RICE UNIVERSITY

Development of iron oxide nanomaterials-based technology for arsenic remediation

by

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ABSTRACT

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In 2005, the Colvin group proposed the use of magnetite nanoparticles for arsenic adsorption. This would allow the reduction of waste significantly with the additional advantage of magnetic-driven separation at low fields. However, despite the efforts of several groups around the world, the use of arsenic sorbents based in nanomaterials is not yet feasible. Still, the study of new iron-based nanomaterials for arsenic uptake has been increasing over the last years. During my PhD program, I have analyzed the performance of magnetite nanoparticles synthesized by several methodologies with both batch experiments and column tests and varying conditions including groundwater with high silica concentrations (Chapter 4). Silica is one of the most common interferences and dramatically decreases the arsenic removal capabilities. My work included the evaluation of arsenic removal capabilities on site (Salamanca, Mexico) and the comparison with commercially available arsenic sorbents under those difficult conditions—[SiO₂] =85ppm and pH=8 (Chapter 3).

In spite of the comparable performance of the nanoparticles to other commercial sorbents, their small-scale production and the lack of a simple filtration
setup motivated us to design a material that could be used under real-world operation conditions. We proposed the use of clusters of nanoparticles in order to benefit of the properties of both the nanoparticles and the bulk material. The understanding of the mechanism of the synthesis, the effect that synthetic parameters have in the cluster size and unit size, and the corresponding effect in arsenic adsorption are discussed in Chapter 5.

Currently, the most pressing needs for groundwater treatment is in developing countries; this forces the use of highly cost-effective strategies. In order to develop a material that can feasibly solve the needs on the field in an inexpensive way, one of the projects was to modify the kitchen synthesis of nanomagnetite previously introduced by our group. Even when in the past a cheap synthesis was achieved, it was a process with several steps and the nanoparticles were not able to absorb arsenic. In this work (Chapter 6), a one-pot synthesis is proposed and studies have shown that the nanoparticles thereby obtained have much better arsenic removal performance than the nanoparticles prepared by thermal decomposition making the material very promising.

Even though the work proposed herein will not solve the problem of arsenic contamination, it provides a grasp of the requirements for the implementation of nanomaterials in water treatment technologies and narrows the gap between design of nanomaterials in the lab and their application on the field.
And that’s why I have to go back
to so many places
there to find myself
and constantly examine myself
with no witness but the moon
and then whistle with joy,
ambling over rocks and clods of earth,
with no task but to live,
with no family but the road.

*End of the World (Wind)* – Pablo Neruda.
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Contents

Acknowledgments ....................................................................................................................... vii

Contents ........................................................................................................................................ ix

List of Figures ................................................................................................................................ xiii

List of Tables ................................................................................................................................. xviii

List of Equations ............................................................................................................................ xix

Nomenclature ................................................................................................................................. 1

Introduction ..................................................................................................................................... 4

1.1. Nanomaterials in water treatment ......................................................................................... 5

1.2. Iron oxide nanomaterials ......................................................................................................... 6

  1.2.1. Iron oxide for water treatment ........................................................................................... 7

  1.2.2. Synthesis of iron oxide nanoparticles ............................................................................... 8

1.3. Arsenic water contamination .................................................................................................. 13

1.4. Arsenic remediation .............................................................................................................. 16

  1.4.1. Interferences for arsenic adsorption ............................................................................... 18

1.5. Evaluation of remediation performance ............................................................................... 20

  1.5.1. Batch experiments ........................................................................................................... 20

  1.5.2. Rapid Small Scale Columns ............................................................................................ 21

1.6. Motivation ............................................................................................................................... 22

Experimental section .................................................................................................................... 24

2.1. Materials ............................................................................................................................... 24

2.2. Synthesis of nanoparticles .................................................................................................... 27

  2.2.1. Thermal decomposition .................................................................................................... 27

    2.2.1.1. Iron oleate synthesis .................................................................................................... 28

    2.2.1.2. Synthesis of nanoparticles ........................................................................................ 28

    2.2.1.3. Transfer of nanocrystals from the organic to aqueous phase ..................................... 30

    2.2.1.4. Coating removal ........................................................................................................ 31

  2.2.2. Co-precipitation from iron salts ....................................................................................... 32

    2.2.2.1. Nanoparticles without surface coatings ................................................................. 33
2.2.1. Polymer coated nanoparticles .............................................................. 34

2.2.3. Solvothermal synthesis ........................................................................ 35

2.2.4. Modified kitchen synthesis for iron oxide nanocrystals ..................... 37

2.3. Physicochemical characterization ............................................................ 39

2.3.1. Transmission Electron Microscopy ......................................................... 39

2.3.2. Scanning Electron Microscopy ............................................................. 40

2.3.3. Dynamic Light Scattering ..................................................................... 40

2.3.4. UV-Vis absorbance .............................................................................. 40

2.3.5. X-Ray Diffraction ................................................................................ 41

2.3.6. X-ray Photoelectron Spectroscopy ....................................................... 41

2.3.7. Raman Spectroscopy ........................................................................... 42

2.3.8. IR Spectroscopy .................................................................................. 42

2.3.9. Thermal Gravimetric Analysis .............................................................. 43

2.3.10. Brunauer–Emmett–Teller (BET) surface area analysis .................. 43

2.3.11. Inductively Coupled Plasma – Optical Emission Spectroscopy ....... 43

2.3.12. Inductively Coupled Plasma – Mass Spectrometry ......................... 45

2.4. Remediation studies ................................................................................ 46

2.4.1. Batch experiments .............................................................................. 46

2.4.1.1. Batch experiments for arsenic ......................................................... 46

2.4.1.2. Dye remediation experiments ........................................................ 49

2.4.2. Rapid Small Scale Column Tests ......................................................... 50

2.4.2.1. Columns with granular materials .................................................... 50

2.4.2.2. Columns with nanoparticles .......................................................... 52

Evaluation of current arsenic sorbents ......................................................... 55

3.1. Introduction .............................................................................................. 55

3.2. Materials characterization ....................................................................... 57

3.3. Selection of the field site ......................................................................... 62

3.4. Batch experiments .................................................................................. 63

3.5. Column tests .......................................................................................... 68

3.6. Prediction of the arsenic adsorption behavior in the presence of competitive ions ........................................................................................................ 78

3.7. Feasibility study ...................................................................................... 80
3.8. Optimizing the use of commercial magnetite nanoparticles ........................................... 84
3.9. Conclusions.................................................................................................................. 95

Iron oxide nanoparticles for arsenic removal ................................................................. 98

4.1. Introduction............................................................................................................... 98
4.2. Synthesis of nanoparticles....................................................................................... 100
4.3. Effect of surface coating......................................................................................... 101
4.4. Effect of synthetic methodology ............................................................................ 109
4.5. Effect of particle aggregation .................................................................................. 115
  4.5.1. Batch experiments.................................................................................................. 116
  4.5.2. Column tests......................................................................................................... 120
4.6. Conclusions.............................................................................................................. 127

Clusters of Iron oxide nanoparticles for arsenic removal ............................................. 130

5.1. Introduction.............................................................................................................. 130
5.2. Solvothermal synthesis........................................................................................... 132
5.3. Reproducibility ....................................................................................................... 135
5.4. Modification of synthetic parameters....................................................................... 137
5.5. Evolution of the reaction through time................................................................. 141
5.6. Temperature effect .................................................................................................. 150
5.7. Cooling effect........................................................................................................... 154
5.8. Proposed mechanism of reaction............................................................................ 158
5.9. Applications in arsenic removal.............................................................................. 162
5.10. Conclusions............................................................................................................. 168

The synthesis of iron oxide nanoparticles from everyday ingredients ....................... 171

6.1. Introduction.............................................................................................................. 171
6.2. Optimizing synthesis using everyday ingredients................................................. 172
  6.1. Forming larger quantities of nanoparticles............................................................. 178
  6.2. Environmental applications.................................................................................... 187
    6.2.1. Arsenic adsorption.............................................................................................. 187
    6.2.2. Dye remediation studies.................................................................................... 189
6.3. Conclusions............................................................................................................. 192
Appendix A ................................................................. 193
Appendix B ................................................................. 201
List of Figures

Figure 1.1 Crystalline structure of iron oxides................................................................. 6
Figure 1.2 XRD for iron oxides.......................................................................................... 7
Figure 1.3 Different types of nano-Iron oxides. ................................................................. 9
Figure 1.4 Scheme of the thermal decomposition reactions.............................................. 10
Figure 1.5 Schematic representation of water soluble nanoparticles ..................... 11
Figure 1.6 Scheme for the co-precipitation synthesis....................................................... 12
Figure 1.7 Scheme of the solvothermal synthesis......................................................... 13
Figure 1.8 Distribution of arsenic groundwater contamination................................. 14
Figure 1.9 Eh-pH diagram for aqueous As species......................................................... 15
Figure 1.10 Arsenic oxyanions as a function of pH....................................................... 16
Figure 1.11 Structural conformations for the bond As-O-Fe in iron oxides..... 17
Figure 1.12 Silica and arsenic adsorb onto iron oxides similarly in a similar fashion................................................................. 19
Figure 2.1 Thermal decomposition synthesis procedure.............................................. 29
Figure 2.2 Schematic representation of a co-precipitation reaction setup..... 34
Figure 2.3 Preparation of reaction mixture for solvothermal synthesis of magnetite nanoclusters ................................................................. 36
Figure 2.4 Solvothermal synthesis procedure............................................................... 37
Figure 2.5 Modified kitchen synthesis. ........................................................................ 38
Figure 2.6 Experimental procedure for adsorption isotherms ........................................ 47
Figure 2.7 Modification of batch experiments for liquid samples......................... 49
Figure 2.8 Assembly of the columns............................................................................ 51
Figure 2.9  Setup of columns in the field and small scale.............................................. 52
Figure 2.10 Preparation of the nMag for column.......................................................... 54
Figure 3.1 SEM images of commercial sorbents.............................................................. 58
Figure 3.2 XRD of commercial sorbents. ........................................................................ 59
Figure 3.3 XPS of commercial sorbents ........................................................................... 60
Figure 3.4 Arsenic isothermal experiments with and without Silica present 64
Figure 3.5 Arsenic removal from Salamanca groundwater ............................................. 66
Figure 3.6 Columns of commercial sorbents in the lab ................................................. 69
Figure 3.7 Columns of commercial sorbents in Salamanca ........................................... 73
Figure 3.8 Column breakthrough curves of main interferences in groundwater.................. 75
Figure 3.9 Determination of minimum dosage for optimal arsenic removal. 85
Figure 3.10 Determination of minimum contact time for arsenic removal..... 86
Figure 3.11 Regeneration conditions for commercial nanoparticles......................... 88
Figure 3.12 Regenerated versus native nanoparticle performance. ......................... 89
Figure 3.13 Effect of the regeneration of nanoparticles in column setup........... 91
Figure 3.14 Effect of the addition of calcium cations in the mitigation of the silica effect................................................................. 93
Figure 3.15 Effect of calcium cations in the performance of magnetite nanoparticles in column setup ................................................................. 94
Figure 4.1  Size-controlled synthesis of nMag. ............................................................... 100
Figure 4.2 Shape-controlled synthesis of nMag. ............................................................ 101
Figure 4.3 TEM image and isotherms of nMag-PAMPS ............................................. 102
Figure 4.4 Schematic representation of water soluble nMag systems........ 104
Figure 4.5  Determination of water transfer conditions..........................105
Figure 4.6  nMag with different coatings..........................................................106
Figure 4.7  Effect of nanoparticles surface coating on arsenic adsorption.....108
Figure 4.8  Magnetite nanoparticles prepared by different synthetic methods. ..........................................................110
Figure 4.9  Adsorption isotherms of magnetite nanoparticles prepared by different synthetic methods. ..........................................................110
Figure 4.10  SEM images of nMag-covered beads. .............................................113
Figure 4.11  Column experiments of magnetite nanoparticles prepared by different synthetic methods. ..........................................................114
Figure 4.12  TEM images of magnetite nanoparticles with different dispersion degrees.........................................................................................117
Figure 4.13  Effect of aggregation of nanoparticles in arsenic adsorption. .....118
Figure 4.14  nMag-covered beads after treatment with super hydride..........121
Figure 4.15  nMag-covered sand after treatment with super hydride..........122
Figure 4.16  nMag-sand column.........................................................................124
Figure 4.17  SEM images of active bed of magnetite/sand columns.............125
Figure 4.18  Sand column experiments of magnetite nanoparticles.............125
Figure 5.1  The clusters of nanoparticles are hollow structures.....................133
Figure 5.2  The size and shape of the clusters is controlled by the synthetic parameters.........................................................................................134
Figure 5.3  Repeatability of the clusters synthesis ............................................135
Figure 5.4  Reproducibility of the clusters synthesis.......................................136
Figure 5.5  Effect of the urea and polymer concentrations in the unit and cluster size.........................................................................................137
Figure 5.6  Effects of temperature and volume in the unit and cluster sizes. 139
Figure 5.7 Adding water to reaction mixture changes the cluster and unit sizes ................................................................. 140
Figure 5.8 Evolution of the reaction mixture during 24h ......................... 141
Figure 5.9 SEM images of reaction at different times ........................................... 142
Figure 5.10 Clusters formation during reaction time ........................................ 143
Figure 5.11 TEM images of reaction at different times ..................................... 143
Figure 5.12 Nanoparticles formation during reaction time ............................. 144
Figure 5.13 Histograms of clusters size at different reaction times .............. 145
Figure 5.14 Evolution of clusters size at different reaction times .................. 146
Figure 5.15 XRD of the synthetic product at different reaction times .......... 147
Figure 5.16 Raman of the synthetic product at different reaction times ...... 148
Figure 5.17 FT-IR of the synthetic product at different reaction times .......... 149
Figure 5.18 Temperature effect in the clusters of nanoparticles synthesis .. 150
Figure 5.19 XPS of the material synthesized at different temperatures ...... 151
Figure 5.20 Fe2p and O1s spectra of the material synthesized at different temperatures ........................................................................... 152
Figure 5.21 Raman of the material synthesized at different temperatures ... 154
Figure 5.22 Cooling effect in synthesis carried out at 285°C ......................... 155
Figure 5.23 Cooling effect in synthesis carried out at 200°C ......................... 156
Figure 5.24 Proposed mechanism for the synthesis of clusters of IO-NPs ..... 159
Figure 5.25 Clusters used for arsenic adsorption with the same unit size .... 163
Figure 5.26 Effect of the cluster size in arsenic adsorption performance ...... 163
Figure 5.27 Clusters used for arsenic adsorption with the same cluster size 164
Figure 5.28 Effect of the unit size in arsenic adsorption performance .......... 165
(Figure 5.29 Clusters used for the column experiment..................................166
Figure 5.30 Column breakthrough curves of arsenic and vanadium in groundwater ..................................................................................................................167
Figure 6.1 Modifying the synthesis of nMag....................................................173
Figure 6.2 Varying the Fe precursor in the modified kitchen synthesis...........174
Figure 6.3 Scale up of the modified kitchen synthesis......................................175
Figure 6.4 DSC plots for thermal decomposition and modified kitchen synthesis reactions .................................................................................................................176
Figure 6.5 Arsenic adsorption isotherms for the MKS-NPs.........................178
Figure 6.6 The purification of MKS-NPs is the limiting step .........................179
Figure 6.7 SEM and TEM of the MKS-s.........................................................180
Figure 6.8 XRD of the MKS-s.........................................................................182
Figure 6.9 Raman of the MKS-s .....................................................................183
Figure 6.10 XPS elemental scans of the MKS-s.............................................184
Figure 6.11 TGA the MKS-s after washing process........................................185
Figure 6.12 Arsenic adsorption for the MKS-s..............................................188
Figure 6.13 Column of MKS-s with Salamanca groundwater.......................189
Figure 6.14 Chemical structure of selected dyes ............................................190
Figure 6.15 Dye remediation performance of MKS-s and TiO2 .....................191
List of Tables

Table 3.1 Summary of physicochemical characterization of sorbents .......... 61
Table 3.2 Summary of the parameters obtained from isotherm experiments ................................................................. 65
Table 3.3 Summary of the parameters for column experiments ......................... 70
Table 3.4 Comparison of the adsorption capacities obtained from column experiments .............................................................................................................. 72
Table 3.5 Comparison of the adsorption capacities obtained from batch and column experiments .............................................................................................................. 80
Table 3.6 Cost analysis of using arsenic sorbents in Salamanca, Mexico ........ 82
Table 4.1 Summary of nanoparticles size with the different coatings .......... 107
Table 4.2 Summary of the parameters of isotherm experiments for magnetite nanoparticles ........................................................................................................ 111
Table 4.3 Summary of the parameters for nanoparticles-beads column experiments ........................................................................................................ 115
Table 4.4 Summary of the parameters for nanoparticles-sand column experiments ........................................................................................................ 126
Table 6.1 Elemental quantification after washing cycles .............................. 186

Table A. 1 Elemental analysis of several Salamanca wells during 2011 ........ 194
Table A. 2 Elemental analysis of several Salamanca wells during November 2012 .................................................................................. Error! Bookmark not defined.
Table A. 3 Elemental analysis of several Salamanca wells during June 2013 ........................................................................................................ 197
Table A. 4 Elemental analysis of Well 2 in Salamanca ................................ 200
List of Equations

Equation 1.1  Point of Zero Charge .................................................................................. 8
Equation 1.2  Adsorption capacity formula ..................................................................... 20
Equation 1.3  Langmuir model equation ......................................................................... 21
Equation 1.4  Advection-dispersion equation .................................................................. 22
Equation 1.5  Solution for ADE by Ogata and Banks .................................................... 22
Equation 3.1  Formula for fitting experimental data in column experiments. 70
Equation 3.2  Calculation of the treatment cost for arsenic removal ............................. 81
Equation 3.3  Calculation of the volumetric amount of sorbent required for arsenic removal .................................................................................................................. 82
# Nomenclature

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
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<tbody>
<tr>
<td>ADE</td>
<td>Advection-Dispersion Equation</td>
</tr>
<tr>
<td>BET</td>
<td>Brunauer, Emmett and Teller method</td>
</tr>
<tr>
<td>BV</td>
<td>Bed Volume</td>
</tr>
<tr>
<td>CNC</td>
<td>Colloidal Nanoparticle Clusters</td>
</tr>
<tr>
<td>$D$</td>
<td>Coefficient of hydrodynamic dispersion</td>
</tr>
<tr>
<td>DI Water</td>
<td>Deionized Water</td>
</tr>
<tr>
<td>DLS</td>
<td>Dynamic Light Scattering</td>
</tr>
<tr>
<td>DMA</td>
<td>Dimethylarsinate, $(\text{CH}_3)_2\text{AsO(OH)}$</td>
</tr>
<tr>
<td>EBCT</td>
<td>Empty Bed Contact Time</td>
</tr>
<tr>
<td>EPA</td>
<td>Environmental Protection Agency</td>
</tr>
<tr>
<td>exp</td>
<td>Experimental</td>
</tr>
<tr>
<td>Fe-oleate</td>
<td>Iron oleate</td>
</tr>
<tr>
<td>FTIR</td>
<td>Fourier Transform Infrared spectroscopy</td>
</tr>
<tr>
<td>$h$</td>
<td>hour</td>
</tr>
<tr>
<td>ICP-EOS</td>
<td>Inductively Coupled Plasma – Optical Emission Spectrometer</td>
</tr>
<tr>
<td>ICP-MS</td>
<td>Inductively Coupled Plasma – Mass Spectrometry</td>
</tr>
<tr>
<td>IO-NPs</td>
<td>Iron Oxide Nanoparticles</td>
</tr>
<tr>
<td>JCPDS</td>
<td>Joint Committee on Powder Diffraction Standard</td>
</tr>
<tr>
<td>$L$</td>
<td>Length</td>
</tr>
<tr>
<td>LOD</td>
<td>Limit of Detection</td>
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LOQ  Limit of Quantification
MCL  Maximum Contaminant Level
min  min
MKS  Modified Kitchen Synthesis
MKS-NPs  Nanoparticles prepared by Modified Kitchen Synthesis
MKS-s  Solid obtained from the Modified Kitchen Synthesis
MMA  Methylarsonate, \( \text{CH}_3\text{AsO(OH)}_2 \)
MW  Molecular weight
nMag  Nano Magnetite
nMag-PAA  Nano Magnetite – coated with PAA
nMag-PEG  Nano Magnetite – coated with PEG
nMag-PEI  Nano Magnetite – coated with PEI
NA  not applicable
ND  not determined
NP  nanoparticle
NPs  nanoparticles
NOM  Natural Organic Matter
OA  oleic acid
ODE  \(1\)-octadecene
PAA  Poly(Acrylic Acid)
PAA-Na  Poly (acrylic acid) sodium salt
PAMPS  poly(2-acrylamido-2-methyl-1-propanesulfonic acid)
PEG  Polyethylene glycol
<table>
<thead>
<tr>
<th>Acronym</th>
<th>Description</th>
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<tbody>
<tr>
<td>PEI</td>
<td>Polyethyleneimine</td>
</tr>
<tr>
<td>PMMA</td>
<td>Poly(methyl methacrylate)</td>
</tr>
<tr>
<td>POE</td>
<td>Point of entry</td>
</tr>
<tr>
<td>POU</td>
<td>Point of use</td>
</tr>
<tr>
<td>PZC</td>
<td>Point of Zero Charge</td>
</tr>
<tr>
<td>Q</td>
<td>Flow rate</td>
</tr>
<tr>
<td>$Q_s$</td>
<td>Linear velocity</td>
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<tr>
<td>QC</td>
<td>Quality control</td>
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<tr>
<td>QCM-D</td>
<td>Quartz Crystal Microbalance with dissipation</td>
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<tr>
<td>$R$</td>
<td>Retardation factor</td>
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<tr>
<td>RSSCT</td>
<td>Rapid Small Scale Column Tests</td>
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<td>Safety Data Sheet</td>
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<td>Technical Data Sheet</td>
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<td>TEM</td>
<td>Transmission Electron Microscope</td>
</tr>
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<td>Thermogravimetric Analysis</td>
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<td>Total Organic Carbon</td>
</tr>
<tr>
<td>UV/Vis</td>
<td>Ultraviolet-Visible Spectroscopy</td>
</tr>
<tr>
<td>XPS</td>
<td>X-ray Photoelectron Spectroscopy</td>
</tr>
<tr>
<td>XRD</td>
<td>X-ray Diffraction</td>
</tr>
<tr>
<td>$\mu$</td>
<td>micro</td>
</tr>
<tr>
<td>$\rho$</td>
<td>Density</td>
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Chapter 1

Introduction

Since its inception nanotechnology has been defined by the breadth of potential applications that can benefit from materials with dimensions between one and one hundred nanometers. The novel optical, catalytic, and magnetic properties of nanomaterials has found relevance in areas as diverse as biomedical imaging\(^1\) and energy technology.\(^2,3,4\) This community has characterized the potential for engineered nanomaterials to interact negatively with the environment, as well as explored how the unique properties of small scale matter can address environmental challenges. Examples of successful environmental nanotechnology applications include the development of photocatalysts that can harvest energy from the sun for water splitting or CO\(_2\) reduction,\(^5\) as well as novel platforms for sensing existing and emerging pollutants.\(^6\)
1.1. Nanomaterials in water treatment

Nanomaterials can improve both traditional drinking water treatment strategies, such as filtration, as well as offer new approaches to processes such as desalination. This work has revealed two significant barriers for widespread application of nanomaterials in this arena: their cost, and their largely uncharacterized environmental impact. The latter issue has been the subject of targeted research in many countries, and is being slowly resolved through more sophisticated and informed regulations. The former issue remains. It is not so much that there is no benefit to the application of nanomaterials in water treatment processes. Indeed many have analyzed the need for improved water treatment processes and have identified opportunities for the use of nanomaterials in confronting these challenges. However, these benefits must be realized at extremely low cost and large scale in order for widespread adoption.

Until very recent work by this group and others, many of the early examples of nanotechnology-enabled water treatment exploited only the larger surface to volume ratios available in nanoscale materials. Examples include the improvement of Fenton-like reactions in advanced oxidation, by giving new functionalities to membranes, or by reducing the energetic consumption in desalination. In addition, any water treatment process that relies on the sorption of materials to surface interfaces clearly can benefit from the high surface areas available in nanomaterials. Also important has been the ability to improve sorption efficiency
and selectivity through functionalization of surfaces to further improve affinity or selectivity.\textsuperscript{15}

**1.2. Iron oxide nanomaterials**

Materials containing iron have been widely used in environmental applications\textsuperscript{16} such as organic remediation\textsuperscript{17}, chromium reductive precipitation,\textsuperscript{18} and arsenic sorption.\textsuperscript{19} In addition to their higher surface areas, the use of iron oxide nanomaterials offers other advantages including the possibility of magnetic separation and material regeneration.\textsuperscript{20,21,22}

![Crystalline structure of iron oxides.](image)

**Figure 1.1** Crystalline structure of iron oxides.

The crystalline structures for $\alpha$-$\text{Fe}_2\text{O}_3$, $\gamma$-$\text{Fe}_2\text{O}_3$, and $\text{Fe}_3\text{O}_4$ are shown. Red spheres represent $\text{O}$. For hematite and maghemite, $\text{Fe}^+$ in octahedral sites are green spheres, $\text{Fe}^+$ in tetrahedral sites are black spheres. For magnetite, octahedral and tetrahedral sites are represented in black and green, respectively. Taken from Wei \textit{et al.}\textsuperscript{23}

There are at least eight crystal structures that can be described as “iron oxide”.\textsuperscript{24} When the term iron oxide is used in literature, especially in nanotechnology, it refers to either $\alpha$-$\text{Fe}_2\text{O}_3$ (hematite), $\gamma$-$\text{Fe}_2\text{O}_3$ (maghemite), or
Fe$_3$O$_4$ (magnetite). Figure 1.1 shows the crystalline structure for each oxide form. Ambiguity in the terminology stems from both the spontaneous oxidation of magnetite to maghemite in the presence of oxygen, as in (1), and the similarity of the XRD diffractogram between $\gamma$-Fe$_2$O$_3$ and Fe$_3$O$_4$ (Figure 1.2).

$$Fe_3O_4 + 2H^+ \rightarrow \gamma Fe_2O_3 + Fe^{2+} + H_2O \quad (1)$$

Figure 1.2 XRD for iron oxides.

