

Bold and Small: Using Nanotechnology for Magnetic Filtration of an Inorganic Pigment Liquid Slurry

By

Aaron H. McRorie

B.S., Indiana Wesleyan University, 2009

A REPORT

Submitted in partial fulfillment of the requirements for the degree

MASTER OF SCIENCE

Department of Chemical Engineering

College of Engineering

KANSAS STATE UNIVERSITY

Manhattan, Kansas

2018

Approved by:

Major Professor

Dr. James H. Edgar

Abstract

As a chemist who values purity of product, I have decided to look into various methods of filtration to ensure purity of final product. One such method is magnetic filtration of metallic impurities. For certain applications, the presence of ferromagnetic iron can increase magnetic susceptibility of certain items and therefore it must be removed selectively. One possible method of filtration that will bind much more selectively than a generic magnet is the use of nanoparticles. The following report is the research into what would be the best method of magnetic filtration using nanoparticles in a liquid slurry.

Table of Contents

List of Figures.....	iv
List of Tables.....	v
List of Attachments.....	vi
Acknowledgments.....	vii
Dedication.....	viii
CHAPTER 1 - Introduction	
A. Background.....	1
B. Issue at Hand.....	2
CHAPTER 2 – Experimentation	
A. How the Nanoparticles are prepared.....	3
B. Experiment Set-up.....	3
C. Process.....	7
D. Additional Testing.....	11
CHAPTER 3 – Comparison of Models and Experimental Data	
A. Consistency.....	11
B. Effects of Packing Density.....	11
C. Effect of Surface Properties.....	14
CHAPTER 4 – Conclusion.....	17
References.....	19

List of Figures:

Figure 1. Schematic of Magnetic Extraction Unit¹.....4

Figure 2. Schematic of Filter Cartridge and Filtrate¹.....5

Figure 3. Schematic of Full Magnetic Filter (Cartridge and permanent magnets)¹.....7

Figure 4. Filtration efficiency as function of the packing density of the metallic wool packed in the filter cartridge with a main water flow of 1000 +/- 100 L/h” and no magnetic field¹.....12

Figure 5. Filtration efficiency as a function of packing density of the metallic wool packed in the filter cartridge with a main water flow of 1000 +/- 100 L/h with a magnetic field¹13

Figure 6. Filtration efficiency with and without magnetic field applied on the filter (magnetic and mechanic filtration) over 10 min with 50 g metallic wool packed ($q= 0.37\text{g/cm}^3$) in the cartridge and a main water flow of 1000 +/- 100 L/h. ¹.....14

Figure 7. Nanoparticle removal efficiency with standard flow rate and standard packing density of filter (0.37 g/cm^3)¹.....15

List of Tables:

1. Stability of the injection concentration during different experiments ¹	8
2. Comparison between different magnetic filtration processes ¹	16

List of Attachments:

Appendix 1: Particle Functionalization Process.....21

Appendix 2: Reduced Flame Synthesis.....23

Acknowledgments:

I'd like to extend a special thanks and my heartfelt gratitude to the members of my supervisory committee to include Dr. Placidus Amama, Dr. Jennifer Anthony, and especially Dr. James Edgar for all of their generous advice throughout this whole process!

Dedication:

I would like to dedicate this entire document to my loving wife, Theresa. Without her selfless love and undying devotion I would have never made it this far in life and I wouldn't be half the man I am.

Love you Theresa!

Chapter 1. Introduction

A. Background:

In an industrial setting, filtration is an essential portion of the production process to ensure a pure final product. Impurities can cause significant issues with applications associated with that product. In order to ensure that the impurities do not make it to the final product and therefore the customer, a company must ensure that the proper procedures are in place to filter out those impurities. To determine the best method of filtration, this report pulls together research from other previously conducted experiments to begin testing the validity of nanoparticle magnetic filtration as a method of selectively filtering out impurities.

One of the original applications of magnetic filtration was reported by J.H.P. Watson². He used a magnetic filter of stainless steel wool with a magnetic field of around 0.1 to 0.15T for the direct application of industrial sewage treatment.² He used ferromagnetic particles to breakup sludge in sewage treatments to expedite the process and decrease the need for large settling tanks. In his work he illustrated how effective steel wool activated by an external magnetic field was at filtering out magnetic nanoparticles. The first principle to be established in the filtration is explained quite well in the following statement: “The fundamental element in the extraction process is the interaction between a magnetic wire and a small ferromagnetic particle in a uniform background field.”² This initial understanding demonstrated how an activated magnetic wire with a surrounding magnetic field could remove a specific series of particles (say, Fe_2O in the case of J.H.P Watson): a new method of filtration was developed. Since then the medical field has elaborated on this concept for a variety of diagnostic methods. One such example is the detox of heavy metals in liquids using carbon coated metal nanomagnets.³

The formation of the nanomagnets to specifically target certain metals can be done through ‘reduced flame synthesis’ which produces a “graphene-like carbon-coated cobalt metal nanoparticles (20-40 nm diameter) with an onion-like core/shell structure.”⁴ This method is derivative of the flame synthesis method for pigmentary titania. Further explanation of this

method is covered in section 2A “How the Nanoparticles are Prepared” and Appendix 2. This method is scalable to an industrial level, because it is cost efficient and effective. It has been proposed for removing trace valuable metals from industrial wastewater for recycling purposes. To date it has had a successful efficiency rate of 99% removal of valuable metals in certain studies.⁴

B. Issue at Hand:

The primary goal is to remove the impurities in-process, but if that proves too difficult or not cost-effective, then a secondary goal is to generate a process for filtering the samples to quantitatively determine the impurity content. If that secondary goal is determined to be the best method, then a smaller-scale variant of this experiment can be performed on a sample of slurry collected from the main process. This sample would be filtered to determine the amount of iron present. Limited previous research had shown that higher magnetic characteristics in the slurry can be traced to higher levels of trace iron.

The slurry is paramagnetic. Its limited response to a magnet is acceptable for the process it is used for. To clarify, the product can be affected by a magnet in its pure state, but the response is so limited that a very strong magnet would be required. The magnetic field must be optimized so it only filters out particles with trace Fe, and not pure particles. The filtration method must effectively capture all trace elements without inhibiting the process or introducing more impurities in the process. The impurities contained in the initial raw material are expected to be the same as the final product based on stoichiometry. An initial, unverified estimate is 600 PPM Fe. The product itself is mildly magnetic and if attracted to a strong magnet (especially bigger particles) while the Fe infused particles will experience an even stronger attraction. Therefore, a medium to low strength magnet will need to be tested to determine the necessary setting for optimal filtration. Additionally, the ‘large vs small particles’ discussion further mandates that the filtration process occur during the slurry stage so that (in theory) all of the particles will be small and un-clumped to prevent magnetic filtration based on size alone.

Chapter 2. Experimentation

Goal: to determine the necessary variables and the proper size/composition of nanoparticles for most cost effective and most efficient removal of iron.

