

REMOVAL OF ARSENIC, PHOSPHATE AND  
CHROMATE FROM WATER BY IRON FUMARATE

By

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REMOVAL OF ARSENIC, PHOSPHATE AND  
CHROMATE FROM WATER BY IRON FUMARATE

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Abstract: Water is often called the “universal solvent” for its ability to dissolve a wide range of chemicals. Water may therefore contain a wide variety of dissolved substances. Often, these may be toxic compounds such as arsenic which can turn groundwater into poison. Other compounds may not harm us directly, but may lead to dangerous changes in the environment (phosphorus).

We have developed a family of compounds based on an iron fumarate coordination polymer. The material was synthesized in a precipitation reaction from the reaction of ferric chloride and disodium fumarate. Synthesis was carried out in water at room temperature, open to the atmosphere. The empirical formula is believed to be  $\text{Fe}(\text{C}_4\text{H}_2\text{O}_4)(\text{OH}) \cdot 0.5\text{H}_2\text{O}$ . Iron fumarate has been shown to react with phosphate, arsenate, arsenite and dichromate. It represents an advantage over other iron based materials due to ease of synthesis and high capacity for pollutants (phosphate capacity was found to be 690 mg  $\text{PO}_4^{3-}$  / g iron fumarate). The capacity of iron fumarate for dichromate was found to be 26.3 mg Cr(VI) / g iron fumarate.

In the case of arsenate, the material was optimized by changing the iron to fumarate ratio. Several different materials were synthesized and tested. The material synthesized that showed the highest capacity was  $\text{Fe}_4(\text{C}_4\text{H}_2\text{O}_4)_3(\text{OH})_6$  (capacity of 200.9 mg As / g iron fumarate). A relationship was then determined from four of the highest capacity materials. The relationship was used to determine the optimum iron to fumarate ratio for the reaction between iron fumarate and arsenate. The estimated optimum material is  $\text{Fe}_5(\text{C}_4\text{H}_2\text{O}_4)_4(\text{OH})_7$ .

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## CHAPTER I

### INTRODUCTION

Water is absolutely essential to life as we know it. As humans, we require water regularly, and suffer dehydration in a very short time without it. We extract large amounts of water from the hydrosphere daily for use in agriculture, manufacturing, plumbing and a myriad of other applications. When the water has served its purpose, it is sent back into the environment, carrying with it whatever solutes we have added to it. Our use of water invariably changes this precious resource. In addition, water is not static in the environment, and will pick up various chemicals from the biosphere, geosphere and the atmosphere. Water, so important to life, is constantly in a state of flux. Therefore, water quality is an important problem. The demand for clean water is always increasing due to a growing world population. While this is occurring, there is increasing pollution due to urbanization and poor water management practices. There is a clear need to develop technologies for the removal of toxins from water. Heavy metals pose a special problem, in that they are elements, and thus will not break down into harmless substances with time. Clearly there is a need to develop technology to remove heavy metals from water.<sup>1</sup>

Iron oxides and their derivatives are often used to treat contaminated water. Iron oxides, hydroxides and oxyhydroxides are found all around us. Iron is the fourth most abundant element in the earth's crust, and its oxides are spread throughout the environment. Iron oxides are also fairly complex. There are 17 known iron oxides, hydroxides and oxyhydroxides. These vary in

crystal structure, degree of hydration and composition.<sup>2</sup> Many of the polymorphs of iron oxides are kinetically accessible due to similar overall thermodynamic stability. Therefore, any of a number of them may be formed naturally, depending on how much water is present, particle size and chemical environment.<sup>3</sup>

The two most thermodynamically stable iron oxides are hematite ( $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>) and goethite ( $\alpha$ -FeOOH). They are formed naturally as transformations from other iron oxides. Goethite possesses a distorted hexagonal/orthorhombic structure.<sup>1</sup> It is thought that goethite has two different kinds of active sites. There are triply coordinated Fe<sub>3</sub>OH and Fe<sub>3</sub>O sites. These may be represented as Fe<sub>3</sub>OH<sup>-1/2</sup> and Fe<sub>3</sub>O<sup>-1/2</sup>.<sup>4</sup>

Hematite ( $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>) is the most thermodynamically stable iron oxide, and many thermal transformations of other iron oxides lead to the formation of hematite. It has a hexagonal unit cell structure and is isostructural with corundum.<sup>1</sup> This structure can be thought of as built up by pairs of FeO<sub>6</sub> octahedra.<sup>5</sup>

Magnetite has the formula Fe<sub>3</sub>O<sub>4</sub> and contains mixed valence iron, with two Fe(III) and one Fe(II). It is ferrimagnetic, and has been known to display magnetic properties for hundreds of years. Magnetite has an inverse spinel structure with alternating layers of octahedral and mixed tetrahedral/octahedral irons.<sup>1,6</sup> Maghemite,  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>, has a structure similar to magnetite, but all of the irons are Fe(III). To compensate for the oxidation of iron, cation vacancies are distributed randomly in the octahedral sites in the crystal structure.<sup>5</sup> It is important to note that magnetite and maghemite may mix to form solid solutions.<sup>5</sup>

Akaganeite ( $\beta$ -FeOOH) is isostructural to hollandite.<sup>5</sup> The general formula is FeO<sub>0.80</sub>(OH)<sub>1.20</sub>Cl<sub>0.20</sub> · 0.13H<sub>2</sub>O. In akaganeite, FeO<sub>3</sub>(OH)<sub>3</sub> octahedra share edges to form double chains parallel to the b axis. This forms tunnels in which chloride ions reside, held in place by hydrogen bonding. These chlorides may be involved in ion exchange reactions. The ability of akaganeite to adsorb

and ion exchange makes it a flexible material. It can selectively exchange only certain ions, while those too large to fit in the channels may sorb onto the surface.<sup>1</sup>

Lepidocrocite ( $\gamma$ -FeOOH) has a layered structure. Formation of lepidocrocite is kinetically favorable.<sup>1</sup> Lepidocrocite is made up of double chains of  $\text{Fe}(\text{OOH})_6$  octahedra, where the double chains share edges with each other. These double chains agglomerate into sheets, which are held together by hydrogen bonding.<sup>5</sup>

Ferrihydrite is often formed in precipitation reactions. It is one of the less stable of the naturally occurring iron oxides, but becomes much more stable as particle size decreases.<sup>3</sup> The particle size of ferrihydrite is  $\leq 5$  nm. There is ongoing controversy regarding the structure and formula of ferrihydrite. This probably stems from the fact that it is so poorly crystalline. It is known that there are two primary forms of ferrihydrite, “six-line” and “two-line”, referring to the number of peaks on an X-ray diffraction spectrum. These peaks are very broad, especially for two-line ferrihydrite.<sup>7</sup> The formula is estimated to be  $\text{Fe}_5\text{HO}_8 \cdot 4\text{H}_2\text{O}$ . It is thought that high surface area and coordination make it an especially reactive iron oxide. While core irons are octahedral, surface irons are thought to be tetrahedral and will readily bind with a variety of contaminants.

Zero valent iron is simply iron in its elemental state. It is often used as nanoparticles. Zero valent iron has a standard redox potential of  $-0.44$  V, and this allows it to participate in redox reactions and it can also produce Fenton’s reagent in situ. It is thus used as a reductant and an adsorbent.<sup>8</sup>

Zero-valent iron reacts with arsenic through various processes, including adsorption, co-precipitation and reduction.<sup>9</sup>

## CHAPTER II

### ARSENIC

Arsenic in the environment exists in one of four oxidation states. These include arsenite (+III) and arsenate (+V), and more rarely elemental arsenic (0) and arsine (-III).<sup>10</sup> Arsenic is a strong chalcophile however, and thus it is primarily found in the positive oxidation states.<sup>11</sup> The oxidation state of aqueous arsenic is primarily governed by redox chemistry.

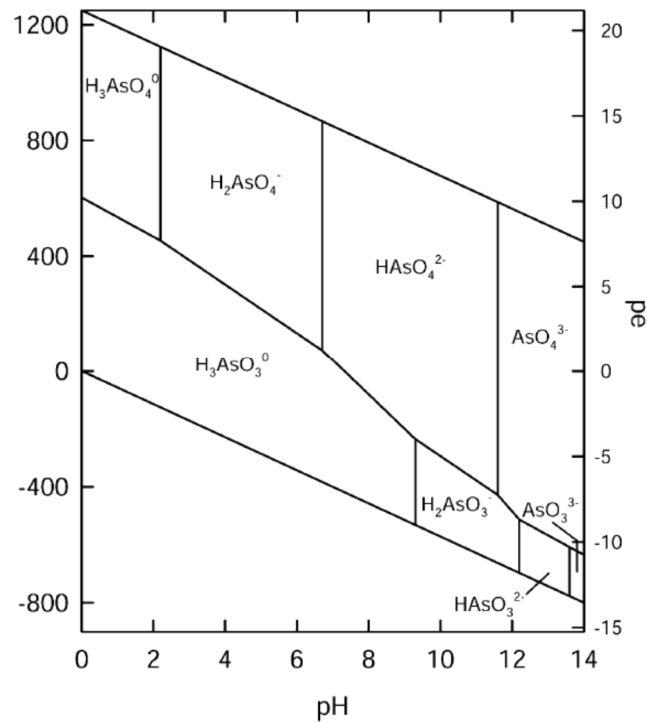


Figure 1. Pourbaix diagram for arsenic<sup>12</sup>

As seen in **Figure 1**, arsenate tends to form at more basic, oxidizing conditions. Arsenite occurs at acidic, reducing conditions. The most important forms of arsenate are monoprotic and diprotic arsenic acid ( $\text{HAsO}_4^{2-}$  and  $\text{H}_2\text{AsO}_4^-$ , respectively). In surface waters, dissolved oxygen often leads to arsenate formation, and it is therefore the most common form. Reducing bacteria can convert arsenate to arsenite, and also may produce arsenosugars. Anthropogenic pollution and natural geologic processes each contribute significantly to levels of arsenic in the environment.<sup>12</sup>

Arsenic is the 20<sup>th</sup> most abundant material in the earth's crust. As a strong chalcophile, it is most commonly found in the minerals arsenopyrite, arsenolite, orpiment, claudetite, arsenic pentoxide, realgar and scorodite. It occurs in over 200 other mineral forms.<sup>11</sup> The most common ore is arsenopyrite ( $\text{FeAsS}$ ), which is often arsenic rich.<sup>12</sup>

Arsenic has a variety of uses to man. It is primarily used today as a wood preservative in the form of chromated copper arsenate, which is a mixture of the oxides of arsenic, chromium and copper.<sup>13</sup> It is estimated that as much as 70% of arsenic produced is used in this way. Another 22% is used in agricultural chemicals. This includes feed additives for swine and poultry, pesticides and herbicides. Other important uses of arsenic include gallium arsenide, a semiconductor and Fowler's solution, a treatment for psoriasis.<sup>11</sup>

Unfortunately, arsenic is toxic to man. While the toxicity is minimal for some organic forms such as arsenosugars, the toxicity of others is extremely high. The most dangerous form is considered to be arsine gas. It is extremely pyrophoric as well as toxic. Thankfully, it is not often encountered. The primary forms of interest to this study are arsenate and arsenite, as these are found in water, and may be consumed with food from plants. Studies have found that arsenite is 60 times more toxic than arsenate.<sup>14</sup> Contrary to the normally observed trend, organoarsenic compounds are usually less toxic than inorganic forms.