XRD diffractogram for $\alpha$-Fe$_2$O$_3$ (red), $\gamma$-Fe$_2$O$_3$ (blue), and Fe$_3$O$_4$ (purple) are shown. Taken from Wei et al.$^{23}$

For our purposes, the term iron oxide refers to maghemite or magnetite.

1.2.1. Iron oxide for water treatment

There are several naturally occurring iron ores. Most common are the oxyhydroxides: goethite ($\alpha$-FeOOH), akaganeite ($\beta$-FeOOH), lepidocrocite ($\gamma$-FeOOH) and the oxides: wüstite (FeO), hematite ($\alpha$-Fe$_2$O$_3$), maghemite ($\gamma$-Fe$_2$O$_3$), ferrihydrite (5Fe$_2$O$_3$$\cdot$9H$_2$O), and magnetite (Fe$_3$O$_4$).$^{24}$ Even though the crystalline structure of
these iron oxides and oxyhydroxides are different, their surfaces are remarkably similar.\textsuperscript{25} They are dominated by iron hydroxyl groups whose extent of protonation depends upon the pH of the solution.\textsuperscript{26}

\[
\text{FeOH}_2^+ \leftrightarrow H^+ + \text{FeOH} \quad pK_a_1 \quad (2)
\]
\[
\text{FeOH} \leftrightarrow H^+ + \text{FeO}H^- \quad pK_a_2 \quad (3)
\]

The values pK\textsubscript{a1} (2) and pK\textsubscript{a2} (3) vary with mineral composition. Usually, iron oxyhydroxides and oxides have values of Point of Zero Charge (PZC) between 5.5 and 9.6.\textsuperscript{27} Reported values of PZC for magnetite are close to 6.4\textsuperscript{26}, which makes it an ideal candidate for remediation of oxyanions in natural water.

\[
PZC = \frac{pK_a_1 + pK_a_2}{2}
\]

\textbf{Equation 1.1 Point of Zero Charge}

\textbf{1.2.2. Synthesis of iron oxide nanoparticles}

The synthesis of iron oxide nanoparticles (IO-NPs) has advanced significantly in recent years because of their many potential applications.\textsuperscript{28} There are several methodologies for the preparation of IO-NPs including co-precipitation, microemulsion, hydrothermal synthesis, solvothermal synthesis, sonolysis, sol-gel reactions, microwave-assisted synthesis, thermal decomposition, aerosol methods and electrochemical methods.\textsuperscript{23} Each of these possess particular advantages ranging
from cost to ease of preparation to nanoparticle quality. In this work, thermal decomposition, co-precipitation, and solvothermal synthesis were utilized to generate the nanomaterials shown in Figure 1.3.

![Diagram of nano-Iron oxides]

**Figure 1.3 Different types of nano-Iron oxides.** Different types of nanostructures can be obtained by varying synthesis techniques including (i) monodisperse nanoparticles, (ii) aggregates of nanoparticles or (iii) clusters of nanoparticles.

Thermal decomposition is performed at high temperatures using iron carboxylate salts; its products are very uniform and non-aggregated nanocrystals (Figure 1.3.i). This technique was first reported by Bawendi *et al.*\(^{29}\) for the preparation of quantum dots. They described the injection of organometallic reagents into a hot solvent for nucleation, followed by slow growth for the formation of uniform and nearly monodisperse nanocrystals. A similar mechanism is observed for the synthesis of IO-NPs as described in Figure 1.4. In 1999, Alivisatos *et al.*\(^{30}\) described a similar method for the preparation of transition metal oxide nanocrystals, including $\gamma$-Fe$_2$O$_3$. In this case, they used metal cupferron (salt of N-nitroso-N-phenylhydroxylamine) complexes as a single precursor. Additionally, in
2001, Hyeon et al.\textsuperscript{31} demonstrated the synthesis of $\gamma$-Fe$_2$O$_3$ nanocrystals by thermal decomposition of iron pentacarbonyl in oleic acid. Colvin et al.\textsuperscript{32} reported size controlled synthesis of iron oxide nanocrystals through decomposition of an iron carboxylate precursor (iron (III) oleate) prepared \textit{in situ} at a high temperature.

\begin{figure}
\centering
\includegraphics[width=\textwidth]{figure1.png}
\caption{Scheme of the thermal decomposition reactions.}
Precursors are mixed to allow formation of monomers that accumulate until nucleation seeds form. Resulting seeds grow over time within a narrow size distribution. Taken from Ling \textit{et al.}\textsuperscript{33}
\end{figure}

Iron oxide particles synthesized in organic phases can be transferred to water using fatty acid bilayers\textsuperscript{34} (Figure 1.5.i) or amphiphilic polymers\textsuperscript{35,36} (Figure 1.5.ii). However, this protocol is costly, even when carboxylate salts can be prepared from metal chloride salts,\textsuperscript{37} which reduces cost and also facilitates the preparation of larger quantities of material.
Figure 1.5  Schematic representation of water soluble nanoparticles
Schematic representation of a nanoparticle transfer to water by (i) bilayer and (ii) polymeric coating. Taken from Prakash et al.34 and Yu et al.36, respectively.

Co-precipitation generally forms nanoparticles with morphologies shown in Figure 1.3.ii. This method was first reported by Stroeve et al.38 for the preparation of Fe₃O₄ nanoparticles in aqueous solutions without surfactants. The nanoparticles are precipitated when the reaction (4) occurs.

\[
2Fe^{3+} + Fe^{2+} + 8H^+ \rightarrow Fe_3O_4 + 8H_2O \quad (4)
\]

Several modifications of this method have been reported including the use of surfactants39 and polymers40 to control the aggregation of the nanoparticles. However, this has proven to be difficult given as it is difficult to prevent the formation of small aggregates such as those in Figure 1.6. is usually observed. The initial pH and temperature of the iron salt mixture solution are the primary determinants of the composition and size of the nanoparticles.41 Variations such as the use of surfactants and ammonia as a base enables the straightforward preparation of inexpensive ferrofluids.42
Small aggregates of nanoparticles can be prepared by the addition of a base to a Fe\(^{2+}\) and Fe\(^{3+}\) mixture in the presence of a polymer. Modified from Reference 40.

The solvothermal method occurs in a stainless steel vessel that can be pressurized to high temperatures and pressures. The resulting materials are generally well-defined and homogeneous aggregates of nanoparticles as illustrated in Figure 1.3.iii. This method was first reported by Li et al.\(^{43}\) in 1997 for the preparation of quantum dots. In 2003, the Gao et al.\(^{44}\) reported the use of the solvothermal reaction for the preparation of 8nm and 11nm IO-NPs, where the size was determined by the surfactant used. When ternary surfactant combinations were used, spherical aggregates were formed.\(^{45}\) Although the formation of these clusters of nanocrystals is not entirely understood, Figure 1.7 gives a general overview of the probable mechanism. Initially, microspheres of amorphous precursor are formed; as time passes, particles crystallize from the external toward the internal surface until no amorphous material remains.
Figure 1.7  Scheme of the solvothermal synthesis. Precursors are mixed and introduced in a close reactor for the formation of soft microspheres. Small nanoparticles crystallize on the surface until all inside precursors are deposited in a hollow system. Modified from Bian et al.\textsuperscript{46}

1.3. Arsenic water contamination

Arsenic is one of the worst inorganic pollutants found in water. Both As(III) and As(V) interfere with essential biological functions. In particular, As(III) deactivates enzymes with sulfhydryl groups and As(V) competes with phosphate groups in cell reactions. Long-term exposure damages most organ systems.\textsuperscript{47} Skin lesions, blackfoot disease, diabetes and a large number of nervous, hepatic, hematological and renal system effects have been observed following chronic arsenic exposure.\textsuperscript{48} Arsenic is considered a group I carcinogen for humans as it is known to cause lung, skin, and bladder cancers and has been associated with kidney,
liver, and prostate cancer.\textsuperscript{49} For this reason, the World Health Organization has established a provisional guideline value of 0.01mg/L for arsenic in drinking water. This value remains provisional as of 2011 because most arsenic removal techniques cannot achieve a lower value.\textsuperscript{50}

Although contamination of groundwater with arsenic may result from anthropogenic activities such as mining, most incidences are naturally occurring and result from changes in the geochemistry surrounding wells.\textsuperscript{51} While incidences in India and Bangladesh are usually the first come to mind when arsenic contamination is discussed, arsenic in groundwater is a worldwide problem. High concentrations of arsenic in groundwater have been reported around the world\textsuperscript{52} and Figure 1.8 depicts the most troublesome arsenic contamination areas.

\textbf{Figure 1.8} Distribution of arsenic groundwater contamination. Areas in blue are lakes. Taken from Smedley \textit{et al}.\textsuperscript{53}
Depending upon redox (Figure 1.9) and pH (Figure 1.10) conditions, arsenic is found in water as inorganic species such as arsenic acids (H$_3$AsO$_4$, H$_2$AsO$_4^-$, HAsO$_4^{2-}$ and AsO$_4^{3-}$) and arsenious acids (H$_2$AsO$_3$, H$_2$AsO$_3^-$, HAsO$_3^{2-}$ and AsO$_3^{3-}$). Less commonly arsenic may also be found in organic forms including methylarsonate (CH$_3$AsO(OH)$_2$, MMA) and dimethylarsinate ((CH$_3$)$_2$AsO(OH), DMA). MMA and DMA are commonly observed in the urine of people exposed to large amounts of arsenic as they are metabolic byproducts of arsenic exposure. Inorganic species are more toxic, especially those that contain arsenic in the +3 oxidation state. For this reason, arsenic removal techniques focus on the elimination of arsenate and arsenite, and their corresponding protonated species.

![Eh-pH diagram for aqueous As species.](image)

**Figure 1.9** Eh-pH diagram for aqueous As species. System As–O$_2$–H$_2$O at 25°C and 1 bar total pressure. Taken from Smedley *et al.*
Figure 1.10  Arsenic oxyanions as a function of pH.  
Protonated species of arsenite (i) and arsenate (ii) as a function of pH at an ionic strength of approximately 0.01 M. Redox conditions correspond to indicated oxidation states dominating the speciation in both cases. Modified from Smedley et al.53

1.4. Arsenic remediation

Since the EPA lowered the maximum contaminant level (MCL) for arsenic to 0.01mg/L in 200154, several techniques have been tested for arsenic removal to parts per billion levels. The most pressing needs are in developing countries where the treatment of groundwater must be performed in individual wells. For these point-of-use applications, an easy-to-handle and cost-effective technology is required. Currently, adsorption is the only technique that meets these needs55 and the only method to remove both As (III) and As (V) species effectively.56 In 2007, Mojan et al.57 published an exhaustive review of materials used as arsenic sorbents highlighting titanium, aluminum, and iron oxides as the most promising along with
some activated carbons. Of these options, iron oxide sorbents are the most widely used due to their low cost and their relative natural abundance.\textsuperscript{58} For these reasons, arsenic removal capacities of iron minerals such as goethite (FeOOH), lepidocrocite ($\gamma$-FeOOH), ferrihydrite (FeOOH$\cdot$0.4H$_2$O), magnetite (Fe$_3$O$_4$), hematite (Fe$_2$O$_3$) and amorphous iron oxides (hydrous ferric oxides, HFO) have been characterized. Much is now know about the mechanism, kinetics, and desorption properties.\textsuperscript{26,59,60}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure11.png}
\caption{Structural conformations for the bond As-O-Fe in iron oxides. Arsenic can bond iron oxides in three conformations: (i) bidentate corner-sharing (binuclear), (ii) bidentate edge-sharing (mononuclear), and (iii) monodentate complexes. The images at the top correspond to geometrical representations calculated from density functional theory; simplified representations are given below for easier visualization. Modified from Fendorf \textit{et al.}\textsuperscript{59} and Sherman \textit{et al.}\textsuperscript{61}}
\end{figure}

As previously mentioned, the surfaces of all iron (hydr)oxides are similar. When arsenic is adsorbed in their surface, all show the same structural conformations.\textsuperscript{61} Figure 1.11 shows how arsenate bonds iron (hydr)oxides in three
conformations: (i) bidental corner-sharing (binuclear), (ii) bidental edge-sharing (mononuclear), and (iii) monodentate complexes. The most stable form are monodentate complexes and the bidentate corner-sharing complexes are the least stable.

1.4.1. Interferences for arsenic adsorption

In addition to arsenate and arsennite, there are other oxyanions that interact with iron (hydr)oxides. Nitrate (NO$_3^-$), phosphate (PO$_4^{3-}$), bromate (BrO$_3^-$), sulfate (SO$_4^{2-}$), silicate (SiO$_4^{2-}$), and perchlorate (ClO$_4^-$) are some the most common oxyanions found in drinking water. As in the case of arsenic oxyanions, these ions bind iron ores to form mono- and bi-dentate complexes (such as silicate in Figure 1.12).$^{62}$ Removal of oxyanions such as phosphate (PO$_4^{3-}$), chromate (CrO$_4^{2-}$), vanadate (VO$_4^{3-}$), and selenate (SeO$_4^{2-}$) by iron (hydr)oxides has been extensively characterized$^{63}$ and shown to have a profound impact on arsenic removal processes.

Oxyanions can also interfere with methods that seek to remove arsenic uptake through co-precipitation with iron. Ciardelli et al.$^{64}$ reported that silicate has the worst effect in arsenic removal, followed by phosphate and the sulfate having no effect. Performance decreased even more when both silicate and phosphate were present. Roberts et al.$^{65}$ determined that iron salt dosages must be increased up to six times the minimum when silicate and phosphate are present in groundwater. Similar results have been observed in arsenic uptake by adsorption when oxyanions such as phosphate and silica are present. Chowdhury et al.$^{66}$ reported that
concentrations as low as 2mg/L of phosphate can decrease the removal efficiency by 20 percent when using magnetite/maghemite nanoparticles. In 2012, Maiti and et al. reported a similar trend when using laterite (an iron and aluminum mineral) as arsenic sorbent. They demonstrated that the effect of silica at environmentally significant concentrations is worse than that caused by phosphate, bicarbonate, or sulfate.

![Figure 1.12](image)

**Figure 1.12** Silica and arsenic adsorb onto iron oxides similarly in a similar fashion.

Surface complexes of As(V), As(III) and Si(OH)₄ on iron oxides. H, O, Fe, As, and Si are represented by grey, red, blue, purple, and yellow, respectively. Taken from Gao et al.
1.5. Evaluation of remediation performance

1.5.1. Batch experiments

To assess the adsorption capacity of any sorbent, adsorption isotherm experiments must be performed. A solution containing the analyte of interest is kept in equilibrium with a known amount of sorbent for a specific time. Several samples are exposed to different concentrations, and the adsorption capacity is calculated for each point. The adsorption capacity, $q$, is defined as:

$$q = \frac{(C_{eq} - C_0) \cdot V}{m_s}$$

Equation 1.2 Adsorption capacity formula

$C_{eq}$ and $C_0$ are the analyte concentration at equilibrium and at the beginning respectively, $V$ is the volume of solution used and $m_s$ is the mass of the sorbent. The experimental data is then fitted to an isotherm model. All curves presented herein are described well by a Langmuir isotherm model which assumes that a contaminant binds in a uniform monolayer onto a homogeneous surface. This model was chosen because nanoparticle sorption properties are often modeled in this way. Experimental data when described by a Langmuir model provides the parameters $q_{max}$ and $k_L$, which correspond to the maximum capacity of the analyte that the material can adsorb and a constant related to the system. The mathematical form of the Langmuir model is:
21

\[ q = q_{max} \frac{C_{eq}k_L}{1 + C_{eq}k_L} \]

Equation 1.3 Langmuir model equation

1.5.2. Rapid Small Scale Columns

Most sorbents are used in a fixed-bed treatment system. In this case, contaminated water travels through the inlet of a column packed with the sorbent and other matrices; purified water is recovered at the outlet. The dynamics of the contaminant removal are defined by sorbent’s adsorption capacity thus making column studies important for projecting the performance of materials in the field. Most arsenic sorbent evaluations reported in the literature have been performed in pilot-scale columns. These experiments can last several months for good arsenic sorbents. On a smaller scale, rapid small-scale column tests (RSSCT) are an effective way to quantify the performance of an arsenic sorbent in only a few days or weeks. In a typical RSSCT column experiment, water with a semi-constant concentration of analyte feeds into the column with a specific flow rate and samples are collected at predetermined time intervals. The concentration of analyte in the outlet water increases following a sigmoidal curve. The data can be adjusted to an one-dimensional advection-dispersion equation (ADE), which is the standard model for contaminant transport. The equation that describes the one-dimensional dispersion of a contaminant in a granular media is:
\[
\frac{\partial C}{\partial t} = D_x \frac{\partial^2 C}{\partial x^2} - v_x \frac{\partial C}{\partial x}
\]

**Equation 1.4 Advection-dispersion equation**

The solution proposed by Ogata in 1961\(^2\) and used in this work is the following:

\[
\frac{C(x,t)}{C_0} = \frac{1}{2} \left( \text{erfc} \left( \frac{Rx - v_xt}{\sqrt{4RD_xt}} \right) + \exp \left( \frac{v_xRx}{D_x} \right) \text{erfc} \left( \frac{Rx + v_xt}{\sqrt{4RD_xt}} \right) \right)
\]

**Equation 1.5 Solution for ADE by Ogata and Banks**

Where \(C(x,t)\) (concentration at a certain position and time), \(C_0\) (initial concentration), and \(t\) (time) are given by the experimental data, \(v_x\) (flow velocity) and \(x\) (length of the flow path) are known, and \(R\) (retardation factor) and \(D_x\) (coefficient of hydrodynamic dispersion) are the parameters. \(R\) is related to the time the column can run effectively and is dimensionless. \(D_x\) is a second-order tensor that incorporates both the properties of the porous media and the fluid flow.\(^3\)

1.6. **Motivation**

Arsenic contamination in groundwater is a widespread problem with dire consequences for human health. Nanotechnology is uniquely suited to address this global health challenge. In 2006, Colvin *et al.*\(^4\) proposed the use of magnetite nanoparticles for arsenic adsorption. The large sorption capacities of the small scale materials offered a substantial decrease in the amount of arsenic-laden waste to
dispose of; additionally magnetic driven separation at low external fields made the removal process more energy efficient (e.g. no pumps were required). Major challenges remaining to address include the availability of large scale and cost-effective material production as well as site-specific difficulties identified in field trials of nanomaterials. The work presented herein addresses these challenges.

Three issues will be addressed in the next several chapters:

1. Identification of the technical requirements for applying nanoparticles as sorbents in the field, and characterization of their performance with water containing multiple ions in addition to arsenic. Chapters 3 and 4.

2. Design of nanomaterials that meet many of the needs identified from field studies of arsenic removal by nanoparticles. Chapter 5.

Chapter 2

Experimental section

2.1. Materials

Synthesis of nanomaterials. Iron(III) chloride (FeCl₃, 97%), iron(II) chloride tetrahydrate (FeCl₂•4H₂O, 98%), iron(III) chloride hexahydrate (FeCl₃•6H₂O, 97%), oleic acid (OA, technical grade, 90%), 1-octadecene (ODE, technical grade, 90%), urea, ethylene glycol (anhydrous, 99.8%), were purchased from Sigma-Aldrich; Poly (acrylic acid) sodium salt (PAA-Na, Mw = 6,000) was procured from Polysciences, Inc; sodium oleate was acquired from Fischer Scientific. Ethanol 190 proof (95%, KOPTEC), was acquired from VWR. Hexanes (certified ACS grade) and acetone (certified ACS grade) were purchased from Fisher Scientific. For the kitchen synthesis reaction, olive oil, HEB brand, was purchased from a local grocery store.

Surface modification of nanomaterials. Poly (acrylic acid), sodium salt (PAA-Na, Mw = 15,000), polyethyleneimine (PEI, branched, Mw = 25,000), and
polyethylene glycol (PEG, Mw = 10,000) were purchased from Polysciences, Inc. Super hydride solution (1.0M lithium triethylborohydride in THF) was procured from Sigma Aldrich.

*Inductively Coupled Plasma (ICP) Analysis.* Nitric acid (HNO₃, 70%, purified by redistillation, >99.999% trace metals basis) and hydrogen peroxide (H₂O₂, 30wt% in H₂O) were required for sample digestions. Standards for ICP were purchased from Sigma Aldrich. These include: arsenic (TraceCERT, 1000mg/L As in nitric acid), iron (TraceCERT, 1000mg/L Fe in nitric acid), sulfur (TraceCERT, 1000mg/L S in H₂O), silver (TraceCERT, 1000mg/L Ag in nitric acid), phosphorous (TraceCERT, 1000mg/L P in H₂O), chromium (TraceCERT, 10,000mg/L Cr in nitric acid), lead (TraceCERT, 1000mg/L Pb in nitric acid), mercury (TraceCERT, 1000mg/L in nitric acid), silicon (TraceCERT, 1000mg/L Cd in nitric acid), and multiple element standard solutions #4 (TraceCERT, 40mg/L Al, 40mg/L As, 100mg/L B, 40mg/L Ba, 10mg/L Be, 10mg/L Cd, 10mg/L Co, 20mg/L Cr, 20mg/L Cu, 100mg/L Fe, 10mg/L Mn, 20mg/L Ni, 40mg/L Pb, 100mg/L Se, 100mg/L Tl, 40mg/L V, and 100mg/L Zn in 10% nitric acid), and #3 (TraceCERT, 2000mg/L Ca, 200mg/L K, 400mg/L Mg, and 1000mg/L Na in 5% nitric acid).

*Commercial arsenic sorbents.* The commercial sorbents were provided from the manufacturing companies: Bayoxide E3 from AdEdge Technologies; FerrIX AE33 from Purolite Int. Ltd; and NXT-2 from EP Minerals. Ferroxide Black 78P was purchased from Rockwood Pigments.

*Arsenic adsorption experiments.* The arsenic and silica stock solutions were prepared by dissolving arsenic (V) oxide (As₂O₅, +99.9%) and sodium metasilicate
nonahydrate (Na$_2$SiO$_3$•9H$_2$O, ≥98%) in deionized (DI) water with 4g/L sodium hydroxide (NaOH, 99.99% trace metals basis). Solutions for batch experiments were prepared by dilution of stock solutions with DI water; pH was adjusted with nitric acid (HNO$_3$, 70%, ≥99.999% trace metals basis) and sodium hydroxide (NaOH, pellets, semiconductor grade, 99.99% trace metal basis). Sodium nitrate (NaNO$_3$, 70%, ≥99.0%) and calcium chloride (CaCl$_2$, anhydrous, ≥96.0%) were also used in arsenic adsorption experiments. All reagents were purchased in Sigma-Aldrich.

*Salamanca water.* Groundwater from Salamanca, Mexico was used for batch and columns experiments both in-field and in-lab conditions. For in-field conditions, the water was taken from the inlet and transferred to a 20L plastic container, where it was brought to room temperature and exposed to air before experimental use. For laboratory experiments the raw groundwater was transported in 1L plastic containers in small coolers during transportation to Rice University. After arrival the water was kept at room temperature. Prior to experimental use the groundwater was filtered with a Puradisc 25 syringe filter (0.2μm polyethersulfone, PES, membrane) from Whatman. For the batch experiments, water was taken from the container and spiked, when needed, with the arsenic stock solution.

*Dye remediation experiments.* Congo red (Congo Red 4B, dye content, ≥85%), rose bengal (4,5,6,7-Tetrachloro-2’4’,5’,7’-tetraiodofluorescein disodium salt, dye content 95%), methyl red (2-(4-Dimethylaminophenylazo)benzoic acid), orange II (4-(2-Hydroxy-1-naphthylazo)benzenesulfonic acid sodium salt, dye content ≥85%), and methyl blue (Acid blue 93) were purchased from Sigma Aldrich.
**Column experiments.** Glass wool for laboratory use was purchased from Sigma Aldrich. PMMA beads (poly(methy methacrylate), MW 75,000, 200 micron) were acquired from Polyscience, Inc. Three types of sand – sea washed (Fisher chemical), pure (40-100 mesh, ACROS Organics), and standard (EMD Millipore) – were procured from Fisher Scientific. Borosilicate columns, 10mm x 100mm and 10mm x 400mm, were fitted with an adjustable endpiece (Omnifit Labware). Plastic frits (10mm x 50μm PTFE) were purchased from Diba Industries Ltd. Masterflex L/S Computer-Compatible Digital pumps (with Easy-Load 3 Pump Head, 600rpm) and Masterflex tubing (Tygon, LFL, L/S 14) were acquired from Cole-Palmer.

### 2.2. Synthesis of nanoparticles

The iron oxide nanocrystals described in this thesis were prepared using three different methods as described below.

#### 2.2.1. Thermal decomposition

A typical thermal decomposition reaction consists of two steps: the preparation of a precursor – iron oleate – and the crystallization and growth of nanoparticles. The methodology is based on synthetic procedures previously reported in 2004 by Colvin *et al.*\(^{32}\) and Hyeon *et al.*\(^{75}\)
2.2.1.1. Iron oleate synthesis

Iron oleate was prepared by first dissolving ferric chloride hexahydrate (FeCl₃•6H₂O, 30mmol, 8.1g) and sodium oleate (120mmol, 36.5g) in DI water (75mL) forming a pale yellow emulsion. Then ethanol (75mL) was added and the solution was magnetically mixed for ten minutes; the pale yellow emulsion becomes an orange solution. Finally, hexane (150mL) was added; after a few minutes the polar phase was clear and the organic phase was dark orange. The reaction mixture was kept at reflux conditions (60°C) for four hours. The resulting dark orange solution was washed five times with DI water using a separatory funnel (30mL) to remove excess of sodium oleate, Na⁺ and Cl⁻ ions in solution. Afterwards the iron oleate in hexane was divided into 10mL aliquots and placed in 50mL Corning polyethylene terephthalate (PET) centrifuge tubes; 30mL of acetone was added to each tube and the resulting two-phase mixture was vortexed for one minute. The iron oleate solutions were centrifuged at 11,000rpm for 15 minutes and the supernatant was discarded; the process was repeated three times. The resulting dark brown solution (iron oleate in hexane) was then stored in a clear glass container under room temperature. The final concentration was measured by Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-EOS) as described in section 2.3.11; the iron concentrations were usually in the range of 10-20g/L.