A. How the nanoparticles are prepared

The nanoparticles used in this study were synthesized by the method described in the article "Scaling up Magnetic Filtration and Extraction to the Ton per Hour Scale Using Carbon Coated Metal Nanoparticles."¹ It involves a reduced flame synthesis method. Refer to Appendix 2 for specifics on the process. After the synthesis, the particulates were dispersed in a 10% HCl and water solution and stirred for 5 days.¹ This procedure ensures a carbon coating is properly applied. To ensure the process is complete I.I. Herrmann et. al.⁶ recommend that the HCl be changed out each day. The nanoparticles were recovered from the solution with a neodymium based magnet and treated for functionality.¹ See Appendix 1: 'Particle Functionalization Process' for further details.

B. Experiment Set-up

Two 1000 liter tanks were set-up to hold the water for the before and after the process steps. A pump pushes water from tank A to tank B through the magnetic filtration unit which consists of a filtration portion, an adsorption portion, and an injection point for the magnetic nanoparticles.¹ See Figure 1.

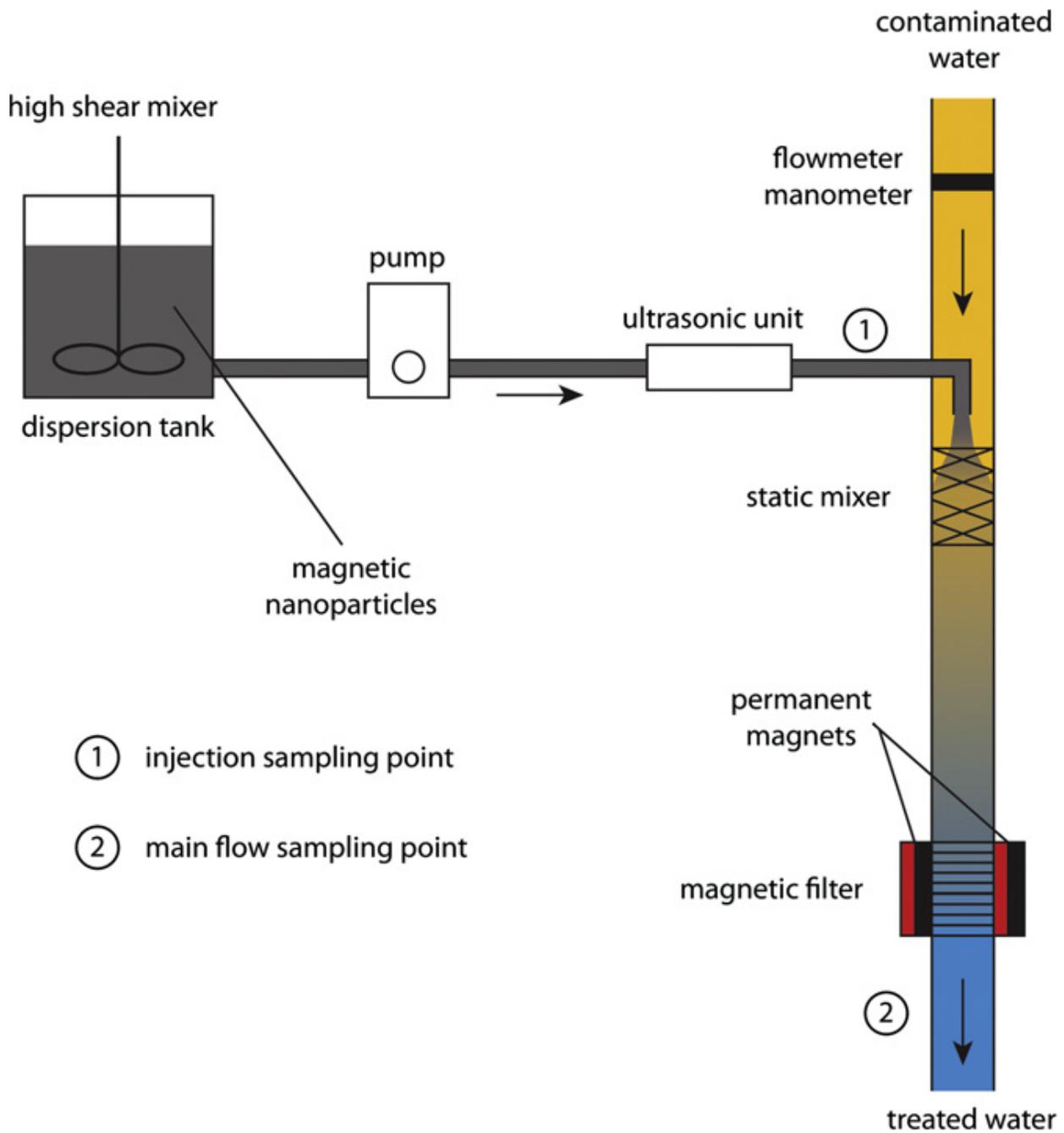


Figure 1: Schematic of Magnetic Extraction Unit¹

As illustrated by the schematic, the nanoparticles are already mixed in the 15 L dispersion tank with a high shear mixer to keep the particulate fully mixed. The static mixer

makes certain that the nanoparticles are fully dispersed as they are injected into the flow to ensure full exposure of the particles to the slurry and therefore maximum filtration.¹ The ultrasonic unit between the pump and the injection point keeps the particulate fully mixed and prevent agglomeration of particles. The proper settings for the ultrasonic unit (Heilscher, UIP 250)¹ were previously determined in a study performed by members of the French Institute of Sciences and Techniques. In their study, the use of pulse or continuous pulse irradiation did not affect deconglomeration as both were equally efficient at an amplitude of 30%.⁸ The injection point is a T junction connected directly into the main flow. This runs immediately into the static mixer followed by a flowmeter and manometer to further track specifics on the flow.¹ The flow rate and pressure were monitored to see if they played a part in fluctuations of results. Before reaching tank B, the slurry flowed through a magnetic filter composed of a cartridge filled with steel wool. The specifics of the filter are as follows: Volume of cartridge: 135 cm³, stainless steel wool: (DIN 1.4460, fiber lengths: 20 cm, diameter: 0.06mm, magnetic saturation: 80A m²/g). Figure 2 further illustrates the filtration unit below:

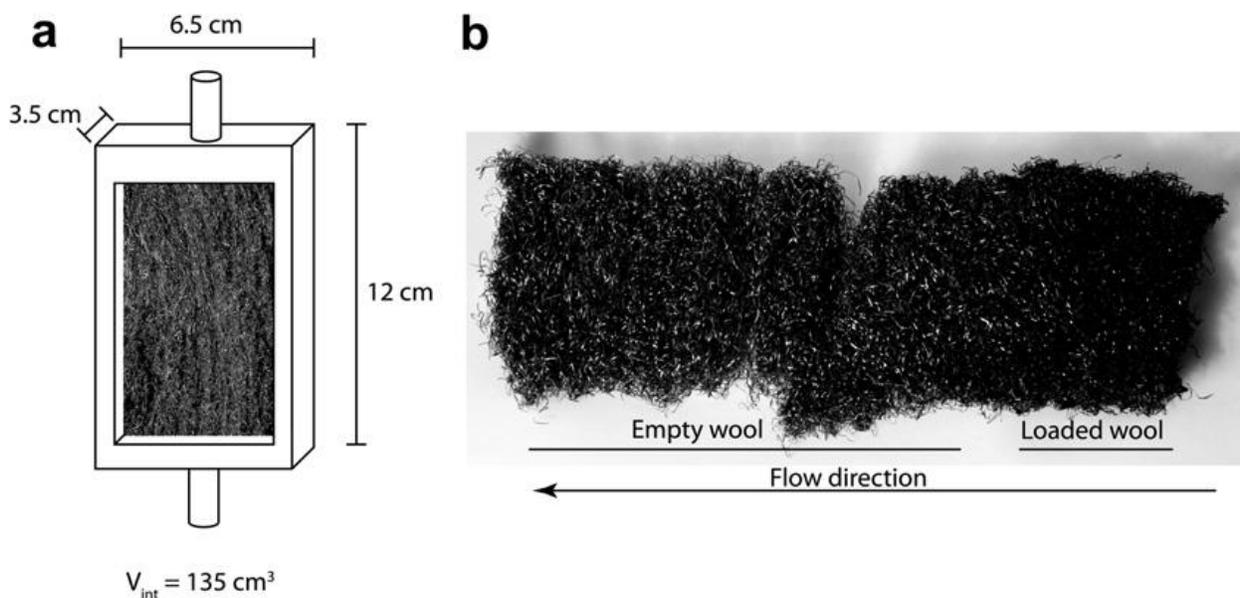


Figure 2. Schematic of Filter Cartridge and Filtrate. A: Dimensions of the Filter Cartridge. B: Visual of Wool Composition with Captured Particles.¹

Section “a” of the figure demonstrates the general dimensions of the filter cartridge for

replication purposes while section “b” of the figure demonstrates the steel wool after initial testing to show the capture of the particulates. The side of the steel wool that was first introduced to the flow of particulate is loaded with nanoparticles while the side downstream has far less (if any) particulate in it and therefore demonstrates that the filtration was at least largely complete.

The combined magnet and filter housing itself was created in-house and is shown in Figure 3. The housing apparatus holds the two permanent magnets and the steel wool cartridge. The magnets were designed to produce a 0.4-0.5 T uniform flux density while the steel used for the housing itself has a magnetic permeability of 4000 H/m (Henries per meter).¹ This makes certain that the magnetic field is contained within the tube and cylinder rather than permeating other regions. Once a complete run is pumped through the filtrate the entire housing is removed so the steel wool can be cleared to recover the particulates. Further research will need to be conducted to determine how much particulate can be run through the device before either the filter becomes clogged, or the filter becomes so saturated that particles start leeching into the exit flow, or the flow rate is partially inhibited.

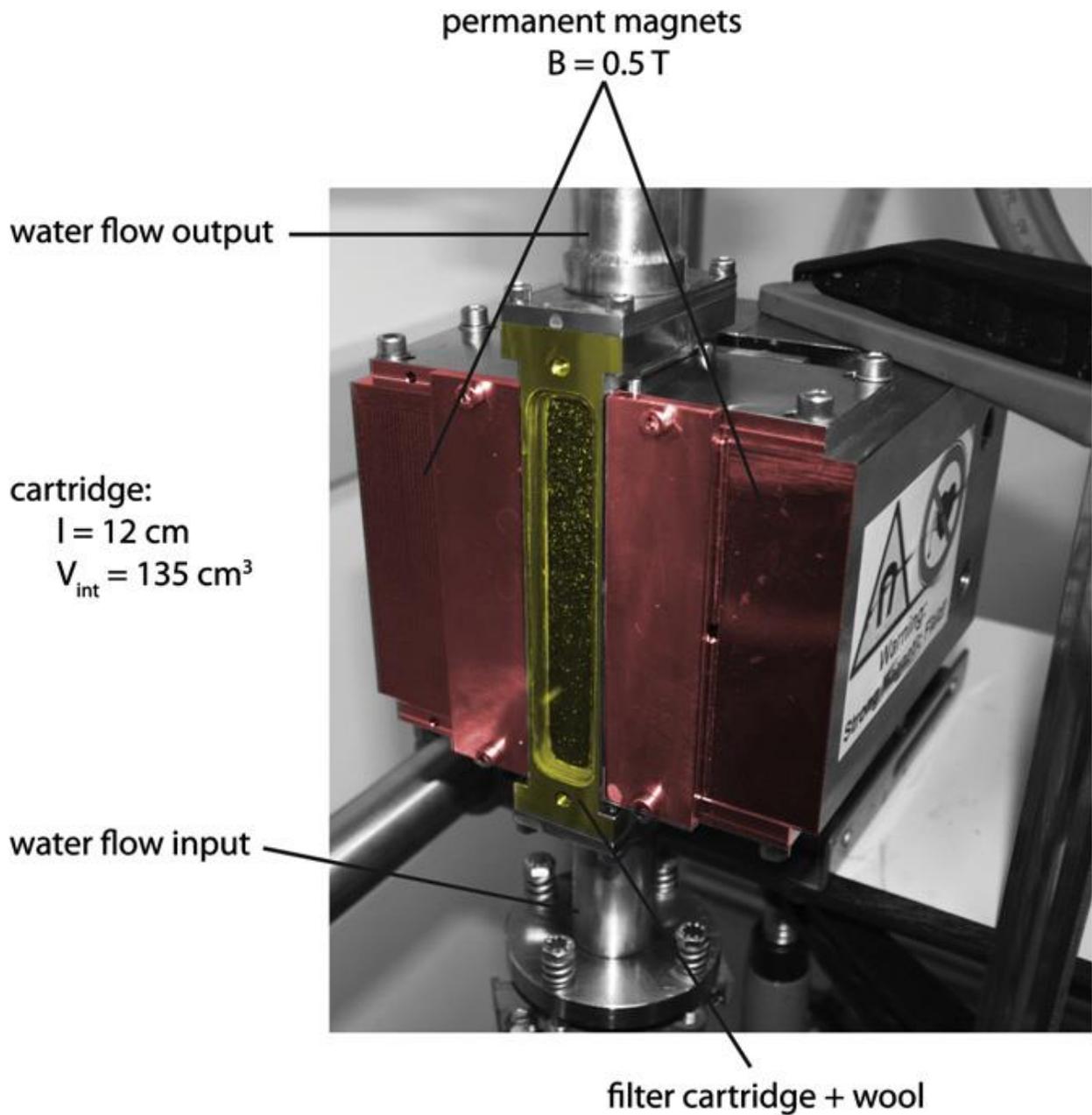


Figure 3: Schematic of Full Magnetic Filter (cartridge and permanent magnets) ¹

C. Process

In order to test the ability of the injector to pump the particulates in a stable and consistent manner into the main flow, a series of tests were run with 5L flowing through the

main flow between tanks A and B. Samples were taken at physical sample point 1 (See Figure 1 above) at three different times to ‘determine the particle concentration and homogeneity before entering the main flow.’¹ The three different time points were the beginning, middle, and end of the flow time period wherein the main flow occurred between tank A and tank B. While the experiments were not comprehensive, the average concentrations and standard deviations determined during a variety of injector speeds and main flow speeds demonstrated the consistency of the particle concentrations over time. The averages are reported in Table 1.¹

Experiment	Main Flow Speed	Injector Speed (rpm)	Average Co Conc. (ppm)	Standard Deviation (ppm)	Standard Deviation % of Average
1	600	200	367	14	4%
2	600	300	337	42	12%
3	1000	300	1020	63	6%
4	2800	600	841	97	12%
5	2800	600	857	67	8%

Table 1: Stability of the Injection Concentration during different experiments¹

To prevent false results via cobalt ions, two samples were taken from the same point at each setting. The first sample was dried and digested in 2 mL of HNO₃ to acquire the full concentration of cobalt (regardless of whether it was bonded to the nanoparticles as a coating or acting as free ions). The second sample at each setting was centrifuged for 2 hours at 2500 rpm to separate the nanoparticles from the rest of the water. Since the second sample contained only the cobalt ions, the resulting concentration was subtracted from the total concentration in the first sample of each setting to determine the cobalt that coated the nanoparticles. Therefore the average concentration of nanoparticles entering the main flow at each setting is presented in Table 1.¹ These data points demonstrate that the particle concentrations at the injection point did not vary over time despite different average concentrations based on flow rates. The standard deviation for each value was below 15% and therefore once an ideal injection concentration (based on flow rate) is determined, that

average is considered consistent throughout each experiment.