Trivalent arsenic is chemically soft and may bind to S – H groups in enzymes. The enzymes are inhibited and rendered ineffective.<sup>10</sup> The toxicity of arsenate primarily stems from its chemical similarity to its lighter group member, phosphorus. Our bodies use phosphorus to synthesize DNA, as an energy currency, and as a component of bones and teeth. Arsenate is similar enough that it will bind to ADP and become incorporated into DNA. Macroscopically, arsenic is a carcinogen that is known to cause kidney and cardiac failure, attack the nervous system, and cause various cancers.

One of the hardest hit areas in the world is the Bengal Basin in Asia, where concentrations up to 3.2 mg / L in the water have been reported.<sup>15</sup> Arsenic in this area arises from unconsolidated settlements. Naturally occurring arsenic is bound to sediments and clays, and is released into drinking water.<sup>16</sup> This has been called the “greatest mass poisoning in history,” with up to 36 million people being affected.<sup>17</sup> This contrasts to the arsenic problem in Chile, where concentrations may reach 21.8 mg / L in river water. These exceptionally high levels are due to geothermal inputs and evaporation. Oxidizing conditions lead to arsenate being the primary form. Arsenic is a problem in many other areas as well, such as the southwestern United States.<sup>12</sup>

There are many methods that may be used to combat arsenic dissolved in water. These include membrane separation, biosorbents, coagulation and precipitation, ion exchange, and adsorption. While it is useful to explore all avenues, and there are cases where any of the mentioned methods may be ideal, adsorption is generally considered to be the most promising method. It avoids the high cost of membrane separation and the sludge formation of coagulation/precipitation processes. Ion exchange may also be expensive. Biosorbents are exciting, inexpensive, but they take time to grow, and only remove arsenic as far down as the roots. Adsorption is commonly explored as the best option, due to its simplicity and effectiveness at high or low concentrations. It is generally inexpensive and versatile.<sup>18</sup>

Materials for absorption may be derived from agricultural or industrial byproducts. While inexpensive, these materials often have low capacities for arsenic.<sup>19</sup> Other materials used include activated carbon, and aluminum- and iron-based materials. Iron is an ideal choice of material for a sorbent because arsenic has a strong binding affinity for it. We have synthesized an iron based sorbent for arsenic extraction from water. It is ideal because it is synthesized from inexpensive and non-toxic starting materials. The synthesis takes place in room temperature water open to the atmosphere. Our material is also highly effective for removing arsenic.

### **Literature Review**

Lakshmipathiraj *et al.* studied the adsorption of arsenate onto goethite prepared from the oxidation of ferrous carbonate. It was determined that adsorption occurred initially via diffusion, and later by chemical modes. The Langmuir isotherm model was determined to provide the best fit for the sorption process. Capacity for arsenate was found to be 4.8 mg As(V) / g solid.<sup>20</sup>

Mamindy-Pajany and coworkers studied arsenate adsorption onto zero valent iron, goethite, hematite and magnetite. They looked at the effect of pH and concentration, and also whether the reaction was reversible or not. Rate of adsorption was found to correlate with the iron content of the adsorbents, with the order being goethite ( $\alpha$ -FeOOH, 1.4 mg/g) < hematite ( $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>, 0.8 mg/g) < magnetite (Fe<sub>3</sub>O<sub>4</sub>, 2.0 mg/g) < zero valent iron (Fe, 0.3 mg/g). A Langmuir model was found to properly model the adsorption behavior. Based on desorption experiments, arsenic was most strongly adsorbed to hematite.<sup>21</sup>

Lenoble *et al.* studied the reaction between arsenic and various materials, including goethite, amorphous iron hydroxide, and clays pillared with iron and titanium. Capacities and the effects of pH on the adsorption of arsenate and arsenite were studied. Amorphous iron hydroxide had the highest capacities of arsenic removal for both forms (28 mg/g As(III), 7 mg/g As(V)). Goethite removed 22 mg/g As(III) and 4 mg/g As(V). The iron and titanium pillared clays both had a



capacity of 13 mg/g for arsenite, and 4 and 3 mg/g for arsenate. Arsenite was removed from pH 4 to 9, most effectively at acidic pH.<sup>22</sup>

Giménez and coworkers studied the sorption of arsenate and arsenite onto goethite, hematite and magnetite under various conditions. Equilibrium was reached in under two days for all materials, with hematite reaching equilibrium relatively slowly. A Langmuir isotherm was found to fit with all reactions and sorbents. Hematite was found to exhibit the highest capacity for both forms of arsenic (1.8 mg/g arsenate and 0.6 mg/g arsenite), with the results being even better under acidic conditions. Magnetite removed 0.8 mg/g arsenate and 0.6 mg/g arsenite. Goethite removed 0.5 mg/g arsenate and 0.4 mg/g arsenite.<sup>23</sup>

## **Experimental**

Iron fumarate was prepared from iron chloride hexahydrate from Fisher, fumaric acid from Eastman (98%) and sodium hydroxide from Fisher. All water used in the experiments was purified by reverse osmosis and ion exchange. Synthesis of iron fumarate was carried out in water open to air at room temperature. The synthesis of iron fumarate is a simple precipitation reaction in which an aqueous solution of sodium fumarate and sodium hydroxide is added to one of iron chloride to immediately yield a precipitate. In a typical synthesis, 300. mmol of NaOH was dissolved in 300 mL of deionized water. Upon dissolution, 100. mmol of fumaric acid was added. This was stirred to dissolution, forming a solution of 100. mmol sodium fumarate and 100. mmol of NaOH. In a separate flask, 100 mmol of iron chloride hexahydrate was dissolved in 300 mL of deionized water. Upon dissolution of the iron chloride and the fumaric acid, the solutions were mixed. The fumarate solution was added to the iron chloride solution, with immediate precipitation of the iron fumarate. The solution was then vacuum filtered using a fine glass frit. The precipitate was washed with deionized water until the conductivity of the filtrate stabilized,

and then dried. The dried, washed product was then ground using a mortar and pestle to maximize the surface area for sorption experiments. The yield was 93.86%.

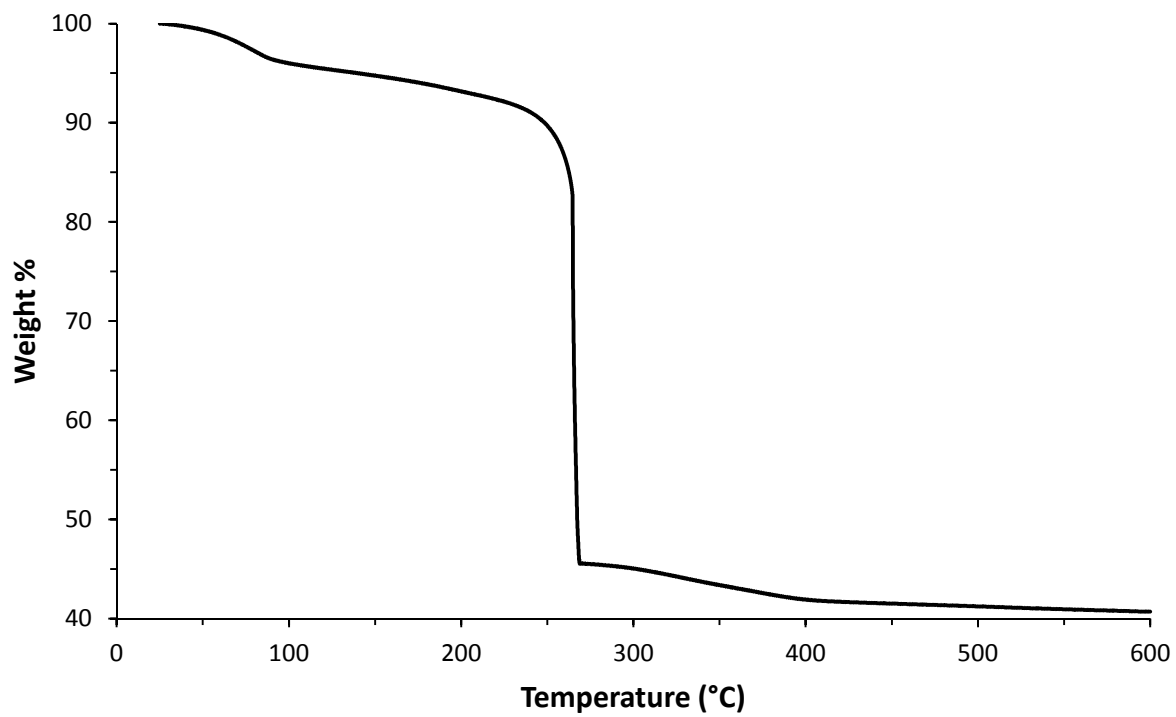
Monopotassium arsenate (from Sigma) was used to prepare arsenate samples. The required mass of  $\text{KH}_2\text{AsO}_4$  was dissolved in purified water. When lower concentrations were needed, these were obtained by dilution of a more concentrated arsenate solution. For arsenite, the proper mass of arsenic trioxide (Mallinckrodt) was dissolved in purified water. The dissolution of arsenic trioxide is thermodynamically favorable, but kinetically slow.<sup>24</sup> It was therefore necessary to heat these solutions while stirring for up to 3 days to dissolve the arsenic trioxide. The solution was then filtered using a fine glass frit to ensure that no undissolved arsenic trioxide remained.

Iron fumarate was characterized by thermogravimetric analysis using a Mettler-Toledo TGA-DSC 1. Infrared spectra were obtained using a Nicolet Magna 750 IR spectrometer.

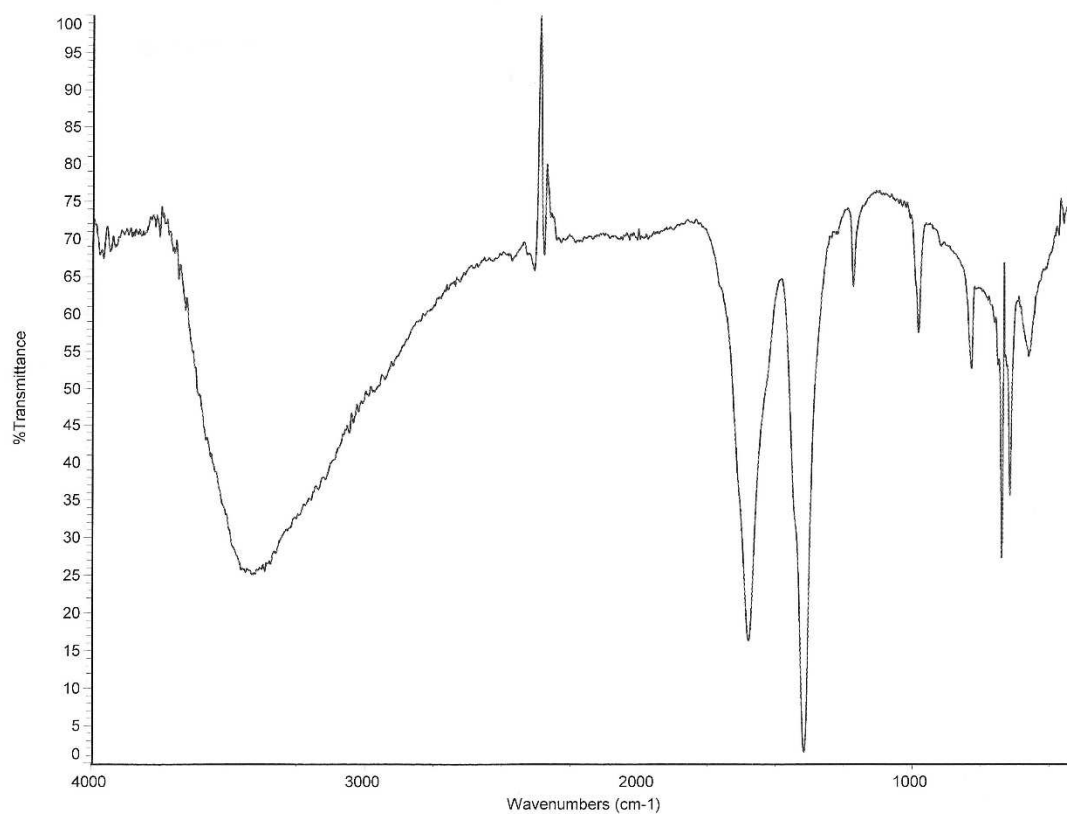
Concentration of arsenic in solution was found using a Varian GTA120/AA240Z graphite furnace atomic absorption spectrometer.

