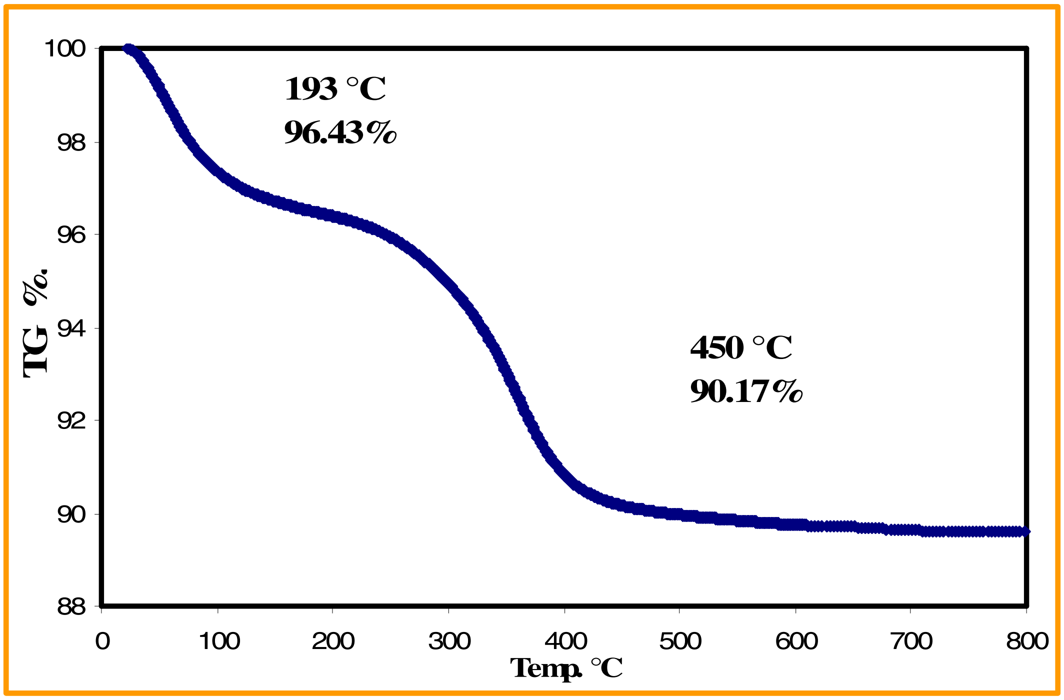


Figure 3-13: TGA pattern of MNAS-20

Mercaptopropyltrimethoxysilane (MPS) was used as another reagent to coat magnetite particles. It is different from the previous reagent in that the organic group is a mercaptopropyl group. The same procedure was used as that for synthesis of MNAS-10 and MNAS-20. Firstly, the prepolymer was prepared by hydrolysis and condensation of MPS using hydrochloric acid as a catalyst as in Figure 3-14.

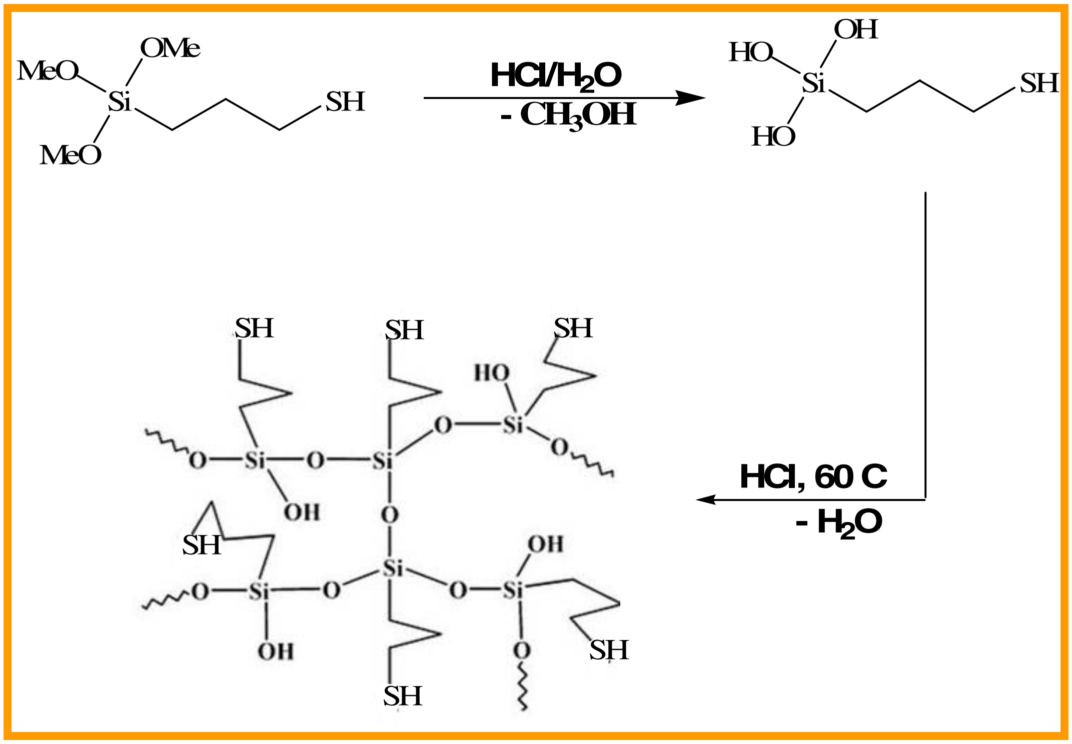


Figure 3-14: Cartoon exemplifying the preparation of MPS

The product is sticky oil of mercaptopropylsilsesquioxane (PMPS) with the general formal of [mercaptopropyl- $SiO_{1.5}]_X$, and it is insoluble in water. The PMPS was diluted with ethanol to produce a coating solution of 20 wt % PMPS that was designated PMPS-20. Then, PMPS-20 solution was mixed with magnetite particles and heated to 280 °C. High temperature induces silsesquioxane to coat the surface of magnetite particles via their hydroxyl groups. The prepared magnetic extractant from the PMPS-20 coating solution was designated as MNTS-20.

In this situation, not all organic groups were decomposed during the curing period with high temperature. The magnetite particles were coated by ormosil as confirmed by FTIR spectroscopy. The FTIR spectrum of the MNTS-20 extractant indicated the presence of absorption bands at 2381 cm^{-1} and 2622 cm^{-1} that are characteristic of a stretching vibration for thiol groups, and the peak at 1069 cm^{-1} was due to Si-O stretching vibration. Moreover, the bands displayed from 3588-3059 cm^{-1} are a feature of O-H band stretching vibration that might indicate the existence of silanol groups that remain after reaction. This mean PMPS is more thermally stable than PAEAPS and some of organic groups survived the high temperature.

Testing of Magnetic Extractants for Uranium Removal from Aqueous Solution

The Langmuir isotherm equation was applied to calculate the molar capacity of the magnetic extractant. Thus, the number of moles of UO_2^{2+} bound per unit mass of extractant was determined. The Langmuir isotherm is expressed as equation 1-3:

$$\frac{[Uc]}{[Ub]}=\frac{b}{[Ux]}+\frac{[Uc]}{[Ux]} \qquad \textbf{1-3}$$

Where $[U_c]$: the equilibrium concentration in aqueous phase (mol/L).

$[U_b]$: the number of moles of UO_2^{2+} adsorbed per unit mass of extractant.

$[U_x]$: the maximum adsorption of UO_2^{2+} at monolayer coverage per unit mass of extractant.

b: an adsorption equilibrium constant that can be determined experimentally.