2.2.1.2. Synthesis of nanoparticles

Low-dispersion magnetite nanoparticles (nMag) were prepared by the thermal decomposition of the iron oleate precursor. In a typical reaction, 1mmol Fe-
oleate was mixed with oleic acid (4mmol), and 10mL 1-octadecene (ODE); over 90 minutes the solution was heated from room temperature to 315°C and kept to produce uniform (5–10% standard deviation in diameter) iron oxide nanocrystals. A thermal controller provided feedback to ensure a stable temperature.

![Thermal decomposition synthesis procedure.](image)

The iron oleate precursor is prepared under reflux conditions (i) and after purification a dark orange, viscous solution is obtained (ii). The precursor is used to prepare nMag at 315°C; this decomposition is signaled by the production of white vapors above the solution (iii). The product after purification is a dark black hexanes solution (iv). Shown here is a solution which is approximately 1g/L in iron.

The iron oxide nanocrystals could be precipitated from this solution using acetone, and then after centrifugation could be dispersed again in hexanes. As an example, the solution produced after heating the iron oleate was divided into 5mL aliquots and placed 50mL centrifuge tubes; 20mL of acetone and 20mL of ethanol were added to each tube and vortexed for one minute and centrifuged at 6,000 rpm in a Thermo Scientific brand benchtop centrifuge for 15 minutes. The clear to pale yellow supernatant was decanted and the solid brown or black precipitate was dispersed again in 5mL of hexanes. The cycle of dispersion followed by sedimentation was repeated three times and the resulting black colloid, referred to
here as “nMag”, was stored in closed 20mL glass vials. The final concentrations of iron in hexanes were measured by ICP-EOS and were usually around 1g/L.

2.2.1.3. Transfer of nanocrystals from the organic to aqueous phase

The phase transfer process described here was inspired by a method published by Yu et al. in 2006. In contrast to this existing literature this approach does not leave the organic ligands at the surface intact; instead the aim was to affect a ligand exchange that would lead to the removal of the largely hydrophobic oleic acid surface coating. Three different polymer solutions were applied to this water dispersion method: PEG (2g/L), PAA (10g/L) and PEI (2g/L). The ideal conditions with respect to concentration of polymer and mixing methods varied as a function of polymer and particle dimension; for this reason the process was generally optimized in small aliquots of 1mL, before scaling up the water transfer. The results and rationale behind this optimization are described in section 4.3 of this thesis.

As an example, varying volumes (0.25 to 2mL) of polymer solution were added to 1mL of nMag ([Fe]~5g/L) and diluted to 5mL of water in 8mL glass vials. Solutions were sonicated (Hielscher Ultrasound Technology probe sonicator, 1 cycle, 80% amplitude) for 10 minuntes. The solutions are then stirred overnight using a magnetic stirrer resulting in the complete evaporation of the organic phase (hexanes). Some aggregated particles may form in this process, and for this reason the remaining solution is centrifuged at 11k rpm for 30min in 2mL microcentrifuge tubes (Eppendorf brand). The efficiency of this transfer process can be determined
by the dividing the iron concentration in the final aqueous solution by the iron concentration in the starting hexanes solution, adjusted for volume.

Once the phase transfer process is optimized for polymer concentration and mixing time, a large-scale water transfer can be performed with similar results. For example, ten 20mL vials with 2mL of nMag were mixed with the corresponding optimal volume of polymer; the aqueous phase volume is brought to 12 ml with DI water. These solutions were sonicated (Hielscher Ultrasound Technology probe sonicator, 1 cycle, 80% amplitude) for 20min and under overnight stirring in open vials the hexane phase evaporated. The aqueous solutions were then combined into 50mL centrifugation tubes and centrifuged for 30min at 11,000 rpm. The aqueous supernatant was collected and could be stored in glass bottles until use. Iron concentrations were determined by ICP-EOS as described in section 2.3.11.

2.2.1.4. Coating removal

Nanoparticles prepared by thermal decomposition are coated by oleates bound to the surface available irons. This coating contributes substantially to the sample content, in effect lowering the concentration of iron in a solid sample. This dilution of the solid-state iron oxide can complicate solid-state characterization methods focused on the inorganic part of the sample. For this reason, nanoparticles were sometimes stripped of their organic coatings following the procedure outlined below.

Five milliliters of nanocrystals solution (in hexanes) was placed in 50mL Corning polyethylene terephthalate (PET) centrifuge tubes. A plastic 12 ml syringe
(Thermo Scientific Luer-lock syringe) was used to measure out 5mL of super hydride solution. Super hydride is extremely reactive, and water and humidity in the needle must be avoided. The procedure is carried out in a chemical hood by an operator equipped with a face shield, coat, safety glasses and chemically resistant gloves. It should always be completed when there is another person in the laboratory. The hydride was delivered slowly to the iron oxide solution over two minutes from the syringe through a 0.2μm PES syringe filter, which replaced the needle tip. While bubbles of what presumably was hydrogen were observed during addition of hydride, they soon stopped after which time the tube was closed and placed in a bath sonicator for 10 min. Then 20mL of ethanol was slowly added to the tube, again resulting in bubbling, and after this abated the mixture was sonicated for 10 min more. Acetone was used to bring the volume to 45mL and the solution was centrifuged at 11,000rpm for 15min. 5mL of hexanes were added and mixed with help of a vortex. This procedure was repeated at least 3 times after which time no bubbles were seen after super hydride addition.

2.2.2. Co-precipitation from iron salts

Magnetite nanoparticles by co-precipitation can be prepared by two methods depending on whether a stabilizing surface coating is required. In this work, NPs synthesized by both methods were used. Both approaches described below modified the procedure described by Stroeve et al.\textsuperscript{38} in 1996.
2.2.2.1. Nanoparticles without surface coatings

Two hundred milliliters of a 1M NaOH solution was added to a 500mL round flask. This solution was deoxygenated for 30min and then was magnetically stirred (400rpm) at 80°C until use.

A 50mL solution of 0.2M Fe$^{3+}$ and 0.1M Fe$^{2+}$ was prepared by mixing FeCl$_3$•6H$_2$O (2.7g) and FeCl$_2$•4H$_2$O (1.0g) with DI water. The solution was deoxygenated for 30min and warmed to 80°C. Subsequently, using a 60 ml syringe, the solution was added drop by drop to a flask with the NaOH solution. During addition, the reaction mixture was kept at 80°C and was stirred vigorously using a magnetic stir plate. When the addition was finished, the reaction was kept at 80°C for an additional thirty minutes and during that time it developed a deep black color. The solution was then allowed to cool to room temperature under slower mixing conditions. The solution was then transferred to a 50mL centrifuge tube, and a neodymium magnet was used for a few seconds to concentrate a black solid powder. 100mL of DI water were added to this solid and the nanoparticles were redispersed after vigorous manual mixing. This process of solid product collection via a magnet, followed by redispersion into deionized water, was repeated until the pH of the supernatant was 7. The particles were stored as a solid material and stored in a desiccator and used within a week. After longer times, the black solid changed to brown color due to the oxidation to maghemite. The mass of dry solid typically corresponded to a yield of 80% based on the starting iron salt concentrations.
2.2.2.1. Polymer coated nanoparticles

This procedure is very similar to the preparation described in the prior section with minor modifications. Specifically a stabilizing polymer, PEG or PEI, was added during the formation of the nanoparticles.

A 40mL 1M NaOH solution was prepared in a 100mL round flask and deoxygenated. It was heated for 30min to 80°C on a magnetic stir plate operating at 400rpm.

A 0.2M Fe³⁺ and 0.1M Fe²⁺ solution was prepared by dissolving FeCl₃•6H₂O (541mg) and FeCl₂•4H₂O (199mg) in 10mL of a 2g/L polymer solution. The solution was deoxygenated for 30min and warmed to 80°C. Afterwards the solution was added drop by drop from a 12 ml syringe to the flask with the NaOH solution. During this addition the reaction mixture was kept at 80°C subjected to vigorous
stirring via a magnetic stir plate (800rpm). When the addition was finished, the black and homogeneous solution was kept at 80°C for 30min after which time it was allowed to cool to room temperature under moderate mixing conditions (400rpm). The solution was then transferred to a 50mL centrifuge tube, where the NPs were concentrated with the help of a magnet in a manner similar to that described in the previous section. 40mL of DI water were added to redisperse the NPs with vigorous manual mixing; then, the NPs were collected again with the magnet. The washing step was repeated until the pH of the supernatant was 7. Then, 10mL of DI water was added and the solution was transferred to a 20mL vial and purged with nitrogen. These particles were typically stable for about a month under these conditions; after longer periods the nanoparticles precipitated.

2.2.3. Solvothermal synthesis

The procedure here presented is largely based off of work reported by Yu et al. in 2006.° A single reaction mixture containing iron salts was first prepared and divided into four equal parts. A 100mM Fe³⁺ solution was prepared by adding FeCl₃·6H₂O (2.29g) to 85mL ethylene glycol (Figure 2.3.i). The solution was kept at a 65°C and 400rpm to accelerate the dissolution of iron chloride. After 30min, the solution was a bright orange (Figure 2.3.ii); then PAA-Na (1.02g) was added to reach a 2mM final polymer concentration. The rate of mixing was then increased to 800rpm. After 45min, the solution was clear and homogeneous except for a few white aggregates of PAA-Na collected at the top of the solution (Figure 2.3.iii).
Finally, urea (5.10g) was added to a 1M final concentration; after 45min, the solution was homogenous and had a reddish brown color (Figure 2.3.iv).

![Figure 2.3 Preparation of reaction mixture for solvothermal synthesis of magnetite nanoclusters](image)

(i) FeCl₃·6H₂O is added to ethylene glycol until complete dissolution. (ii) After 30min a bright orange solution is observed, and then PAA is added. (iii) After 45min, most of the PAA is dissolved (some small aggregates are found at the top) and the solution is now a dark orange; urea is then added. (iv) After 45min, the urea is fully dissolved and the solution is now a reddish dark brown.

Twenty milliliters of the reaction mixture (Figure 2.4.i) were loaded into a 50mL Cr-Ni-Ti alloy hydrothermal autoclave reactor (Col-Int Techn) with a Teflon liner (Figure 2.4.ii). It was very important to carefully tighten the top of the autoclave. The reactor was then placed into a preheated oven for 24h. Temperatures between 145°C and 285°C were used. After heating, the autoclave was allowed to fully to room temperature before unsealing its top. This step was completed in a hood as the reaction mixture evolved many nitrogen-based gaseous products. Using a glass pipette (Figure 2.4.iii), the reaction mixture was transferred to a 20mL glass vial. The solid product was collected on the side of the vial magnetically, and the supernatant was disposed. The first supernatant is very dark and viscous (Figure
2.4.iv). The magnet was taken away, and the clusters were redispersed in ethanol. The last two steps were repeated until the supernatant is clear. To avoid oxidation, the clusters were dried and kept under vacuum in a desiccator.

![Figure 2.4](image)

**Figure 2.4 Solvothermal synthesis procedure.**
The reaction solution(i) is introduced to a Teflon liner, which is then placed inside the stainless steel autoclave(ii). After the reaction is over, and the reactor has cooled down, the solution is transferred (iii) to a 20mL vial, where the particles are washed and concentrated using a small magnet (iv).

The final product morphology and dimensions were a sensitive function of the reaction temperature, concentration of iron salt, reaction time, polymer and urea concentration. These trends are described in Chapter 5.

### 2.2.4. Modified kitchen synthesis for iron oxide nanocrystals

This synthetic methodology was based on the procedure published by Yavuz *et al.* in 2010. Several variations will be described in Chapter 6, and the final optimized approach is described below.

100mmol of FeCl₃•6H₂O were added to 300mL olive oil (Figure 2.5.i) The mixture was kept stirring (400rpm) at 120°C overnight which removes any water present from the iron precursor. The clear and yellow-brown solution was then
subjected to increasingly higher temperature until it reached 230°C where it was allowed to equilibrate for ten minutes; at 270°C, the reaction was allowed to equilibrate for ten minutes more. The solution changed to a darker color as temperature increased. White vapors were observed after temperature reached 270°C. The final reaction occurred at 315°C for 24h. Initially the reaction was very vigorous with extensive bubbling (Figure 2.5.ii), but after four hours became quiescent. After cooling to room temperature the black reaction mixture consisted of two phases (Figure 2.5.iii): a viscous black solution and a black solid. The solid was easily separated using a magnet (Figure 2.5.iv).

![Figure 2.5](image)

**Figure 2.5** Modified kitchen synthesis.
Reaction mixture before (i), during (ii) and after reaction (iii). The recovered solid is magnetic as expected (iv).

The purification of the liquid phase was very challenging. The black solution was divided into 5mL aliquots and placed in 50mL centrifuge tubes; 20mL of acetone and 20mL of ethanol were added to each tube and the mixture was vigorously mixed, followed by centrifugation at 6,000rpm for 15min. The
supernatant was decanted; then another 40mL of acetone and ethanol (1:1 by volume) were added. The purification process was repeated until the supernatant was clear. The resulting black colloid (nMag) was stored in hexanes under ambient conditions.

2.3. Physicochemical characterization

The solid products from the reactions described previous were subjected to extensive structural, microscopic, chemical and optical characterization. Since most of the materials were magnetic, magnetic characterization was also performed. Additionally some techniques were used to complement the characterization of their applications. All of these methods are described below, and the results and discussion are presented in the following chapters.

2.3.1. Transmission Electron Microscopy

*All TEM images were taken by Gabriela Escalera or Dr. Seung Soo Lee

TEM samples were prepared by dropping the solution (10 to 20 µL) onto ultra-thin carbon type-A 400 mesh copper grids (Ted Pella Inc.). The TEM micrographs were taken on a JEOL 2100 field emission gun TEM operated at 200 kV with a single tilt holder. Typically, the size and size distribution data were obtained by counting more than 1000 particles using Image J, in images taken at 40K magnification. However, for the clusters in Chapter 5, the size and size distribution
data were obtained by counting approximately 100 particles using images taken at 15K magnification.

2.3.2. Scanning Electron Microscopy

*All SEM images were taken by Arash Bahloul or Dr. Zuzanna Lewicka*

Solids were placed on SEM mounts using carbon tape without a gold surface coating. SEM images were obtained on an FEI Quanta 400F Field Emission Scope at 10.0 kV. Images at magnifications between 100x and 100,000x were usually acquired.

2.3.3. Dynamic Light Scattering

The hydrodynamic diameter of the nanoparticles, both in hexane and water, was measured using a Malvern Zen6300 Zetasizer NanoS equipped with a 633 nm laser. Because of the sensitivity of this technique to dust and other impurities, the measurements were performed in triplicate. The zetasizer software automatically optimized the measurement for the number and length of each scan. The refractive index and absorbance (at 633nm) for the analyzed materials is an important input parameter for calculating nanoparticle dimensions via light scattering. For these nanoparticles we took 2.42 as the refractive index and 0.2 for the absorbance. The particle size was calculated from the average of the number mean and the standard deviations over three measurements.

2.3.4. UV-Vis absorbance

A Varian Cary 5000 UV/Vis/NIR Spectrometer was used to obtain optical absorbance data. The optical absorbance data was obtained from 300nm – 800nm
with a measurement speed of 600 nm/min (unless otherwise stated). Samples were run in poly(methyl methacrylate), PMMA, disposable 4.5mL or 2.5mL cuvettes (10mm path length). All samples were run with a baseline correction scan on an identical cuvette filled with the corresponding solvent (blank) on both beams and then with a blank sample in the rear beam position during analysis.

2.3.5. X-Ray Diffraction

X-ray powder diffraction (XRD) patterns were obtained using a Rigaku D/Max Ultima II Powder Diffractometer. Spectra were usually taken from 10 to 80 degrees. The XRD uses a Cu Ka radiation (1.54 Å) and generated at 40 kV and 40 mA. Data was collected on the instrument using a 5 mm diameter x 0.2 mm deep Rigaku zero-background sample holder. Specific collection times were dependent on the sample. In all cases fixed time (FT) mode was used with points every 0.025 degree. For nMag samples, FT of 20s per point was used while a FT of 10s was used for commercial samples; FTs of 5s was used for co-precipitation particles and clusters. Jade 10.0 software was used to remove background and match expected magnetite peaks (JCPDS 00-019-0629).

2.3.6. X-ray Photoelectron Spectroscopy

XPS data was collected using a PHI Quantera XPS. Samples were evaporated onto aluminum foil and interrogated with an X-ray spot size of 200µm. Pass energy was 140eV for survey scans and 26eV for elemental scans. All scans utilized electron and ion neutralizers. Time for data collection varied according to sample
composition. Typically, a fast scan (14 min) was first taken and then areas for Carbon, Oxygen and Silicon were analyzed with between 20 and 30 scans. The Iron range was usually measured with 40 scans. Due to its low concentration, Arsenic areas required 50 scans. The data was processed using PHI Multipak 7.0.

2.3.7. Raman Spectroscopy

The Raman spectra were collected with a Renishaw inVia Raman Microscope. Unless otherwise stated, a 785 nm laser with a 1200 lines/mm filter was used. Powder samples were placed onto an aluminum foil substrate for measurements. Spectra were collected using a 50X lens with the laser set at 1% power for over 20 min and the range covered was from 200 to 2000 cm\(^{-1}\). Each spectrum was an average of 3 acquisitions with 10 accumulations. Oxidation of magnetite was observed when laser power intensity was increased as the typical peak for magnetite evolved to three peaks of maghemite.

2.3.8. IR Spectroscopy

Fourier transform infrared spectroscopy (FT-IR) was recorded on a Thermo Nicolet NEXUS 670 FTIR spectrometer using a diamond ATR element. Solids were deposited over the ATR element. Spectra were acquired with a resolution of 4 cm\(^{-1}\) and 64 scans. Transmission spectra were taken from 400-4000 cm\(^{-1}\); absorption spectra from 350-900 cm\(^{-1}\). Data was processed using the OMNIC software available from the manufacturer.
2.3.9. **Thermal Gravimetric Analysis**

Thermo-gravitmetric Analysis (TGA) was carried out using TA Instruments SDT Q-600 Simultaneous TGA/DSC instrument using an alumina pan as a solid sample holder. Samples were maintained at 35°C for 10 min for instrument stabilization. The samples were then heated to 800°C at a rate of 10°C/min under N₂ or air, depending on the experiment.

2.3.10. **Brunauer–Emmett–Teller (BET) surface area analysis**

BET surface area analysis was carried out on an automated Quantachrome Autosorb 3B Surface Analyzer. A specific mass of solid (a few milligrams) was introduced into a glass bulb-ended tube and heated under vacuum at 200°C for several hours to remove surface adsorbed contaminants. The sample was then cooled with liquid nitrogen and analyzed by measuring the volume of N₂ gas adsorbed at specific pressures. The surface area was calculated automatically using an Autosorb 3 software program.

2.3.11. **Inductively Coupled Plasma – Optical Emission Spectroscopy**

The particle concentrations were measured by a Perkin Elmer Optima 8300 Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES) equipped with an autosampler. All measurements were carried out with calibrations that yielded R² > 0.9999 and a LOQ lower than 0.2 mg/L. Iron was measured simultaneously at two wavelengths, 273.955nm and 238.204nm, in a radial mode. Calibration curves usually had standards between 1-60 mg/L.
Sample preparation was carried out by adding 1mL of HNO₃ trace metals to 50µL of nMag solutions. The sample was mixed for 1h under mild heating (around 70°C, using a hot plate); in some cases 1mL of concentrated nitric acid was added for an additional hour. Over time the hexanes evaporated leaving a clear (transparent or yellow) aqueous phase was left. This solution was transferred to a 10mL volumetric flask and diluted. Samples were filtered with a 0.2µm PES syringe and stored in 15mL centrifuge tube. If the magnetite nanoparticles were stabilized in water, 200µL of sample was used and there was obviously only a single phase. Solid samples (around 5mg) were more difficult to dissolve and required 5mL of concentrated nitric acid. Samples described in Chapter 6 required a pretreatment of the solids with H₂O₂ followed by overnight heating and mixing.

High arsenic concentrations (ppm level) and silicon concentrations were simultaneously measured also by ICP-OES. All measurements were carried out using calibrations with an R² > 0.9999 and a LOQ lower than 0.1mg/L for As and 0.2mg/L for Si. Both elements were measured simultaneously at two wavelengths: 188.979nm and 228.812nm for As, and 251.611nm and 252.851nm for Si. Arsenic was measured in an axial configuration, while silicon in a radial one. Calibration curves usually had standards between 0.5-20mg/L for As and 2-100mg/L for Si.

Sample preparation required acidification of the solutions: 0.15mL of 70% HNO₃ (trace metals basis) was added to 10mL of solution yielding a 1% nitric acid solution. All samples were filtered prior to acidification with a 0.2µm PES syringe filter.
2.3.12. Inductively Coupled Plasma – Mass Spectrometry

Arsenic and other element concentrations were measured by a Perkin Elmer Nexion 300 Inductively Coupled Plasma-Mass Spectrometer (ICP-MS) equipped with an autosampler. All measurements were carried out using calibrations with an $R^2 > 0.9999$ and a LOQ lower than 0.2μg/L. Arsenic was measured either by itself or in a multielement solution. In both cases, calibration curves usually had standards between 1-200μg/L of As. The concentration for the other elements corresponded to the Multielement standard solution 3 (Sigma Aldrich). Because this analysis was frequently carried out with large numbers of samples, quality control (QC) standards were run every 25 samples.

As chloride is an important interference to arsenic – due to the polyatomic ion $^{40}\text{Ar}^{35}\text{Cl}^+$ contributes to the $^{75}\text{As}$ signal $-^{78}$, when groundwater was measured the standard mode was changed to the KED (Kinetic Energy Discrimination) mode. In the KED mode, both ions are passed through a cloud of inert gas molecules; the $^{40}\text{Ar}^{35}\text{Cl}^+$ will collide more frequently with the inert gas atoms than will $^{75}\text{As}$ ion, due to its larger size. Therefore, the interference signal will be reduced.

Sample preparation consisted in the acidification of the solutions: 0.15mL of 70% HNO$_3$ (trace metals basis) were added to 10mL of solution to yield a 1% nitric acid solution. All samples were filtered prior to acidification with a 0.2μm PES syringe filter.
2.4. Remediation studies

Batch experiments and column tests were carried out to evaluate the different materials. The results are presented and discussed in Chapters 3 through 6.

2.4.1. Batch experiments

Several kinds of batch experiments were performed depending on the information required, the form of the material (solids or solutions) or the analyte of interest (arsenic or dye). Details of these variations are given below.

2.4.1.1. Batch experiments for arsenic

The sorption capacity of a material was determined by measuring the difference in concentration between the initial and final solutions; adsorption for the isotherm studies and desorption for the quantification of regeneration. Arsenic was measured either by ICP-MS or ICP-EOS if its concentration was lower or higher than 1mg/L, respectively.

2.4.1.1.1. Regeneration experiments

Five grams of commercial nanoparticles (Ferroxide Black 78P) were saturated with 500mL of arsenic solution with and without silica. To reach saturation, solutions were mixed as appropriate at room temperature for 24h. Then, any solids were filtered and dried under vacuum. To remove the arsenic and silica
sodium hydroxide was used. NaOH at different concentrations was required both with and without NaNO₃.

To evaluate regeneration, 100mg of a saturated sorbent was stirred with 30mL of a sodium hydroxide solution for 4h or 20h depending on the experiment. The mixture was decanted for 10min., 10mL of the supernatant was filtered with a 0.45μm PES syringe filter. 1mL of the filtered solution was diluted with 9mL of 1% nitric acid.

2.4.1.1.2. Adsorption isotherms using solid sorbents

A known amount of solid was weighed in a 50mL centrifuge tube (Figure 2.6.i), and then 40mL of the relevant contaminant solution was added. This solution was not generally homogeneous, and was mixed on a magnetic stir plate for at least four hours (Figure 2.6.ii).

Figure 2.6  Experimental procedure for adsorption isotherms
The solid is weighed into the centrifuge tube(i) where the solution of interest will be added. Then, the tube is mechanically mixed for 4h(ii). The solution is filtered using a syringe filter and transferred to a new 15mL centrifuge tube(iii). After acidification, the sample concentration is measured by ICP.

The mixture was left in repose for a few seconds so the solid would settle and 10mL of the supernatant was filtered with a 0.45μm PES syringe filter (Figure
2.6.iii). This sample was acidified with HNO₃ trace metals and evaluated by ICP to determine the arsenic concentration (Figure 2.6.iv). For a single isotherm curve at least 7 points were collected at each arsenic concentration using sample quantities between 4 and 200mg. All measurements were repeated in triplicate.

2.4.1.1.3. Adsorption isotherms using NPs solutions

To obtain isotherms for dispersed nanoparticles the prior methodology was necessarily altered. In order to compare to the results with solid samples, the concentration of the arsenic solutions were adjusted downwards. Typically seven solutions were prepared in the desired range of concentrations. For a single point, 6mL of a contaminant solution (usually arsenic) was added to a 12mL centrifuge tube. Then a volume of nanoparticles solution was added (usually smaller than 1mL). After mechanical mixing for 4h at room temperature, the samples were filtered using an Anatop Plus 25 Syringe Filter (0.02μm polypropylene, PP, membrane) from Whatman. This process could take up to 30min. When the solution of nanoparticles is in hexanes, the volume of nanoparticle solution was added was usually smaller than 0.1mL (depending on the sample nanoparticle concentration) (Figure 2.7.1). The volume of NPs added was not considered. As Figure 2.7.ii shows, during mixing the color of the solution was homogeneous. At the end, some of the color was retained in the aqueous phase. When possible, the organic phase was separated by a transfer pipette before filtration. After filtration, the solution was left open for 30 min to assure the hexane completely evaporated prior to acidification.
(i) The NPs solution is added to the arsenic solution. (ii) During mixing, the sample seems homogeneous. (iii) Some minutes after the mixing stops, the remaining hexanes solution can be separated from the aqueous phase.