## **Results and Discussion**

The results from the thermogravimetric analysis are shown in **Figure 2**. An initial loss of about 4.6 % occurred between 30°C and 85°C, corresponding to the loss of a half of a molar equivalent of water of hydration. Between 85°C and 240°C gradual weight loss occurred to give a weight loss of 4.4 % that is likely due to the release of another half an equivalent of water of hydration. Above 240°C, the fumarate began to oxidize eventually leading to a sharp weight loss at 265°C. The corresponding loss of 58.2 % represents the loss of one organic fumarate ligand. Finally, the loss of 8.7 % from 265°C to 600°C represents dehydroxylation. The empirical formula was found to be  $\text{Fe}(\text{C}_4\text{H}_2\text{O}_4)(\text{OH}) \cdot 0.5\text{H}_2\text{O}$ .



**Figure 2. Thermogravimetric trace for iron fumarate.**



**Figure 3. The infrared spectrum of iron fumarate  $\text{Fe}(\text{C}_4\text{H}_2\text{O}_4)(\text{OH})$**

The material was also characterized by infrared spectroscopy (**Figure 3**). The peak at  $3410\text{ cm}^{-1}$  is from an O-H stretch. The peaks at  $1600\text{ cm}^{-1}$  and  $1396\text{ cm}^{-1}$  are due to C = O anti-symmetric and symmetric stretching of the fumarate ion, respectively. The peak at  $981\text{ cm}^{-1}$  also provides evidence for the inclusion of carboxylic acid in the material, as this peak is a H-C=C out of plane bend.

X-ray powder diffraction performed on the iron fumarate showed no peaks, indicating that the material is amorphous.

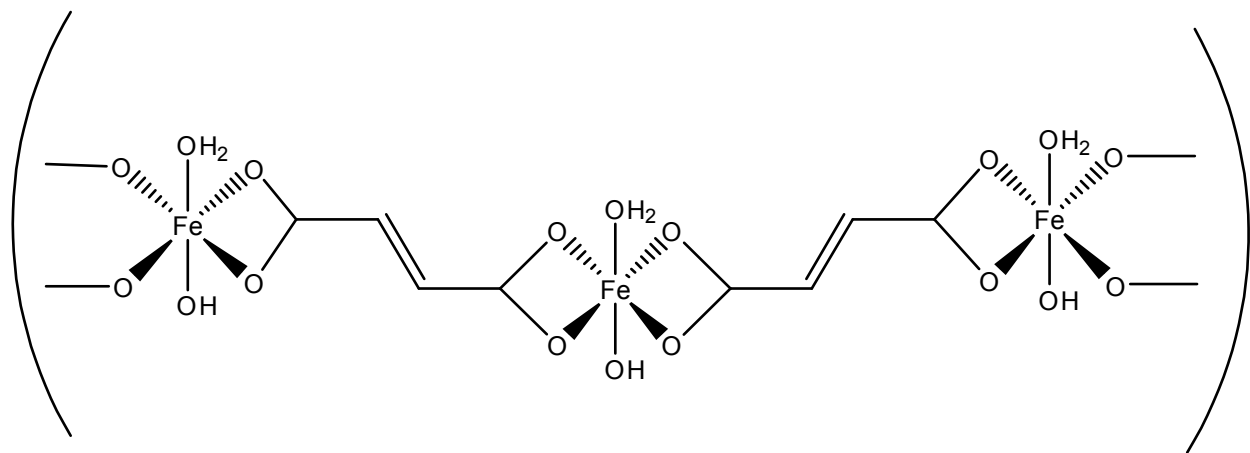
The material thus formed is believed to occur by the following reaction:



**Equation 1. Preparation of iron fumarate  $\text{Fe}(\text{C}_4\text{H}_2\text{O}_4)(\text{OH})$**

First, the fumarate sodium salt is formed by dissolving the sodium hydroxide and fumaric acid together. The products of the reaction are sodium chloride and water. The reaction takes place at room temperature in deionized water, and is thus a very green reaction.

A possible structure for the iron fumarate coordination polymer is:



**Figure 4. Proposed structure of  $\text{Fe}(\text{C}_4\text{H}_2\text{O}_4)(\text{OH})$**

Initially, it was necessary to determine how long it took for the reaction between iron fumarate and arsenate to reach equilibrium. To do this, arsenic stock solution and iron fumarate was added to several vials. One could be removed each day, and the arsenic concentration checked. Once the change in arsenic concentration between two successive days was small, the reaction was

considered to be at equilibrium. Four batch reactions were prepared, with 15 mL 500 µg/L arsenate and 50 mg iron fumarate  $\text{Fe}(\text{C}_4\text{H}_2\text{O}_4)(\text{OH})$  added to each 20 mL scintillation vial. Each day, one vial was removed. To stop the reaction, the mixture was filtered with a 0.2 µm nylon syringe filter. The treated solutions were then analyzed on a Varian 240Z graphite furnace atomic absorption spectrometer. The concentration of arsenic after a day was determined to be 9.2 µg/L, and for days 2 through 4 the concentration was below the detection limit. To ensure the reactions were carried to completion, it was assumed that equilibrium was reached after 2 days.

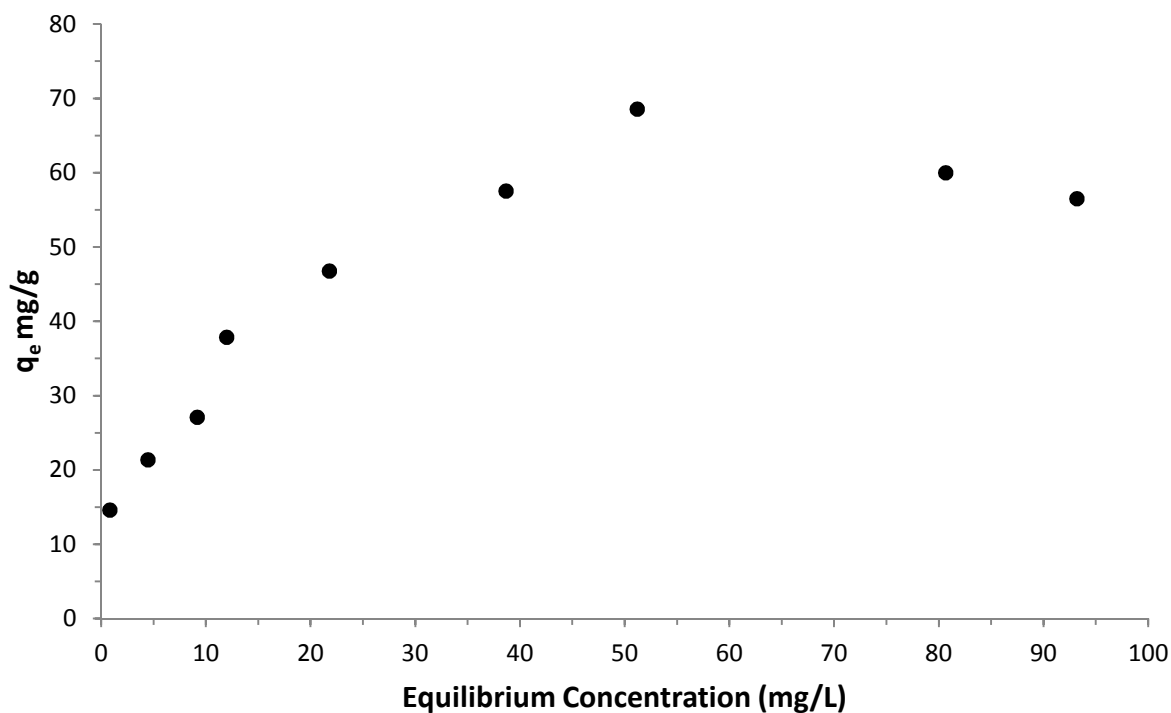
Once the time to equilibrium was determined, batch experiments were performed to find a sorption capacity. Arsenate solution of 110.9 mg / L (20 mL) and varying weights of iron fumarate were used. At a small enough weight of iron fumarate, arsenic would saturate the material, and the change in arsenic adsorbed per gram of iron fumarate would stay the same. This is given by the equation:

$$q_t = \frac{(C_0 - C_t)V}{m}$$

**Equation 2. Capacity equation.**

To estimate the capacity at time t, the change in concentration ( $C_0 - C_t$ ) is multiplied by the volume of the sample, giving the milligrams of arsenate adsorbed. When this is divided by the weight of material used, the weight of arsenic adsorbed per weight of adsorbent used ( $q_t$ ) is obtained.

The sorption isotherm for  $\text{Fe}(\text{C}_4\text{H}_2\text{O}_4)(\text{OH})$  is shown in **Figure 5**.



**Figure 5. Capacity curve for  $\text{Fe}(\text{C}_4\text{H}_2\text{O}_4)(\text{OH})$  reacted with arsenate**

The capacity is estimated to be 68.5 mg/g. There is some error in the last three points that is magnified by dilution. Thus, iron fumarate shows a good capacity for arsenate adsorption, comparing favorably to many other adsorbents.<sup>19</sup>

Once the capacity of  $\text{Fe}(\text{C}_4\text{H}_2\text{O}_4)(\text{OH})$  for arsenate was found, it became desirable to optimize the iron fumarate for arsenic sorption. This has to do with iron fumarate being amorphous. The material is not locked into a set stoichiometry by a regular crystal structure, so the iron to fumarate ratio may be varied.