The molar capacity of the magnetic extractant was assessed by plotting U_c versus Uc /U_x. The resulting plot is linear and the slope of this line is used to determine the maximum uptake, which is of the form of mmole of uranium adsorbed per one gram of extractant. As example, Figure 3-15 illustrates the uptake ability MNSA-20 using the Langmuir isotherm.

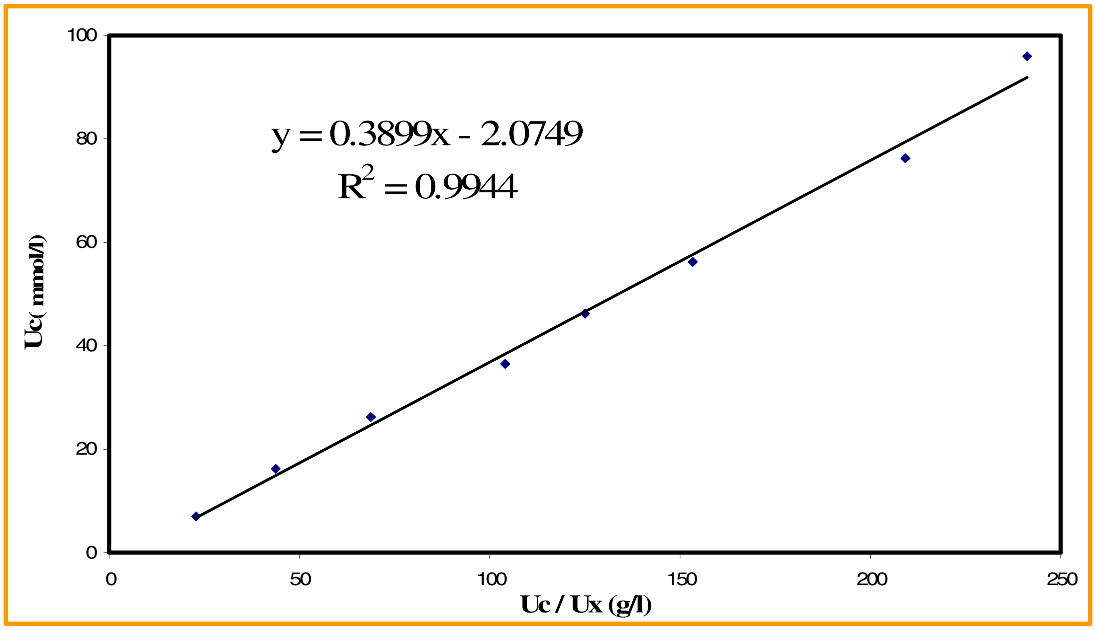


Figure 3-15: The ability of MNSA-20 for uptaking uranium

The procedure to assay the molar capacity of the extractant consists of four stages. First, a range of stock solutions of UO_2^{2+} concentrations [Us] were prepared in range from 0.01 M to 0.1 M, and were used to prepare the calibration standard curves. Then, 10 g of aliquots UO_2^{2+} solutions were mixed with 0.1 g of each synthesized extractant with stirring for two hours, which proved to be a sufficient time to reach equilibrium. The ratio of extractant to uranium solution was kept low (1:100 times). The third stage is the magnetic filtration for mixtures. Finally, the concentration of UO_2^{+2} in the permeate [Uc] (the equilibrium concentration) was measured by UV-visible spectroscopy. The wavelength for the absorption measurements was observed at the maximum visible light absorption (λ_{max}), which for uranium is at 415 nm.

Table 3-1 summarizes the ability of uptaking uranium by the synthesized magnetic extractants. First of all, the ability of uncoated magnetite nanoparticles was tested for uptaking uranium from water. These particles show no affinity for removal of uranium. As a consequence, magnetite particles play just one role as a magnetic property provider. All synthesized extractants were effectively shown to remove uranium contaminants from water. Indeed, some extractants showed a powerful ability to extract uranium from water.

Table 3-1

Results from treatment of aqueous solutions of uranium with magnetic extractants and their surface area

Extractant	**Capacity of Uptaking (mg/g)**	**Surface area (m^2/g)**	**Capacity of Uptaking (mg/m^2)**
Uncoated magnetite	**0.0**	**56.8**	**0.0**
MNSA-20	**152.08**	**59.2**	**2.6**
MNSA-10	**105.29**	**51.4**	**2.01**
MNST-20	**142.50**	**14.5**	**9.9**
AEAPS-MN	**1,250**	**1.5**	**822.4**
PyAEAPS-MN	**850**	**1.3**	**674.6**

The increased ability for adsorption of uranium for AEAPS-MN and PyAEAPS-MN over the other extractants can be attributed to hard/soft acid base principles. The AEAPS-MN and PyAEAPS-MN particles have spherical shape from TEM and SEM, and the size of the particles ranged from about 10 to 20 nm with the mean size of about 12 nm. The mean surface area of a single particle is about 450 nm^2 (calculated from $S = 4\pi R^2$ where R is the mean radius of particles). The TGA of them (as AEAPS-MN in Figure 3-4) shows that about 38 % of extractant particle is a silane polymer which has a high density of reactive amino groups on the surface of the extractant. The existence of the amino groups, which can reduce the surface energy of magnetite nanoparticles, leads to an improvement in uniformity and control of the particles agglomeration since the amino group is a strong electron donor that can adsorb the UO_2^{2+} ions from water. Consequently, this leads to a marked improvement in the ability of AEAPS-MN and PyAEAPS-MN for removal of uranium, where the uptaking ability of extractants is 125 % and 85 % by weight, respectively.

The other extractants (MNAS-10, MNAS-20, and MNTS-20) performed very well compared to values in the literature. The surfaces of MNAS-10 and MNAS-20 are anionic in water near neutral pH. Therefore, the uranyl ions are electrostatically adsorb to the extractant surface. Although, the MNTS-20 has at least four times less surface area than MNAS-20, it has about the same uptake capacity (mg/g), and it has triple times the uptake capacity per meter square of extractant. The enhanced adsorption of MNTS-20 over the MNAS extractants can be attributed to the fact that the surface of the MNTS-20 has SH groups that act as electron donors.

3.7 Conclusions

Supermagnetic nanoparticles were prepared by co-precipitation from ferrous and ferric electrolyte solutions at high pH. The resulting particles had diameter of 10-20 nm. They were coated by silane reagents to generate novel magnetic extractants that can act as single component magnetic filtration aids. The synthesized magnetic extractants effectively removed uranium and, by extrapolation, other radioactive metals from water. Fruitfully, the ability of some of the extractants exceeds about 100 % weight of uptaking uranium. These results are also promising in that the extractants have other potential applications (e.g. catalysts, drug delivery agents, etc.) as well.

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CHAPTER 4

Removal of Heavy Metals (Mercury and Copper) Pollutants from Water Using Magnetic Filtration

4.1 Introduction

The aim of this chapter is the development of magnetic extractants for use in removal of heavy metals from water. In the last century, the global interest in the concentration of the heavy metals in aquatic environments has increased due to environmental and public health problems. Most of the heavy metal contaminants are waste products of industrial and metallurgical processes such as the effluents from electroplating and metal finishing operations where large amounts of heavy metals are discharged daily into the environment. Heavy metals can easily contaminate a water system due to their high solubility in water.

Heavy metals are a group of chemical elements (metal or semimetal) that have a relatively high density (specific gravity) and are toxic at low concentrations such as copper, mercury, lead, nickel, cadmium, platinum, and zinc. Heavy metals can be naturally found in the Earth's crust. They are highly stable in the environment and, therefore, they tend to accumulate in soils and sediments. Heavy metals may enter the human body from ingested contaminated food, using contaminated water for drinking or irrigation, air, or by absorption through the human skin. As a consequence, metals interfere with the function of organs and affect the human health. Even though some heavy metals, such as zinc, copper, chromium, iron, and manganese, are required by the human body in tiny amounts for human metabolism, they can be toxic in larger amounts. Following are some details about mercury and copper which have been selected as representative heavy metals.