The primary set of experiments for determining magnetic filtration efficiency were performed with the following parameters: initial nanoparticle concentration (in dispersion tank), amount of stainless steel in cartridge, surface properties of nanoparticles, and magnetic influence (whether the magnet is activated or not). The consistent settings were as follows: the main flow rate between tank A and B was constant at 1000 +/- 100 L/h of tap water; the dispersion tank is initially filled with 10 L of DI water; and the shear mixer is set to 10,000 rpm. The changing variables were as follows: The dispersion tank is filled with either 0.5 or 1 g/L of cobalt nanoparticles; the injection pump is set to 245 ml/min for the 0.5 g/L of nanoparticle concentration and set to 500 ml/min for the 1.0 g/L nanoparticle concentration.¹

The filter efficiency was evaluated in a series of experiments performed with different amounts of steel wool to include: 86, 50, 27, and 0 grams. The samples were taken after 1 minute of feeding each time.¹ To calculate the filter efficiency, the concentration of the particles that made it through the filter were divided by the total initial concentration prior to injection. Each packing weight was tested both with and without the magnetic field leading to a total of 8 experiments for this section. The experiment with no packed steel wool and no magnetic field was the baseline for the concentration.

Any variations appear to be due to flow disturbance noted between the injection system and the main stream. This makes sense since there is a guaranteed pressure drop in the injection system whenever a sample is pulled. Fortunately, these variations were not enough to affect the overall results of the process.¹

First, the efficiency of the wool packing density on the filtration process was tested without applying a magnetic field. The parameters used were a main flow rate of 1000 L/h, an initial concentration of 1 g/L nanoparticles in dispersion tank, and an injection flow of 500 ml/min.¹ These parameters remained consistent throughout the process regardless of packing density. The results are presented in the “results” section in conjunction with Figure 4¹. Next, the same experiments were performed with the magnetic field present. The same conditions

as before without the magnetic field were employed with the same packing densities once again, samples were collected after approximately 1 minute of running time to establish equilibrium. Samples were collected at the exit flow of the filter cartridge every 3 minutes for a total of 3 samples each. The reported values were averaged.¹

Experiments were performed to determine how the filter efficiency changed with time. 10 minute run times both with and without magnetic filtration were tested. Ten minutes was chosen as the amount of time based on a portion of the “additional testing” in section D. To ensure stability in a dispersed form, “chemically modified magnetic nanoparticles (C/Co-PEI-IDA)”¹ were tested because they are more hydrophilic and therefore more stable in water. Figure 4 shows that the filter efficiency decreases somewhat rapidly with time when a high particle concentration is introduced and the magnetic field is not present. This was expected because any filter that is steadily bombarded with a high concentration over a large period of time will start to either lose efficiency (more particulate gets through) or will lose pressure and velocity (get clogged). Both are symptoms of filter saturation. Without the magnetic field this could present a problem. That being said, the magnetic field when introduced at a strength of 0.5T, created a consistent removal efficiency of 97.5%.¹ As figure 6 demonstrates, the ppm of cobalt in the fluid exiting the cartridge with no magnetic field (mechanical filtration) was approximately 6.5-7 ppm after three minutes; then steadily rose to 8 ppm at 7 minutes and rocketed to 12 ppm after 10 minutes. This was with a starting concentration of approximately 17 ppm, determined with no filter at all. With the same starting concentration, the magnetic filtration appears to even improve over time by starting with approximately 0.20 ppm at 3 minutes, dropping to approximately 0.15 ppm after 7 minutes and approximately 0.07 ppm after 10 minutes. The initial filtration efficiency of the mechanical filtration was approximately 50%, and dropped quickly. In contrast, with the magnetic field the efficiency jumped to 97.5%.¹

D. Additional Testing:

A series of additional control experiments were conducted to confirm the reliability of the injection system. In these experiments, 5 L of the dispersion containing the nanoparticles was injected into the main flow and measured the time required to inject it. The pump speed of the main flow was varied between 600 L/h and 2800 L/h. The results indicated that the speed at which the particulate was injected increased linearly with the rate of the main flow increased.¹ Fortunately, this confirmed that the pump for the injection flow is sufficient for the task and is not overwhelmed by the main flow from tank A to tank B.

To test the effect of the surface properties on the filtration efficiency, tests were run using functionalized particles (with coating) for 10 minutes and tests using uncoated particles for 20 minutes. The results confirmed that there were few enough particulates in the water after a 20 minute duration; 10 minutes was sufficient for each experiment.¹

Chapter 3. Comparison of Models and Experimental Data

A. Consistency

The results in Table 1 confirm that the injection concentration (as measured by average particulate concentration in parts per million) was consistent. The averages (though different between each test) had very small standard deviations (no more than 15%).¹ This proved not only the consistency of the injector pump, but also the ability for the high shear mixer and ultrasonic unit to keep the concentration consistent through the duration of the experiment.

B. Effects of Packing Density

According to the results (Figure 4¹), without the magnetic field, the metal wool packing density has a significant influence on the physical filtration of particles. As can be seen, the

concentration sampled after the filtration cartridge is significantly higher when no steel wool is present. With no magnetic filtration and no physical filtration, the sampled concentration was approximately 17 ppm after 1 minute of particle feeding. This result by itself seems inconsequential, until compared to the resulting concentration when various packing densities of steel wool are applied. At a packing density of 0.2 g/cm^3 , the concentration of particles sampled after 1 minute decreased to 10.3 ppm. For a packing density of 0.37 g/cm^3 , the concentration of particles sampled after 1 minute decreased to 5.4 ppm. That is, almost half of the particles with almost double the density. This portion is somewhat linear. Yet after increasing the packing density to 0.64 g/cm^3 , the particle concentration decreased to 3.2 ppm^1 which continues the linear aspect of the graph to a lesser extent.