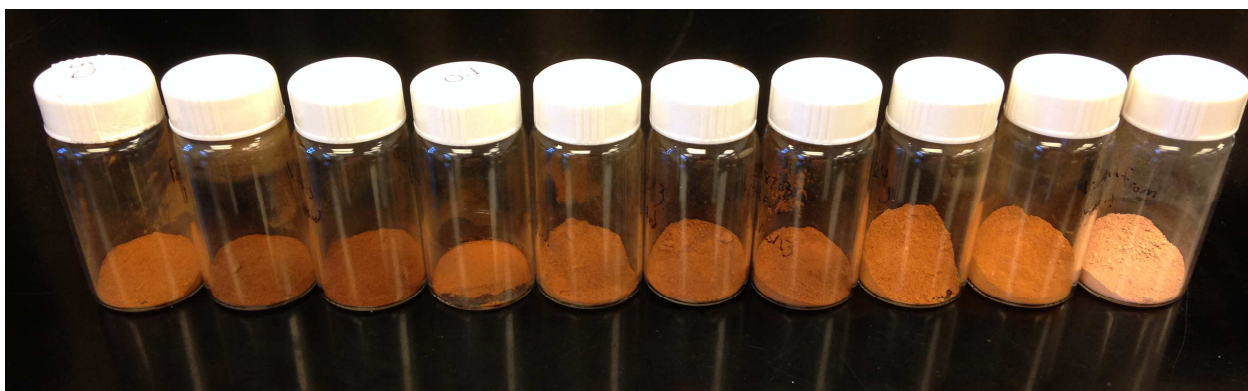
Using the same materials and methods listed above, several new iron fumarates were prepared. The same number of moles of iron and sodium hydroxide were used as before, but different amounts of fumaric acid were used in the synthesis. As before, a solution of ferric chloride in 300 mL of water was prepared, and a second solution of sodium fumarate and sodium hydroxide was

prepared in another 300 mL of water. Also as before, the fumarate solution was added to the iron solution. The precipitates formed immediately and were washed and dried. We were concerned that the materials were becoming hydrated by too much water during washing, and so the materials were washed with 500 mL of water and allowed to dry. They were then ground with a mortar and pestle.

A list of all of the prepared iron fumarates is shown in **Table 1**. The formulas are estimated based on the weight of each chemical used in the synthesis.

$\text{Fe}_2(\text{C}_4\text{H}_2\text{O}_4)(\text{OH})_4$	$\text{Fe}_7(\text{C}_4\text{H}_2\text{O}_4)_4(\text{OH})_{13}$	$\text{Fe}_3(\text{C}_4\text{H}_2\text{O}_4)_2(\text{OH})_5$	$\text{Fe}_{10}(\text{C}_4\text{H}_2\text{O}_4)_7(\text{OH})_{16}$
$\text{Fe}_4(\text{C}_4\text{H}_2\text{O}_4)_3(\text{OH})_6$	$\text{Fe}_5(\text{C}_4\text{H}_2\text{O}_4)_4(\text{OH})_7$	$\text{Fe}_8(\text{C}_4\text{H}_2\text{O}_4)_7(\text{OH})_{10}$	$\text{Fe}_{12}(\text{C}_4\text{H}_2\text{O}_4)_{11}(\text{OH})_{14}$
$\text{Fe}_{25}(\text{C}_4\text{H}_2\text{O}_4)_{24}(\text{OH})_{27}$	$\text{Fe}(\text{C}_4\text{H}_2\text{O}_4)(\text{OH})$	$\text{Fe}_2(\text{C}_4\text{H}_2\text{O}_4)_3$	

**Table 1. A list of prepared iron fumarates**



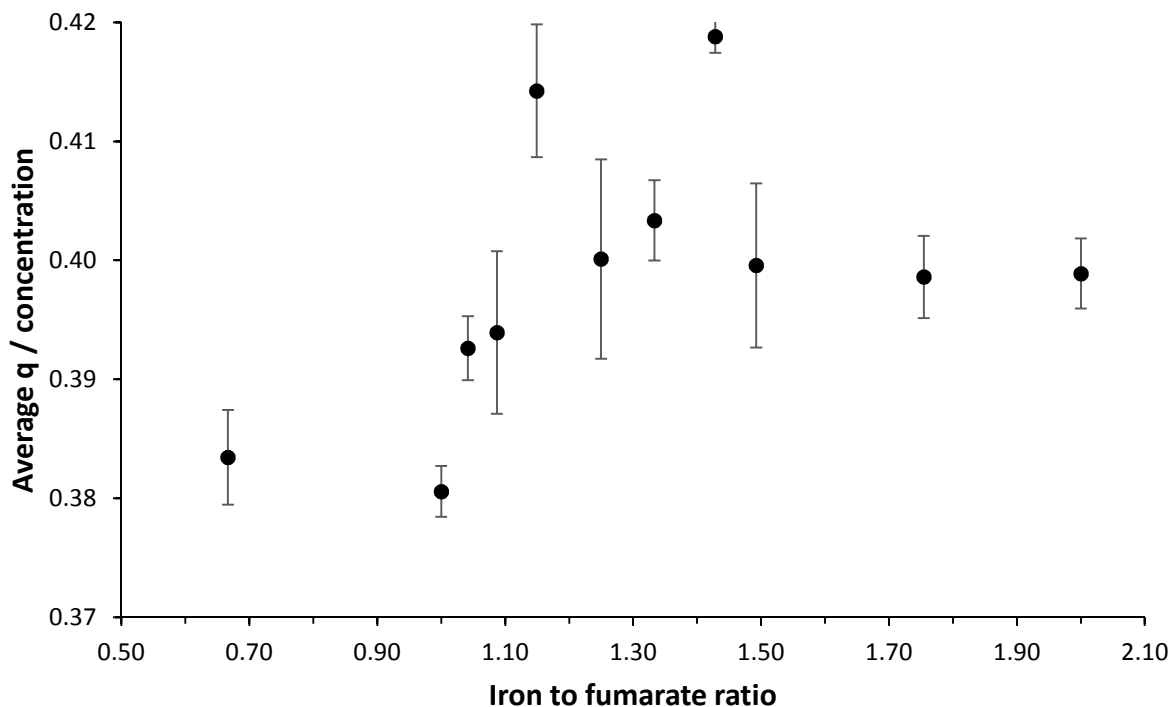
**Figure 6. A picture of the prepared iron fumarates organized by theoretical iron content.**

**Iron(III) rich materials are on the left.**

The new materials were initially tested to get an idea for their arsenic capacity. To do this, 50 mg of the iron fumarate samples were reacted with 20 mL of 100 ppm arsenate solution. Solids were allowed to react with solution for a week while the mixture was stirred. At the end, mixtures were



filtered using 0.2  $\mu\text{m}$  nylon syringe filters. Each material was tested three times. Results are shown in **Figure 7**.



**Figure 7. Initial test of prepared iron fumarates for arsenic sorption**

After this, it was decided to test three materials which showed a high binding affinity for arsenic. Capacity curves for these three iron fumarates can be seen in **Figures 8 - 10**. In **Figure 8**, it can be seen that the first part of the curve for  $\text{Fe}_3(\text{C}_4\text{H}_2\text{O}_4)_2(\text{OH})_5$  is more steep than for  $\text{Fe}(\text{C}_4\text{H}_2\text{O}_4)(\text{OH})$ . The final capacity is also higher, at 152 mg As/g. The same is true for  $\text{Fe}_4(\text{C}_4\text{H}_2\text{O}_4)_3(\text{OH})_6$ , where the final capacity is 201 mg As/g. For  $\text{Fe}_8(\text{C}_4\text{H}_2\text{O}_4)_7(\text{OH})_{10}$ , the curve is very steep. Almost all of the arsenic was removed after a 12 mg treatment (99.6% removed). The graph was plotted on a logarithmic scale to show curvature. Capacity is 187 mg/g.

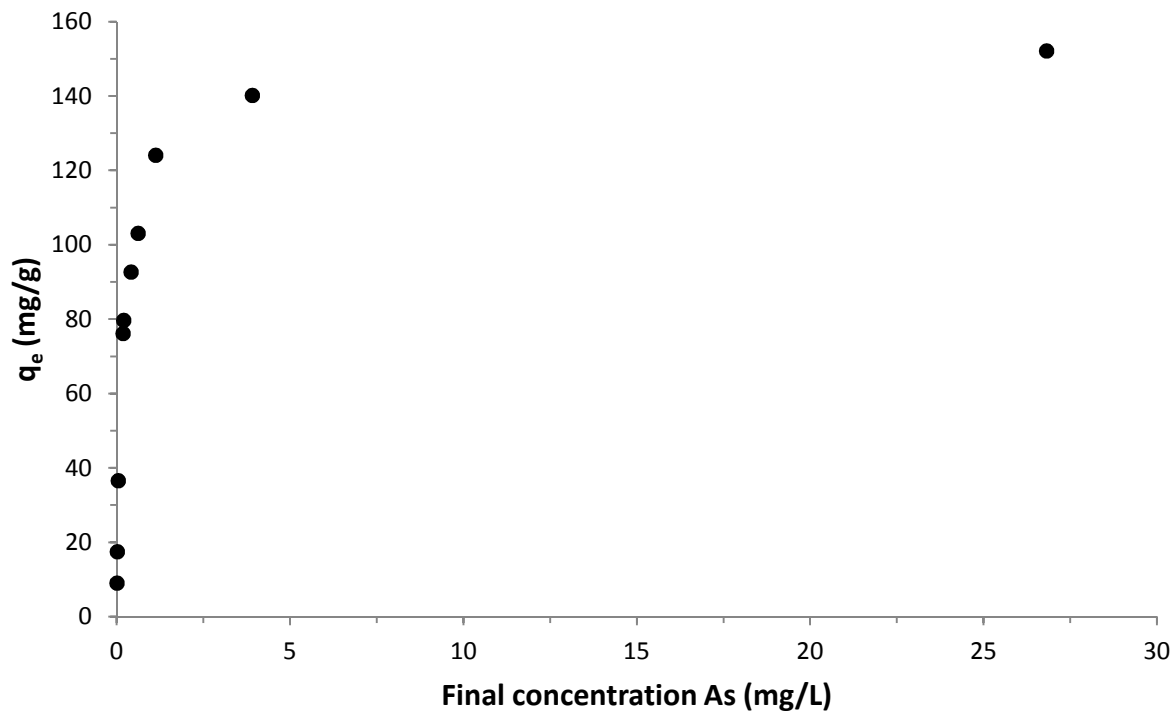


Figure 8. Capacity curve for  $\text{Fe}_3(\text{C}_4\text{H}_2\text{O}_4)_2(\text{OH})_5$