Mercury is one of the transition metals and is a shiny, silver-gray metal that is liquid at room temperature. It has eighty electrons and rarely occurs free in nature. Also, it is the heaviest known elemental liquid since its density is 13.534 $g{\cdot}cm^{-3}$ at room temperature. Mercury can exist into three oxidation states that are zero, one, and two. The monovalent state is less common than the others and it can be found as diatomic Hg_2^{II}. Salts mercury compounds can occur as inorganic or organic materials, the latter being more toxic such as methyl mercury. Mercury possesses a high affinity for sulfur and thus cinnabar (HgS) is the most common ore in the environment.

Mercury is released into the environment through natural processes such as volcanic activity, weathering of rocks, disposal of certain products (batteries, medical products, and thermostats), and industrial wastes. These releases have been primarily from chemical and allied industries. The EPAs Toxic Chemical Release Inventory reported that mercury releases to land and water totaled nearly 68,000 lbs from 1987 to 1993.[1] Mercury and its compounds are highly toxic to humans, especially elemental mercury and methyl mercury. Humans can be exposed to mercury via absorption through the skin, respiration, or ingestion. Mercury can affect the central nervous system, mouth, teeth, and gums. It can also damage the heart, liver, and kidney. The EPA has set the maximum contaminant level (MCL) as 2 ppb.

Copper occurs naturally as one of the most important metals for industry since it has excellent electrical and heat conductivity. Copper and its alloys are used to make different products that can be used in households, such as wire and plumbing pipes. The atomic number of copper is 29, and its density is 8.96 $g{\cdot}cm^{-3}$. Copper can exist as Cu^{+1} (cuprous) or Cu^{+2} (cupric). Copper (II) is the most stable and forms blue or blue-green solutions. Humans are mainly exposed to copper through the consumption of water coming from copper plumbing pipes. The EPA has set the maximum contaminant level goal (MCLG) copper as 1.3 ppb. Exposure to high levels of copper can cause nausea, vomiting, and diarrhea. A very high level of copper can cause damage to the liver and kidneys, and might lead to death.

A variety of physical and chemical treatment techniques have been used for the removal of heavy metals from water. These include chemical precipitation, ion exchange, activated carbon adsorption and membrane filtration. Although, these methods have advantages they also present some limitations. The details of some of the methods that are widely used for removal of heavy metals will be explained with more attention being given to mercury and copper. The chemical precipitation method is widely used for removal of heavy metals in industrial plants. The method depends on increasing the pH of the treated water. Consequently, the dissolved metal ions are converted into insoluble metal hydroxide precipitates and the resultant solid (sludge) is then settled out and removed.[2] Common reagents can be used to precipitate metals including alkalis, and sulfides such as lime, magnesia, NaOH, $NaHCO_3$, Na_2CO_3, Na_2S, H_2S, NaHS, or FeS.[3]

Tunay reported the ability of using hydroxyl precipitation for removal of copper, nickel, and cadmium.[4] They also used Ca(II) as a ligand-sharing agent for ethylenediamine-tetraacetic acid (EDTA) and nitrilotriacetic acid (NTA).

Sodium or potassium dimethyldithiocarbamate, or other sulfur containing reagents, are widely used for removal of mercury from water by forming insoluble complexes.[5] The precipitates with mercury can be easily removed from water, but they have to be removed immediately or mercury will leach out into the solution.[6] Furthermore, sulfur-containing reagents might decompose to release more toxic materials into the water environment.[7] Additionally, a large amount of chemical is needed and a large amount of sludge is produced that requires additional treatment.

Ion exchange methods are used to remove heavy metals by using an exchanger that can be natural or synthetic. Reversible interchange of ions occurs between the exchanger and the contaminated water. A research group reported the synthesis of an ion exchanger that was functionalized by thiol groups that was useful for removal of trace concentrations of mercury from water.[8] Another group examined lithium-, sodium-, potassium-, rubidium- and cesium- based Y zeolites for removal of copper ions from water.[9] Ion exchange has some limitations since contaminated water requires pretreatment to remove suspended solids prior to the treatment by a resin, and it is not applicable for high metal concentrations.[10] Additionally, it is not cost effective and not all heavy metals are removable by this method.

Adsorption technology clearly is the best alternative for removal of heavy metals from water. Metal ions are transferred from the water to the surface of the adsorbents (solid) and are bound by physical or/and chemical interactions. There are several varieties of adsorbents reported in the literature includes natural materials, agricultural waste, industrial by-products, and activated carbon.[11-14]

Although, all of these above methods have some advantages, researchers are still looking for a system that is economical to operate, requires little equipment, has no harmful impact on the environment, and does not pose safety and health problems to workers. This thesis addresses methods to synthesize appropriate magnetic extractants which can eliminate heavy metals from water.

4.2 Experimental

All reagents were ACS reagent grade and were used without further purification. Water was purified by reverse osmosis and deionization. Toluene was HPLC grade and was used as received. 3-[2-(2-Aminoethylamino)ethylamino]propyltrimethoxysilane, and mercaptopropyltrimethoxysilane were used to coat magnetite nanoparticles, and diphenylthiocarbazone, carbon tetrachloride,and sulfuric acid were used to assess the mercury concentration. Also, mercury acetate and copper acetate were used to prepare work solution. Figure 4-1 illustrates the reagents structures that were not described previously.

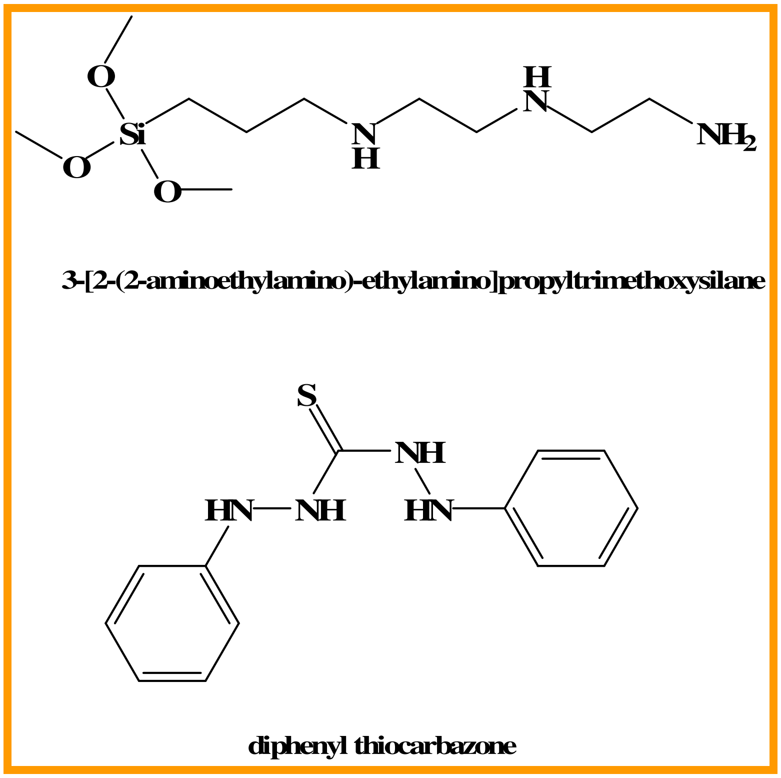

Figure 4-1: Reagent structure

Magnetic filtration was performed using the same method described in the previous chapters. The extractants were characterized using several techniques that are described in Chapters Two and Three. Additionally, IR and Raman spectroscopies were also used.