2.4.1.2. Dye remediation experiments

The experiments with dyes were very similar to the methods described in section 0. A known amount of solid was weighed in a 50mL centrifuge tube. Then, 40mL of the dye solution were added. Mixing at room temperature was carried out in a mechanical mixer for 4h. Subsequently, 10mL of the supernatant was filtered with a 0.45μm PES syringe filter. Finally, the sample was analyzed with the UV-Vis spectrometer. In this case only a few concentrations were measured – in triplicate – allowing the percent removal to be determined.
2.4.2. Rapid Small Scale Column Tests

All the columns in this work were run under similar conditions. They were packed as described below depending on the active material; once packed, DI water was run in an ascendant flow overnight to remove any air bubbles. Because the column had an adjustable end piece, extra space that developed due to material re-accommodation could be eliminated by adjusting the top end. The flow was changed from ascending to descending immediately before starting the experiment.

Once running, the flow rate was kept at Empty Bed Contact Time (EBCT) of 2min and monitored every hour by weighing the water flow. As needed, the programmed flow rate was increased; however, if the flow rate had to be increased more than three times the desired flow rate during the course of an experiment, the experiment was aborted.

For every time point, 1 bed volume of sample was collected, filtered using a 0.45μm PES syringe filter, and acidified to yield a 1% nitric acid solution. The feed solution was also samples (filtered and acidified) every time that the feeding tank was refilled. For columns run in the field, the acidified samples were stored in a freezer at 4°C and subsequently transported in a cooler to Rice University where the ICP analysis was performed.

2.4.2.1. Columns with granular materials

All the columns were packed as shown in Figure 2.8. The column with the retaining cap was mounted in a retort stand. Then, a small amount of glass wool was added to fill the bottom centimeter.
Figure 2.8  Assembly of the columns.
The column bottom to top. A retaining cap is adjusted to ensure there is no empty volume, followed by 1 cm of glass wool. Then at least 10 cm of support material (PMMA beads or sand) are added followed by the desired volume of active material. A second layer of support material is added with another centimeter of glass wool. An adjustable end piece assembly is used at the top, and this permits the column length to be adjusted in the event that the materials compact further under flow.

Ten centimeters of the column was filled with the support material – either PMMA beads or sand – and soft tapping during this process ensured the materials were uniformly placed. The desired bed volume – usually 10 cm – was filled with the
active material; like with the support, mechanical agitation ensured that the material bed was compacted. A second layer of support material was added – this usually was longer than 10 cm – followed by a centimeter of glass wool. The adjustable end piece was then added to close the column and tubing (L/S 14, 1.6 mm internal diameter) was connected to both ends and one end was placed in the pump compartment while the other end led to the feeding tank as shown in Figure 2.9.i.

![Figure 2.9 Setup of columns in the field and small scale.](image)

(i) A typical setup in the field is shown. 20 mL plastic containers feed the columns. (ii) Image of a small scale column.

### 2.4.2.2. Columns with nanoparticles

The limited quantity of nanoparticles available from the synthetic strategies described previously required a modification in the column set-up. Specifically, the overall column volume has to be adjusted in order to minimize the material mass requirements. These microscale columns are shown in Figure 2.9.ii. Besides their size they are otherwise identical in composition to the larger columns.
2.4.2.2.1. Packing solid nanoparticles

Solid nanoparticles were mixed with the relevant support media (either PMMA beads or sand) prior to introduction into the column. Mixtures of 10w% and 20w% were typically employed; aimed total mass was usually higher than 10g to assembly active media beds for 7cm or longer. After adding the nanoparticles to the support media – in a 15mL centrifuge vial –, the tube was shaken vigorously by hand for a minute, placed in a bath sonicator for 30 minutes, and then agitated for a day in a mechanical mixer. This mixture was introduced into the column as the active materials in a manner identical to that described in the previous section.

2.4.2.2.2. Packing liquid nanoparticles

The methodology in this section follows the same logic as the previous section. Nanoparticles were incorporated into the support media so as to lead to a homogenous dispersion with few or no aggregates.

To achieve a homogeneous loading, a known volume of highly concentrated nMag solution was added in small aliquots to the support media during several days. The addition of the first nMag aliquot to PMMA beads is shown in Figure 2.10.i; Figure 2.10.ii shows the same sample after 1min of manual and vigorous stirring. Then the sample was dried overnight in a desiccator under vacuum. Figure 2.10.iii shows the sample with a 0.5w/w% load of nMag. Figure 2.10.iv shows the same sample with a 2w/w% concentration of nMag. The highest concentration of nanocrystals that could be incorporated into the support materials in a uniform
fashion was 5 w/w%. Typically this required twenty days of preparation as each aliquot adds around 0.25w/w%.

**Figure 2.10 Preparation of the nMag for column**

The nMag is added to the support media, in this case PMMA beads, (i) and then mixed (ii) and let to dry in a desiccator under vacuum. After several additions, the mixture looks very homogenous, at 0.5w%, (iii) and becomes darker as concentration increases (iv), 2.0w%.
Chapter 3

Evaluation of current arsenic sorbents

3.1. Introduction

Arsenic is recognized as one of the most serious contaminants in drinking water. The global scope of this problem makes that the potential benefits of effective arsenic remediation sizable. The success of remediation depends on the technology used; these technologies fall into several categories: ionic exchange, electrokinetics, membrane filtration, oxidation, phytoremediation, coagulation-flocculation, and adsorption. Of these, adsorption remains the most simple and cost-efficient; it can be used in existing water treatment installations and it allows the sorbents to be reused after regeneration. Consequently, the selection of the sorbent is one of the most important factors in making the remediation process feasible. Selection of the right sorbent involves several considerations, including chemical nature, the specific surface area, pore size structure, surface chemistry, co-existing ions present, and
Taking these considerations into account, iron oxide nanomaterials, such as nanomagnetite or hydrous ferric oxide, are ideal for heavy metal remediation.

The nature of arsenic contamination creates several obstacles to treatment. Naturally occurring arsenic enters water sources, usually groundwater, when solubilized from soil matrices; it can thus be found in a wide range of surface and groundwaters. In contrast, anthropogenic arsenic can be introduced from surface soils that have been treated with arsenic to enhance plant growth (a common practice in the 1800s). These diverse origins, and the diverse reducing and oxidizing conditions they represent, make it difficult to design one treatment technology for arsenic. For example, in the case of Bangladesh, the highest concentrations of arsenic are found in reducing groundwater and hence As(III) speciation. It has been hypothesized that arsenic is released to groundwater by the reductive dissolution of arseniferous iron oxyhydroxides. In other cases arsenic is found in oxidizing environments, where it is predominantly As(V). This is the case for most sites in Latin America, which are usually in areas of volcanic activity.

Interfering ions found in the water sources can also create problems for arsenic remediation. For example, when arsenic is treated in Bangladesh with oxidized aquifer sediments, naturally occurring phosphates compete with arsenic oxyanions and diminish the effectiveness of sorbents. In Latin America, native silica concentrations are the biggest challenge for arsenic removal. The geothermal water sources in Mexico and Argentina have very high silica loadings ([Si]=10-528mg/L) compared to Bangladesh and India ([Si]=6-42mg/L). The higher salinity and temperatures of the waters, in combination with the silica levels, result
in poor performance of traditional remediation techniques. Research in this area has focused on the development of sorbents effective for these particular circumstances. The use of iron oxide nanomaterials has been established as a viable option for remediating arsenic, even when sites present challenging conditions and communities have few resources to spend on water treatment.

This chapter compares the performance of iron oxide nanomaterials to more conventional commercial sorbents in conditions commonly found in Latin America. Of particular interest in this work is the activity of sorbents in the presence of high concentrations of silica. Our prior work at field sites in Mexico revealed this interfering ion to be the most significant issue facing large-scale deployment of iron-based sorbents. We selected a field test in Salamanca, Mexico to confirm and complement the findings from the lab.

### 3.2. Materials characterization

Ferroxide Black 78P from Huntsman, a food grade certified commercial magnetite, was selected as a benchmark for experimental design. This material, which will be referred to simply as Ferroxide, is a black solid made of spherical micro sized grains (Figure 3.1.i); Figure 3.1.v shows aggregates of particles with dimensions around 100nm. The X-ray diffraction (XRD) spectrum in Figure 3.2.a corroborates that the magnetite is the crystalline structure of the material. X-ray photoelectron spectroscopy (XPS) spectrum shows no evidence of any kind of coating; only iron (710-725eV, Fe2p region), oxygen (520-540eV, O1s region), and a
small amount of magnesium (295-315eV, Mg KLL region) are present (Figure 3.3). This information corresponds to what was reported in the Technical Data Sheet (TDS) from Huntsman.\textsuperscript{91}

Also, three commercial iron oxide commercial sorbents were selected for comparison: Bayoxide E33 from AdEdge Technologies, FerrIX AE33 from Purolite Int. Ltd., and NXT-2 from EP Minerals. For simplicity, they will be referred to as Bayoxide, Purolite and NXT, respectively.

**Figure 3.1** SEM images of commercial sorbents.
SEM images show the morphology of Ferroxide Black 78P (i, v), Bayoxide E33 (ii, vi), FerrIX A33E (iii, vii), and NXT-2 (iv, viii) at low and high magnification, respectively.

The Bayoxide material is a brown solid formed of irregular grains roughly microns in size (Figure 3.1.ii); at higher magnification, these appear very homogenous and highly porous (Figure 3.1.vi). The XRD spectrum in Figure 3.2.b indicates the material is goethite. Figure 3.3 shows the XPS survey spectrum, which finds only iron and oxygen. This supports the data given by AdEdge Technologies in their technical specifications.\textsuperscript{92}
Figure 3.2  XRD of commercial sorbents.

Diffractograms of Ferroxide Black 78P (a), Bayoxide E33 (b), FerrIX A33E (c), and NXT-2 (d) are shown. The diffraction patterns of magnetite (blue, JCPDS 00-019-0629) and goethite (red, JCPDS 00-029-0713) are shown for reference.

The Purolite material is formed of microspheres (Figure 3.1.iii) and has a light brown color. On their surface, the beads appear very irregular, large, and porous (Figure 3.1.vii). Figure 3.2.c shows that the structure is mostly amorphous, which was expected from the organic resin support, but the presence of hydroxo hydroxides can be ratified from the small peaks observed. In the XPS wide scan, carbon (280-295eV, C1s region), nitrogen (390-405eV, N1s region), and chlorine (195-205eV, C1s region) are observed in addition to the expected iron and oxygen (Figure 3.3). These results correspond with the composition reported in the Safety
Data Sheet (SDS) from Purolite Int. Ltd.,\textsuperscript{93} which states the product is between 9-12\% hydrated iron oxide and 23-46\% polyvinyl benzyl trimethyl ammonium chloride, with the remainder being water. Because their high water content, and the need to weight them in the field, the beads were dried in air under sunlight before using them.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{xps_commercial_sorbents.png}
\caption{XPS of commercial sorbents}
\end{figure}

Survey scans of Ferroxide Black 78P, Bayoxide E33, FerrIX A33E, and NXT-2; all the peaks for Fe (710-725eV) and O (520-540eV) were observed.

The NXT material is a reddish brown powder formed of granules with a few microns in size (Figure 3.1.iv); at higher magnification, these appear irregular and seem to be composed by smaller uneven particles (Figure 3.1.viii). Figure 3.2.d
shows that the powder is mostly amorphous; the presence of a small peak at 29 degrees suggests some crystalline structure may be present, but it is either a small fraction of the sample or extremely small so that scattering is not strong. The XPS survey spectrum, in Figure 3.3, corroborates the presence of iron, oxygen and lanthanum (825-865 eV, La3d region); as well, a trace amount of carbon can be detected. This information agrees with the composition reported in the SDS from EP Minerals, which states the product is a mixture of lanthanum hydroxide and hydrated ferric oxide.94

Table 3.1 shows a summary of the characterization. In addition to the elemental composition, crystalline phase, and morphology individually discussed, the Langmuir surface area measured using a BET instrument is also included.

<table>
<thead>
<tr>
<th></th>
<th>Langmuir surface area (m²/g)</th>
<th>Elemental analysis</th>
<th>Crystalline phase</th>
<th>Morphology</th>
</tr>
</thead>
<tbody>
<tr>
<td>Huntsman</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ferroxide Black 78P (Ferroxide)</td>
<td>4</td>
<td>Fe, O, Mg</td>
<td>Fe₃O₄</td>
<td>Agglomerated nanoparticles</td>
</tr>
<tr>
<td>AdEdge technologies Bayoxide E33 (Bayoxide)</td>
<td>260</td>
<td>Fe, O</td>
<td>FeO(OH)</td>
<td>Mesoporous material</td>
</tr>
<tr>
<td>Purolite</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>FerrIX A33E (Purolite)</td>
<td>124</td>
<td>Fe, O, C, N, Cl</td>
<td>Amorphous</td>
<td>Microspheres</td>
</tr>
<tr>
<td>EP Minerals</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NXT-2 (NXT)</td>
<td>453</td>
<td>Fe, La, O, C</td>
<td>Amorphous</td>
<td>Mesoporous material</td>
</tr>
</tbody>
</table>

Table 3.1  Summary of physicochemical characterization of sorbents
Results obtained by BET (Langmuir area), XPS (elemental analysis), XRD (crystalline phase) and SEM (morphology).
3.3. Selection of the field site

Because this study is focused on remediating arsenic contamination in oxidizing groundwaters, we placed great emphasis on selecting appropriate research sites. Two locations in Mexico, the city of Guanajuato and the city of Salamanca, provided us with local support from city officials, as well as sites contaminated with arsenic. The two areas are distinct in the nature of the arsenic contamination and its impact on the local drinking water. In Guanajuato state groundwater wells are highly contaminated with arsenic, but these sources can be diluted with surface waters free of arsenic for drinking. Salamanca relies entirely on groundwater and is thus quite sensitive to any sources of arsenic in well sites. In addition, Salamanca’s water system is fed by more than 100 small wells, each of which provides the perfect environment for small-scale field tests. Furthermore, most of the wells do not comply with the Mexican regulation for arsenic (25 ppb).

In 2011, eight wells in Salamanca were randomly selected and analyzed for arsenic and other elements; the detailed analysis is shown in Appendix A (Table A. 1). Because of the consistent high concentration of arsenic, the high temperature (more than 30°C), and the representative concentration of silica, well 2 was selected for field-testing. In 2012 (Table A. 2) and 2013 (Table A. 3) a larger number of wells were analyzed, with well 2 being one of the three with the most challenging conditions. Table A. 4 shows that the concentrations observed in well 2 have been consistent during the last four years. In this context, there were two significant factors that we hypothesized would impact the efficacy of the arsenic sorbents: the
presence of silica, which is well known to interfere strongly with sorbents designed for arsenic, and the combined interference from the many other anions found in this water.

### 3.4. Batch experiments

Batch experiments measure the equilibrated sorption (e.g. removal) of arsenic onto solid phase sorbents and provide a measure of the sorption capacity, or the amount of arsenic that can be adsorbed versus the weight of sorbent. Three conditions were evaluated in these experiments: interactions between sorbents and aqueous solutions of arsenic controls; sorption of arsenic when silica was present and the sorption of arsenic in groundwater collected from the field sites described previously. Preliminary studies ruled out pH as a major factor in arsenic adsorption to surfactants over the range of interest in these sites, or between 6 and 8.

Figure 3.4.i shows the adsorption capacities of the commercial sorbents under different concentrations of arsenic at pH 7. This is the best-case scenario for any sorbent as arsenic has no competition for surface adsorption. Under these ideal circumstances, the performance of these sorbents as determined by their sorption capacity scales directly with the available surface area (Table 3.1). NXT, the highest surface area material, has a much greater adsorption capacity than Purolite and Bayoxide, which are very similar in value. Ferroxide has the smallest adsorption.

When silica is present, however, the surface area of the samples has less of an impact on their performance (Figure 3.4). NXT and Bayoxide both had diminished sorption, but only slightly. In contrast, the performance of the Purolite material
decreased substantially while the already poorly performing Ferroxide decreased only slightly. While other researchers have found that silica does diminish arsenic adsorption to a wide variety of surfaces, the results shown here are much more significantly impacted.\textsuperscript{98,99} It is important to note that here the silica concentrations ([SiO\textsubscript{2}]=85g/L) were set to be similar to those found in Salamanca groundwater (Table A. 4); these are higher concentrations than usually reported in literature (5-30mg/L).\textsuperscript{65,64,68}

![Figure 3.4](image)

**Figure 3.4  Arsenic isothermal experiments with and without Silica present**
(i) An isotherm of arsenic adsorption of the commercial sorbents was measured under ideal conditions – only arsenic at pH=7. (ii) The same experiment was run under the presence of silica ([SiO\textsubscript{2}]=85g/L).

Though parameters can be extracted from the Langmuir model, the results should not be taken as highly precise. Most critically the model assumes that as a sorbent binds to a surface, its concentration in solution falls. In this case, the concentration of silica is too high in comparison with the arsenic and does not change significantly over the course of the experiment. Still, as a comparison the
derived values of $q_{\text{max}}$ and $k_L$ from Equation 1.3 are given in Table 3.2. This assumption is very suitable for Bayoxide and NXT, where the value of $q_{\text{max}}$ decreases by a negligible proportion; however, the values for $k_L$ decrease by nearly 50% when silica is present in the solution. Notably, in the case of Ferroxide the presence of silica does not affect the equilibrium ($k_L$) considerably, but it does decrease the total sites ($q_{\text{max}}$) available for adsorption by a third. For Purolite, the effect is massive: it decreases the equilibrium ($k_L$) and the total sites ($q_{\text{max}}$) by one quarter.

<table>
<thead>
<tr>
<th>Isotherm condition</th>
<th>$q_{\text{max}}$ (mg/g)</th>
<th>$k_L$ (L/mg)</th>
<th>$q_{10}$ (µg/g)</th>
<th>$q_{100}$ (mg/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rockwood Pigments</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ferroxide Black 78P</td>
<td>Arsenic</td>
<td>0.62</td>
<td>31.44</td>
<td>148</td>
</tr>
<tr>
<td></td>
<td>With Silica</td>
<td>0.20</td>
<td>28.37</td>
<td>44</td>
</tr>
<tr>
<td></td>
<td>Salamanca</td>
<td>N. D.</td>
<td>N. D.</td>
<td>N.D.</td>
</tr>
<tr>
<td>AdEdge technologies</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bayoxide E33</td>
<td>Arsenic</td>
<td>7.78</td>
<td>1.99</td>
<td>152</td>
</tr>
<tr>
<td></td>
<td>With Silica</td>
<td>7.19</td>
<td>1.07</td>
<td>76</td>
</tr>
<tr>
<td></td>
<td>Salamanca</td>
<td>3.37</td>
<td>1.23</td>
<td>38</td>
</tr>
<tr>
<td>Purolite</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>FerrIX A33E</td>
<td>Arsenic</td>
<td>8.32</td>
<td>2.04</td>
<td>166</td>
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<tr>
<td></td>
<td>With Silica</td>
<td>2.15</td>
<td>0.51</td>
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<td></td>
<td>Salamanca</td>
<td>7.12</td>
<td>0.89</td>
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<td>EP Minerals</td>
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<td></td>
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<tr>
<td>NXT-2</td>
<td>Arsenic</td>
<td>20.21</td>
<td>1.13</td>
<td>226</td>
</tr>
<tr>
<td></td>
<td>With Silica</td>
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<td>0.48</td>
<td>96</td>
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<td></td>
<td>Salamanca</td>
<td>3.04</td>
<td>0.86</td>
<td>26</td>
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</table>

### Table 3.2 Summary of the parameters obtained from isotherm experiments

A summary of the parameters ($q_{\text{max}}$ and $k_L$) obtained by fitting the experimental data to a Langmuir model is shown. The adsorption capacities observed at 10ppb and 100ppb, $q_{10}$ and $q_{100}$, are also included.

Figure 3.5.i shows the arsenic removal efficiency of the sorbents when added to Salamanca water in a 10L/g treatment dosage. We anticipated that the performance would parallel that observed for the pure arsenic and silica samples.
Based in the observations when only arsenic and silica are present, it was expected that NXT would have the best performance and Purolite the worst after the commercial nanoparticles. However, the trend observed when using Salamanca water was different: Purolite showed the best performance (18.8%), followed by Bayoxide (14.0%), and then by NXT (14.6%). The Ferroxide, as expected, had the lowest removal efficiency, 4.4% and was not further evaluated. To understand better this trend, isotherms with spiked Salamanca water were performed (Figure 3.5). Spiked Salamanca water refers to the addition of a miniscule volume of arsenic stock solution to increase the arsenic concentration without affection the other concentrations.

![Graphs showing arsenic removal efficiency and isotherms](image)

**Figure 3.5  Arsenic removal from Salamanca groundwater**

(i) The removal efficiency of the commercial sorbents was measured with Salamanca groundwater at a dosage of treatment of 10L/g. (ii) An isotherm was carried out under real groundwater conditions by fortification of Salamanca water with arsenic.

The isotherms follow the same trend of the single point experiment: Purolite had superior adsorption over Bayoxide, and Bayoxide had a slightly better
performance than NXT. When looking at the values of $q_{\text{max}}$ and $k_{L}$, we observe the opposite to what we see with the isotherms in presence of silica: $q_{\text{max}}$ of both Bayoxide and NXT decreases significantly, much more so than for NXT. On the contrary, the $q_{\text{max}}$ of Purolite decreases only 15%. The decrease in the value of $k_{L}$ is highest for Purolite (56%), then Bayoxide (38%), and then NXT (24%); interestingly, the $k_{L}$ values are higher than in the isotherms with only arsenic and silica for the three sorbents.

The effects that silica has on $q_{\text{max}}$ and $k_{L}$ values in both synthetic and natural water for the three sorbents suggests that there are different ions in competition with arsenic for surface sites on the sorbents. The cases of Bayoxide and NXT are similar: in the presence of only silica we observed competitive adsorption for the same sites. When other ions are introduced, however, there are either fewer sites for adsorption (suggesting additional competitive adsorption) or the promotion of the silica adsorption in the presence of more ionic media. The latter possibility is more consistent with the data. Specifically, the ions that could compete with arsenic for adsorption (e.g. nitrate, phosphate) are present only at very low concentrations in the test waters (less than 2ppm for nitrate and 15-66ppb for phosphate). Their direct competition cannot explain the substantial drop in $q_{\text{max}}$ and $k_{L}$ values. In the absence of other ions, the silica outcompetes arsenic for surface binding due to its very high concentrations. When other ions are present, silica is even more effective at surface adsorption. This is not too surprising as silica precipitation and coating onto surfaces is often accelerated by the presence of ions such as $\text{Mg}^{2+}$ and $\text{Al}^{3+}$.100,101
Even when the batch experiments can give a general prediction of the behavior of a sorbent, kinetic effects are not considered. Also, the values of $q_{max}$ and $k_L$ cannot be used for a direct comparison to what can be found in a column configuration. For that reason, two extra values were calculated for all isotherms and are also expressed in Table 3.2: $q_{10}$ and $q_{100}$. These values represent the adsorption capacities predicted by the fitting at concentrations of $[As]=10\mu g/L$ and $100\mu g/L$. The significance of these values is that $q_{100}$ would be the maximum expected capacity for when a column is fully saturated when in contact with Salamanca groundwater; and $q_{10}$ would be the expected capacity for when a column Environmental Protection Agency (EPA) maximum contaminant level (MCL).

### 3.5. Column tests

Batch experiments are useful for rapid comparison and analysis of sorbents; however, evaluating the sorption process under flow conditions in a column is closer to the application envisioned in the field. Rapid Small Scale Column Tests (RSSCTs) (see Chapter 2, p. 50) were performed in the lab with a solution of arsenic ($[As]=100\mu g/L$) and silica ($[SiO_2]=85mg/L$) at pH 7 with two sorbents: the Ferroxide nanoparticles and the Bayoxide material (Figure 3.6).

Even though the Ferroxide did not performed satisfactorily in the batch experiments, they were evaluated in a column configuration. In Figure 3.6.i the arsenic breakthrough is shown, and the details of the experimental parameters such as the length of the column (L), the bed volume (BV) size and the flow rate (Q) used
are given in Table 3.3. In this table, the derived parameters, $R$ (retardation factor) and $D$ (coefficient of hydrodynamic dispersion), as well as the coefficient of determination ($r$) of the fit the data with the advection-dispersion equation (ADE, see Chapter 1, p. 21) (red line) are given.

**Figure 3.6  Columns of commercial sorbents in the lab**

RSSCTs of Ferroxide (i) and Bayoxide (iii) were carried out with a feeding solution [As]=100μg/L and [SiO₂]=85mg/L at pH 7. The corresponding cumulative adsorption capacity ($q$) is reported in (ii) and (iv), respectively.

As discussed in section 1.5.2, the experimental data from the columns could be described by a one-dimensional advection-dispersion model (Equation 1.4). However, the Ogata and Banks solution (Equation 1.5) was not used. Instead, the
simplification of Equation 1.5 proposed by Ogata and Banks (Equation 3.1) because it simplified greatly the modeling process; the omission of the second term should not introduce errors greater than experimental error.  