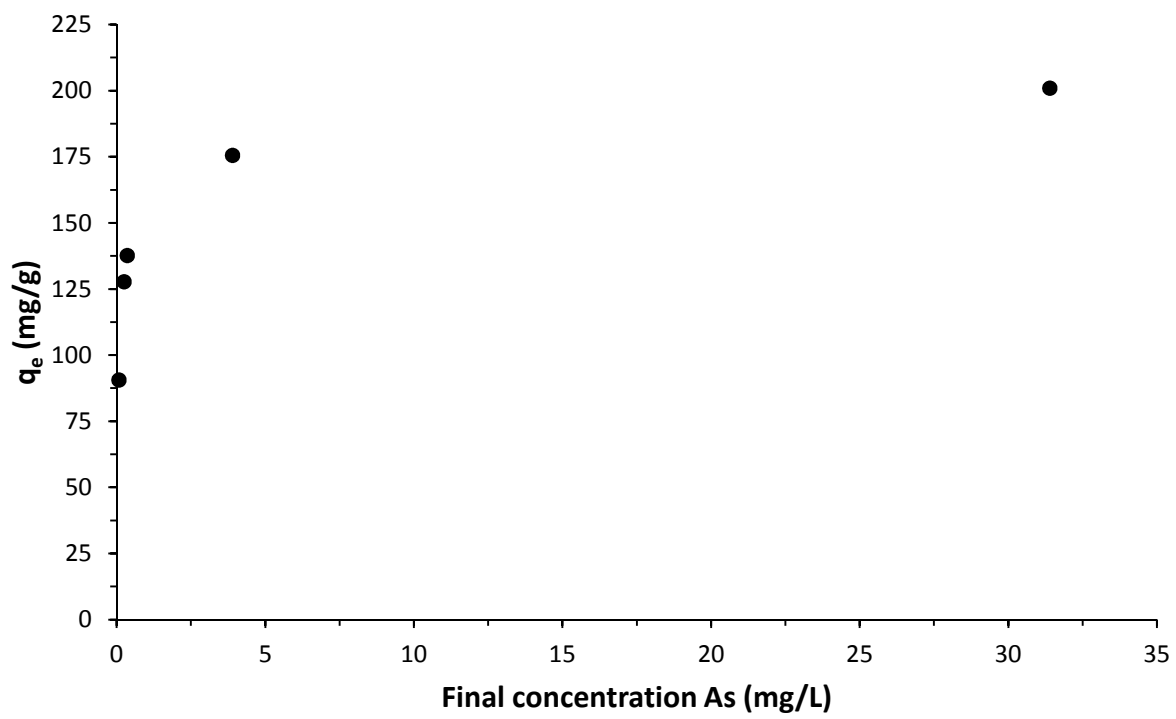
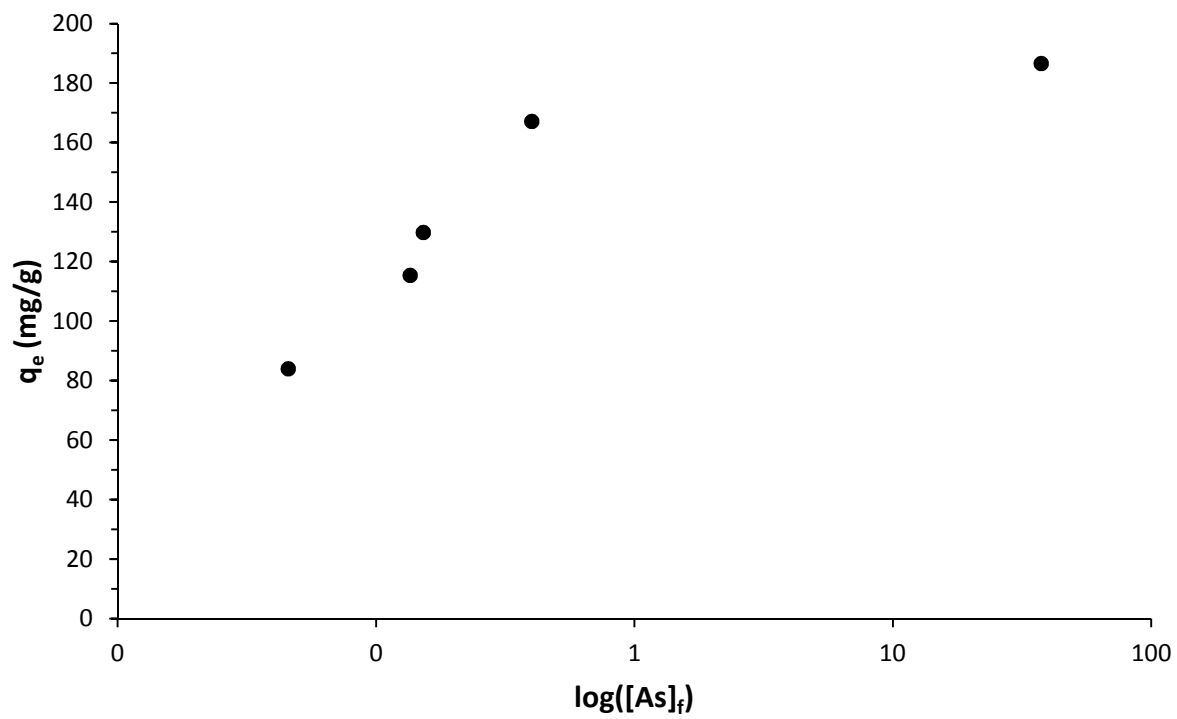
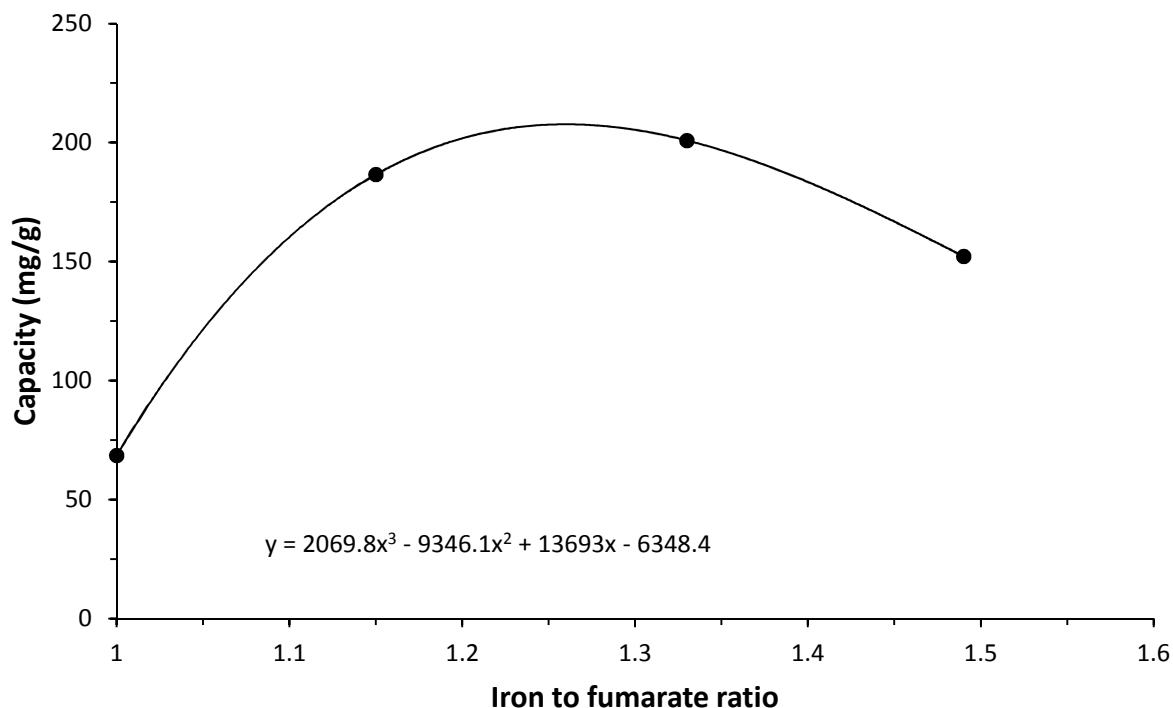


Figure 9. Capacity curve for  $\text{Fe}_4(\text{C}_4\text{H}_2\text{O}_4)_3(\text{OH})_6$



**Figure 10. Capacity curve for  $Fe_8(C_4H_2O_4)_7(OH)_{10}$**



**Figure 11. Relationship between capacity and material composition**

The estimated capacities from the four tested materials were plotted vs. the iron to fumarate ratio in the material. When this is done, a curve is obtained, as can be seen in the **Figure 11**. This implies that there is an optimum iron to fumarate ratio where the capacity is the highest. To find this, a third order polynomial was fitted to the points. The equation for this polynomial was:

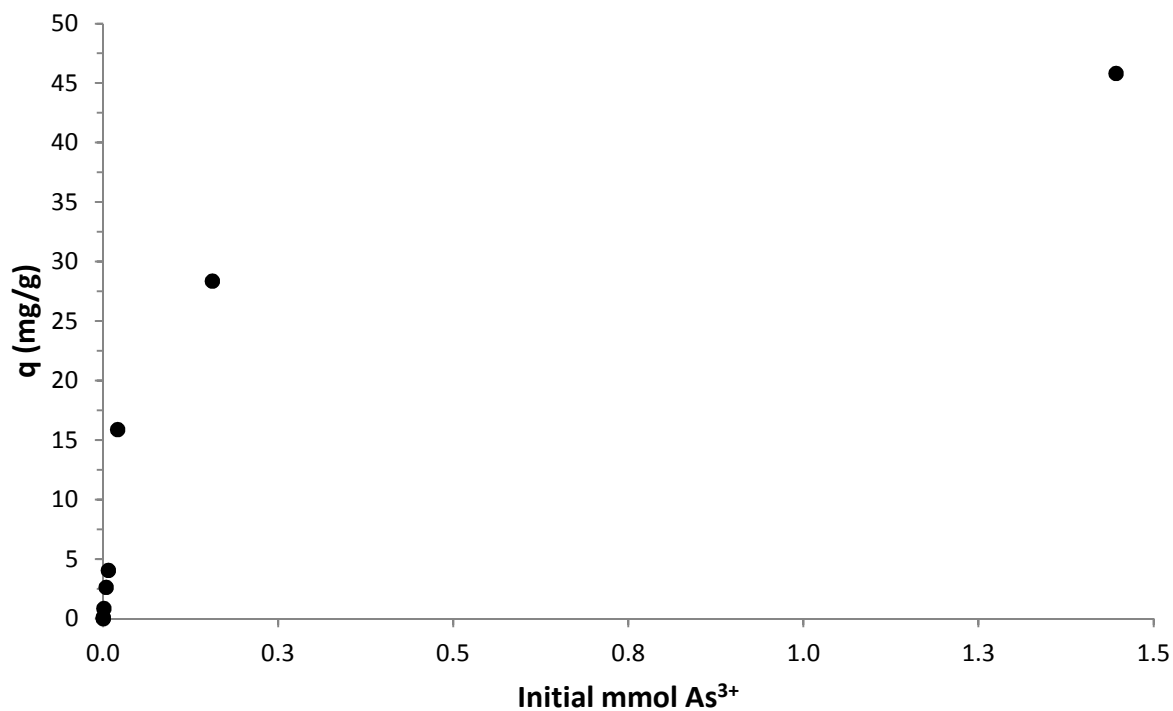
$$y = 2069.8x^3 - 9346.1x^2 + 13693x - 6348.4$$

**Equation 3. Relationship between capacity and material composition**

When the derivative was taken and set equal to zero, it was found that  $x = 1.26$ . This corresponds to  $\text{Fe}_5(\text{C}_4\text{H}_2\text{O}_4)_4(\text{OH})_7$ . This material has been previously synthesized, and was tested in the initial test of the new materials. It was not the highest material in that experiment, although it was near the top. When the material is challenged it may prove to be the optimum iron fumarate for arsenate removal. The predicted capacity for this material is 207 mg/g.

The reactivity of iron fumarate  $\text{Fe}(\text{C}_4\text{H}_2\text{O}_4)(\text{OH})$  towards arsenite was also investigated. First, an experiment was conducted to determine how long it takes for the reaction between arsenite and iron fumarate to reach equilibrium. Fifteen mLs of  $500 \mu\text{g/L As}^{3+}$  was added to four 20 mL scintillation vials. To this, 50 mg of iron fumarate was added. The mixture was stirred, and every day a vial was removed. To stop the reaction, the mixture was filtered with a  $0.2 \mu\text{m}$  nylon syringe filter. The treated solutions were then run on a Varian 240Z graphite furnace atomic absorption spectrometer. After four days, 94.3% of the arsenite had been removed. The difference in the arsenite concentration change between days 3 and 4 was less than 1%. It was therefore assumed that equilibrium was achieved in four days.