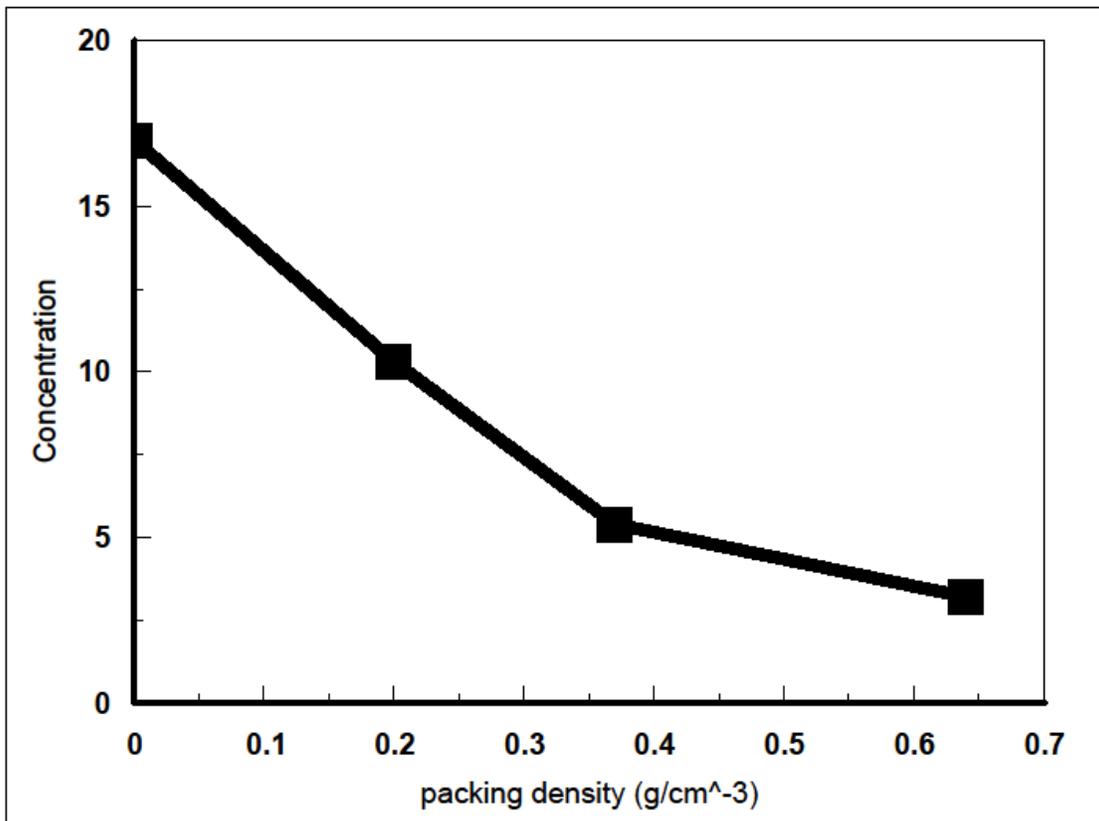


Figure 4 Filtration efficiency as function of the packing density of the metallic wool packed in the filter cartridge with a main water flow of $1000 \pm 100 \text{ L/h}$ and no magnetic field¹

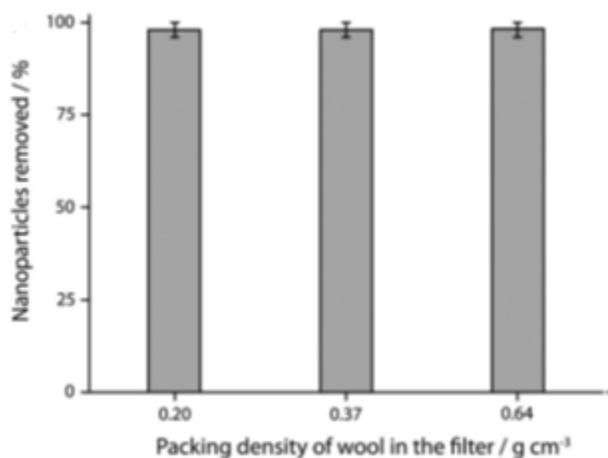


Figure 5. Filtration efficiency as a function of packing density of the metallic wool packed in the filter cartridge with a main water flow of 1000 +/- 100 L/h with a magnetic field¹

When the magnetic field was applied with each of the packing densities under the same conditions, the variance in filtrated particles almost entirely disappeared. The percent of nanoparticles removed was nearly 98% consistently regardless of the packing density (Figure 5¹). Over 98% (with a variance of +/- 1%) of the particles were filtered out by the magnetic filter regardless of packing density.¹ So for each packing density where wool was present, the filtration efficiency was the exact same within 1%. The variance between the packing densities was less than the variance within their own tests. This not only verifies the efficiency of the magnetic portion of this filtration, but also allows a much simpler determination of packing density based on flow interference rather than a balance between efficient filtration and flow. Since the packing density did not affect the variance, a packing density of 0.37 g/cm³ was used for all subsequent tests to minimize the pressure loss¹ and any flow issues that would be associated with a higher density. This middle packing density was able to attract nearly all nanoparticles with less likelihood of early oversaturation.

The high-shear mixer in the dispersion tank created enough mechanical stress on the nanoparticles that some were damaged and this led to a cobalt ion concentration of 0.2 ppm after filtration. This concentration stayed consistent throughout all successive experiments.¹ Considering how easily the color properties can be altered in the pigments that this is to be

used on, this may be a disqualifying flaw unless a less stress-inducing stirring mechanism can be introduced. Another possible solution would be to find a coating that is inert in how it affects color and physical properties in the pigments. But that is a concept for future experimentation.