<table>
<thead>
<tr>
<th>Location</th>
<th>L (cm)</th>
<th>BV (mL)</th>
<th>Q (cm/min)</th>
<th>R (cm/min)</th>
<th>D (cm/min)</th>
<th>r</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ferroxide</td>
<td>Lab</td>
<td>27.9</td>
<td>21.83</td>
<td>10.01</td>
<td>57</td>
<td>95.3</td>
</tr>
<tr>
<td></td>
<td>Salamanca</td>
<td>25.5</td>
<td>20.03</td>
<td>6.53</td>
<td>9</td>
<td>265.2</td>
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<tr>
<td>Bayoxide</td>
<td>Lab</td>
<td>22.8</td>
<td>18.87</td>
<td>8.02</td>
<td>8900</td>
<td>10.9</td>
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<tr>
<td></td>
<td>Salamanca</td>
<td>10.1</td>
<td>7.93</td>
<td>3.86</td>
<td>3186</td>
<td>12.4</td>
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<td>Purolite</td>
<td>Lab</td>
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<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td></td>
<td>Salamanca</td>
<td>21.0</td>
<td>16.49</td>
<td>10.02a</td>
<td>N.A.</td>
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<tr>
<td>NXT</td>
<td>Lab</td>
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<td>---</td>
<td>---</td>
</tr>
<tr>
<td></td>
<td>Salamanca</td>
<td>9.9</td>
<td>7.78</td>
<td>3.88</td>
<td>5770</td>
<td>32.3</td>
</tr>
</tbody>
</table>

Table 3.3  Summary of the parameters for column experiments
The table shows a summary of the parameters used and obtained (R, D and r) by fitting the experimental data to an advection diffusion model. a: flow rate targeted for that column.

\[
\frac{[\text{As}]_x}{[\text{As}]_0} = \frac{1}{2} \text{erfc} \left(\frac{RL - Q_x(EBCT \ast x)}{\sqrt{4RD(EBCT \ast x)}}\right) 
\]

Equation 3.1 Formula for fitting experimental data in column experiments

\([\text{As}]_x/[\text{As}]_0\) is the ratio of outlet concentration over initial arsenic concentration, which corresponds to the y-axis, and it is dimensionless; \(\text{erfc}()\) is the complementary error function; \(R\) is the retardation factor, and is dimensionless; \(L\) is the length of the active area in the column, in cm; \(Q_x\) is the linear velocity of the fluid through the column, in cm/min; \(D\) is the dispersion coefficient, in cm/min; and
instead of time, \( t \), \( EBCT^* x \) is used. EBCT is the empty bed contact time, in \( \text{min}/\text{BV} \), and \( x \) are the number of bed volumes, \( \text{BV} \). These correspond to the x-axis in the graphs.

Figure 3.6.ii displays the cumulative adsorption capacity for Ferroxide. Two important values are taken from this kind of graph, \( q_{\text{stop}} \) and \( q_{10} \), and summarized in Table 3.4. \( q_{\text{stop}} \) is the final adsorption capacity when the column is stopped; ideally it would correspond the value when completely saturated, but not all column experiments were carried out to a final value of \( [\text{As}]_f/ [\text{As}]_0 = 1 \). On the other hand, \( q_{10} \) is the adsorption capacity when a \( [\text{As}] = 10 \mu \text{g/L} \). In the case of Ferroxide, the cumulative capacity is calculated considering only the weight of the sorbent.

In Figure 3.6.iii and Figure 3.6.iv the same kind of graphs, the arsenic breakthrough curve and the cumulative adsorption plot, are shown for Bayoxide. In contrast to the Ferroxide material, Figure 3.6.iii shows a large “flat” area where a substantial volume of contaminated water is being treated and no arsenic is released in the outflow water. The number of bed volumes treated before reaching the MCL (around 6,000 BVs) is in good agreement with what is reported in the literature: a decrease from 40,000 BVs to 20,000 BV when the silica concentration increases from 45 mg/L to 60 mg/L. In Figure 3.6.iv, it is evident the column did not reach saturation, but even then the final cumulative capacity (\( q_{\text{stop}} = 1.09 \mu \text{g/g} \)) is greater than predicted by the isotherm with Salamanca water (\( q_{100} = 0.35 \mu \text{g/g} \)).

Column experiments with Salamanca groundwater were performed with the four sorbents and both the breakthrough curves and cumulative adsorption capacity plots are shown in Figure 3.7.
Table 3.4  Comparison of the adsorption capacities obtained from column experiments

A summary of the adsorption capacities obtained at the columns when stopped ($q_{stop}$) and when they reach $[As]_{out}=10\mu g/L$ ($q_{10}$) is shown. The values obtained from the isotherms with Salamanca water is also presented for comparison. a: $q_{stop}$ for isotherms is the value observed at $[As]_e=100\mu g/L$ ($q_{100}$); b: isotherm with Salamanca water was not run for the Ferroxide, the value was then taken from the isotherm with only arsenic and silica at pH 7; c: this value was then observed when the column stopped before reaching saturation.

Figure 3.7.i shows the arsenic breakthrough curve for the Ferroxide material with Salamanca groundwater. As expected, the performance was worse than observed with synthesized water in the lab; the retardation factor decreased from 53 to 11 (Table 3.3). The final cumulative adsorption capacity (Figure 3.7.ii), $q_{stop}$ decreased from 0.10mg/g to 0.02mg/g (Table 3.4); these results clearly indicate that the Ferroxide Black 78P is not a viable commercial sorbent for arsenic under these challenging waster chemistry conditions.
Figure 3.7  Columns of commercial sorbents in Salamanca

RSSCTs of Ferroxide (i), Bayoxide (iii), and NXT (v) were carried out with groundwater from Salamanca as a feeding solution. The corresponding cumulative adsorption capacities (q) are reported in (ii), (iv), and (vi), respectively.
Figure 3.7.iii displays the breakthrough curve for arsenic of the Bayoxide material with Salamanca groundwater. As anticipated, the number of bed volumes treated decreased when going from the lab to Salamanca; $R$ went from 8900 to 3186 (Table 3.3). The coefficient of hydrodynamic dispersion, on the other hand, did not change considerably; $D$ went from 10.9 cm/min to 12.4 cm/min. This small change is possibly related to the fluctuation in the experimental data observed at bed volumes higher than 3800BV. These fluctuations are due to the fact that the column was run for three weeks at a field site and some nights had to be stopped for several hours. In Figure 3.7.iv it is evident the column was stopped close to reaching saturation. Even when the $q_{stop}$ value is lower than the one observed in the column run in the lab; it is much bigger than predicted by the isotherm $q_{100}$ (Table 3.4). The same trend is followed with $q_{100}$ values: sorbents tested for arsenic removal using Salamanca water have half of the capacity found in the idealized laboratory experiments.

During field trials the water chemistry conditions do change, and to understand how these might be influencing the data the concentrations of other possible interfering ions were monitored. There are several ions that interfere with arsenic removal in addition to silica. The most common are phosphate, selenium and vanadium; the three of them were measured during the column run but the selenium concentration was very close the detection limit. Figure 3.8.i shows the breakthrough curve for silica; as expected, saturation is reached promptly but value of $[\text{SiO}_2]_{out}/[\text{SiO}_2]_{in}$ is kept around 0.9, which indicates continued adsorption of silica. Figure 3.8.ii shows the breakthrough experimental data for P and V. In both
cases, the outlet concentration increases almost linearly; which indicates a minimum adsorption is occurring.

Figure 3.8  **Column breakthrough curves of main interferences in groundwater.**

The breakthrough curves of the main interferences in the field columns of Bayoxide and NXT are shown; silica, (i) and (iii), phosphorous (black squares) and vanadium (red circles), (ii) and (iv), respectively.

Figure 3.7.v shows the arsenic breakthrough curve for the NXT material with Salamanca groundwater. Contrary to the behavior found in the isotherm experiments, the retardation factor is bigger for NXT ($R=5770$) than Bayoxide ($R=3186$) (Table 3.3). Similar to the other field column experiments, there are
fluctuations in the data at bed volumes higher than 3800BV for similar reasons. Even without the variations, it is evident that dispersion plays a bigger role in controlling sorption in the column: $D$ is 32.3 cm/min for example. Figure 3.7.vi shows that the cumulative adsorption capacity of NXT is very similar to the Bayoxide (Figure 3.7.iv); however, the experiment with NXT had to be halted before NXT reached its maximum adsorption capacity. Even so, $q_{stop}$ (0.73 mg/g) is almost three times what was predicted by the isotherm $q_{100}$ (0.24 mg/g) (Table 3.4). The same outcome is observed with $q_{100}$ values, the column one is almost eight times better than that predicted by the isotherm. As anticipated the silica concentration in the column outlet increases rapidly (Figure 3.8.iii), but there is no indication of significant adsorption. However, that is not the case for phosphorous and vanadium (Figure 3.8.iv). With the exception of the overshoot peak (e.g. increase in the normalized concentration around 1500 BVs) in the data for phosphorus, which is typical for competitive systems\textsuperscript{103}, adsorption for both V and P occurred until the column was stopped without being close to saturation.

In the case of the Purolite material, column experiments comparable to the ones described previously were not possible. After a few hours the flow started to decrease rapidly and eventually stopped; analysis of the arsenic concentration at 586 BV found it lower than the detection limit. For that reason, a breakthrough curve is not shown. An attempt to repeat this study with Purolite found the same result. Previous studies have reported a 34% decrease in the arsenic adsorption capacity of Purolite when silica is present in a concentration of 20 mg/L and a 52% decrease when also there is presence of phosphate\textsuperscript{104}. Moreover, performance can decrease
~48% when the concentration of silica increases 10mg/L. For this reason, Purolite is not recommended by its distributor for use in water with silica concentrations larger than 20mg/L. Regardless, $q_{stop}$ was calculated at 0.03mg/g (Table 3.4).

The unusual results seen with the Purolite material may be caused by the propensity for silica monomers (e.g. silicic acid) to condense into oligomers and polymers at high concentration (higher than 120mg/L). Condensation of silica into dimers and oligomers is also possible at even lower concentrations if the pH is basic. In 2012, Christl et al. reported that this polymerization was also observed in silica adsorbed onto iron (hydr)oxide surfaces when equilibrated for several days with silica solutions with concentrations as low as 40mg/L. Higher concentrations of silica resulted in even faster surface condensation. In a comment on the previous paper, SenGupta et al. made emphasis on how the adsorption of polymeric species of silica would be really difficult to revert and how in a column set up the accumulation of silica in the bottom of a column would favor the conditions for dimerization. This phenomenon has been observed in other systems when arsenic and silica are present in solution. It is possible that what was observed in the Purolite column follows a mechanism similar to described by SenGupta. In that case, the presence of the anionic exchange resin – the support material of the sorbent – provided conditions more favorable for enhanced surface polymerization that only the iron-hydroxo superficial groups. An XPS analysis of the material of the column was done to confirm this hypothesis but no conclusive results were obtained.
3.6. Prediction of the arsenic adsorption behavior in the presence of competitive ions

The last section demonstrated the significant, negative impact that silica and other interfering ions can have on arsenic removal by iron oxide sorbents. It also highlighted that in spite of the similar composition, the four materials exhibited very different behavior with respect to the magnitude of the interfering ion effects and the response to the interplay of the different ions. Integrating these observations into a mechanistic model would be of great value to both the practical application of these sorbents, as well as the design of improved sorption materials.

There are several models proposed for surface adsorption. These include Langmuir isotherm models altered for competitive adsorption of multiple ions, ideal solution theories and more macroscopic thermodynamic approaches. The application of such models to arsenic adsorption in the presence of interferences has been explored. Typically such studies focus on the impact of silicate, phosphate and silica on arsenate removal as they, like arsenic, are large anions. Hsu et al. defined and measured factors that reflect the competitive adsorption on As(V) removal using iron oxide coated sand and estimated the effects of various mixture of ions. More recently, the competitive adsorption of As(V) and As(III) has been studied. However, these estimates were generally predictive only when the conditions were idealized.

One of the assumptions made was the fact that an isotherm with groundwater would give a closer idea of what would happen in a column set up with
the same water. For that reason, in Table 3.4 relevant values ($q_{\text{stop}}$ and $q_{10}$) of the columns were put together and compared with the equivalent obtained from the isotherm with Salamanca groundwater. Nevertheless, after what was observed with the Purolite material, where the isotherm with Salamanca water predicted a much better performance than with the solution of arsenic and silica, and the results from were devastating probably because of the effect of the silica, a step back was taken. For Purolite, the results suggested that the factor that was expected to have the bigger impact, in fact did. To verify this observation, the $q$ values obtained from the isotherm with a solution of arsenic and silica and from the columns with Salamanca water are summarized in Table 3.5.

The comparison is of more value than the one made in Table 3.4. In the case of the Purolite material, the performance observed is actually only a third part of expected, instead of the 1 in 20. In the case of Bayoxide, the performance in the column is actually a 20% higher than expected ($q_{\text{stop}}$), instead of the 237% based in the isotherm with Salamanca groundwater; a 20% increase actually can be justified for kinetics effects present only in the column. The $q_{10}$ value is 4 times bigger than predicted instead of 8. For the NXT, the predictions are closer to observed. For $q_{10}$ value the observed/predicted ratio passes from 8 times to 2. For $q_{\text{stop}}$ the column only reached $[\text{As}]_{\text{stop}}/[\text{As}]_{0} = 0.8$, and the value is very close to expected. Because an isotherm with Salamanca water for the Ferroxide material was not carried out, the analysis does not change.
<table>
<thead>
<tr>
<th></th>
<th>Experiment</th>
<th>$q_{\text{stop}}$ (mg/g)</th>
<th>$q_{10}$ (µg/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>岩木粉黑78P</td>
<td>Isotherm - Silica</td>
<td>0.15</td>
<td>44</td>
</tr>
<tr>
<td></td>
<td>Column - Salamanca</td>
<td>0.02</td>
<td>5</td>
</tr>
<tr>
<td>阿多吉技术</td>
<td>Isotherm - Silica</td>
<td>0.69</td>
<td>76</td>
</tr>
<tr>
<td>Bayoxide E33</td>
<td>Column - Salamanca</td>
<td>0.83</td>
<td>317</td>
</tr>
<tr>
<td>普鲁利特</td>
<td>Isotherm - Silica</td>
<td>0.10</td>
<td>11</td>
</tr>
<tr>
<td>FerriX A33E</td>
<td>Column - Salamanca</td>
<td>0.03&lt;sup&gt;a&lt;/sup&gt;</td>
<td>N. D.</td>
</tr>
<tr>
<td>EP Minerals</td>
<td>Isotherm - Silica</td>
<td>0.92</td>
<td>96</td>
</tr>
<tr>
<td>NXT-2</td>
<td>Column - Salamanca</td>
<td>0.73&lt;sup&gt;a&lt;/sup&gt;</td>
<td>207</td>
</tr>
</tbody>
</table>

Table 3.5 Comparison of the adsorption capacities obtained from batch and column experiments.

A summary of the adsorption capacities obtained at the columns when stopped ($q_{\text{stop}}$) and when reach a [As]$_{\text{out}}$=10µg/L ($q_{10}$) is shown. The values obtained from the isotherms with Salamanca water is also presented for comparison. a: this value was then one observed when column stopped without reaching saturation.

A full predictive and mechanistic model is beyond the scope of this work; however, as these comments suggest the data provide a clear direction for future refinements in experiments and modeling.

3.7. Feasibility study

In The data presented here, specifically the $q_{10}$ value measured in the field using Salamanca water makes it possible to calculate a treatment cost for these materials. Equation 3.2 shows the approach:
\[
Treatment\ Cost \left[ \frac{\$}{m^2} \right] = \frac{Media\ cost \left[ \frac{\$}{Kg} \right] \times 1000 \left[ \frac{L}{m^3} \right]}{q_{10} \left[ \frac{\mu g}{g} \right] \times 1000 \left[ \frac{g}{Kg} \right]} \times (\left[ As \right]_0 - \left[ As \right]_{target}) \left[ \frac{\mu g}{L} \right]
\]

**Equation 3.2 Calculation of the treatment cost for arsenic removal**

Where the *media cost* is the market price of the sorbent during 2013; \( q_{10} \) is the adsorption capacity obtained at the columns when they reach a \([As]_{out}=10 \mu g/L\); \([As]_0\) and \([As]_{target}\) are the initial arsenic concentration and the targeted arsenic concentration, this last usually is determined by the local MCL. Despite the treatment cost is based on data from columns with Salamanca groundwater, the formula does not take into account that (i) regeneration cycles can decrease the calculated price; (ii) fluctuations in inlet water chemistry such as inlet arsenic concentration, pH, temperature, and other seasonal variations, may affect removal; and (iii) pressure build-up may occur more readily in full-scale columns and require backwash cycles that perturb the mass-transfer zone within a column.

In Table 3.6 the treatment costs, as well as the parameters used for their calculation, for the Ferroxide, Bayoxide and NXT materials are reported. In addition, it is important to remark the cost here estimated is only related to the sorbent; operational and other factors are not been considered for this assessment. Farrell reported a similar analysis in 2014.\(^9\) However, there are two main differences: the values for the adsorption capacity are from a column experiment, which makes the analysis more realistic; and regenerations are not considered in this cost analysis. Regenerations would decrease the treatment cost for all materials, but there is not
enough information as yet to characterize its overall effectiveness in a treatment process.

The volume of material ($V_m$) needed to treat water during a month was calculated using Equation 3.3. The water consumption for a month, $W_{C_m}$, was calculated using a typical well flux of 20L/s; it would be expected that the $V_m$ would be smaller than the size of the filtration column in the individual wells. For the reported values of $V_m$ and treatment cost, the initial and target arsenic concentration were $[\text{As}]_0=90\mu\text{g}/\text{L}$ and $[\text{As}]_{\text{target}}=10\mu\text{g}/\text{L}$.

$$V_m \ [\text{m}^3] = \frac{([\text{As}]_0 - [\text{As}]_{\text{target}}) \left[\frac{\mu\text{g}}{L}\right]}{q_{10} \left[\frac{\mu\text{g}}{g}\right]} \times \frac{W_{C_m} \ [\text{m}^3]}{\rho \left[\frac{\text{Kg}}{\text{m}^3}\right]} \times \frac{1000 \left[\frac{L}{\text{m}^2}\right]}{1000 \left[\frac{\text{g}}{\text{Kg}}\right]}$$

**Equation 3.3 Calculation of the volumetric amount of sorbent required for arsenic removal**

<table>
<thead>
<tr>
<th></th>
<th>$q_{10}$ $(\mu\text{g}/g)$</th>
<th>Media cost $($/\text{Kg})$</th>
<th>$\rho$ $(\text{Kg}/\text{m})$</th>
<th>$V_m$ $(\text{m})$</th>
<th>Treatment cost $($/\text{m})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ferroxide</td>
<td>5</td>
<td>5.5</td>
<td>700</td>
<td>1185</td>
<td>88</td>
</tr>
<tr>
<td>Bayoxide</td>
<td>317</td>
<td>16.5</td>
<td>472</td>
<td>27.7</td>
<td>4.2</td>
</tr>
<tr>
<td>NXT</td>
<td>207</td>
<td>19.4</td>
<td>720</td>
<td>27.8</td>
<td>7.5</td>
</tr>
</tbody>
</table>

**Table 3.6 Cost analysis of using arsenic sorbents in Salamanca, Mexico**

$q_{10}$: Adsorption capacity obtained at the columns when they reach a $[\text{As}]_{\text{out}}=10\mu\text{g}/\text{L}$; Media cost: price in the market in 2013; $\rho$: density was obtained from the SDS or TDS provided from the manufacturers; $V_m$: volume of sorbent required to reduce the $[\text{As}]$ from 90 to 10µg/L with a water consumption of 20L/s for a month; treatment cost: estimated cost per cubic meter of water treated. As the $q_{10}$ value for Purolite was not obtained, it was not considered in this analysis.
Based on the estimated treatment costs (Table 3.6), the Bayoxide material is the most cost-efficient with a treatment cost of $4.2 per cubic meter of contaminated water. This cost is too excessive as 1728 meter cubed of water are treated each day at one well site alone; and the city is supplied for more than one hundred wells, that would imply more than 172,000 cubic meter of water per day. This cost is excessive for a developing country for which a practical water treatment process should be at most $0.10 per cubic meter. In addition, a filtration reactor at least 28m³ should be implemented at a remote well facility in order to change or regenerate the material once per month. This may be a challenge in a city like Salamanca that relies on more than 100 wells. Also important is the amount of waste generated; if the material is not regenerated, 2800m³ of sorbent with high arsenic content would have to be disposed every month. Even when a similar amount of the material is required, NXT follows it with almost double of the cost ($7.5 per cubic meter). Far behind the Ferroxide material has a ludicrous cost of $88 per cubic meter and a monthly volumetric amount of sorbent required of 1185m³ per well.

This analysis indicates that while Bayoxide E33 and NXT-2 can remove arsenic from water in these prototypical Latin American sites, their high cost makes them impractical for immediate application. There remains a need for a material that can remove high arsenic concentrations in the presence of interfering ions (particularly silica); in a cost effective manner; without the generation of large amounts of waste. Iron oxide nanocrystals are particularly promising emerging systems for meeting these needs and their performance is described in the next
section. Unlike the Ferroxide commercial materials, which also possess nanoscale features of iron oxide, the materials of interest here are non-aggregated and highly crystalline.

3.8. Optimizing the use of commercial magnetite nanoparticles

Before evaluating extremely small and uniform nanocrystals for arsenic removal, the commercial material, Ferroxide, was used to explore and optimize the experimental design. Its low cost and its high-purity certification make it a candidate for field applications and it can be readily sourced in large quantities.

The relative amount of sorbent material to arsenic can influence sorbent performance. Using Ferroxide we explored the optimal ratio in batch experiments. Figure 3.9 shows a study to determine the minimum dosage to obtain at least a 90% removal ([As]_{eq}/[As]_{in}<0.1). A solution with only arsenic ([As]_{in}=98\mu g/L) at pH 7 was used. Four contact times were tested: 1min (pink), 5min (violet), 10min (purple) and 30min (grey) – lines are shown for easier visualization. When the dosage is higher than 1.5g/L, the removal of arsenic is almost 100%. At dosages lower than 1g/L, differences are observed. As expected, the longer the contact time is, the more efficient the adsorption is; however, the data at 1min do not follow this trend. The adsorption when the contact time is 10min is slightly better than the one with a contact time of 5min. This data illustrate the importance of kinetics in surface adsorption. Arsenic is adsorbed rapidly onto nanoparticles, probably as a monodentate complex with iron; it takes between 5 and 10 minutes for this
complexation to equilibrate to the more stable bidentate complex. After equilibration longer than thirty minutes, isotherm measurements are free from kinetic effects and can be measured using sorbent concentrations lower than 1g/L.

Figure 3.9  Determination of minimum dosage for optimal arsenic removal

Several contact times were used to determine the arsenic removal efficiency at different dosages. Dosages below 1g/L are desired. Insert shows a larger view of the area of interest. Initial arsenic concentration was 98µg/L, at pH 7.

Farrell at al explored the ideal conditions for incorporating nanocrystals onto a sand column;114 20w/w% was the maximum amount reported to run the columns without backpressure issues. This value was the maximum loading used for nanoparticle columns. Farrell also reported the use of two residence times: 3.6 and 36 min. As expected, the column with longer residence time had a smaller value of hydrodynamic dispersion coefficient. However, a more extensive study of the influence of the contact time was made (Figure 3.10), the goal was to find the smaller contact time that provided a good adsorption performance.
Figure 3.10 Determination of minimum contact time for arsenic removal
Contact times between 1 and 30 min were tried to determine the minimum time where arsenic removal was optimal. The experiment was performed in an ideal solution with only arsenic ([As] = 98µg/L) at pH 7 and a solution that had arsenic with Silica present ([As] = 75µg/L, ([SiO₂] = 50mg/L) at pH 8.

Two solutions were selected to test the minimum contact time required: arsenic ([As] = 98µg/L) at pH 7, and arsenic in presence of silica ([As] = 75µg/L, ([SiO₂] = 50mg/L) at pH 8. A first order reaction was used to fit the experimental data in both conditions. In the case of the solution with only arsenic, the model fit almost perfectly up to three minutes. After this time there is an increase in the remaining concentration of arsenic, which then decreases at 30min. When silica is present, the fitting is very good and the arsenic concentration remains stable at a concentration around 40µg/L, after a contact time of 3min. In both cases, the difference between the remaining arsenic concentration between 2min and 3min is
very small. Taken together, this data suggests a contact time of 2min offers the most
efficient residence time for column experiments.

Also important for larger scale use of arsenic sorbents are (a) the ability to
reuse the nanoparticles and (b) mitigation of the silica effect.\textsuperscript{95,115} Because Ferroxide
Black 78P could be sourced in large quantities, this material was used as a
benchmark for later studies with much smaller and non-aggregated iron oxide
nanocrystals.

Regeneration conditions for nanocrystals were developed around the
hypothesis that strongly basic conditions would strip surface bound arsenic without
changing the surface iron oxide. Five grams of the Ferroxide was exposed to a high
arsenic concentration solution for 24h. It was then dried under vacuum and
separated into several aliquots to be treated with different conditions: including
different NaOH concentrations, variable ionic strength (using NaNO\textsubscript{3}) and
temperature. Specific ranges for these variables were based on published
regeneration conditions for other iron oxide sorbents.\textsuperscript{104,116,117} Ferroxide loaded
with arsenic was exposed to the regeneration solutions for one hour, the solids were
physically filtered, and the remaining solution was analyzed for its arsenic
concentration. The results of this experiment are shown in Figure 3.11.

As expected, the regeneration is greatest at high concentration of NaOH and
at elevated temperatures; also, the presence of NaNO\textsubscript{3} has a small positive effect.
Considering cost and energy usage, the best regeneration condition identified was
treatment with a 2w/w\% NaOH solution at room temperature.
Regeneration conditions

Figure 3.11  Regeneration conditions for commercial nanoparticles. Temperature, NaOH concentration and ionic strength were the variables considered.