An attempt was then made to obtain the arsenite capacity of  $\text{Fe}(\text{C}_4\text{H}_2\text{O}_4)(\text{OH})$ . For each batch treatment, 15 mL of arsenite solution and 50 mg iron fumarate was used. The initial concentration of arsenite was varied. The reactions were carried out in 20 mL scintillation vials. The reaction was allowed to carry on for 4 days, after which it was assumed equilibrium had been reached, as indicated above. To stop the reaction, the mixture was filtered with a  $0.2 \mu\text{m}$  nylon syringe filter. The treated solutions were then analyzed on a Varian 240Z graphite furnace atomic absorption spectrometer, diluted if needed with purified water. The reaction was carried out three times for each initial concentration to get an average.



**Figure 12. Capacity curve for Fe(C<sub>4</sub>H<sub>2</sub>O<sub>4</sub>)(OH) reacted with arsenite**

The results can be seen in **Figure 12**. Fe(C<sub>4</sub>H<sub>2</sub>O<sub>4</sub>)(OH) does in fact show activity for sorption of arsenite. There was significant error at the higher concentrations. Up to 100 mg/L As<sup>3+</sup>, however, there is a good trend. The capacity for arsenite is estimated to be 45.8 mg As<sup>3+</sup>/g solid.

### **Conclusion**

In conclusion, a material from the reaction from iron(III) chloride and fumaric acid has been prepared. The material is likely a coordination polymer made of alternating units of iron and fumarate. This insoluble compound has been reacted with arsenate, and demonstrated an arsenic capacity of 68.5 mg/g. By varying the ratio of iron to fumarate, new iron fumarates were prepared which show increased activity towards arsenate. The highest material tested has an estimated capacity of 201 mg/g, which is extremely high. The capacities of the iron fumarates were graphed

versus the iron to fumarate ratio, and a new trend is observed. It appears that the optimum material for an iron fumarate system for arsenate removal is  $\text{Fe}_5(\text{C}_4\text{H}_2\text{O}_4)_4(\text{OH})_7$ .

## CHAPTER III

### PHOSPHATE

Phosphorus is the sixth most abundant element in the human body.<sup>25</sup> As phosphate, it is utilized in the synthesis of DNA and as an essential part of the body's system of transferring chemical energy. As a result, it is a crucial element for life. Crops require it to grow, so it must be added to the soil as a component of fertilizer. Any phosphate that is not taken up by the plant is wasted. It is then flushed into ponds, lakes, streams and rivers. As a result, bodies of water may have a significantly higher concentration of phosphate than is natural. Another source of phosphate in the environment is from ranches, where the waste phosphate from the animals is excreted from the body and eventually flushed into water systems in the same way as the fertilizer. These are known as non – point sources. Phosphate sources may also be point sources, such as waste streams from industry (production of semiconductors), and even sewage flows from cities.<sup>26,27</sup>

In all of these cases, as the levels of phosphate increase in natural systems, changes in the water biology may begin to occur. Phosphorus is commonly the limiting nutrient in water systems, and thus an increase in phosphate concentration enables additional plant growth. Algae and some bacteria are able to rapidly grow and use up the phosphorus. This results in a substantial increase in surface algae. The algae block sunlight and can lead to the death of plants below. The algae uses up all of the available nutrients and begins to die. The degradation of the algae depletes the dissolved oxygen in the water, and this leads to the death of many other organisms. This process



is known as eutrophication. In addition, cyanobacteria blooms that can result from phosphate excess often produce extremely toxic compounds.<sup>26</sup>

To prevent eutrophication, it is necessary to avoid the release of materials that generate these growth limiting nutrients into the hydrosphere. Very often the growth limiting nutrient is phosphate.<sup>26</sup> With this in mind, we designed an insoluble compound to sorb phosphate from water. The intention is to use this compound to treat water before it is returned to natural water systems. The compound must be non – toxic and must not release harmful substances back into the water. Ideally, the compound will also be inexpensive.

Iron was chosen as a good metal to try to prepare a sorbent. This is due to the fact that iron is inexpensive and non – toxic. In addition, many naturally occurring phosphate minerals are iron phosphates. (E) – butenedioic acid, or fumaric acid, was chosen as a useful ligand. Fumaric acid is a food acid, and is part of the citric acid cycle. Fumaric acid can be found in plants of the genus *Fumaria*, and in bolete mushrooms.<sup>28</sup> Fumarate has an ideal structure for the structure of the insoluble compound. It is a trans – dicarboxylic acid. It may bind to metals in a bidentate fashion using both terminal carboxylic acid groups. The locked linear structure of fumaric acid thus allows it to form insoluble compounds.

### **Literature Review**

Previously, Eskandarpour, *et al.* used schwertmannite ( $\text{Fe}_8\text{O}_8(\text{OH})_6(\text{SO}_4)$ ) that had been activated by an acid treatment process to remove phosphate from deionized water.<sup>29</sup> The material was able to be separated from solution using a magnet, and regenerated for further use. The capacity of schwertmannite for phosphate was improved from 100 mg/g to 136 mg/g by the acid treatment.

Kang, *et al.* used goethite, hematite and ferrihydrite to remove phosphate from wastewater samples and laboratory prepared samples.<sup>30</sup> Ferrihydrite was able to remove significantly more

phosphate than the other iron oxides, with a capacity of 19.4 mg/g. Ferrihydrite also showed a high selectivity for phosphate. The materials were able to be regenerated and reused.

Rentz, *et al.* used iron oxides produced by microbes to remove phosphate from water.<sup>31</sup> Iron oxides were obtained from microbial mats which formed at the interface of the anoxic/oxic zones in wetlands. The phosphate solutions were prepared from deionized water. The capacities for phosphate varied widely, and ranged from 46.9 to 165 mg/g. The sorption kinetics followed a pseudo 1<sup>st</sup> order model.

Xiong, *et al.* prepared ferrihydrite-modified diatomite for use as a phosphate adsorbent.<sup>32</sup> The diatomite surface was treated with sodium hydroxide, and ferrihydrite was then deposited on the surface. Specific surface area increased from 24.77 to 211.1 m<sup>2</sup>/g. The material was tested at pH of 4 and 8.5. The ferrihydrite-modified diatomite worked best at the lower pH, with a capacity of 37.3 mg P/g solid.

## **Experimental**

Iron chloride hexahydrate and sodium hydroxide were purchased from Fisher. Fumaric acid was purchased from Eastman (98%). Sodium phosphate monobasic monohydrate was purchased from Fisher (98.8%). All water used was purified by reverse osmosis and ion exchange. Synthesis of iron fumarate was carried out in purified water at room temperature in open air. In a typical synthesis of iron fumarate, 300 mmol sodium hydroxide was added to 300 mL of water. Upon dissolution, 100 mmol of fumaric acid was added to this and stirred to dissolution. In a separate flask, 100 mmol iron(III) chloride hexahydrate was added to deionized water and stirred to dissolution. While stirring, the fumarate solution was added to the iron chloride solution. A pink – red precipitate immediately formed upon mixing. This product was collected via vacuum filtration using a fine glass frit. It was washed with deionized water until no chloride was detected

by testing the sample with silver nitrate solution (formation of silver chloride). The product was then dried at room temperature under vacuum.

Iron fumarate was characterized using thermogravimetric analysis to determine its empirical formula, and by infrared spectroscopy to reveal structural data. These results were previously covered in Chapter 2.

## **Results and Discussion**

An experiment was performed to determine how long it took the reaction of phosphate with the iron fumarate to reach equilibrium. Three batch experiments were started at the same time, and one was removed each day. For each reaction, 15 mL of 219 mg/L stock solution was added to 50 mg iron fumarate. The concentration of phosphate was determined by a DR/890 Hach colorimeter, using the molybdovanadate method. It was shown that the reaction reached equilibrium in 2 days, with the difference in the percent concentration change being 0.1% between days 2 and 3.

To determine the capacity of iron fumarate for phosphate, a series of batch experiments were performed where the initial concentration of phosphate was increased, while holding the volume of solution and weight of iron fumarate used for treatment constant. At a high enough concentration of phosphate, the adsorbent will be saturated with phosphate, and it will have reached its capacity for phosphate. Capacity may be represented as  $q$ :

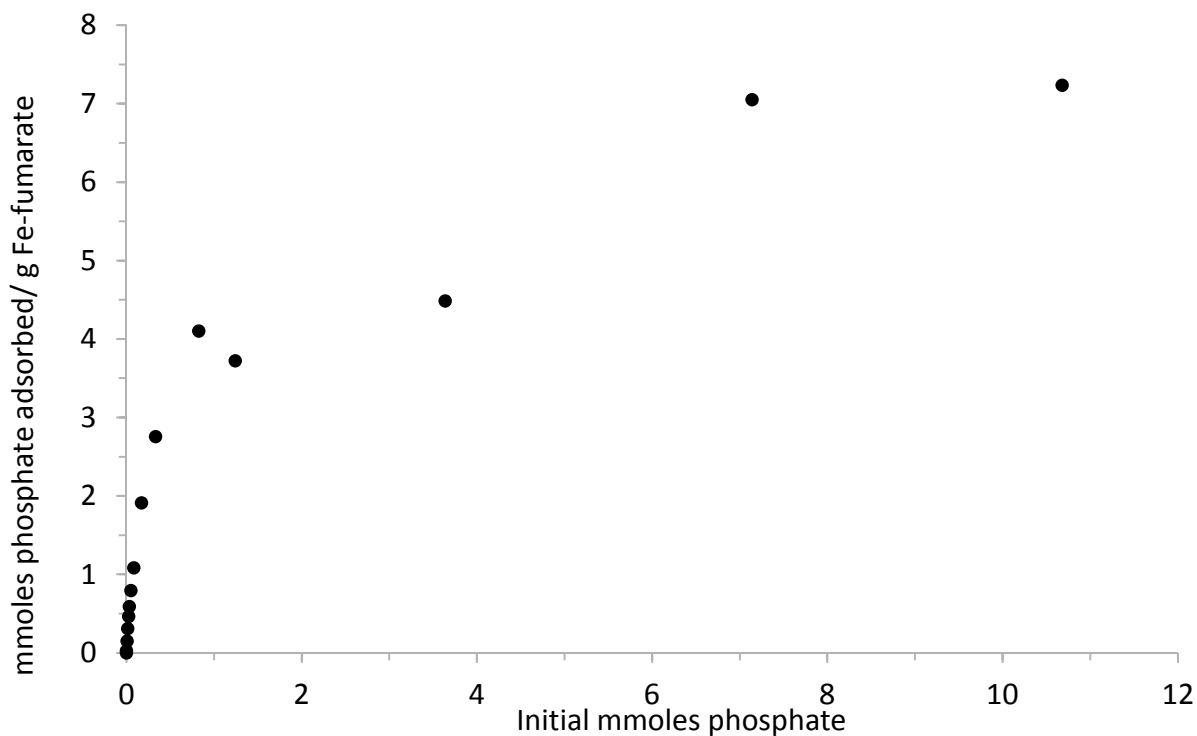
$$q_t = \frac{(C_0 - C_t)V}{m}$$

**Equation 2: Capacity equation**

When  $q$  is graphed versus the initial concentration of phosphate, a curve is obtained. The top, level part of this curve corresponds to the capacity of the material for phosphate.