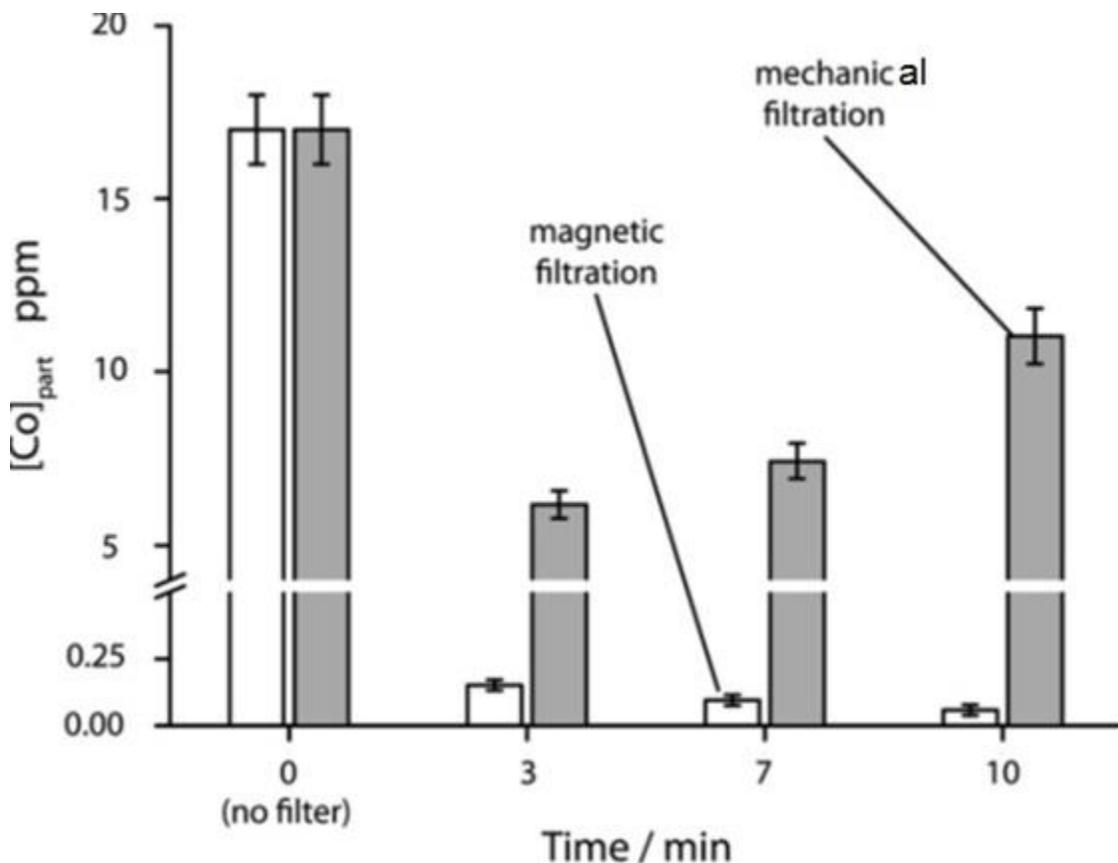


Figure 6. “Filtration efficiency with and without magnetic field applied on the filter (magnetic and mechanic filtration) over 10 min with 50 g metallic wool packed ($q= 0.37\text{g}/\text{cm}^3$) in the cartridge and a main water flow of $1000 \pm 100 \text{ L}/\text{h}$.”¹

C. Effect of Surface Properties

The performance of the filter was not altered greatly by the nanoparticle surface properties. This was demonstrated by coating the cobalt nanoparticles with two different types of carbon. One was left as prepared by the manufacturer (Nanostructured & Amorphous Materials, Inc) and the other was surface modified.¹ The overall efficiency of the filter was greater than 98%¹ for the ‘as-prepared particles’ when injected continuously for 20 minutes.

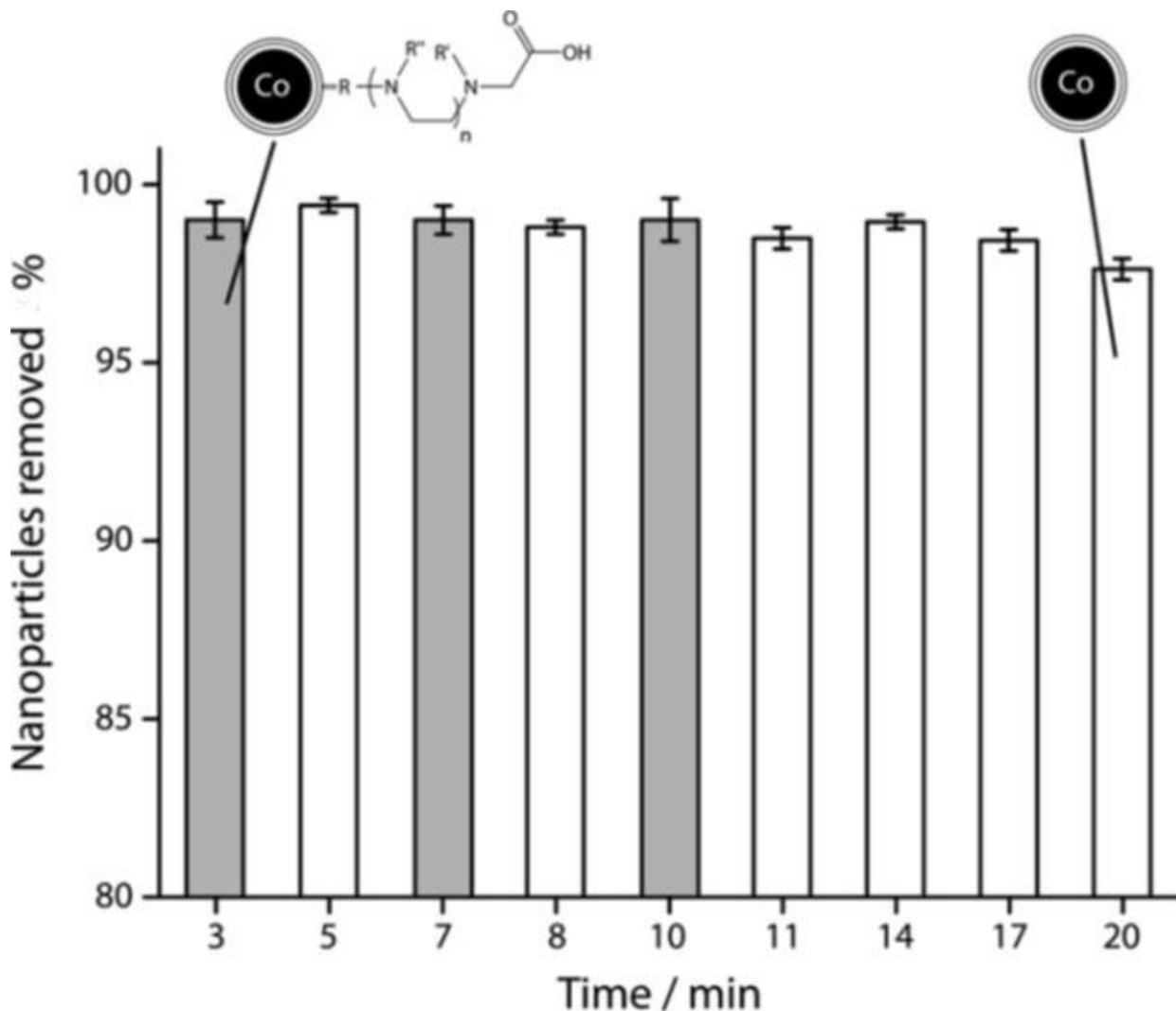


Figure 7. Nanoparticle removal efficiency with standard flow rate and standard packing density of filter (0.37 g/cm^3)¹ The ‘as prepared particles’ are the white bars while the ‘modified’ particles (Co-PEI-IDA surface coating) are the grey bars. Both sets of particles maintained filtration efficiency of approximately 98% and there was no significant change in efficiency based on the type of surface.

A direct comparison between the work of Caterina C. Borghi et al²⁴, V. Badescu et al⁵², Robert M. Wingo et al⁵⁷, and Cafer T. Yavuz et al⁵⁸ in table 2 aligns all of the pertinent properties in a table to determine the most advantageous sized particle (micro vs nano) and the best core element. This shows that microparticles have the distinct advantage of easier collection at a faster flow rate, but have the disadvantage of less surface area overall.¹ For the relatively fast flow of our current systems with only trace elements being filtered, the

microparticles would be the best option. Fortunately, there is a third option, metallic carbon coated nanoparticles. These find a middle ground between the two options by having a higher specific surface area while maintaining a higher bulk magnetic saturation when compared directly to iron oxide. This allows greater filtration (over 97%)¹ in a rapid flow rate that is comparable to the microparticles while still acquiring most of the ions to be filtered due to the higher surface area.