Three types of samples were used for comparing the efficiency of the regeneration for the optimized conditions above: virgin Ferroxide, spent Ferroxide (the saturation was carried out with the procedure described above, using the solutions that would be used for the isotherm experiments), and the regenerated sample of Ferroxide (the saturation step was followed with the regeneration using a 2% NaOH solution). Note that the spent and regenerated samples were washed and dried under vacuum before the isotherm experiment. Two solutions were used to
evaluate the adsorption capacities of the regenerated materials: a solution of only arsenic ([As] = 1085 µg/L), and a solution of arsenic in the presence of silica ([As] = 290 µg/L, [SiO₂] = 50 mg/L). Both solutions were at pH 7. Results for the isotherm with only arsenic are shown in Figure 3.12.i. As expected, the regenerated material performed better than used material not subject to regeneration; also, the regenerated material was not as effective at arsenic removal as the freshly prepared system. The same trend is found when silica is present (Figure 3.12.ii); however, the difference between the regenerated and the spent material is minimal. This effect is consistent with the assessment that deposition of silica onto iron oxide at high concentration would lead to coatings that would be very difficult to remove.¹⁰⁸

![Figure 3.12](image)

**Figure 3.12  Regenerated versus native nanoparticle performance.**
The arsenic adsorption isotherm of virgin (black square), regenerated (blue circle) and spent (red triangle) of magnetite nanoparticles are shown with prepared solutions without (i) and with silica present(ii). Initial solution for (i) was [As] = 1085 µg/L, and [As] = 290 µg/L, [SiO₂] = 50 mg/L for (ii); both at pH 7.

These batch isotherm experiments were confirmed with column studies. Specifically, a solution with an arsenic concentration of 90 µg/L and a silica concentration of 100 mg/L with a pH=7 were treated with columns using fresh and
regenerated materials. Figure 3.13i shows the performance of the column before (first cycle) and after regeneration (second cycle). Though the regenerated column breakthroughs arsenic before the fresh column, the volume treated before the outlet water reaches the MCL (10µg/L) is a somewhat larger due to the decrease of the hydrodynamic dispersion coefficient, $D$. However, a definitive conclusion cannot be obtained from these experiments since the volume treated before saturation is too low to observe a clear effect. A similar experiment was run in Salamanca (Figure 3.13.ii) under similar conditions ([As]~90µg/L, [SiO₂]~90mg/L, pH=7.9). In this case, the breakthrough curves between the fresh and regenerated materials were indistinct from one another. To further characterize the regeneration efficiency, the cumulative percent of arsenic recovered during the regeneration process was calculated for both columns. In the case of the column run in the lab (Figure 3.13.iii), almost 80% of the arsenic adsorbed was recovered; for the column used in the field at Salamanca (Figure 3.13.iv) only 50% was recovered.

These results corroborate the observations from batch experiments: that regeneration after silica exposure is not very effective. However the cumulative adsorption capacities before and after regeneration of the column material reveal an interesting detail. Both lab (Figure 3.13.v) and Salamanca (Figure 3.13.vi) columns reached their theoretical capacity, corrected for the amount of arsenic released during regeneration. Also the shapes of the cumulative curves at low bed volumes are very similar. Even when the total amount of arsenic adsorbed will not be the same after regeneration the behavior before reaching the MCL, usually at the beginning of the mass transfer zone, will be very similar.
Figure 3.13  Effect of the regeneration of nanoparticles in column setup.

The breakthrough curves of columns prepared with 20%wt. Ferroxide columns before and after regeneration (first and second cycle) with synthetic water in the lab (i) and with groundwater in Salamanca (ii). (iii) and (iv) show the arsenic recovered from the columns during regeneration of lab and on-site columns, respectively. (v) and (vi) show the cumulative adsorption capacity from the columns with synthetic and groundwater columns, respectively; the line represents the theoretical capacity expected after regeneration.
It is important to note that these studies were completed with a poorly performing commercial sorbent chosen for its similarity in structure to isolated nanocrystals. This limits the information that can be deduced from the breakthrough curves. This hypothesis would have to be proven with a material with better performances. As well, a different condition for regeneration could improve the decrease in the regeneration efficiency observed when silica is present; the difference in regeneration efficiency observed between the NaOH 2% solution at room temperature and the NaOH 10% solution at 50°C observed in Figure 3.9 could be different in real water conditions.

The second concern to address to make iron oxide nanoparticles a more suitable candidate for arsenic removal is the mitigation of the silica effect. Pretreatments of the groundwater with alumina and activated carbon were studied by Farrell in Guanajuato water ([As]=7-30μg/L, [SiO₂]~50mg/L, pH=7.3) to decrease the silica effect without any success. An increase in arsenic adsorption onto iron oxide surfaces has been reported in the presence of divalent cations such as zinc, magnesium and calcium. The mechanism that allows this increase in adsorption is not clear. In the case of the zinc cations it has been proposed that a zinc-arsenate complex is formed in solution and it is more likely to be absorbed onto magnetite, the same could be true for Ca²⁺. The effect of calcium cations in the presence of silica was studied. Figure 3.14 isotherm experiments with four different conditions were performed: only arsenic; arsenic and silica ([SiO₂]= 50mg/L); and arsenic, silica ([SiO₂]= 50g/L) and calcium, the last one at two different concentrations 25mg/L and 50mg/L. Fitting the experimental results to the
Langmuir adsorption model, it was found that the total amount of arsenic adsorption in the presence of silica or silica and calcium is not significantly different. However, the $k_L$, which is correlated with the chemical equilibrium, drops significantly when silica is present and increases as calcium cations are added to the As and SiO$_2$ solution. This trend could be explained by an electrostatic effect: the presence of Ca$^{2+}$ decreases the repulsion present between magnetite already occupied with arsenate anions$^{119,120}$ (negatively charged) and allows the adsorption of more negative anions.

![Figure 3.14](image)

**Figure 3.14  Effect of the addition of calcium cations in the mitigation of the silica effect.**

The arsenic adsorption isotherm of Ferroxide with only arsenic (black square), arsenic and silica (red triangle) and arsenic, silica and calcium with a concentration of 25mg/L (pink star) and 50mg/L (purple pentagon). Silica concentration was constant in all the initial solutions, [SiO$_2$]= 50mg/L; all initial solutions were adjusted to pH 7.
Columns were run with a synthetically prepared solution (Figure 3.15.i) – [As]=90μg/L, [SiO₂]=100mg/L, pH=7– and Salamanca water (Figure 3.15.ii); when calcium was added, the final concentration of calcium cations was 20mg/L. As shown in Figure 3.15.i, in the lab column, there is a positive effect of using Ca⁺ to mitigate the silica effect. However, when this experiment was repeated using Salamanca water (Figure 3.15.ii) both columns, with and without Ca⁺, had a similar behavior. In Salamanca groundwater, the effect of 20mg/L of Ca⁺ ions in addition to the 10.4mg/L already present (Table A. 4), may not be significant because of the large background of other ions. These would mask the electrostatic effect observed when using water with less net ionic strength.

**Figure 3.15** Effect of calcium cations in the performance of magnetite nanoparticles in column setup.

The breakthrough curves of columns prepared with 20%w Ferroxide columns with (red circles) and without (black squares) the addition of calcium cations, [Ca⁺]=50mg/L, in the lab (i) and in Salamanca (ii) are shown. A small mitigation effect is observed when using synthetic water, but it is not seen when using groundwater.
3.9. Conclusions

The work discussed in this chapter provides a point of reference for the work to be reported in the next ones. The use of four commercially available arsenic sorbents allowed the identification of the main parameters that affect arsenic adsorption: a commercial available nanomaterial formed of close to 100nm magnetite nanoparticles, Ferroxide Black 78P (Huntsman); a mesoporous material mainly composed of goethite, Bayoxide E33 (AdEdge Technologies); an amorphous iron oxide prepared in situ an ionic exchange resin, FerrIX (Purolite Int. Ltd.); and a mesoporous material with a mixed composition of lanthanum hydroxide/iron oxide, NXT-2 (EP Minerals). Although they all are primarily iron (hydr)oxides, and adsorption is expected to occur in the iron-hydroxo groups in the surface, they behave very differently because of their composition and the nature of their support media.

Batch experiments were performed in the lab to study the effect of silica on arsenic adsorption of these materials. A simple Langmuir model that included the competitive adsorption of silica was used to fit experimental data. For all of the materials, arsenic adsorption was reduced in the presence of silica. However, the trend observed in the laboratory was not observed in the more complex water chemistry of the field site Salamanca groundwater. This site presents many challenges because of its high pH, high concentration of silica and presence of other possible interferences. When trying to relate the results in batch experiments with groundwater to column tests with the same water, correlation was not successful.
The case of the Purolite material was the more extreme and helped to understand the reason. In the batch isotherm with groundwater, Purolite was the material with the best performance; despite that with only arsenic it was the second best one, and its performance significantly decreased when silica was present. When used in a column set up, the column stopped only after a few hours because of a drastic drop in the water flow. After further analysis, it was concluded that silica was the reason of this bad performance. This suggested that the behavior in the column would be dictated for the parameter that affected the arsenic adsorption the most, in this case silica. When comparing the results obtained in batch experiments with lab solutions with silica for the other materials, a better correlation between the batch and column experiments was done. This is a major conclusion as indicates that as long as the parameter with major effect in the adsorption process is identified and its effect is characterized in batch experiments, an empirical prediction of the behavior in columns could be done.

An important focus of this chapter was to consider the feasibility of applying arsenic sorbent materials in actual groundwater, in this case drawn from a prototypical site in Salamanca, Mexico. It was found that materials as Bayoxide and NXT can treat water with the conditions presented by the selected site, but the cost of this treatment is not viable for developing countries. In addition, the amount of waste generated by using these sorbents would be enormous (more than 2800m³ of sorbent per well per month). This suggests that there is still room for improvement, and much smaller and more isolated iron oxide nanocrystals could offer an important alternative for water treatment under these conditions.
To lay the groundwork for further studies of nanocrystals, commercial nanoparticles (Ferroxide Black 78P) were used to optimize a number of experimental conditions surrounding residence time, sorbent concentration, and regeneration procedures. These commercial systems also offered a test-case for evaluating proposals for silica mitigation, such as the addition of calcium to test waters. Though regeneration is not complete in column setups with Salamanca water, before breakthrough starts it is similar before and after regeneration. This permits the treatment of similar amounts of water until reaching MCL in several cycles. On the other hand, the solution proposed for the mitigation of silica, the use of Ca\(^+\) ions, while promising in the laboratory was not effective in real water. These studies not only provide insights into what existing technologies may offer to communities who face issues with arsenic contamination in drinking water, but also lay a foundation for characterizing the performance and feasibility of newer materials based on isolated and highly uniform iron oxide nanocrystals.
Iron oxide nanoparticles for arsenic removal

4.1. Introduction

This chapter focuses on the technical evaluation of iron oxide nanoparticles (IO-NPs) as arsenic sorbents. In particular, it examines nMag, which has previously shown great potential in batch experiments under lab conditions. While some extant research examines this potential, the studies performed under real conditions remain quite limited. In 2006, the Colvin group became the first researchers to propose using magnetite nanoparticles for arsenic adsorption, which because of the sorbent’s large surface produced very little waste material. This approach carried the added advantage of magnetically driven separation at low external fields. Further studies of the size dependent arsenic adsorption and desorption were published, which indicated that decreasing the size of magnetite particles...
dramatically enhanced its arsenic adsorption capacity. Based on this knowledge, in 2008 a collaboration in Guanajuato, Mexico between Rice University and the Center for Water Technology Innovation in Guanajuato (CITAG) was established with the final goal of performing pilot scale experiments for arsenic removal from drinking water using magnetite nanoparticles. Farrell published the results of this collaboration in 2014. In order to demonstrate the efficacy of this process, Farrell used commercial nanoparticles that were too aggregated to reflect the results obtained for smaller and more dispersed nanoparticles. An outstanding question remained which was the utility of the smaller nanoparticles for arsenic remediation.

Moreover, despite the large number of nanomaterials that show potential for environmental applications, in particular those that are iron based, and the variety of possible applications reported in recent years, few studies have examined performance under realistic field conditions. Habuda-stanić and Nujić published a review of arsenic removal research using nanoparticles in early 2015. The authors reviewed studies of nearly 100 nanomaterials that were conducted between 2011 and 2014. They found that most of the research only reported bench performance, asserting that full-scale application is still decades away. This chapter thus explores the potential of IO-NPs as arsenic sorbents under conditions that are close to full-scale deployment, and compares bench experiments so common in the research community to the findings from field sites.
4.2. Synthesis of nanoparticles

Thermal decomposition was the method of synthesis used in this study. It is the preferred method of synthesis to prepare nMag as it yields highly uniform nanocrystals\textsuperscript{32} that are easily transferred to water using fatty acid bilayers\textsuperscript{34} or amphiphilic polymers\textsuperscript{35,36}. The specific method of nMag synthesis that was employed in this study is reported in section 0. By changing parameters such as iron precursor concentration, reaction temperature, reaction time, and the ratio between iron precursor and surfactants, size and shape were controlled, as shown Figure 4.1 and Figure 4.2, respectively.

![Figure 4.1](image)

**Figure 4.1  Size-controlled synthesis of nMag.** By changing the reaction conditions, nanocrystals of varying dimensions can be produced. TEM images of four sizes are shown below: (i) 6nm, (ii) 13nm, (iii) 18nm, and (iv) 24nm. The size distribution is shown below each image.
Figure 4.2  Shape-controlled synthesis of nMag.
By changing the reaction conditions, the shape of the nanoparticles can be modified. TEM images are shown of nanospheres and nanocubes close to 14nm (i, ii) and 19nm (iii, iv).

4.3. Effect of surface coating

The effect of different surface coatings on the particles’ adsorption capacity and removal efficiency was examined in this study. The work was limited to the evaluation of spherical, as opposed to cubic, nanoparticles because of these samples were easier to transfer into water. nMag with a size of 21±2nm (Figure 4.3.i) was transferred to water using the amphiphilic copolymer PAMPS-LA (poly-2-acrylamido-2-methylpropane sulfonic acid, lauryl acrylate) as described in section 2.2.1.3. A schematic representation of the NP-polymer system is shown in Figure 4.3.ii; the chemical structure of the polymer is displayed below the scheme. This polymer was selected for its stability in high salinity solutions.124
Figure 4.3  TEM image and isotherms of nMag-PAMPS
(i) TEM image of water soluble nMag coated by a PAMPS-LA system. (ii) Isotherms of nMag-PAMPS exposed to arsenic synthetic water with and without silica present. Two-step isotherms were observed when using the system nMag-PAMPS-LA.

Arsenic adsorptions were performed with and without silica present (Figure 4.3.ii). However, its adsorption capacity for arsenic, $47.9 \text{mg As/g magnetite}$, was significantly lower than that reported previously for nMag-Brij 30$^{117}$ and nMag-Igepol CO-630$^{125}$. In addition, evidence of a two-step isotherm was observed, as phenomenon also observed by Yean et al.$^{117}$ Multistep Langmuir isotherms are usually observed when the contaminant adsorbate enhances the affinity of the surface to the adsorbate.$^{126}$ It was inferred that this effect was related to the bilayer system that was present in both nMag-surfactant/polymer systems, and that the second step occurs when the bilayer coating is destabilized and the iron oxide surface becomes more accessible. This would explain why the step occurs at higher arsenic concentration for the PAMSP-LA polymer coating. One would expect this surface coating to be far more stable than the one formed by the smaller Brij 30
surfactant. Because of this poor performance, future work focused on polymers that employed ligand exchange (e.g. the complete removal of the organic coating) as a water transfer strategy.\textsuperscript{127}

To observe the effect of the surface coating in a simplistic manner, three polymers were selected because of their biocompatibility\textsuperscript{127} and the charge: polyacrylic acid (PAA, negative charged), polyethylene glycol (PEG, neutral), and polyethylimine (PEI, positive charged). In Figure 4.4, the schematic representation of the NP-polymer systems (not to scale) and the chemical structures of the polymer are shown. In the case of the negatively charged polymer, one carboxylate will replace the oleate group on the surface of the nMag (Figure 4.4.i); because of the charge repulsion, the polymer will attempt to stretch out as much as possible as shown in Figure 4.4.iii. This is not the case when the polymer has no charge: PEG polymer agglomerates and chains can interact with each other, forming a fleecy surface as shown in Figure 4.4.iv. In the case of the PEI used, the polymer is branched, which gives the system a steric interaction in addition to the charge repulsion. This will generate a less compact surface coating as shown in Figure 4.4.v.
Figure 4.4  **Schematic representation of water soluble nMag systems.**
nMag (i) was transferred to water using polymers. PAMPS-LA covers nMag (ii) with a bilayer system. When using ligand exchange for water transfer, the polymer replaces a few chains of the oleic acid. PAA, PEG, and PEI were used. In nMag-PAA (iii), the negative chains of PAA should limit the polymer packing at the interface. In nMag-PEG (iv), PEG is expected to wrap the particle. In nMag-PEI (v), the positive chains are branched, which make the individual chains more voluminous. The chemical structure of the polymer is shown below each corresponding particle.

The conditions for water transfer of each polymer were determined in every sample on a small scale by determining the ratio of polymer/nMag that would generate the highest water transfer efficiency. As shown in Figure 4.5.i the ideal condition for PEG is clearly 2mmol\textsubscript{PEG}/mol\textsubscript{Fe}. However, in the case of PAA (Figure
4.5.ii) the phase efficiencies are very similar at different polymer/nMag ratios (mmol\text{polymer}:mol_{Fe} is used for easier quantification). We selected a relatively low concentration of polymer since the solution becomes cloudy at higher concentrations. A similar behavior was observed with PEI. Once the ideal condition was found, the process was scaled up to generate enough water-soluble nanoparticles (100mg) for the adsorption experiments. It is important to note that this process was carried out for each sample that was transferred to water, not only that which is presented here. The ideal mmol\text{polymer}:mol_{Fe} for every sample was below 5.

![Graphs showing water transfer efficiency vs. mmol\text{polymer}/mol_{Fe}]

**Figure 4.5  Determination of water transfer conditions.**
The optimization for the water transfer of nMag is studied for each nMag sample. Examples of this optimization for PEG (i) and PAA(ii) are shown.
Figure 4.6  nMag with different coatings.
An organic sample of nMag (i) was transferred to water using PEG (ii), PAA (iii), and PEI (iv) by ligand exchange. The size distribution is shown below each image.

For the analysis of the surface coating, a sample with a very small nMag was selected so as to maximize the surface fraction of the sample (Figure 4.6.i). Although the size distribution was broader, the smaller diameter materials were often formed in large quantities fulfilling the practical needs for sorbent evaluation studies. The samples transferred to water by PEG (Figure 4.6.ii), PAA (Figure 4.6.iii) and PEI (Figure 4.6.iv) were larger than the original sample (Table 4.1). As shown in Figure 4.6 even while the average diameters of the water-soluble nMag grow as the polymer coatings are added, the overall size distributions remains the same as the as-prepared sample. The hydrodynamic diameter of each sample (nMag, nMag-PEG, nMag-PAA, and nMag-PEI), measured by DLS, is reported in Table 4.1. It is important to remark that DLS cannot accurately measure the hydrodynamic diameters below 10nm, but the obtained values follow the trend that the real values should have therefore they are used for comparison. For the water-soluble
nanoparticles, the hydrodynamic diameters of nMag-PEG and nMag-PAA are very similar. Both PEG (Mw=10,000) and PAA (Mw=15,000) have a similar weight and each are linear polymers. In contrast, nMag-PEI is bigger because of the larger molecular weight of PEI (Mw=25,000) and its branched geometry. The diameter increase is too small to be accounted for by aggregation of nanoparticles; additionally the TEM micrographs after transfer to water show that the particles remain isolated (Figure 4.6).

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<thead>
<tr>
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<th>Core diameter (nm)</th>
<th>Hydrodynamic diameter (nm)</th>
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<tbody>
<tr>
<td>nMag</td>
<td>3.6 ± 1.6</td>
<td>8.8 ± 1.3</td>
</tr>
<tr>
<td>nMag-PEG</td>
<td>7.4 ± 2.0</td>
<td>36.8 ± 5.7</td>
</tr>
<tr>
<td>nMag-PEI</td>
<td>5.8 ± 1.8</td>
<td>63.8 ± 3.6</td>
</tr>
<tr>
<td>nMag-PAA</td>
<td>5.6 ± 2.3</td>
<td>27.3 ± 1.5</td>
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Table 4.1  **Summary of nanoparticles size with the different coatings.**
The core and hydrodynamic diameters were measured for the particles in hexane, and after transfer to water using PEG, PEI and PAA coatings.

Because of the amount of material required, instead of full isotherms adsorption experiments in batch were performed at only significant concentrations and are reported in removal efficiency in Figure 4.7. The removal efficiency is calculated by the remaining arsenic concentration in solution, after equilibration time, normalized by the initial arsenic concentration; the result is reported in percent values. Three initial concentrations of arsenic were used to evaluate the effect of surface coating: 0.02mg/L, 0.2mg/L, and 1.8mg/L. The removal efficiency of
the four systems (nMag, nMag-PEG, nMag-PAA and nMag-PEI) is shown in Figure 4.7.i. Results coincide with the expectations of the study: the negatively charged nanoparticles show low removal efficiency at any arsenic concentration. The removal efficiencies for the positively charged and neutral nanoparticles are very similar: greater than 90% for both systems at the three selected concentrations.

**Figure 4.7 Effect of nanoparticles surface coating on arsenic adsorption.** Removal efficiency (i) and adsorption capacity (ii) are shown for the nanoparticles nMag, nMag-PEG, nMag-PAA, and nMag-PEI at three different initial arsenic concentrations: 0.02mg/L (cyan bars), 0.2mg/L (dark gray bars), and 1.8mg/L (orange bars).

When comparing the adsorption capacities (Figure 4.7.ii), the same trends are observed: nMag-PAA has extremely low adsorption capacities, whereas nMag-PEG and nMag-PEI have very similar adsorption capacities. The capacities of nMag-PEG and nMag-PEI are quite high for the equilibrium concentration at the conclusion of the experiment, around 200μg/L. However, neither the capacities nor the removal efficiency of the neutral particle system (nMag-PEG) are similar to that
found for the particle with no coating (nMag). Although this uncoated control sample was not fully dispersed in the water, we speculate that a ligand exchange between the carboxylate surface groups and the arsenate could have occurred thus explaining its surprising performance. After the experiment was concluded (Figure 2.7.iii), some nanoparticles were aggregated and remained in the bottom of the tube. This may have occurred because when carboxylates are replaced by arsenate on the particle surface the nanoparticle is no longer soluble in hexane or in water.

Although the results were promising using nMag-PEG or nMag-PEI, because of the samples’ high cost and long preparation times, other methods of IO-NP synthesis were explored.

### 4.4. Effect of synthetic methodology

To examine the effect of synthetic methodology, nMag performance was compared for particles prepared by thermal decomposition, coprecipitation and hydrothermal methods. Those prepared by a hydrothermal method were purchased from Rockwood Pigments. TEM images of the IO-NPs used are shown in Figure 4.8. Nanoparticles (NPs) prepared by thermal decomposition were disperse and around 20nm (Figure 4.8.i). NPs prepared by coprecipitation were sonicated in water to prepare the TEM grid (Figure 4.8.ii); even then, small aggregates (around 200nm) of nanoparticles around 10nm were observed. Large aggregates of nanoparticles around 100nm were observed for those prepared by a hydrothermal method (Figure 4.8.iii). Adsorption isotherms without and with silica were carried out for
the three materials, which are shown in Figure 4.9. The summary of the parameters obtained when the experimental data were fitted to a Langmuir model is presented in Table 4.2.

![TEM images of magnetite nanoparticles](image1)

**Figure 4.8** Magnetite nanoparticles prepared by different synthetic methods.

TEM images are shown of magnetite nanoparticles prepared by thermal decomposition (i), coprecipitation (ii), and hydrothermal (iii). Because of the aggregation present in the last two samples, size distribution was not determined.

![Adsorption isotherms](image2)

**Figure 4.9** Adsorption isotherms of magnetite nanoparticles prepared by different synthetic methods.

Adsorption isotherms without (i) and with silica (ii) are shown for nanoparticles prepared by thermal decomposition (purple circles), coprecipitation (cyan triangles), and hydrothermal (black squares).
Table 4.2  Summary of the parameters of isotherm experiments for magnetite nanoparticles

A summary of the parameters ($q_{\text{max}}$ and $k_L$) obtained by fitting the experimental data to a Langmuir model (Figure 4.9) is shown. The adsorption capacities observed at 10ppb and 100ppb, $q_{10}$ and $q_{100}$ are also shown.

When comparing their performance, it is evident that the two particles prepared in the lab performed better than the commercially sourced sample (Figure 4.9.i). This is undoubtedly related to their size, but also to their aggregation state. The largest and most heavily aggregated nanoparticles show the poorest performance. However, despite the fact that NPs prepared by coprecipitation (CPT) are smaller than nMag, they do not have the expected higher adsorption capacities. This is likely due to their high level of aggregation and the consequent inaccessibility of their surfaces.

When analyzing the performance further, the four parameters summarized in Table 4.2 provide different information: $q_{\text{max}}$ is related to the total active sites for adsorption in the surface; $k_L$ provides information about how favored adsorption is; while $q_{10}$ and $q_{100}$ are the capacities of the material at 10ppb and 100ppb, which are significant as correspond to the maximum contaminant level (MCL) and the approximate arsenic concentration Salamanca groundwater, respectively.
In the presence of arsenic only, it was observed that the capacities at arsenic concentrations of 10ppb \((q_{10})\) and 100ppb \((q_{100})\) are higher for the smaller particles (CPT). In contrast, the dispersion of the particles for the maximum capacity \((q_{\text{max}})\) shows a significant difference (Table 4.2), \(q_{\text{max}}\) is greater for nMag. When silica is present in solution (Figure 4.9.ii), the general trend remains the same: NPs prepared in the lab still perform better than those that were purchased. However, the effect is different. In the case of the commercial particles, the silica presence decreased the adsorption capacity by a third, while having little effect on the \(k_L\) parameter. For the particles prepared in the lab, the decrease in the \(q_{\text{max}}\) was only 10% or less in both cases. However, the biggest difference was observed in the \(k_L\) values, where nMag was not affected and the CPT decreased to nearly one third. When silica is present, the adsorption capacities of the dispersed nanoparticles at environmentally significant arsenic concentrations (10ppb and 100ppb) are nearly double when comparing nMag with CPT (Table 4.2).