4.3 Preparation of Extractants

Preparation of Mercaptopropylsilsesquioxane Coated Magnetite Nanoparticles

Magnetite nanoparticles (7.02 g) were added to a solution of mercaptopropyltrimethoxysilane (2.5 g) in toluene (30 ml). The reaction mixture was then stirred using a mechanical stirrer at 80 °C for 24 hours. Afterwards, the derivitized material was isolated by filtration, washed extensively with toluene to remove unattached molecules, and was dried in an oven at 65 °C. The material, designated MERS-MN, was obtained in yield of 7.61 g. IR (KBr, cm^{-1}): 3669 (w), 3307 (m), 3044 (m), 2902 (m), 2818 (m), 2392 (s, br), 2296 (w), 2022 (w, br), 1764 (w), 1570 (w), 1437 (s, sh), 1366 (s, sh), 1258 (m), 1079 (m), 903 (w, br), 737(w), 643(m).

Preparation of 3-[2-(2-Aminoethylamino)ethylamino]propylsilsesquioxane Coated Magnetite Nanoparticles

Magnetite nanoparticles (4.0 g) were placed in a hybridization tube along with a solution of 3-[2-(2-aminoethylamino)ethylamino]propyltrimethoxysilane (1.0 g) in toluene (23 g). The mixture was heated to 40 °C for 24 hours while being rotated in a hybridization oven. Afterwards, the derivitized material was isolated by filtration, was washed extensively with toluene, and was dried in an oven at 65 °C. The material was obtained in a yield of 3.63 g of product and will be referred to as TAS-MN. IR (KBr, cm^{-1}): 3666 (w), 3427 (w), 3427 (m), 2949 (w), 2772 (m, br), 2596 (m, br), 2286 (m), 1756 (w), 1585 (m), 1499 (w), 1297 (w), 1144 (s), 1045 (s), 888 (w), 744 (s), 593 (s), 470 (m).

4.4 Testing of Magnetic Extractants

Testing of Magnetic Extractant for Mercury Removal from Water

A range of different concentrations of stock solutions of Hg^{2+} (8 ppm – 20 ppm) was prepared and treated with the synthesized magnetic extractant. The mixtures were stirred for two hours and then were filtered via magnetic filtration. The equilibrium concentrations of Hg^{2+} solutions were assessed by using a colorimetric method. Diphenyl thiocarbazone of 1.95 x 10^{-4} M was prepared in carbon tetrachloride. Then 5 ml of Hg^{2+} was mixed with 5 ml of sulfuric acid (1 N) and then extracted with 10 ml of the diphenyl thiocarbazone solution. UV visible spectroscopy was used to measure the concentration of Hg^{2+} in the permeate solution (the equilibrium concentration) and the absorption measurements was observed at 675 nm.

Testing of Magnetic Extractant for Copper Removal from Water

A range of different concentrations of stock solutions of cupper acetate (Cu^{2+}) (0.03 M – 0.08 M) was prepared and treated with the synthesized magnetic extractant. The mixtures were stirred for two hours and then filtered via magnetic filtration. UV visible spectroscopy was used to measure the concentration of Cu^{2+} in the permeate solution (the equilibrium concentration) and the absorption measurements was observed at 640 nm. The Langmuir isotherm equation was applied to calculate the adsorption capacity of the magnetic extractants.

4.5 Results and Discussion

The focus of this chapter was to describe the extraction of mercury (II) and cupper (II) ions from contaminated water by using magnetic extractants via magnetic filtration. Magnetite nanoparticles were used as the source for magnetism in the synthesized extractants. The magnetite nanoparticles were synthesized by mixing Fe(II) and Fe(III) salts in a high pH aqueous solution. All details and characterization of the synthesized magnetite particles were extensively discussed in Chapter Three.

Two different silane reagents were used to coat the magnetite particle surfaces since silane reagents are able to link covalently to a hydroxylatd surface.[15] It is well known from the literature that magnetite particles that are synthesized by co-precipitation have extensive qualities of hydroxyl groups on the surface via contact with aqueous solution. Consequently, these groups can be easily coupled with any silane reagent by the formation of Fe-O-Si covalent bonds.[16]

Mercaptopropyltrimethoxysilane reagent was used to coat the magnetite nanoparticles. The mentioned reagent was utilized in Chapter Three, where the reagent was used to synthesize the prepolymer prior to coating magnetite particles. This procedure reduces the number of the functional groups on the surface of the particles. In order to increase the number of functional groups, the reagent was reacted with magnetite particles at low temperature to graft the functional groups on the magnetite particles surfaces. Figure 4-1 illustrates the reaction between the magnetite nanoparticles and the mercaptopropyltrimethoxysilane reagent. The material will be referred to as MERS-MN.

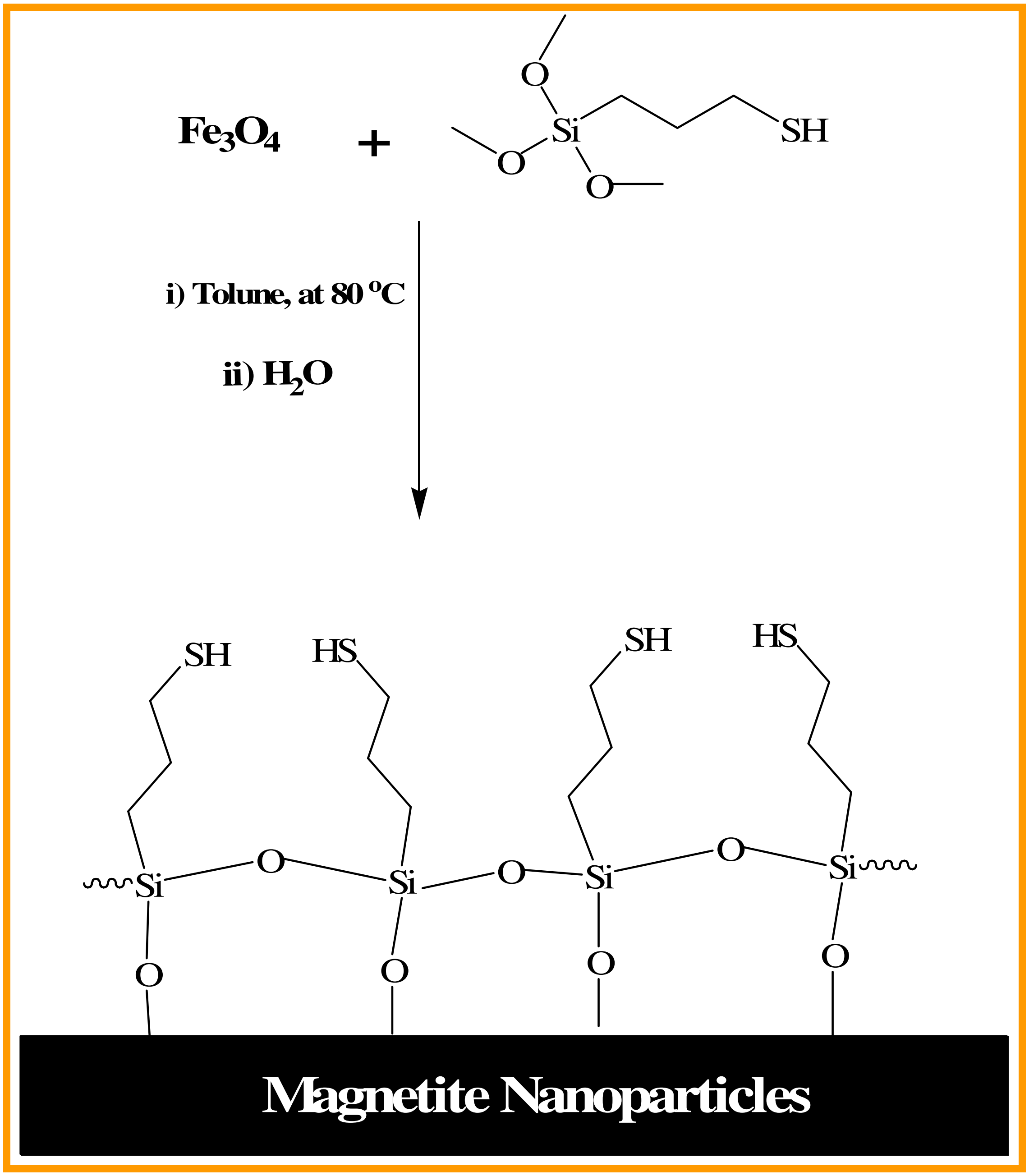

Figure 4-2: Cartoon exemplifying the reaction between the reagent and the magnetite nanoparticles