Comparison between different magnetic filtration processes								
Size	Material	Ref.	primary particle size (nm)	SSA (m/g)	Flow (cm/s)	Mag field strength (T)	# Passage in the filter	Filtration efficiency (%)
Micro	Magnetite	24	5000	2	15	0.5	2	99.9
Micro	Hematite	24	1000	15	15	0.5	8	99.6
Micro	Hematite	24	500	19	15	0.5	8	99.4
Micro	Magnemite	52	500	5	0.2	0.5	1	98.1
Nano	Magnetite	58	26	170	0.1	1.3	1	90
Nano	Magnetite	57	6	192	-	1	1	>37
Nano	Magnetite	57	11	105	-	1	1	>95
Nano	Magnetite	57	20	58	-	1	1	>99
Nano	Cobalt	1	23	29	12	0.5	1	>97.5

Table 2 Comparison between different magnetic filtration processes ^{1,31}

To further expand on the data contained within Table 2, the results of five different research projects were combined to determine the best particle material and size to be used for magnetic filtration based on a series of criteria, most importantly the comparable filtration efficiency and surface area. The majority of the micro particles were over 99% efficient in filtration because their larger size experiencing a greater effect from a magnetic field. In contrast, the nanoparticles were less efficient because their smaller size led to less of a magnetic effect. The nanoparticles had the distinct advantage of an overall larger surface area, which allows more ions to bind to them. It is difficult to pinpoint an exact perfect balance, but

the clear result of the metallic carbon coated nanoparticles classifies them as a prime candidate.

Chapter 4. Conclusion

In order to discover a more efficient method of filtering out potentially magnetic and therefore harmful iron impurities, I have extensively reviewed several studies on the ability of nanoparticles in a magnetic filter as a method of continuously extracting specific undesired metal ions from a liquid slurry. While there are several possible solutions to pursue, the most promising for the specific problem at hand was investigated in depth. The results show that it is possible to achieve at least 98% filtration without significantly interfering with the flow by using a specific density of magnetic material (0.37 g/cm^3) with a 0.5T strength magnet.¹ The efficiency was further increased by using a carbon-coated cobalt-core nanoparticles. The cobalt-core was the primary source of magnetic reactivity to the field, but if cobalt contamination of the pigment or wastewater is a concern the core could be replaced by an iron carbide core. The ironic issue with this is that the motivation behind this study is to extract iron.

A potential problem is that the high-shear mixer in the dispersion tank for the injection portion can break apart nanoparticles and therefore expose the cores. These 'exposed cores' can escape the filtration system in small amounts. This leads to the question of whether there is enough original contaminant to justify this risk, or if the risk of more iron being exposed to the system through these 'exposed cores' outweighs the filtration benefit. So further research will be required to determine if cobalt contamination in small amounts will affect the color or physical properties of the final product or not. Additional research is required as to how much the iron core particles would contaminate the final product via the shear stress exposing them vs the benefit of filtration.

The system proved to be quite stable; it provided consistent filtration even with varying filtration densities with the magnetic field activated. The filtration efficiency only declined during periods without the magnetic field (mechanical filtration only). The main flow was

highly consistent and the pressure drops due to injection and sampling were minimal and had no significant bearing on the results. The surface properties of the nanoparticles did not affect filtration itself and only served to vary the amount of targeted ions absorbed. For an application that is only seeking to absorb trace elements, we can afford to use less expensive micro-particles with a smaller surface area and higher filtration rate. We are much more concerned with not allowing the nano/micro-particles to escape the filtration system than we are about capturing vast amounts of iron ions.

Even if not directly applied to our production process (with thousands of gallons pushing through), the cost of nanoparticles, filtration/magnet resources, and cleaning of the filtrate would be astronomical for very small gain. Instead of using this filtration method continuously, samples would be selectively tested from slurries when quality control is key. The difficulty with this test method is that in order to measure levels of iron attached to the nanoparticles, their initial weight must be known, the amount of nanoparticles that have passed through the filtration system or never reached the filtration system must be estimated as a variable, and finally the nanoparticles must be completely recovered from the filtration cartridge in order to get an accurate measurement. With this many variables on such a small scale of measurement, a much more robust system with fewer variables or at least better controls on collection of nanoparticles must be in place before accurate quality control tests can be run.

So in conclusion, this method represents a significant improvement and a step in the right direction, but simultaneously requires a significant amount of further research before it can be applied directly. A few examples of studies that will need to be performed for further consideration are as follows: a 'less stress-inducing' stirring method (to prevent nanoparticles from fragmenting and passing through the filter), other filtrate materials that can be cleaned and replaced easily, and coatings for nanoparticles that absorb Fe but are inert to the pigment in case pieces fall off.

References

(1)

Rossier, Michael, Marcel Schreier, Urs Krebs, Beat Aeschlimann, Roland Fuhrer, Martin Zeltner, Robert N. Grass, Detlef Günther, and Wendelin J. Stark. "Scaling up magnetic filtration and extraction to the ton per hour scale using carbon coated metal nanoparticles." *Separation and Purification Technology* 96 (2012): 68-74. doi:10.1016/j.seppur.2012.05.024.

(2)

Watson, J. H. P. "Magnetic filtration." *Journal of Applied Physics* 44, no. 9 (1973): 4209-213. Doi:10.1063/1.1662920.

(3)

Aposhian, H.V."DMSA and DMPS-Water Soluble Antidotes for Heavy Metal Poisoning." *Annual Review of Pharmacology and Toxicology* 23, no.1 (1983): 1933-215.

(4)

Rossier, Michael, Fabian M. Koehler, Evagelos K. Athanassiou, Robert N. Grass, Markus Waelle, Karin Birbaum, Detlef Günther, and Wendelin J. Stark. "Energy-Efficient Noble Metal Recovery by the Use of Acid-Stable Nanomagnets." *Industrial & Engineering Chemistry Research* 49, no. 19 (2010): 9355-362. doi:10.1021/ie101117c.

(5)

Oskuee, Reza K., Ali Dehshahri, Wayne T. Shier, and Mohammad Ramezani. "Alkylcarboxylate Grafting to Polyethylenimine: A Simple Approach to Producing a DNA Nanocarrier with Low Toxicity." *The Journal of Gene Medicine* 11, no. 10 (2009): 921-32. doi:10.1002/jgm.1374.

(6)

Herrmann, Inge K., Robert N. Grass, Dmitry Mazunin, and Wendelin J. Stark. "Synthesis and Covalent Surface Functionalization of Nonoxidic Iron Core-Shell Nanomagnets." *Chemistry of Materials* 21, no. 14 (2009): 3275-281. doi:10.1021/cm900785u.

(8)

Nguyen, Van Son, Didier Rouxel, Rachid Hadji, Brice Vincent, and Yves Fort. "Effect of Ultrasonication and Dispersion Stability on the Cluster Size of Alumina Nanoscale Particles in Aqueous Solutions." *Ultrasonics Sonochemistry* 18, no. 1 (2011): 382-88. doi:10.1016/j.ultsonch.2010.07.003.

(10)

Grass, Robert N., and Wendelin J. Stark. "Gas Phase Synthesis of Fcc-cobalt Nanoparticles." *Journal of Materials Chemistry* 16, no. 19 (2006): 1825. doi:10.1039/b601013j.

(24) (as listed in Table 2 per Reference (1))

Borghi, C. Caterina, Massimo Fabbri, Maurizio Fiorini, Maurizio Mancini, and Pier Luigi Ribani. "Magnetic Removal of Surfactants from Wastewater Using Micrometric Iron Oxide Powders." *Separation and Purification Technology* 83 (2011): 180-88. doi:10.1016/j.seppur.2011.09.042.