To confirm these observations, column experiments were performed with Salamanca water drawn from a field site in Mexico. The columns for the nanoparticles purchased and those synthesized by coprecipitation were prepared as described in section 2.4.2.2.1. For the columns with nMag a modification described in section 0 was made. To make sure the PMMA beads were homogenously covered with nMag, SEM images were taken before (Figure 4.10.i) and after (Figure 4.10.ii) the addition of nMag. The presence of nMag changed the contrast of the beads under the electronic microscope, and the coating appears homogeneous as shown in Figure 4.10.ii.
Figure 4.10  SEM images of nMag-covered beads.
SEM images are shown of PMMA beads before (i) and after covering with nMag (ii),
as well as after an in situ treatment with NaOH (iii).

However, when the column made with the nMag-covered beads was run, the
flow rate decreased rapidly after a few hours. This result may be due to the fact that
the excess of organic material present in the sample plugged the porous volume. To
remove the excess of organic material and the oleate groups from the surface of the
NPs, a solution of NaOH 1M was used for backwashing, followed by washing the
column with DI water until pH in the outlet was neutral. When the column was
unassembled, SEM images were taken to observe the effect of NaOH on the nMag-
covered beads (Figure 4.10.iii). In these images, the beads maintained their high
contrast from the nMag coating suggested the particles themselves had not been
stripped off. Also before treatment the beads appeared glued together with
interfaces that were almost joined (Figure 4.10.ii). Such features were absent after
treatment with base.

After the NaOH in situ treatment, the flow was stable and the breakthrough of
arsenic was observed after several bed volumes. To ensure that the organic coating
had been fully removed the sample was also treated with hydride, as described in
section 0. The results for the column experiments are show in Figure 4.11. The
details of the experimental parameters such as the length of the column (L), the bed volume (BV) size and the flow rate (Q) used are given in Table 4.3.

![Figure 4.11](image)

**Figure 4.11** Column experiments of magnetite nanoparticles prepared by different synthetic methods.

RCSSTs were performed with 20%wt nanoparticles loaded in PMMA beads. Nanoparticles prepared by thermal decomposition (i), coprecipitation (ii), and hydrothermal (iii) were used.

Surprisingly, the results for the three columns were very similar. The experimental data and the fitted model are shown in Figure 4.11.i for nMag, in Figure 4.11.ii for the coprecipitation NPs, and in Figure 4.11.iii for the hydrothermal nanoparticles. In Table 4.3, the derived parameters $R$ (retardation factor) and $D$ (coefficient of hydrodynamic dispersion), as well as the coefficient of determination ($r$) of the fitting model (red line), are summarized. Contrary to expectations, the commercial nanoparticles had the largest retardation factor. However, both the commercial and the coprecipitation column had very large values for the coefficient of hydrodynamic dispersion ($D$), which is a direct reflection of the large particle agglomerates. The nMag column had a retention factor that was nearly equal to that measured for the hydrothermally prepared materials. However, the $D$ was smaller.
It can therefore be inferred that the agglomerates of particles were not as large as those present in the other columns. Another interesting fact is that during the assembly of the column and the corresponding prewashing the wash solutions were distinctly orange. This may be a result of residual by-products of the reaction of nMag with the super hydride solution.

<table>
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<th>L (cm)</th>
<th>BV (mL)</th>
<th>Q (mL/min)</th>
<th>R</th>
<th>D (cm/min)</th>
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<td>10</td>
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<td>Hydrothermal</td>
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<td>6.53</td>
<td>11</td>
<td>224.8</td>
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</tr>
</tbody>
</table>

Table 4.3 Summary of the parameters for nanoparticles-beads column experiments.
A summary of the parameters used and obtained ($R$, $D$ and $r$) by fitting the experimental data from Figure 4.11 to an advection diffusion model is shown. Columns were 20%wt nanoparticles loaded in PMMA beads.

Because of the unexpected similarity in the column experiments, a further study was performed to examine the effect that aggregation of the nanoparticles has on both batch and column experiments.

4.5. Effect of particle aggregation

The effect of particle aggregation on adsorption capacity was also examined as part of this study. Among extant research on this topic, the Colvin group has demonstrated over the years that the agglomeration of particles decreases the
adsorption capacity of nanomaterials. This agglomeration is usually observed in commercial nanoparticles; even when breaking the aggregates through sonication helps to improve their capacity, they do not usually compare to the well-dispersed NPs. For this reason, further studies of aggregation were conducted with the NPs prepared in the lab, with special efforts dedicated to evaluating the performance of nMag distributed as evenly as possible over the support media in a column setup.

4.5.1. Batch experiments

To understand the effect of aggregation, thermal decomposition and coprecipitation particles were selected since both systems can be successfully stabilized in water using PEG. TEM images of the samples used are shown in Figure 4.12 Since aggregation in the coprecipitation particles prevented us from measuring size distributions, corresponding diameter distribution histograms could not be generated. Figure 4.12.i shows the nanoparticles prepared by thermal decomposition and suspended in hexanes; the term nMag will be used to refer to this sample. In Figure 4.12.ii, the nMag transferred to water with PEG is shown; this will be referred to as nMag-PEG. In Figure 4.12.iii, the coprecipitation prepared without any surfactant is shown, which will be called CPT. Finally, in Figure 4.12.iv, coprecipitation NPs synthesized in the same conditions as CPT but with PEG present in the solution during the synthesis are shown; this sample will be referred to as CPT-PEG.
TEM images of nMag in hexanes (i) and covered with PEG (ii) show that nanoparticles are fully isolated from each other. In contrast, aggregation is observed in nanoparticles prepared by coprecipitation with non-coating (iii) and PEG coating (iv).

As Figure 4.12 shows, the degrees of agglomeration between the different particles are different. nMag and nMag-PEG are fully dispersed. On the other hand, CPT aggregates are very compact; the nanoparticles can barely be distinguished from each other. In CPT-PEG, aggregates are present but they are more extended; this may be a consequence of drying effects and it is possible that in the solution, they are composed of only a few NPs.

In Figure 4.13, the adsorption performance of the four samples is analyzed. Full isotherms were not performed because of the amount of sample they required. Instead, the removal efficiency of three different concentrations of arsenic was selected for each condition. As in the previous experiments, the first condition selected solely contained Arsenic at pH 7; the second condition used the same solution with silica present in a concentration of 85mg/L. The arsenic removal efficiency was measured for both conditions (Figure 4.13.i shows the performance for arsenic alone and Figure 4.13.iii shows the performance for arsenic and silica). The corresponding adsorption capacities are shown in Figure 4.13.ii for the
condition without silica and in Figure 4.13.iv when silica is present. For sample limitations, nMag-PEG was not analyzed when silica was present.

![Graphs showing arsenic removal efficiency and adsorption capacity](image)

**Figure 4.13 Effect of aggregation of nanoparticles in arsenic adsorption.** Arsenic removal efficiency (i, iii) and adsorption capacity (ii, iv) are shown for the nanoparticles without and with silica present. nMag and coprecipitation nanoparticles (CPT) were studied with and without PEG coating at four different initial arsenic concentrations: 0.02mg/L (cyan bars), 0.2mg/L (dark gray bars), 1.8mg/L (orange bars), and 17.2mg/L (olive bars). When silica was present (iii, iv), [SiO₂] = 90mg/L.

The effect of aggregation is clearly demonstrated in Figure 4.13.i. nMag-PEG, the more dispersed sample, has more than 90% removal efficiency at the three arsenic concentrations analyzed (0.02mg/L, 0.2mg/L, and 1.8mg/L). CPT-PEG
follows very closely, with the efficiency decreasing at the higher concentration. Compared to nMag-PEG, this suggests that the maximum adsorption capacity, \( q_{\text{max}} \), will be lower for CPT-PEG. In Figure 4.13.ii, this hypothesis is supported by the experimental adsorption capacity, where the nMag-PEG is almost four times bigger than CPT-PEG. Surprisingly, the behavior of nMag and CPT are very similar, with the nMag values of removal efficiency and \( q \) being slightly larger. This could be analogous to what was observed in aggregates in solids: the nanoparticles inside the aggregates do not have interaction with the solution and cannot adsorb arsenic. The same process occurs with the nanoparticles inside the small capsules of hexanes that are intrinsically formed when in contact with water.

As shown in Figure 4.13.iii, it was observed that all the efficiencies decreased when silica was present, as expected. At the lowest arsenic concentration (0.02mg/L), the removal efficiency followed the anticipated trend, with the highest performance observed in the dispersed nanoparticles (CPT-PEG), followed by CPT, which was in turn closely followed by nMag. Again, nMag-PEG was not evaluated in this condition because the sample was not large enough. However, it was quite surprising that, despite the effect described with the aggregation of NPs in hexanes, nMag performed best at the higher concentration levels (1.8mg/L and 17.2mg/L). If the capacities observed in Figure 4.13.ii and Figure 4.13.iv are compared, the effect of silica is greater in NPs prepared by coprecipitation; either in solid or dispersed form, the performance decreases by at least half at each level. In addition, it can be inferred that the maximum adsorption capacity will be reached at lower arsenic
equilibrium concentrations, which makes the nMag material very promising even in harsh conditions.

4.5.2. Column tests

A similar strategy as that described in section 4.4 was implemented in order to perform the column tests. nMag was deposited over PMMA beads and, as is shown in Figure 4.10.ii, the coverage was very homogenous. The coverage of NPs over the beads is more evident when the beads are observed at higher magnification. SEM images of the beads’ surface before (Figure 4.14.i) and after (Figure 4.14.ii) adding nMag are shown. Despite the fact that the image is blurred because of the organic composition of the beads, the particles can be visualized because of the brightness of nMag. As proposed in section 4.4, the removal of the oleate coating of the nanoparticles was attempted once it was deposited over the beads. In this case, super hydride solution, a stronger reagent, was used to ensure the complete removal. Degradation of the PMMA beads was observed when the treatment was carried out externally; however, as shown in Figure 4.14.iii, the removal seems to be efficient, and nanoparticles seem to be fixed over the etched beads. Because of the shorter contact time, it was expected that a similar but less aggressive result would be obtained when treatment was carried out directly with the material already mounted in a column setup. However, the degradation observed in the beads was different. In this case, the beads formed a rubber-like material that did not allow the free flow of water. In Figure 4.14.iv, the morphology
of the material is shown. Because of the results obtained with the PMMA beads, a decision was made to attempt the same approach with sand, a simple and inorganic support. The results of the same kind of treatment on sand are shown in Figure 4.15.

![Images of PMMA beads and sand samples](image)

**Figure 4.14  nMag-covered beads after treatment with super hydride.**
High magnification SEM images of PMMA beads before (i) and after covering with nMag (ii); and after an external (iii) and *in situ* (iv) treatment with super hydride solution are shown.

In Figure 4.15.i the smooth surface of the sand is observed before the addition of nMag. In Figure 4.15.ii, the surface is shown with a 1%wt nMag added. NPs can be seen as tiny white points that are homogenously distributed. A control was made to observe the effect of the super hydride on the sand’s surface; Figure
4.15.iii shows that the surface remains smooth. When the treatment is carried out after the addition of nMag, small coarse areas are observed over the smooth surface (Figure 4.15.iv). Although there is evidence of some aggregation occurring, the surface seems homogenous enough for a 1% w/w nMag to sand.

Figure 4.15  nMag-covered sand after treatment with super hydride. High magnification SEM images are shown of sand (i, iii) and nMag-covered sand (ii, iv) before and after an external treatment with super hydride solution.

When the nMag column was washed with water before the experiment began, some mobility of the particles was observed. In Figure 4.16.i, the movement of the nanoparticles can be clearly seen. The NPs were dragged to the top because packing with water occurs from bottom to top. The leaching of nanoparticles during
the experiment is minimum since it is run in a downstream flow; no particles were observed in the bottom part at the end of the experiment. To verify this, SEM samples of the three areas were taken. Figure 4.16.ii shows the top part where some aggregates of particles can be observed. Figure 4.16.iii shows that the active bed is still very homogenous and the roughness provided by the nanoparticles remains after the experiment. In contrast, the bottom part shown in Figure 4.16.iv is very smooth.

Nanoparticles prepared by coprecipitation were purchased and also prepared with sand at 20%wt. The morphology of sand is presented in two magnifications in Figure 4.17.i and Figure 4.17.v as a point of reference. The homogeneity of the 1%wt nMag in sand is displayed in Figure 4.17.ii, and areas highly populated with NPs can be observed in Figure 4.17.vi. In Figure 4.17.iii small and big aggregated of nanoparticles are shown; nanoparticles can be spotted at a higher magnification (Figure 4.17.vii). In Figure 4.17.iv, large aggregates of the hydrothermal nanoparticles can easily be observed; the compactness of these aggregates is clear in Figure 4.17.viii. The SEM images clearly demonstrate that a comparison between the different degrees of aggregation can be established with these three columns.
Figure 4.16  nMag-sand column.
Photograph of a 1%wt nMag-sand column after experiment (i) is shown. The SEM images of the three areas, top (ii), active bed (iii), and bottom (iv), are also shown.

The performance of these columns with Salamanca water is shown in Figure 4.18.
Figure 4.17  SEM images of active bed of magnetite/sand columns.
SEM images of sand covered without (i, v) and with magnetite nanoparticles prepared by thermal decomposition (ii, vi), coprecipitation (iii, vii), and hydrothermal (iv, viii) are shown at higher and lower resolution, respectively.

Figure 4.18  Sand column experiments of magnetite nanoparticles.
RCSSTs were performed with nanoparticles loaded in sand. Nanoparticles prepared by thermal decomposition (i), coprecipitation (ii), and hydrothermal (iii) were used.

The experimental data and the corresponding fitting are shown in Figure 4.18.i for nMag, in Figure 4.18.ii for the nanoparticles prepared by coprecipitation, and in Figure 4.18.iii for the nanoparticles that were purchased. The experimental details and the derived parameters for the three columns are given in Table 4.4.
A summary of the parameters used and obtained ($R$, $D$ and $r$) by fitting the experimental data from Figure 4.18 to an advection diffusion model is shown. Columns made of coprecipitation and commercial nanoparticles were 20%wt in sand; nMag columns were 1%wt.

As expected, the worst performance was shown for the more aggregated nanoparticles, which were prepared through a hydrothermal method (Figure 4.18.iii). For this fitting, only the points below 100BV were considered because of the decrease in the $[\text{As}]/[\text{As}]_0$ ratio; it is not unusual to see this effect in sand columns. The retardation factor ($R$) for this column was 13, and the hydrodynamic dispersion coefficient ($D$) was 73.3 cm/min, which is lower than that observed when the column was prepared with PMMA beads (Table 4.4).

The best observed performance was for the column prepared with coprecipitation NPs, which yielded an $R$ of 145 and a $D$ of 31.8 cm/min. This result represents the increase in bed volumes treated before the outlet arsenic concentration reached the MCL. The $D$ value also suggests that the nanoparticles were more homogenously distributed in comparison with the column reported in section 4.4.

<table>
<thead>
<tr>
<th></th>
<th>$L$ (cm)</th>
<th>$BV$ (mL)</th>
<th>$Q$ (mL/min)</th>
<th>$R$</th>
<th>$D$ (cm/min)</th>
<th>$r$</th>
</tr>
</thead>
<tbody>
<tr>
<td>nMag</td>
<td>7</td>
<td>5.50</td>
<td>2.83</td>
<td>19</td>
<td>6.3</td>
<td>0.976</td>
</tr>
<tr>
<td>Coprecipitation</td>
<td>10.5</td>
<td>8.25</td>
<td>4.08</td>
<td>145</td>
<td>31.8</td>
<td>0.990</td>
</tr>
<tr>
<td>Commercial</td>
<td>25.5</td>
<td>20.03</td>
<td>6.44</td>
<td>13</td>
<td>73.3</td>
<td>0.961</td>
</tr>
</tbody>
</table>

**Table 4.4 Summary of the parameters for nanoparticles-sand column experiments.**
The 1%wt nMag performed better in sand than the 20%wt commercial NPs. Because of the difference in the loading of the NPs in the column, the performance of nMag cannot be directly compared to the 20%wt coprecipitation NPs in sand. However, it is expected that with the same loading, a column with nMag would have a higher retention factor. Nevertheless, a direct comparison between the $D$ values can be performed; as anticipated, when the nanoparticles are more homogenously dispersed, $D$ has a lower value.

Despite the fact that a column with a higher loading of nMag was not completed for technical reasons, this is the first column to document the performance of nanoparticles in column setup. The use of iron oxide-coated sand was previously documented for water treatment, especially for arsenic remediation; however, to our knowledge, the use of nanoparticles in sand columns has not been documented because of the associated technical difficulties. Hristovski et al. reported nanoparticle performance in batch experiments, but when testing in a column relied on a commercial material comprised of nanoparticles modified with an adhesive. While this is a valid strategy, as new nanomaterials are proven to be effective for arsenic removal, their performance should be documented in a column setup similar to that presented here.

### 4.6. Conclusions

This chapter focused on the evaluation of iron oxide nanoparticles (IO-NPs) as arsenic sorbents. Studies were performed that compared the effect of the surface
coating, the type of methodology used to prepare the material, and the degree of aggregation on the samples’ adsorption capacity. As anticipated, these three parameters were profoundly correlated to the performance of the materials as arsenic adsorbents. One of the major conclusions that can be drawn is that the nanoparticles’ arsenic removal efficiency improves with greater nanoparticle dispersion. For this reason, nanoparticles prepared in the lab that can be easily modified were found to perform best in batch experiments.

One of the strategies for dispersing nanoparticles in water involved the use of polymers or surfactants. The results presented here demonstrate the importance of the selection of the surface coating. In particular, neutral or positively charged polymers are needed for arsenic adsorption in order to avoid surface charge from decreasing the performance of the material.

Of the different analyses, nMag were found to have great potential in both batch experiments under lab conditions. Their performance under high silica concentrations was not significantly affected. Efforts were therefore made to evaluate their performance in a column setup. This type of experiment has not been reported in the literature for any other nanoparticle. Although the loading of the column differed from that used for the other types of nanoparticles, the column prepared with nMag performed better than the commercial NPs column.

It is important to recognize that the use of iron oxide nanoparticles, either those prepared in the laboratory or sourced commercially, is not as yet cost effective for the scale required to treat arsenic in drinking water. While nanoparticles offer the advantage of reducing the amount of material used for
treatment, there are numerous technical difficulties associated with the implementing a column-based remediation technology capable of using them. Designing a material that offers the advantages of nanoparticles without the complications is therefore imperative. The following chapters address this objective.
Clusters of Iron oxide nanoparticles for arsenic removal

5.1. Introduction

Design strategies have already been reported for nanoparticles, mainly for specific medical applications. The design usually considers not only the core structure of the nanoparticles, but also the surface modifications and the possibility of assembled structures. This design-for-purpose focus has recently been noticed in the environmental sciences. Particularly, the use for mesoporous materials or nanomaterials aggregated by cooperative self-assembly brings new opportunity for the application of nanomaterials in environmental applications.

One type of mesoporous materials that have gained attention is the hollow nanostructures. Because of their low density and high surface-to-volume ratio, the application of hollow structure in catalysis and sensing, lithium-ion batteries, drug
delivery is of great interest. Their use has also already been reported for the heavy metal and organic remediation, as well as in their application in sensors. However, the preparation of hollow structures usually requires a step of dissolution or etching, or the use of templates.

Another type of nanomaterial that has increasing notice is the colloidal nanoparticles clusters (CNC), because the properties of the individual nanoparticles are kept but also new collective properties are derived from the hierarchical structure. Clear examples of this enhancement are the use the CNC of magnetic nanoparticles in biomedical applications and in lithium-ion batteries. In biomedical applications the use of CNC is preferred over individual nanoparticles because with this organized agglomeration, the particles kept their superparamagnetic properties but have bigger magnetic responsiveness. In the case of their application in lithium-ion batteries is preferred because, in addition to provide the short diffusion pathways for lithium ions that comes from use of nanoparticles, free space that can accommodate volume changes during cycling. However, the formation of these clusters usually requires the clustering of pre-synthesized nanoparticles, either by the self-assembly driven by the surface coating or by the use of hard templates.

Both hollow nanostructures and colloidal nanoparticle clusters have been synthesized using the solvothermal method. The resulting structure depends on the synthetic parameters such as temperature, reaction time and iron salt concentration. During the literature review, it was noticed the main difference between the preparation of both structures was the use of either a surfactant or a polymer favored the formation of clusters. For that reason, the method reported by
Zhang\textsuperscript{141} for the formation of hollow nanospheres was selected. In the original methodology, only iron chloride and urea are mixed in ethylene glycol and treated in an autoclave. Modifications of this method are explored along this chapter, including addition of a polymer, modification of urea and polymer concentration, temperature variation and a time-dependent study with the final goal to understand the mechanism for this reaction. Finally, the performance of the clusters for arsenic adsorption in both batch and column experiments is discussed.

5.2. Solvothermal synthesis

The first hypothesis to confirm was that the presence of a polymer would change the structure from a hollow nanospheres to a cluster of nanoparticles. Unless otherwise stated, most of the similar follow the procedure described in section 2.2.3. In the typical reaction a solution 0.1M of FeCl\textsubscript{3}-6H\textsubscript{2}O and 2mmL of PAA in ethylene glycol is prepared; urea is the added to a final concentration of 1M; the homogeneous mixture is introduced to an autoclave and heated at 200\textdegree C for 24h. The TEM and SEM images of the clusters obtained from that reaction are shown in Figure 5.1.i and Figure 5.1.iii, respectively. When polymer is not added to the mixture, the structures shown in Figure 5.1.ii are obtained; in the SEM images, in Figure 5.1.iv, is more evident that the structures are hollow as some of them show apertures. These pinholes have been reported for other hollow structures due shape fluctuations.\textsuperscript{142}
Figure 5.1  The clusters of nanoparticles are hollow structures
TEM (i, ii) and SEM (iii, iv) images are shown of clusters prepared with the same conditions, the only difference is the presence (i, iii) and absence (ii, iv) of polymer. When polymer is not present, the surface tension is too high and holes appears in the structure; then, the hollow structure is revealed.

It was observed that when polymer was present the shape of the clusters was raspberry-like as shows Figure 5.2.i. By increasing the temperature, the shape is kept but the cluster size and the nanoparticles unit size changes, as shows Figure 5.2.ii. When the same conditions are used with no polymer and less urea, the hollow structure with a thinner shell is formed at low temperature (Figure 5.2.iii) and a single unit with small pores is observed (Figure 5.2.iv) when no polymer and less urea is used at a higher temperature.
Figure 5.2  The size and shape of the clusters is controlled by the synthetic parameters

The nanoparticles and the clusters size changes by modifying the temperature (i, ii). The morphology of the clusters varies by modifying the concentrations of urea and polymer (iii, iv).

Because of difference shapes could be obtained with minimum changes in the synthesis, the effect of each parameter was studied. However, the first concern to address was the reproducibility of the synthesis.
5.3. Reproducibility

The analysis of the repeatability and reproducibility of the reaction is discussed in this section. Preparing a large volume of the reaction mixture and dividing it in three different reactors assessed the repeatability of the reactors. The products of the three reactors set up at 200°C are shown in Figure 5.3.i-iii. After the products were mixed, the sizing of the mixture was carried out; the corresponding histogram is shown in Figure 5.3.iv. The same experiment was performed with reactors for higher temperature. In Figure 5.3.v-vii, the products of the three reactors set up at 285°C are shown. The histogram of the corresponding mixture is displayed in Figure 5.3.viii. In both cases, the standard deviation is around 20%, which is very acceptable even for a single reaction.

Figure 5.3  Repeatability of the clusters synthesis
TEM images of the same synthesis carried out in different reactors at 200°C (i-iii) and 285°C (v-vii) are shown. Histograms of the combined samples are displayed in (iv) for 200°C and (viii) for 285°C.
By preparing three different reactions, at different times, the reproducibility of the reaction was assessed. The TEM images of the three reactions are shown in Figure 5.4.i-iii; the corresponding histogram is showed below the image. In the three reactions, the result presented is the combination of the product of the same mixture run in three different reactors. Thought the histograms vary in shape, the average size varies less than 7%. This is important because for application experiments, large amount of materials is required.

![TEM images](image)

**Figure 5.4  Reproducibility of the clusters synthesis**

TEM images of the same synthesis carried at three different times at 200°C (i-iii) are shown. Histograms are displayed below each image to show the size distribution. Each sample is a combination of the product of the same reaction carried out simultaneously in three different reactors.

Because the reproducibility and repeatability of the reaction was confirmed, the effect of the synthetic parameters in the cluster size and unit size was studied. In most of the results stated below, triplicates were performed for each condition.
5.4. Modification of synthetic parameters

The effects of the urea and polymer concentration were the first parameters to be analyzed. The results are shown in color contour plots in Figure 5.5.