This reaction led to composite materials that consisted of two components. The first component was the magnetite nanoparticles that offered magnetic properties to the composite materials. The second phase was a layer of polymerized silsesquioxane that coated the metal particles. Thus, the extractant surface has pendant mercaptopropyl groups that facilitate removal of mercury ions from water. This procedure was used in Chapters Two and Three where it was extensively discussed.

The FTIR spectrum of the MERS-MN extractant contained absorption bands at 2392 cm^{-1} and 2818 cm^{-1} that are characteristic of a stretching vibration for thiol groups, and a peak at 1097 cm^{-1} that was due to a Si-O stretching vibration. Moreover, the spectra also indicate the possible existence of silanol groups that remain after reaction due to the bands displayed from 3700-3000 cm^{-1}. Comparison of the IR spectra of MERS-MN extractant and the MNTS-20 extractant that is coated by thiol functionalized ormosil showed that the MERS-MN extractant had higher intensity bands in the range 2200–2500 cm^{-1} than the other as shown in Figure 4-3. Thus, the MERS-MN has more thiol groups on its surface as predicted.

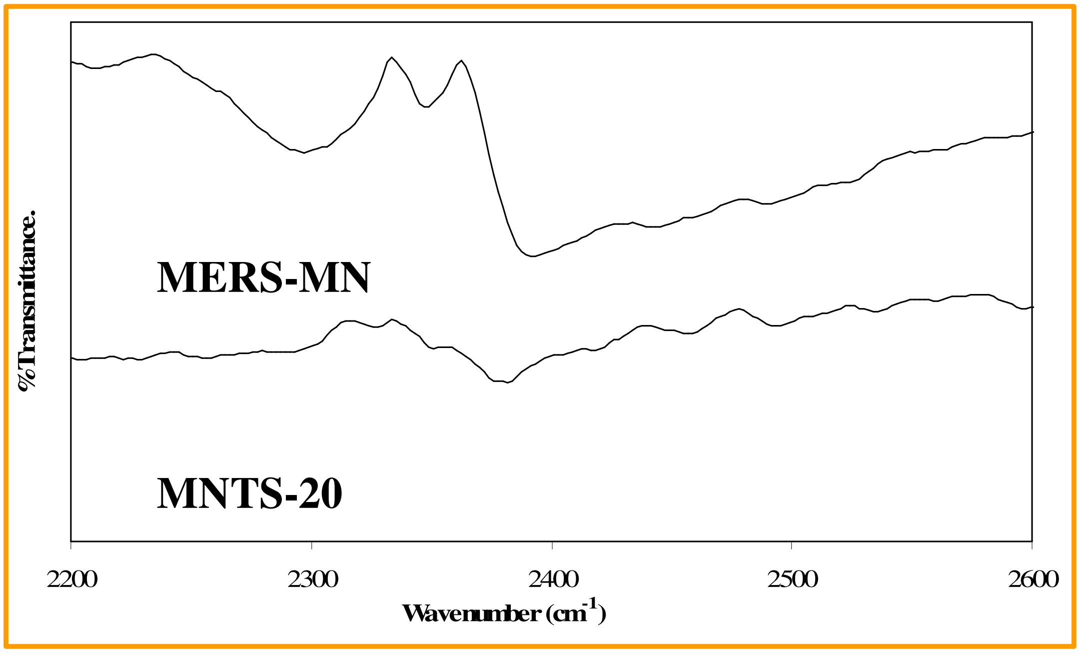

Figure 4-3: IR spectra of MERS-MN and MNTS-20

Thermogravimetric analysis studies of MERS-MN and MNTS-20 extractants were conducted upto 800 °C and are shown in Table 4-1. This confirmed that the surface of MERS-MN extractant had more organic groups than MNTS-20 extractant. Since the resultant in both extractants is hematite coated by silica.

Table 4-1

The Thermogravimetric analysis data of thiol functionalized extractants

Extractant	% weight lost	SSA (m^2/g)
MERS-MN	22.95	21.3
MNTS-20	14.85	14.5

The thiol functionalized magnetite particles have a surface area larger than the amino functionalized magnetite particles. This difference might be explained by the mercaptopropyl groups which aggregated on the magnetite surface in a way to leave cavities and holes. Together the IR data and thermogravimetric analysis confirmed the previous prediction that the surface of MNTS-20 extractant was covered by thiol functionalized ormosil.

3-[2-(2-Aminoethylamino)ethylamino]propyltrimethoxysilane was used as another reagent for coating magnetite particles. This reagent is well-known as a triaminosilane since its structure has three amine groups. The same procedure that was used in Chapter Three to synthesize the extractants at low temperature was used. However, a sealed tube was employed here in the syntheses in order to control the hydrolysis and condensation reactions, since the terminal amine group of the reagent can accelerate the condensation reactions.[17] Although, the terminal amine group can adsorb onto the hydroxyl groups on the magnetite surface, the oxygen atom is easily attached to a silicon atom on another molecule. However the same reactions can occur between two hydrolyzed triaminosilane molecules leading to an increase in condensation. This synthesis led to materials coated by 3-[2-(2-aminoethylamino)ethylamino]propylsilsesquioxane. The magnetite particle surfaces bear amine groups that are attached to the surface by siloxane networks. This extractants will be referred to as TAS-MN.

The IR spectrum of TAS-MN shows absorption bands at roughly 3427 cm^{-1} and 1585 cm^{-1} due to the NH_2 group vibration. The Raman spectrum showed absorption bands for the amine at roughly 2834 cm^{-1} and 1528 cm^{-1}. Also a band at 1295 cm^{-1} due to the C-N stretch (see Figure 4-4) was observed. This confirmed that the particles were successfully coated by the triaminosilane.