(30) (as listed in Table 2 per Reference (1))

Rossier, Michael, Fabian M. Koehler, Evangelos K. Athanassiou, Robert N. Grass, Beat Aeschlimann, Detlef Günther, and Wendelin J. Stark. "Gold Adsorption on the Carbon Surface of C/Co Nanoparticles Allows Magnetic Extraction from Extremely Diluted Aqueous Solutions." *Journal of Materials Chemistry* 19, no. 43 (2009): 8239. doi:10.1039/b913744k.

(31) (as listed in Table 2 per Reference (1))

Cornell, R. M., and U. Schwertmann. "The Iron Oxides: Structure, Properties, Reactions, Occurrence, and Uses Second Ed." 2003. doi:10.1002/3527602097.

(52) (as listed in Table 2 per Reference (1))

Badescu, V., V. Murariu, O. Rotariu, and N. Rezlescu. "Optimization of the Recovery Efficiency in an Axial HGFM Cell with Bounded Flow Field." *Journal of Physics D: Applied Physics* 29, no. 9 (1996): 2515-518. doi:10.1088/0022-3727/29/9/042.

(57) (as listed in Table 2 per Reference (1))

Wingo, Robert M., F. Coyne Prenger, Michael D. Johnson, Joseph A. Waynert, Laura A. Worl, and Tung-Yu Ying. "High-Gradient Magnetic Field Split-Flow Thin Channel (HGFM-SPLITT) Fractionation of Nanoscale Paramagnetic Particles." *Separation Science and Technology* 39, no. 12 (2004): 2769-783. doi:10.1081/ss-200028435.

(58) (as listed in Table 2 per Reference (1))

Yavuz, Cafer T., Arjun Prakash, J.t. Mayo, and Vicki L. Colvin. "Magnetic Separations: From Steel Plants to Biotechnology." *Chemical Engineering Science* 64, no. 10 (2009): 2510-521. doi:10.1016/j.ces.2008.11.018.

Appendix 1:

Particle Functionalization Process

After synthesis, the particles were functionalized as follows. The cobalt core nanoparticles were coated with a polymer shell that altered the surface functionality by using the methodology described by Rossier et. al.⁴ In this method, the nanomagnet surface is coated with a “metal extraction resin-like polymer” that made it easier to attract the desired elements. This was done by first adding 500 mg of the pre-treated (carbon-coated) particles in “40 mL of N,Ndimethylformamide (DMF) (puriss g 99.8%, Fluka) and then added 20 mL of a poly(ethylene imine) (PEI) solution (2 g of PEI; 99%, Mw) 10,000, Polysciences Inc. in 20 mL of DMF”⁴ and stirring for 20 hours at room temperature. This was followed by drying in an “exsiccator above phosphorus pentoxide (98%, ABCR) under vacuum” for ten hours at room temperature.⁴ Then 400 mg of the dried particles were dispersed in 10mL of a dry chloroform mixture created by “dissolving 0.5g of methylisothiocyanate (purum g 98%, Fluka) in 10 mL of dry chloroform (99%, J.T. Baker)”.⁴ This was then placed in an ice bath. The solution was stirred at room temperature while the methylisothiocyanate solution (10 mL) was added drop-wise for two hours. The result was a thiourea-derivatized polyimine surface (CH₃NCS).⁴

Then in order to ensure the PEI (poly(ethyleneimine) coating is secured on the nanoparticles; the researchers dispersed the pre-treated particles (50 grams worth) in a mixture of 600 mL of N,N-dimethylformamide (DMF) (purissP 99.8%, Fluka) and 400mL of PEI solution. The poly(ethyleneimine) solution was a mixture of 25 g of PEI (99%) in 400 ML of DMF).¹ Once the elements were combined, the mixture was stirred for twenty hours at room temperature. When the twenty hours were complete the PEI coated C/Co nanoparticles were separated from the mix using an external magnet.¹ In order to remove any polymer not bonded to the nanoparticles; the nanoparticles were washed with DMF, DI water, and acetone (300 mL of each) and the washed particles were dried at 50 degrees Celsius in a vacuum for at least 12 hours.¹

To further ensure that the nanoparticles are functionalized, another solution was made by first creating three individual solutions as follows: 20 grams of the coated particles dispersed in a solution of 500 mL DMF, a second solution was made by dissolving 10 grams of sodium hydroxide (NaOH) in 300 mL DMF, and the third solution was 20 grams of BrHAc dissolved in 200 mL DMF.⁵ To ensure full dispersion, all three solutions were combined and stirred at room temperature for a total of six hours. Once the particles were removed from the mixture with an external magnet, they were washed with DMF, DI water, and acetone (400 mL each individually) before being dried at 50 degrees Celsius in a vacuum oven.

Appendix 2: Reduced Flame Synthesis

The process of Gas Phase synthesis of cobalt nanoparticles via reduced flame synthesis is as follows:

Precursor preparation.

“Cobalt 2-ethylhexanoate in mineral spirit (S.C. Socetec S. A., 12 wt% Co) was diluted 2:1 (weight/weight) with tetrahydrofuran (Fluka, tech) and filtered (Satorius, fluted filter type 288) prior to use. Conventional flame spray set-up. The Co-carboxylate-based precursor was fed (5 ml min, HNP Mikrosysteme, micro annular gear pump mZR-2900) to a spray nozzle... where it was dispersed by oxygen (5 L/min, Pan Gas tech.) and ignited by a premixed methane-oxygen flame (CH₄: 1.2 l min, O₂: 2.2 L/min, PanGas tech.). The produced particles were separated from the off-gas using glass fiber filters (Schleicher & Schuell, GF6).”¹⁰

Reducing flame spray synthesis.

“The spray nozzle was placed in a glove-box fed with nitrogen (PanGas, 5.0) which was recirculated by a vacuum pump (Busch, Seco SV1040CV) at about 20 m³/h. CO₂ and H₂O were continuously removed from the recycle stream using two adsorption columns, packed with zeolite 4A and 13X (Zeochem), respectively. To avoid the accumulation of CO, NO and other impurities in the glove-box atmosphere a purge gas stream continuously passed through the box... A sinter metal tube (GKN Sintermetalle, inner diameter 25 mm) surrounding the flame... allowed radial inflow of an inert mixing gas (PanGas, CO₂ or N₂, 99.995%) at a flow rate of 25 L/min and stable combustion. A mass spectrometer (Balzers, GAM 400) was applied for the detection of the gas concentration of H₂, N₂, CO₂, NO, NO₂ and O₂. A separate data acquisition and control unit allowed controlling of the mass spectrometer, the liquid feed pump, mass flow controllers (Brooks) for sheath, dispersion and ignition gases as well as temperature of the box atmosphere and the adsorption columns. An oxygen concentration of below 100 ppm (volume/volume) was maintained during all experiments performed in the glove-box. The dispersion, ignition, and combustion of the Co carboxylate based precursor was

performed in the same way as the original flame spray set-up. While keeping a constant dispersing oxygen flow rate (5 L/min) the liquid flow rate was changed from 4.5 ml/min (for $w=1.5$) to 6 ml/min (for $w=2$).¹⁰