For each batch experiment, a total of 15 mL of phosphate stock solution was added to a 20 mL scintillation vial. To this, 50 mg iron fumarate was added. These were allowed to react for 2 days, as this was previously found to be the time needed to reach equilibrium. Results are shown in

**Figure 13.**



**Figure 13. Capacity of iron fumarate for phosphate**

The amount of phosphate bound per gram of sorbent remained unchanged after about 75000 mg/L phosphate. This corresponds to a capacity of about 690 mg/g. This is close to a stoichiometric amount (1.4 mol phosphate per mol iron fumarate), and is more characteristic of a chemical reaction than true sorption. We believe that the reaction may be forming an iron phosphate. Iron phosphate is an insoluble compound, thus allowing it to still be removed from the

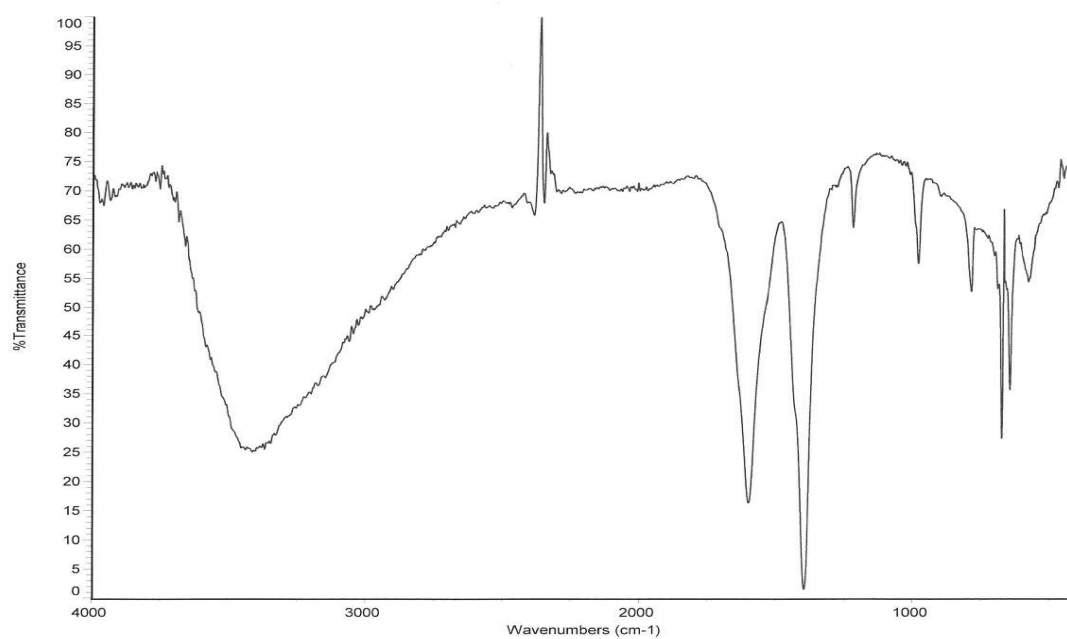
solution. Iron phosphate is a yellow compound (see **Figure 14**). A picture of the reacted iron fumarate product can be seen in **Figure 15**. The product has become yellow, providing evidence to support the argument that iron phosphate is being formed.



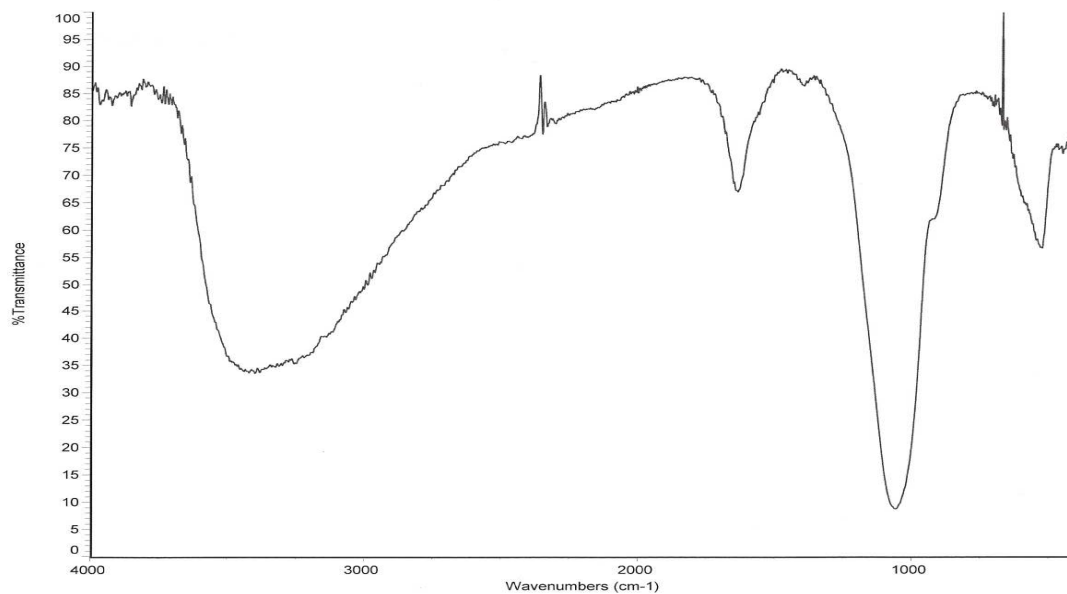
**Figure 14: Iron phosphate pentahydrate,  $\text{FePO}_4 \cdot 5\text{H}_2\text{O}$**



**Figure 15 (above). Unreacted iron fumarate (left) and iron fumarate that has been reacted with an excess of phosphate (shown on right).**

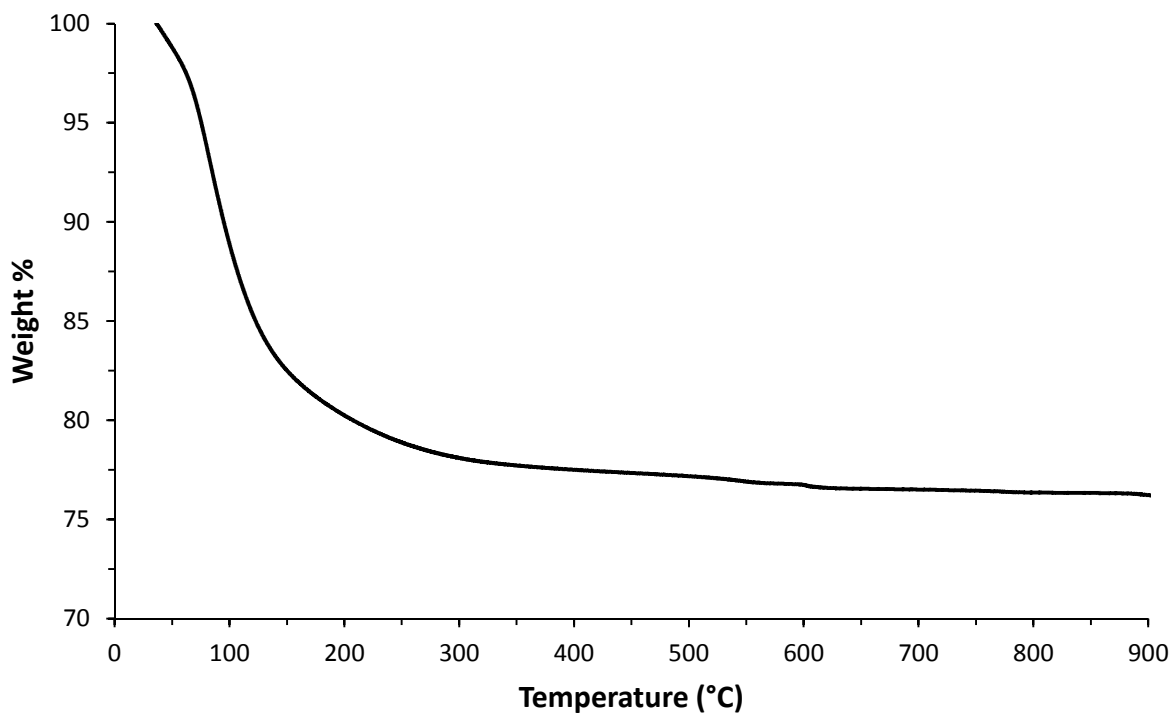


**Figure 16 (above). Infrared spectrum of iron fumarate.**



**Figure 17 (above). Infrared spectrum of iron fumarate reacted with an excess of phosphate.**

An infrared spectrum of the product was obtained. **Figure 16** is for unreacted iron fumarate, and **Figure 17** is for iron fumarate reacted with an excess of phosphate. Notably, the C-O symmetric and anti-symmetric stretching peaks in **Figure 16** ( $1396$  and  $1600\text{ cm}^{-1}$ , respectively) are missing for the phosphate loaded material. The new peak at  $1054\text{ cm}^{-1}$  is a P-O stretch. This provides further support that iron phosphate is being formed, and that phosphate is exchanging with fumarate.



**Figure 18. Thermogravimetric analysis of iron fumarate reacted with an excess of phosphate.**

Thermogravimetric analysis was performed (see **Figure 18** above). There is an initial weight loss of 16% from 27°C to 128°C, indicating loss of water. From 128°C to 600°C, there is further weight loss. The temperature did not get hot enough to decompose phosphate, and so the final product is probably a mixed iron phosphate / pyrophosphate. From this data, the empirical formula of the phosphate loaded sorbent was found to be  $\text{Fe}(\text{HPO}_4)_{1.33}(\text{OH})_{0.33} \cdot 2 \text{H}_2\text{O}$ .

### **Conclusion**

In summary, an iron fumarate compound has been synthesized that shows a high capacity for phosphate. Iron fumarate may be used to efficiently remove phosphate from water and then easily separate the spent material from the water. Evidence suggests that an iron phosphate has been formed from the reaction.



## CHAPTER IV

### CHROMATE

Chromium may be found in nature in the 0, +III and +VI oxidation states, with Cr(III) being the most stable ion. Cr(IV) and (V) exist as unstable intermediates in redox transformations between Cr(III) and Cr(VI). In addition, Cr(II) exists, and it is strongly reducing, but stable enough to have varied chemistry.<sup>33</sup> In water, Cr(III) exists as an octahedral complex. Below a pH of 4, it is  $\text{Cr}(\text{H}_2\text{O})_6^{+3}$ . Increasing the pH leads to hydroxylation and subsequent polymerization.<sup>34</sup> Hexavalent chromium exists as  $\text{HCrO}_4^-$  and  $\text{CrO}_4^{2-}$ , and as  $\text{Cr}_2\text{O}_7^{2-}$ . The ratios of these species depend on the concentration of chromium in the solution and the pH.