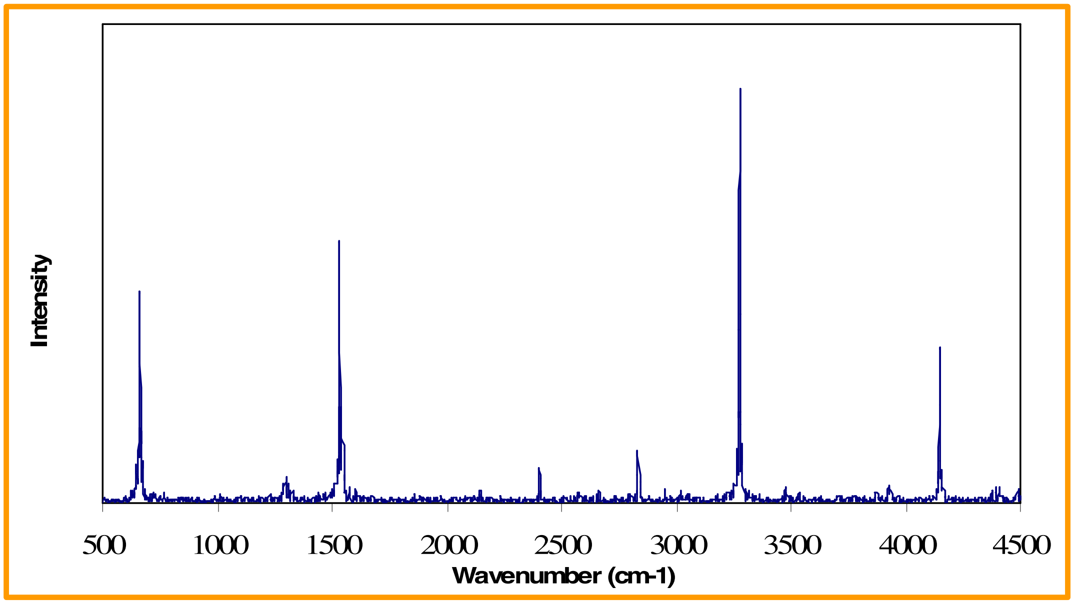

Figure 4-4: Raman spectra from TAS-MN extractant

The thermogravimetric study of the TAS-MN extractant fired at 800 °C shows that the weight loss was 26.26% of its weight. At 800 °C, the organic groups decompose and the magnetite particles were converted to hematite particles that were only coated by silica with no additional organic groups. The percentage of triaminosilane coating can be roughly estimated to be 38%-40%, this is similar to that observed for the diaminosilane coating. Furthermore, the TAS-MN extractant specific surface area was 10.3 m^2/g which is remarkable since it was almost nine times the AEAPS-MN surface area where the coating was diaminosilane. The TAS-MN extractant gave very stable suspensions when stirred with distilled water at natural pH. Particle size was assessed by Dynamic Light Scattering (DLS). Figure 4-5 shows the particle size of the extractant, and the data in the graphs express size distribution by intensity. The TAS-MN particles have an average size of 66.4 nm and polydispersity index of 0.215. The TAS-MN extractant particles have lower size than the particle that was coated by diaminosilane. This result is in agreement with another study that reported triaminosilane-coated flat glass surface has higher surface charge, positive charge at pH = 7, than that coated by diaminosilane.[18]

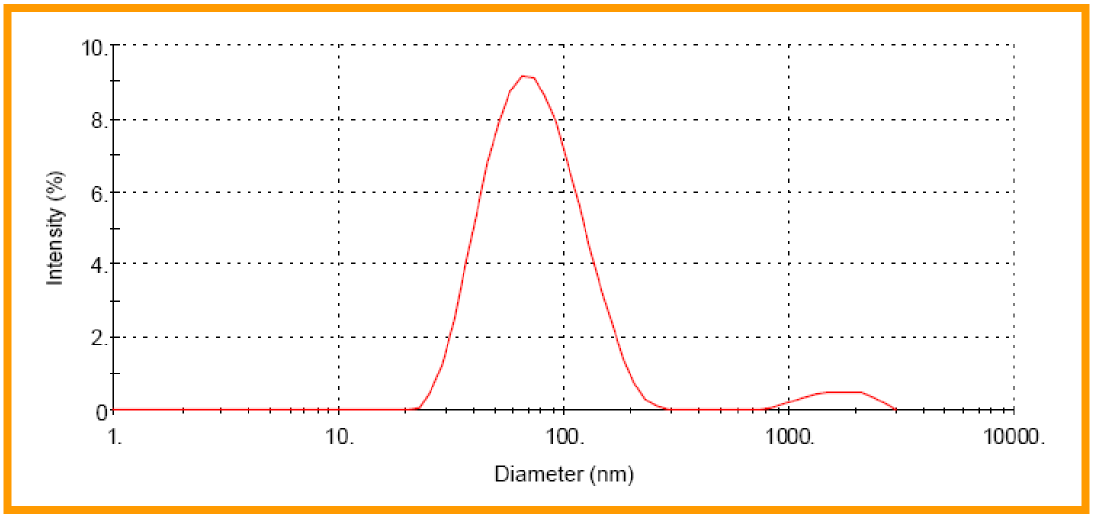

Figure 4-5: DLS graphs of the TAS-MN extractant

Testing of Magnetic Extractants for Mercury Removal from Aqueous Solution

Two extractants functionalized by thiol groups were tested for their ability to uptake mercury ions from water, namely MERS-MN and MNTS-20 extractants. Both of extractants have thiol groups on their surfaces, and the thiol group is well-known for high binding affinity towards mercury ions. The MNTS-20 extractant performed poorly compared with the other extractant (MERS-MN) as predicted. The MERS-MN extractant has larger number of –SH groups that can bind to mercury ions. Figure 4-6 illustrates the ability of both extractants when different masses of each extractant were used to treat an aqueous solution of 12 ppm mercury. It is clear that the MERS-MN (solid line) extractant has the higher ability for removal of mercury ions which increased dramatically with increasing the mass of extractant.

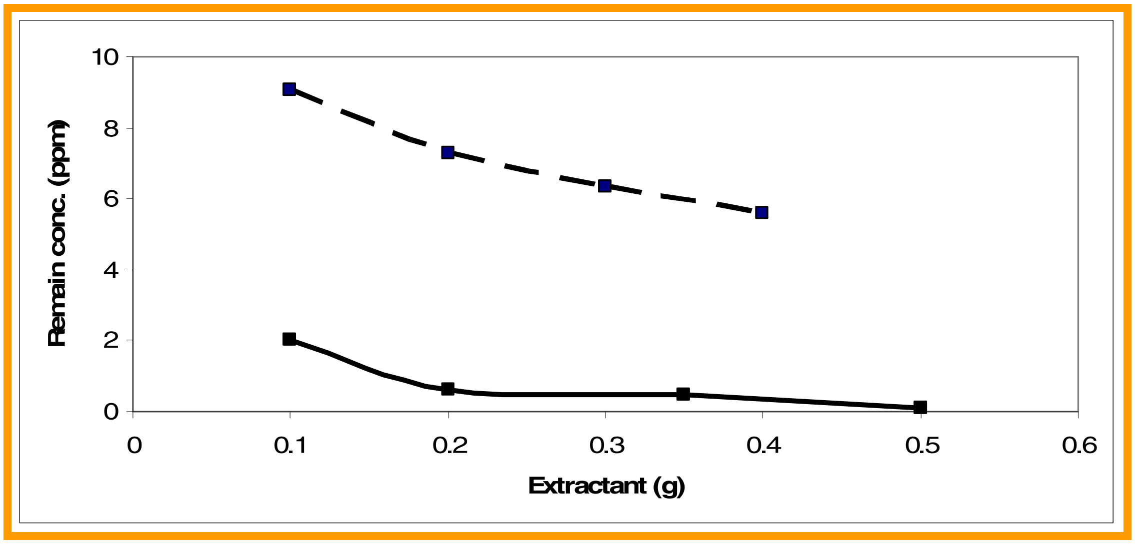

Figure 4-6: The ability of uptaking mercury ions by MERS-MN (solid line) and MNTS-20 (dash line)

The recovery concentrations of the treated solutions were assessed by using a colorimetric method. Diphenylthiocarbazone, which is known as dithizone, was used as an organic colorimetric reagent for this determination. Dithizone is widely used to determine concentrations of heavy metals such as zinc, lead, and mercury.[19] Dithizone (H_2Dz) is insoluble in water but it is soluble in carbon tetrachloride. Moreover, it can form a chelate complex with the mercury ions called mercury dithizonate.

The procedure to assay the ability of the extractants to remove mercury ions from water consists of four steps. First, a stock aqueous solution of Hg^{2+} and dithizone solution in carbon tetrachloride were prepared in 12 ppm and $1.95 \text{ X } 10^{-5}$ M, respectively. Then, 10 g of Hg^{2+} solution was mixed with a specific amount of each synthesized extractant which range from 0.1 g–0.5 g with stirring for two hours, which proved to be a sufficient time to reach equilibrium. The second step was the magnetic filtration for mixtures. In the next step, 5 g of the resulting solution was extracted with 5 g of dithizone solution after acidifying with 5 g of 1 N sulfuric acid. Two phases were produce after 5 minutes of shaking; the lower phase was the dithizone solution which includes mercury dithizonate.

The equilibrium concentration of Hg^{2+} was measured by UV-visible spectroscopy. The wavelength for the absorption measurements was 675 nm. In contrast, many research groups, who used dithizone to determine mercury concentration, usually selected wavelengths around 490 nm.[20,21] This wavelength of 675 nm was selected since dithizone has two peaks. Indeed, mercury dithizonate has just one peak in the same range as in the Figure 4-7.

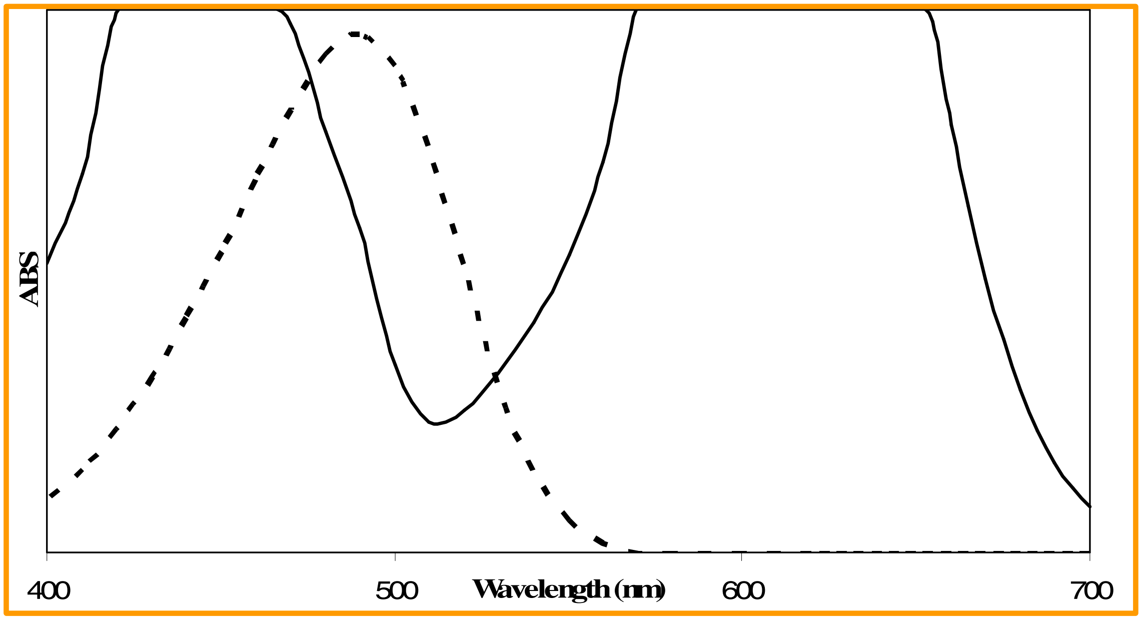

Figure 4-7: Absorbance spectra of dithizone (solid line) and mercury dithizonate (dashed line)

The proposed method is called “reverse mercury determination”. At 675 nm, mercury dithizonate complexes show no adsorption, but there is an effect on absorbance intensities of the peaks that correspond to dithizone. The concentration of unreacted dithizone can be determined from the peak at 675 nm, and the concentration of reacted dithizone can be obtained by subtracting the two concentrations. The result is equal to the concentration of mercury in the sample since the mercury ion forms a chelate complex with two dithizone molecules but the sample dilution corrects for this factor. For instance, Figure 4-8 shows the absorbance spectra of treated solution of 20 ppm mercury along with dithizone. Indeed, the proposed method has less interference from the reacted and unreacted dithizone.

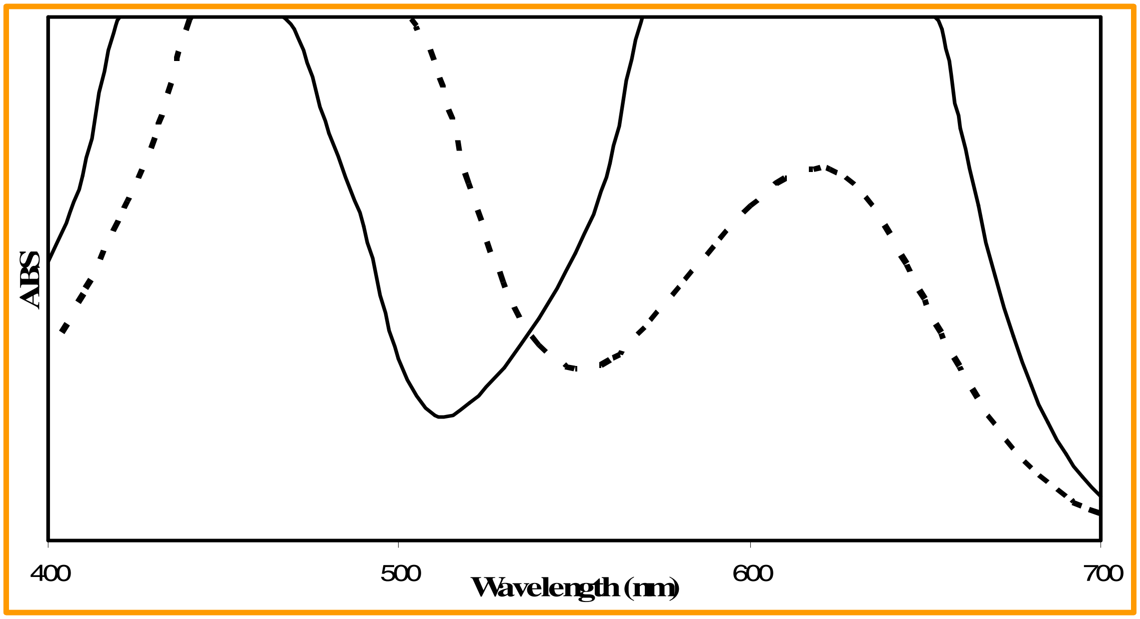

Figure 4-8: Absorbance spectra of dithizone (solid line) and treated solution of 20 ppm mercury(dashed line).

The capacity of the MERS-MN extractant was calculated to be 1.3 mg/g by using the Langmuir equation. This result demonstrates a promising potential for magnetic separation of heavy metals ions from water. The poor uptake ability of MNTS-20 extractant can be attributed primarily to a low concentration of thiol groups loaded on the surface of extractant. Moreover, these results indicated that the siloxane networks have no affinity for adsorption of mercury ions from water.

Testing of Magnetic Extractants for Copper Removal from Aqueous Solution

The TAS-MN extractant was used for removal of copper ions from water since the extractant surface is covered by amine groups. The same procedure to estimate the molar capacity of the extractant that was used in the Third Chapter has been used. First, a range of stock solutions of Cu^{2+} concentrations were prepared [0.03 M to 0.08 M], and were used to prepare the calibration standard curves. Then, 10 g of Cu^{2+}solution was mixed with 0.1 g of TAS-MN extractant with stirring for two hours, which proved to be sufficient time to reach equilibrium. The next step was the use of magnetic filtration of the mixtures. Next, if necessary, Hydrochloric acid [1 M] was added if the filtrate had suspended particles. Finally, the concentrations of Cu^{2+} (the equilibrium concentration) were measured by UV-visible spectroscopy. The wavelength for the absorption measurements was observed at the maximum visible light absorption (λ_{max}), which was at 645 nm. The Langmuir equation was used to assess the uptake capacity of the extractant as in Figure 4-7. The uptake capacity of the TAS-MN extractant was fond to be 83.8 mg/g.