Environmental transformations between Cr(III) and Cr(VI) do occur. As previously noted, Cr(III) is the most stable form, and is the primary naturally occurring form in water. Manganate and permanganate ions are powerful enough to produce Cr(VI). Also, Cr(VI) can be produced by water chlorination at water treatment plants and by photo-oxidation processes.<sup>34</sup> Natural processes where Cr(VI) is reduced to Cr(III) are very important, and are known as “dechromification”. This involves Fe(II) or  $\text{S}^{2-}$  reacting with chromate to produce Cr(III). While Cr(III) is relatively insoluble and often immobilized by natural organic compounds such as humic and fulvic acids, Cr(VI) is highly mobile and soluble.

By far the most important chromium containing ore is chromite,  $\text{FeCr}_2\text{O}_4$ . Chromite may be reduced and transformed into steel. Chrome ochre ( $\text{Cr}_2\text{O}_3$ ) and crocoite ( $\text{PbCrO}_4$ ) are also relatively common. Other noteworthy examples of chromium mineralogy include rubies and emeralds. Rubies are primarily  $\text{Al}_2\text{O}_3$  and emeralds are  $\text{Be}_3\text{Al}_2(\text{SiO}_3)_6$ , but it is the presence of chromium impurities that give these gemstones their color.<sup>33</sup>

Chromium is used primarily as an additive to prepare stainless steel. Other important uses include the production of pigments and inks; indeed, the abundance and variety of brightly colored compounds is how the element got its name. The primary chromium chemical synthesized is  $\text{Na}_2\text{Cr}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$ , which is used to facilitate many of the abundant applications.<sup>33</sup>

Chromium is a trace mineral for the human body; Cr(III) makes up part of the glucose tolerance factor. As such it is necessary for human life. In addition, Cr(III) has been shown to be non-toxic.<sup>35,36</sup> Chromate, however, is an acutely toxic carcinogen. The shape of the chromate anion  $\text{CrO}_4^{2-}$  is similar to  $\text{SO}_4^{2-}$ , and thus passes easily through sulfate channels in our cells. The potent toxicity of chromate is threefold. First of all, it is a strong oxidizing agent and can damage cells in this way. Secondly, cellular reduction of Cr(VI) to Cr(III) occurs with the formation of free radicals, and these can damage the cells also. Finally, upon formation of Cr(III), it is accumulated within the cells to toxic levels. The benign nature of Cr(III) stems from the fact that it is poorly soluble, and from the fact that it cannot pass the cell membrane. Cr(III) formed by the reduction of chromate is thus trapped inside the cell. This trapped chromium builds up in the cell and binds with macromolecules and DNA. Chromate is also very toxic by inhalation.<sup>34</sup> Concentrated chromate can burn holes in the skin.<sup>36</sup> For all of these reasons, it is important to be able to remove chromium from drinking water.

Environmental pollution arises from cooling towers and auto exhaust. As has previously been noted, naturally occurring aqueous Cr(III) may be oxidized by manganese oxides. Elevated levels

of chromate across the US occur at Superfund sites, hundreds of which have chromium as a major contaminant. In fact, most of the chromate in the environment is from anthropogenic sources, as chromate is slowly converted to chromite. Chromate pollution can also come from tanning waste and ore processing

### **Literature Review**

Hu, *et al.* studied chromium adsorption onto maghemite nanoparticles.<sup>37</sup> The nanoparticles were prepared by the sol-gel method. Maghemite has the advantage of being ferromagnetic, and thus magnetic separation could be carried out. The nanoparticles were used for six adsorption/desorption cycles. It was found that chromium was primarily adsorbed as Cr(VI), with little or no reduction to Cr(III). Equilibrium occurred in 15 minutes, and competitive adsorption with other common anions was minimal. Maximum adsorption occurred at a pH of 2.5. A Freundlich isotherm fit the data well.

Hu and coworkers also studied chromium sorption onto surface modified jacobite ( $\text{MnFe}_2\text{O}_4$ ).<sup>38</sup> Nanoparticles were prepared by co-precipitation, followed by a surface redox step. The synthesis yielded 10 nm particles. Equilibrium occurred after just 5 minutes. The optimal pH was 2 with a maximum adsorption of 31.5 mg Cr(VI)/g nanoparticles. A Langmuir isotherm fit the data well. It is believed that adsorption was driven by electrostatic interaction and ion exchange.

Lazaridis et al used alginate-goethite beads to take up chromium.<sup>39</sup> Experiments were carried out using aqueous solutions containing both Cr(III) and Cr(VI). To synthesize the beads, a dispersion of 2% w/v goethite and 1% w/v sodium alginate was stirred into a 0.3 M calcium chloride solution. It was found that The goethite interacted with the Cr(VI) and alginate reacted with the Cr(III). Optimum performance for chromate adsorption was 27.1 mg Cr/g beads at pH of 2.0. Optimum performance for Cr(III) was 30.4 mg Cr/g beads at a pH of 4.0.

## Experimental

Iron chloride hexahydrate (Fisher) was used to synthesize iron fumarate. Fumaric acid was obtained from Eastman (98%) and sodium hydroxide was obtained from Fisher. All water used in the experiments was purified by reverse osmosis followed by ion exchange. In a typical synthesis of iron fumarate, 100 mmol of iron chloride hexahydrate was dissolved in 300 mL purified water. In a separate flask, 300 mmol of sodium hydroxide was added to 300 mL purified water. When all of the sodium hydroxide was dissolved, 100 mmol fumaric acid was added to the water. Upon dissolution, the fumarate solution was added to the iron solution, and a pink-red precipitate was immediately obtained. This was filtered with a fine glass frit and washed with purified water. After washing, the iron fumarate was allowed to dry and was crushed with a mortar and pestle.

Potassium dichromate ( $K_2Cr_2O_7$ ) was purchased from Fisher. To prepare chromate solutions for testing, the required weight of dichromate was dissolved in deionized water. For dilute chromate solutions, a more concentrated solution was prepared and diluted with purified water.

Concentration of chromium was measured with a DR/890 Hach colorimeter, utilizing the 1,5-diphenylcarbohydrazide method.

Iron fumarate was characterized by infrared spectroscopy using a Nicolet Magna 750 IR spectrometer. Thermogravimetric analysis was performed with a Mettler-Toledo TGA-DSC 1. These results have been discussed in Chapter 2.

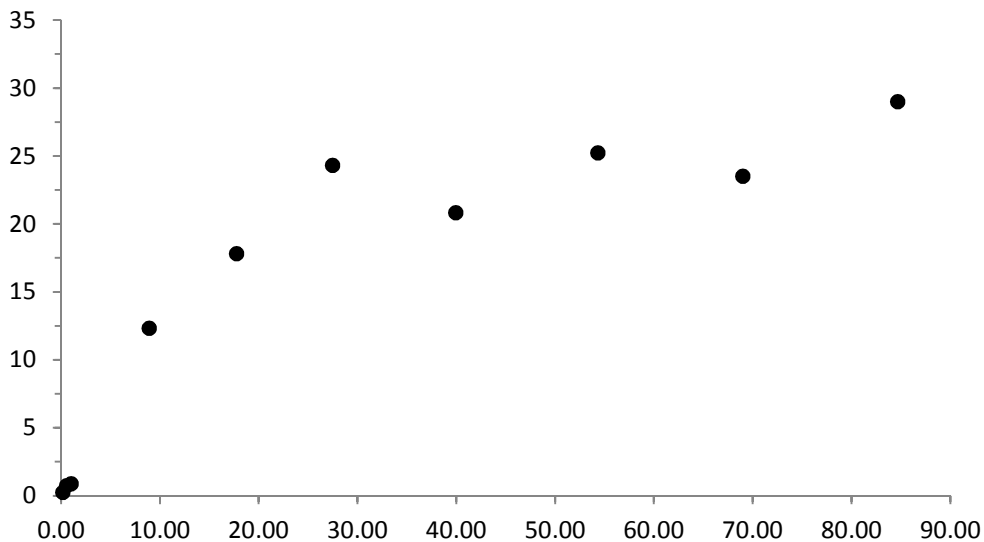
## Results and Discussion

It was necessary to see how long it took the iron fumarate and the chromate to reach equilibrium. To do this, four batch experiments were performed. Each day one sample would be removed and filtered to stop the reaction. Samples were filtered with 0.2  $\mu$ m nylon syringe filters. For each batch experiment, 10 mg of solid was reacted with 20 mL of 500  $\mu$ g/L Cr(VI) solution. The reactions were carried out in scintillation vials.

The concentration of the stock solution was found to be 480  $\mu\text{g/L}$ . After one day, the concentration had fallen to 0.08  $\mu\text{g/L}$ . The concentration at day two was also measured to be 0.08  $\mu\text{g/L}$ . It was therefore determined that it takes less than a day for this reaction to reach equilibrium at these conditions, and future experiments could be carried out for a day.

To determine the capacity of iron fumarate for chromate, different initial concentrations of chromium solution were allowed to react with 10 mg solid. These experiments were performed in 20 mL scintillation vials. The reaction was allowed to go for one day. Each sample was stirred for the duration of the experiment. Concentrations of Cr(VI) were determined using the 1,5-diphenylcarbohydrazide method with a DR/890 Hach colorimeter. To stop the reaction, the samples were filtered with 0.2  $\mu\text{m}$  nylon syringe filters. At higher concentrations, one dilution was necessary to bring the concentration within the working range of the colorimeter.

The results are shown in **Figure 19**.



**Figure 19. The capacity curve for iron fumarate reacted with chromate**

The curve slopes up fairly gently. The sorbent begins to reach its maximum loading at concentrations of around 29 mg/L. With more replicate samples, the random error in the top part

of the graph would likely be smoothed out. By taking the average  $q$  at the two points with the highest concentration, the capacity may be estimated to be 26.3 mg Cr(VI)/g.

### **Conclusion**

Iron fumarate  $\text{Fe}(\text{C}_4\text{H}_2\text{O}_4)(\text{OH})$  has been shown to react with chromate. The reaction proceeds to equilibrium in less than a day. Iron fumarate has a capacity of 26.3mg Cr(VI)/g. This is comparable to the performance of other iron based materials.

## CHAPTER V

### CONCLUSION

Iron fumarate was synthesized from iron chloride hexahydrate and disodium fumarate. It was then tested against various aqueous solutions of arsenate, arsenite, chromate and phosphate. Iron fumarate showed impressive activity against phosphate, with a capacity of 690 mg  $\text{PO}_4^{3-}$  / g. This corresponds to approximately a stoichiometric reaction (1.4 moles phosphate per mole of iron fumarate). It is believed that with phosphate, the phosphate is replacing the fumarate ligand to form insoluble iron phosphate.

Iron fumarate was used to treat chromate solutions. Equilibrium between iron fumarate and chromate was reached in less than one day. Iron fumarate has a capacity of 26.3 mg Cr(VI) / g for chromate.

Iron fumarate was able to remove arsenate and arsenite. It is believed that the arsenate anion replaces a water molecule bound at the iron. Capacities for arsenate and arsenite were 68.5 and 45.8 mg As / g, respectively. Several other iron fumarates of various stoichiometries were prepared by varying the iron to fumarate ratio. Several of these were reacted with arsenate. Capacities were estimated for these, and the results were plotted capacities versus iron to fumarate ratio. A curve was obtained. A third order polynomial was fitted, and the derivative was

taken to find an approximate max. A maximum corresponding to  $\text{Fe}_5(\text{C}_4\text{H}_2\text{O}_4)_4(\text{OH})_7$  was found, and it is estimated that this material should have an arsenate capacity in excess of 200 mg As / g.



## CHAPTER VI

### REFERENCES

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