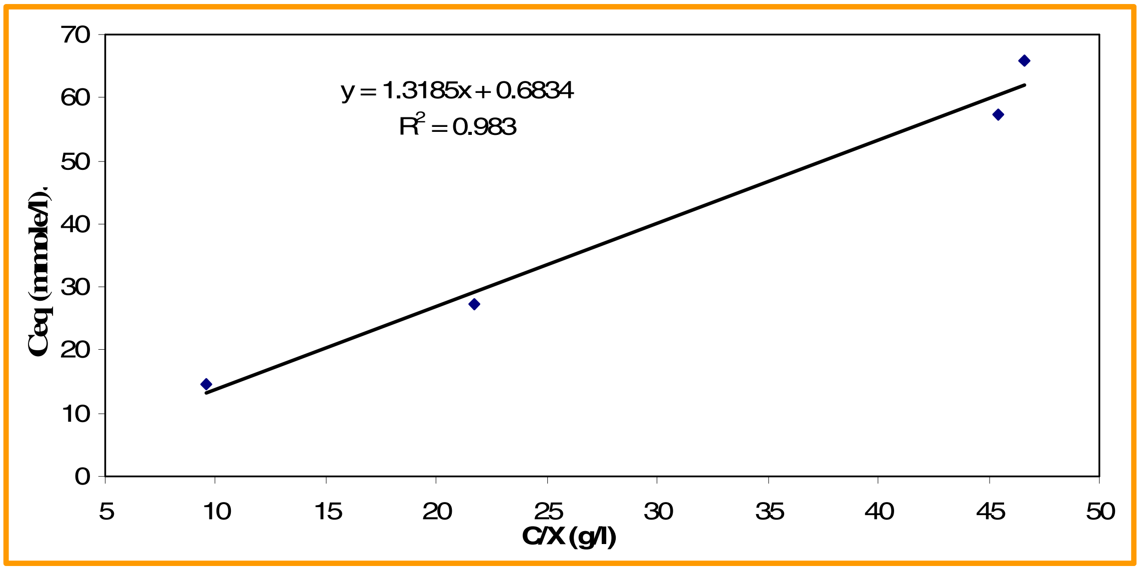

Figure 4-7: The Langmuir adsorption of copper ions by using TAS-MN extractant

4.6 Conclusions

Magnetic nanoparticles were prepared by co-precipitation from ferrous and ferric electrolyte solutions at high pH. Triaminosilane and mercaptolsilane reagents were used to coat magnetite particles to produce successful novel magnetic extractants that can act as single component magnetic filtration aids. The amine functionalized extractant effectively removed copper ions from water, with a capacity of 83.8 mg/g. Thiol functionalized extractants were used for removal of mercury from water, and their ability was promising due to increased the surface area and maximizing of the number of functional groups on the surface. By extrapolation, other heavy metals can be removed by the extractants from water. These extractants have other potential applications in industry as catalysts as well.

4.7 References

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Chapter Five

Conclusions and Future Work

5.1 Conclusions

This work demonstrates the ability of novel synthetic, composite and nanocomposite materials, to act as single-component magnetic filtration aids. Magnetic extractants were synthesized by functionalizing the surface of magnetic substrates with various organosilane reagents and siloxane polymers. In the syntheses, procedure were used that led to extractants that were coated by silica, functionalized silsesquioxane, or functionalized ormosil.

In the first part of this research, novel composite materials based on iron, hematite or magnetite were synthesized for removal of hydrocarbons. The surface of the iron and iron oxides were derivitized to provide hydrophobic active sites for adsorption of hydrocarbons. All extractants demonstrated excellent performance and reduced the concentration of decane in spiked water to the parts per billon level. Indeed, some extractants showed a powerful ability to extract decane from water to achieve a concentration of less than 1 pbb. By extrapolation, numerous other hydrocarbons could be removed from water by the synthesized extractants. Several magnetite-based extractants were demonstrated to remove dyes from water via magnetic filtration. These also showed promise for selective separation of dyes from aqueous solutions.

In the second part of the research, magnetite nanoparticles were prepared by co-precipitation of ferrous and ferric ions by treatment with base. Mercaptosilane and di- and triaminosilanes were used to coat the magnetite nanoparticles in order to produce magnetic extractants that could act as single components magnetic filtration aids. At low temperatures, magnetite particles were coated with functionalized silsesquioxane of the general formal $[RSiO_{1.5}]_X$. At high temperatures, particles were coated with silica or functionalized ormosil. The synthesized magnetic extractants effectively removed radioactive species and heavy metals and, by extrapolation, other metal ions from water. In the case of magnetite nanoparticles coated with diamino functionalized silsesquioxane, the uptake capacity for uranium was as high as 125 % by weight. Moreover, the thiol derivitized extractant showed an uptake capacity for copper ions of 83 mg/g. These results are also promising in that the extractants have other potential applications (e.g. catalysts, drug delivery agents, etc.) as well.

5.2 Future work

The results of the investigation suggest several promising avenues for development of magnetic extractants in the future. One suggestion is increasing the surface area of the extractants with the aim of increasing the active sites on the surface. Additionally, the detailed reaction chemistry between the organosilane reagents and the magnetite particles surfaces requires more investigation to develop enhanced methods to synthesize and control surface properties. The magnetite nanoparticles need further study to prevent their aggregation and to more deeply probe their magnetic properties. The immobilization of other functional groups on the extractant surfaces can potentially increase selectivity.

VITA

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Doctor of Philosophy

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Scope and Method of Study: The objective of this research was the development of new magnetic methods for the removal of contaminants from water via magnetic filtration. These processes provide several advantages such as extremely rapid separations and remote operation that promotes safety and prevents health problems to workers. Since most of the pollutants in water are weakly magnetic or diamagnetic, they are not amenable to magnetic filtration. For this reason, magnetically-active extractants were synthesized that allow the separation of such species via magnetic filtration. In the first aspect of this research, novel composite materials were synthesized based on iron, hematite, or magnetite for removal of hydrocarbons. The surface of the iron and iron oxides were derivitized with alkylalkoxysilane reagents and siloxane polymers in order to provide hydrophobic active sites for hydrocarbons. All extractants demonstrated excellent performance and reduced the concentration of decane in spiked water to the parts per billon level. Indeed, some extractants showed a powerful ability to extract and remove decane concentration to less than 1 ppb. The second aspect involved the synthesis of coated magnetite nanoparticles prepared by treating magnetite nanoparticles with amino- or mercaptomethoxy-silane. The aminosilsesquioxane extractant was functionalized by a pyridine group. The performance of the synthesized extractants was investigated for the removal of radioactive substances (uranium) and heavy metals (mercury and copper) from water. It was found that the resulting materials were highly effective for purifying water contains these toxic metal ions. In the case of magnetite nanoparticles coated with diaminosilane, the uranium uptake can be as high as 125 % by weight.

Findings and Conclusion: Novel composite and nanocomposite materials were determined to be excellent single component magnetic filtration aids**.** The synthesized extractants can also be used for other contaminants and might have other potential applications (e.g. catalysts, drug delivery agents)

ADVOSER'S APROVAL: _____ **Dr. Allen Apblett**: ___________________________