**Figure 5.5** Effect of the urea and polymer concentrations in the unit and cluster size

Contour plots to visualize the effect of urea and polymer concentration in the cluster size (i, ii) and the unit size (iii, iv) are shown for two temperatures, 200°C (i, iii) and 285°C (ii, iv). At low concentrations of polymer, both the cluster and the unit size increase; the same is observed for urea concentrations with a less perceptible outcome. The magnitude of the effect is also sensible to the reaction temperature.
Figure 5.5.i and Figure 5.5.ii show the effect of the urea and polymer concentrations in the cluster size at 200°C and at 285°C, respectively. The trends are similar at both temperatures, but the changes are less drastic at 200°C. The bigger clusters are obtained when no polymer is present and urea concentration is 1M; the biggest ones are obtained at those conditions at higher temperature. When polymer is present, the change in cluster size respect urea concentration is not significant at 200°C. Lower concentrations of urea were not used because the clusters are not longer formed; at 285°C, 0.5M of urea and no polymer, the structure shown in Figure 5.2.iv is formed. A similar case was reported by Yu\textsuperscript{76}: in the dodecylamine (DDA) concentration dependence study, when the concentration of DDA was too low, the formation of rhombic porous nanoparticles was observed. In that case, the DDA was used as a template, at it forms micelles in ethylene glycol; this suggest that urea has a similar role generating the interface for the hollow structure.

Figure 5.5.iii and Figure 5.5.iv show the effect of urea and polymer concentrations in the nanoparticle (unit) size at 200°C and at 285°C, respectively. The trends are less similar than with the cluster size. For both temperatures is true that particle size is smaller when the concentration of polymer is higher. At 200°C is it clear that the concentration of urea has a small effect in the particle size; this is not completely true at 285°C, as when there is not polymer, and urea concentration is 0.5M, the unit size is the same as the cluster size. More experiments should be done to confirm this trend. Higher concentrations of urea and polymer were not tried because of the loading capacity of the reactor. However, it is very clear that the
similar trend in both unit and cluster sizes can be extracted at both temperatures, but changes at higher temperature are more substantial.

The effects of the reaction temperature and the volume of reaction mixture loaded in the reactors in both the cluster size and the unit size are shown in Figure 5.6.

![Figure 5.6 Effects of temperature and volume in the unit and cluster sizes](image-url)

Cluster size (i) and unit size (ii) are directly affected by the reaction temperature. At higher temperature, smaller clusters with bigger nanoparticles. The volume of the reaction seems to have not effect in the cluster size, and a small one in the unit size.

Figure 5.6.i shows that the reaction temperature has a big effect in the cluster size. After 200°C, as the temperature increases, the cluster size decreases when everything else is kept constant. On the other hand, Figure 5.6.ii shows that the reaction temperature has the opposite effect in the unit size. This agree with what previously reported for the preparation of iron oxide nanoparticles by solvothermal synthesis, the higher the temperature is, the bigger the unit size is. Surprisingly, the volume of reaction mixture loaded to the reactor has not significant effect in
neither size. This would allow the generalization of the findings above reported and higher concentrations of urea and polymer could be explored without surpass the loading limitation of the reactors.

As some approaches for hollow nanostructures include steps with hydrothermal synthesis, the addition of water to the reaction was explored. In Figure 5.7, the effect of water added in different amounts is shown.

![Figure 5.7](image)

**Figure 5.7 Adding water to reaction mixture changes the cluster and unit sizes**

Three different reactions ran with the same conditions only varying the amount of water present in the reaction mixture: 0% (i), 7.7% (ii) and 33.3% (iii). At higher percent of water, the unit size decreases. With the presence of a small amount of water, there is aggregation between the clusters; at higher amounts, the disorganize aggregation of particles is preferred.

In Figure 5.7.i, the original reaction – without water – at 285°C is shown; this temperature was selected because more significant changes were observed when varying other parameters at this temperature. Water was added after the iron salt and the PAA are fully dissolved in EG, but before urea is added. Figure 5.7.ii and Figure 5.7.iii show the product when water is 7.7% and 33.3% of the total volume of the reaction mixture. It is clear that the size of the nanoparticles decreases as water
is added in bigger amounts. In addition, the cluster formation is affected; when water is present in a 7.7%, the clusters are smaller, but the boundaries between the clusters are not well defined. No formal clusters are observed when water concentration is higher. This can be explained for the favored dissolution of the polymer in water; the more water is present, the fewer polymer chains are attached to the clusters. This would explain the aggregation of particles at higher concentrations of water and the blurry borders of the clusters at low concentrations of water.

5.5. Evolution of the reaction through time

To fully understand the formation of the clusters, a time-dependent study was carried out at 200ºC. Figure 5.8 shows the reaction mixture after 0, 0.5, 1, 1.5, 2, 3, 4, 6, 8, 12, 16, 20 and 24h in the autoclave. The reaction mixture was transferred from the reactor to the vials as soon as it cooled down and left them for a few hours. Samples after 6h of reaction did not settled and were responsive to a magnet.

Figure 5.8   Evolution of the reaction mixture during 24h
Reactions were started and stopped at the corresponding times. Vials show the reaction mixture after a few hours. Samples of time longer than 6h were magnetic.
The homogeneity of the reaction mixture was also followed with SEM; lower and higher magnification images at different times are displayed in Figure 5.9 and Figure 5.10, respectively. TEM images of the several times were taken at lower (Figure 5.11) and higher magnifications (Figure 5.12) to observe the formation of the clusters.

![Figure 5.9 SEM images of reaction at different times](image)

**Figure 5.9  SEM images of reaction at different times**

SEM images of the reaction mixture were taken at different times. Initial reaction mixture (i) became very homogenous after 30min (ii). Aggregates can be observed at times short times (iii, iv). Areas with microspheres can be observed at times longer than 6h (v, vi). Clusters are the main component after 16h (vii, viii).

The initial reaction mixture (Figure 5.9.i) becomes very homogeneous after 30min (Figure 5.9.ii). At higher magnification both times (Figure 5.10.i-ii) show an amorphous shape mostly because of the large amount of organic. At longer times, 1.5h and 3h (Figure 5.9.iii-iv), the formation of huge aggregates is observed. At higher magnifications, these aggregates seems to be formed of some irregular particles embedded in the organic matrix (Figure 5.10.iii-iv).
Figure 5.10  Clusters formation during reaction time
Higher magnification SEM images were taken to follow the formation of the the clusters. The solution is amorphous at the beginning of the reaction (i, ii); however, elongated and irregular particles are observed at short times (iii-v). Clusters can be observed after 8h(vi), but they are well defined only after 16h (vii, viii).

Figure 5.11  TEM images of reaction at different times
TEM images of samples taken every two hours between 2h-8h (i-iv) and every four hours between 8h-24h (iv-viii) were taken. After 8h well-defined clusters are formed.
When observed with the TEM microscope, at 2h, it is clear these structures form a homogeneous phase in the sample (Figure 5.11.i) and they have a spindle-like structure (Figure 5.12.i). After 4h, spheres, of a few hundred of nanometers in size, appear inside the phase with the spindle-like structures (Figure 5.11.ii). These structures disappear over time (Figure 5.11.iii-v); though at 6h are still significantly present in the reaction mixture (Figure 5.10.v), the phase surrounding the formed clusters seems to be only excess an organic phase (Figure 5.12.ii).

![Figure 5.12 Nanoparticles formation during reaction time](image)

Higher magnification TEM images were taken to observe the formation of the clusters. At t=2h (i), rod-like structures are observed. Microspheres are observed after 6h (ii). After 8h (iii), the spheres are more defined, but particles are not observed until time longer than 16h (iv). At times longer than 20h (v, vi), nanoparticles are very distinct.

At 8h, the clusters are already visible over the organic phase even a low magnification SEM images (Figure 5.9.vi). After 16h, the sample is completely
homogeneous and only microspheres are observed (Figure 5.9.vii-viii). At higher magnification, an improvement in the boundaries and symmetry of the clusters is observed when comparing the ones after 8h of treatment (Figure 5.10.vi) and 16h or higher times (Figure 5.10.vi-vii). After 16h not excess of organic was observed surrounding the clusters (Figure 5.11.vi-viii). Also, it was observed that the size of the clusters decreased over time. To corroborate this observation, histograms of the size of the clusters were made from samples after 8h; they are displayed in Figure 5.13.A.

![Figure 5.13](image)

**Figure 5.13** Histograms of clusters size at different reaction times

The size distribution of clusters during different reaction times were computed for three different reactions (A-C). Size distributions are similar between experiments. The distributions were normalized by area.

Another significant observation was made while comparing the clusters at higher magnification TEM images. At 8h, Figure 5.12.iii, the clusters seem to be formed of an amorphous phase; the surface does not look well defined. At 16h,
Figure 5.12.iv, a thin layer of particles seems to be present in the surface; this layer grows in thickness at 20h, Figure 5.12.v, and it is even ticker at 24h, Figure 5.12.vi.

To confirm these findings, a second similar time-dependent study was carried out. All observations were corroborated. The histograms of the clusters for that study are shown in Figure 5.13.B. Both groups of histograms, A (first study) and B (second study) showed that cluster sizes decreased with time. To better visualize this trend, the average values with the corresponding standard deviation (as error bars) are shown in Figure 5.14.

**Figure 5.14  Evolution of clusters size at different reaction times**
Size at different reaction times were measured for three different reactions (A-C). The trend is similar between experiments: the size slightly decreases from 8h to 24h and keeps constant after 24h.
An increasing in the cluster size is observed from the moment the clusters appear, 8h, to around 16h, where they are more defined. After this moment, their size, and the dispersion of the size, decreased. To determine if the size continue decreasing at longer times, a third study was made with longer times; the corresponding histograms are in Figure 5.13.C. After 24h, the size and the standard deviation showed not significant changes.

Characterization of the structures observed at different times was made using XRD (Figure 5.15), Raman (Figure 5.16) and FT-IR (Figure 5.17).

**Figure 5.15  XRD of the synthetic product at different reaction times**

XRD diffractograms were taken at 2h, 4h, 8h, 16h and 24h. After 8h, the peaks agree with the pattern for magnetite (PDF 03-065-3107), shown in black. The main peak observed at 11 degrees in 2h and 4h agrees with the pattern of FeOCl (PDF 00-024-1005), shown in dark red.
For the samples with a reaction time of 2h and 4h, the XRD diffractogram agrees with the pattern for FeOCl (Figure 5.15). This is not surprising as structures similar as observed in Figure 5.12.i has been reported as nano-spindles of FeOCl; they were observed at the glycerol-assisted forced hydrolysis of aqueous FeCl$_3$ at 145°C.$^{144}$ Those are similar conditions to the ones found during the first hours of herein reported reaction; at lower times, the final temperature (200°C) may not have been reached inside of the reactor. Raman also confirms the FeOCl structure (Figure 5.16); the two peaks match the reported wavenumber for FeOCl prepared at low pressure (390 and 340cm$^{-1}$).$^{145}$

![Raman spectra of the synthetic product at different reaction times](image)

**Figure 5.16**  Raman of the synthetic product at different reaction times
Raman spectra were taken at 2h, 4h, 8h, 16h and 24h. After 8h, the typical peaks of maghemite (704, 499 and 360cm$^{-1}$) are present. The peaks for FeOCl (390 and 340cm$^{-1}$) are well defined at 2h, and still present at 4h.
At 8h and longer times, where only clusters are observed by TEM, the XRD agrees with the pattern for magnetite (Figure 5.15). Raman confirms the structure (Figure 5.16); the peaks agree with the ones reported for the oxidation of magnetite, under the exposition to laser, to maghemite.\textsuperscript{146}

![FT-IR spectra](image)

**Figure 5.17  FT-IR of the synthetic product at different reaction times**

FT-IR spectra in transmittance mode were taken at 2h, 4h, 8h, 16h and 24h. The PAA spectrum (red) is shown for comparison. The peaks corresponding to the $-\text{COOH}$ (nearby 3300 and 1750 cm\(^{-1}\)) are present at short times; after 8h, the peaks observed are the corresponding to the $-\text{COO}^-$ (nearby 1650 and 1590 cm\(^{-1}\)).

The surface functionalization of the clusters was characterized by FT-IR (Figure 5.17). The used PAA/PAA-Na\(^+\) salt was measured as a reference and it is displayed in red; the stretching for $-\text{OH}$ (3300 cm\(^{-1}\)) and both C=O stretches for the carboxylic acid (1750 cm\(^{-1}\)) and the carboxylate (1590 cm\(^{-1}\)) are present.\textsuperscript{147} The peak
for the carboxylic acid decreases with time and it is not present at times higher than 8h. The peak for OH is intense in the samples where the clusters are not formed (2h and 4h) because the excess of EG. Peaks for the symmetric and asymmetric stretches for carboxylate are present (1650 and 1590cm\(^{-1}\)), which indicate PAA is attached to the iron surface with most of the carboxylates present in the chain. A peak at 1060cm\(^{-1}\) is observed at all times due to the Fe-O stretching.

### 5.6. Temperature effect

Though the effect of the temperature in the cluster and unit size was discussed in section 5.4, after discovering the formation of FeOCl as intermediate, the chemical structure of the product of the reaction at different temperatures was studied in more detail. Figure 5.18 shows the structure formed when synthesis was carried out at 145 °C, 180 °C, 200 °C and 285 °C; the rest of the synthetic parameters were kept constant.

![Figure 5.18](image)

**Figure 5.18** Temperature effect in the clusters of nanoparticles synthesis

TEM images of reactions carried out at four different temperatures are shown: 145°C (i), 180°C (ii), 200°C (iii), and 285°C (iv). Spherical structures are observed only when temperature reaction is higher than 180°C.
Spherical structures are observed only when reaction temperature is higher than 180°C; however, particles are only observed when temperature is higher than 200°C. When reaction is carried out at 145°C (Figure 5.18.i), concentric needle-like structures are formed. When reaction is carried out at 180°C (Figure 5.18), the sphere seems to be made of an amorphous solid. Because in those two structures excess of organic seems to be present, XPS survey scans were performed to characterize the element present in the structure (Figure 5.19); the clusters formed at 285°C were also analyzed for comparison.

![Image](image_url)

**Figure 5.19 XPS of the material synthesized at different temperatures**

XPS survey scans were collected for the product of the reactions carried out at three temperatures: 145°C, 180°C, and 285°C. The binding energies for N (~400eV), C (~285eV) and Cl (~200eV), are marked for easier visualization.
Figure 5.19 shows that the amount of N (~400eV), C (~285eV) and Cl (~200eV) present in the purified solids decrease as the temperature reaction is higher; the amount is calculated by the relative intensity of the peaks in comparison to the iron one (~700eV). Contrary to what expected, chlorine relative concentration in the sample prepared at 145°C is very small; at 285 °C, Cl is not longer distinguishable. The relative intensity of N and C is also much lower in the material prepared at 285 °C that the ones prepared at 145°C and 180°C; which agrees with the excess of organic observed by TEM (Figure 5.18). As the bands corresponding to Fe and O were the most intense in the three survey scans, their regions were collected and are displayed in Figure 5.20.

![Fe2p and O1s spectra](image)

**Figure 5.20 Fe2p and O1s spectra of the material synthesized at different temperatures**

Fe2p (i) and O1s (ii) spectra of product of the reactions carried out at three temperatures (145°C, 180°C, and 285°C) are shown. In (i) binding energies for Fe$^{2+}$ (708.4eV) in magnetite and Fe$^{3+}$ (710.3eV) in goethite are marked. The characteristic shoulder for magnetite is not present for the sample prepared at 145°C. In (ii) binding energies for -OH (531.5eV) and O$^-$ (530.3eV) are marked. The peak of the hydroxyl is predominant in the sample prepared at 145°C.
Figure 5.20.i shows the region for the Fe2p binding energies. In the three scans, the presence of Fe(III) is confirmed as the main peak agrees with the average binding energy for Fe(III), 710.3eV. The bump at around 719eV suggest that Fe(III) is present as FeOOH in the structures prepared at 145°C and 180°C; on the other hand, only the one prepared at 285°C shows the typical shoulder of magnetite at 708.4eV, corresponding to the Fe(II) in the structure. This observation are confirmed when analyzing the region for O1s; in Figure 5.20.ii, it is clear that two types of oxygen are present in the samples at different ratios. The binding energies for -OH (531.5eV) and O²⁻ (530.3eV) are marked, and it is clear that the hydroxyl group is the predominant at product prepared at 145°C. This ratio changes in the product prepared at 145°C, as the O²⁻ band is slightly higher that the –OH one; the oxide band is predominant in the clusters prepared at 285°C. To confirm the chemical structures, Raman spectra of the three samples were collected and are displayed in Figure 5.21.

Raman spectra (Figure 5.21) confirmed what observed in Figure 5.20, the product of the reaction at 145°C is FeOOH. The only peak for that spectrum corresponds to the main peak for goethite at 385cm⁻¹. This is not surprising as the formation of hierarchical goethite spheres has been reported by solvothermal methods at low temperature. On the other hand, the clusters prepared at 285°C, show the typical peaks for magnetite (310, 540 and 670cm⁻¹) and the ones for the corresponding partial oxidation under the laser, maghemite (350, 512, 665 and 730cm⁻¹). The peaks for maghemite are much marked for the spheres prepared at 180°C, however, the peak at 350cm⁻¹ is broader than the one at 512cm⁻¹, and could
be overlapping with the main peak for goethite at 385 cm\(^{-1}\); the presence of goethite and maghemite would explain the ratio between –OH and O\(^2-\) observed in Figure 5.20.ii.

**Figure 5.21  Raman of the material synthesized at different temperatures**

Raman spectra of product of the reactions carried out at three temperatures (145\(^\circ\)C, 180\(^\circ\)C, and 285\(^\circ\)C) are shown. The main peaks for magnetite and goethite are marked. The clusters synthesized at 180\(^\circ\)C and 285\(^\circ\)C show the three typical peaks of maghemite (704, 499 and 360 cm\(^{-1}\)). The product of the synthesis carried out at 145\(^\circ\)C agree with the goethite main peak.

**5.7. Cooling effect**

Finally, the last parameter to be study was the cooling rate of the reaction. To assess this effect, a reaction mixture was divided in four reactors and set them up
for reaction at 285°C for 24h; when time was completed, the oven was turned off and the reactors were taken at when the temperature reached different temperatures: 285°C, 200°C, 110°C and 50°C; the reactor were open as soon as the stainless steel autoclave was cool enough. Figure 5.22 shows the TEM images and histograms of each product.

![Figure 5.22](image)

**Figure 5.22  Cooling effect in synthesis carried out at 285°C**

The effect of cooling down a synthesis set up a 285°C was observed in TEM images. After 24h, the synthesis was stopped and the reactor was taken out of the oven immediately (i) and when temperature decreased to 200°C (ii), 110°C (iii) and 50°C (iv). The histograms of the size distribution for each case (from bottom to top) are shown in (v). A barely perceptible size decreasing is observed; a line at 75nm was added to help the visualization of the change.

Though the change in size is very slightly, it is observable that the clusters taken from the oven at 50°C (Figure 5.22.ii) are smaller and more compact that the
ones from the reactor taken from the oven at 285°C (Figure 5.22.iv). This observation is more evident when comparing the histograms (Figure 5.22.v). To corroborate this observation, a similar experiment was setup with bigger clusters. However, as the changes in the previous study were only significant when the temperature difference was considerably different, a second factor was considered: how fast the reactor, outside the oven, was opened. Figure 5.23 shows the results for this study.

**Figure 5.23  Cooling effect in synthesis carried out at 200°C**  
The effect of cooling down a synthesis set up a 200°C was observed in TEM images. After 24h, the synthesis was stopped and two reactors were taken out of the oven immediately: one was opened after 1h (iii) and the other one was left overnight for slow cool down (iv). Other two reactors were left in the oven until the temperature decreased to 90°C and opened after 1h (i) and the other one was left overnight for slow cool down (ii). And the histograms of the size distribution for each case (from bottom to top) are shown in (v).
As in the previously discussed study, a reaction mixture was divided in four reactors and set them up for reaction, this time at 200°C for 24h. When time was completed, the oven was turned off and the two reactors were taken off immediately; the other two were left inside. Figure 5.23.i shows the clusters of the reactor that was left inside the oven overnight; when it was taken of the oven, the autoclave was cool. Figure 5.23.ii shows the clusters of the reactor that was left inside the oven and taken off when temperature reached 90°C; this reactor was open one hour after. Figure 5.23.iii and Figure 5.23.iv shows the clusters from the reactors taken off the oven when time was up (the oven was still at 200°C); the first one was left overnight and open when the autoclave was cool, and the second one was opened 1h later – as soon as the autoclave was cool enough. This variable is possibly more important as the temperature in the reactor surroundings is not the same that inside the reactor; and affects directly the cooling rate. If the reactions are sort from the fastest to the slowest cooling rate, the order is iv> iii>> ii ≥ i. In Figure 5.23.v, the histograms of each case are shown. It is clear than the reactions with slower cooling rates show smaller clusters. Also, it is important to notices that the two pairs of reactions (taken off at 200°C and left in the oven) have similar standard deviations; in both cases the distributions are different. In the case of the slowest cooling (i), there is only one population; in (ii), an amount of clusters seems to have a higher size than the average. The presence of two size populations is more evident in the reaction cooling rates. In the fastest reaction (iv), the mode (350nm) is bigger than the average; in the second fastest reaction (iii), the population the mode (290nm) is smaller than the average.
In addition to the difference in the mode and the average in the reactions with fastest cooling rates, an effect in the polymer coating is visible. In Figure 5.23.iv a thin layer of polymer can be observed in some clusters; this layer is thicker and more evident in Figure 5.23.iii. This difference with the clusters prepared with a slow cooling rate could be rationalized as follow: when the cooling is slow, the gas burble inside the hollow sphere slowly decreases in size and the external shell, nanoparticles and polymer, does the same. When the cooling is fast, the gas burble inside the hollow sphere does not have time to compress. However, if there is a fast decrease in the temperature and then a slow cooling – as in the cases of (iii) –, the polymer in the surface might cool and increase its viscosity, while the burble inside this cluster slowly compresses and so the shell of nanoparticles does. The 1h of slow cooling would explain the small layer of polymer in Figure 5.23.iv, and a thicker one in Figure 5.23.iii.

### 5.8. Proposed mechanism of reaction

Based in the observations in the previous sections, a mechanism for the formation of hollow clusters of nanoparticles is proposed in Figure 5.24. The mechanism is divided in two: the microscopic (i) and nanoscopic (ii) changes.

When following the reaction in the microscopic scale, two changes can be observed: (a) the formation of huge and irregular aggregates – represented in Figure 5.24 as dark orange spheres – (b) and the transformation of aggregates in cluster of particles of a few hundred nanometers in size – represented by dark gray
spheres. The formation of these agglomerates was observed within a few hours of reaction (Figure 5.9.iii-iv) and the conversion to the clusters is observed when the target temperature of reaction is reached inside the autoclave, usually after 8h (Figure 5.9.vi).

![Diagram](image)

**Figure 5.24 Proposed mechanism for the synthesis of clusters of IO-NPs**

(i) The reaction is carried out in a close reactor where an homogeneous polyol solution is transformed in a suspension of microspheres after the solvothermal treatment. (ii) The microspheres formed are a mixture of a intermediary and an amorphous organic phase (dark orange), as time of treatment and temperature increases, the formation of nanoparticles occurs in the external layer. This layer increases with time, until all the material inside the sphere is consumed and nanoparticles are compacted on the surface. Depending in the cooling conditions, the hollow structure compresses to rearrange the packing of the nanoparticles.
The transformation of these huge aggregates to the nano-sized hollow clusters can be explained as follows. First, the formation of smaller and homogenous spheres, composed of an intermediary embedded in an organic amorphous matrix, is observed with longer reaction times; when the target temperature is reached, the crystallization of nanoparticles in the surface starts (c). The hollow structure is formed as a result of a Kirkendall effect, which makes the remaining intermediary inside the particle to dissolve to generate a thicker layer of nanoparticles until it is fully spent (d-e). Finally, because of a cooling effect a contraction in the clusters size is observed (f). Though this proposed mechanism disagrees to the reported mechanism for similar structures,\textsuperscript{151,152,153} other works have reported similar observations to each step; each of them is discussed below in more detail.

The formation of smaller spheres from big agglomerates (b) as the reaction evolves has been reported for other mechanistic studies. In 2008, Cao and Zhu reported the synthesis micro-sized hollow structures formed by nanosheets of a Fe-EG precursor in a microwave-assisted solvothermal method; the synthesis was followed by the thermal decomposition of the precursor to obtain nanostructured $\alpha$-Fe$_2$O$_3$ hollow spheres.\textsuperscript{154} Despite they do not identify their precursor, the XRD presented is similar to the one obtained at earlier times of reaction by this study (Figure 5.15) which agrees with a FeOCl structure; in addition, the nanostructured structures they observed, are similar at the ones observed at the beginning of the reaction (Figure 5.12.i). In 2006, Thomas \textit{et al.}\textsuperscript{155} reported the formation of amorphous carbon spheres covered with metal ions, when glucose is dehydrated during a hydrothermal method; they obtained the metal oxide hollow spheres by
calcination of the carbon spheres. Although the hollow structures herein presented are formed inside the solvothermal reaction, it has been observed that the precursor is embedded in the growing spheres of amorphous organic material (Figure 5.10.iv, Figure 5.11.iii) a times lower that 8h, when the temperature is still increasing inside the reactor. Despite further studies has to be made to corroborate this, from the time-dependent and the temperature studies, it is believed that the chemical structure changes from FeOCl to $\alpha$-FeOOH, to a mixture of $\alpha$-FeOOH/$\gamma$-Fe$_2$O$_3$, and then to Fe$_3$O$_4$, as those were the chemical structures found when reaction run during 24h at 145$^\circ$C, 180$^\circ$C and >200$^\circ$C (Figure 5.20, Figure 5.21).

The crystallization starting from surface of the cluster was observed by TEM as the evolution of the clusters was followed after 8h (Figure 5.12.iii-vi). This agrees with a Kirkendall effect. This effect has been observed in metallurgy for decades and consists in the diffusion of one phase in another. Alivisatos group$^{156}$ first reported this effect in nanostructures, in the diffusion of metallic Co nanoparticles to CoO and Co$_3$S$_4$ hollow nanoparticles. The Kirkendall effect has more recently used to prepare hollow structures such as metallic nanotubes by diffusing the metal precursor to a carbon coating.$^{157}$ This kind of effect was reported as one of the steps in the solvothermal synthesis of core-shell TiO$_2$ spheres.$^{46}$ Though it was not reported as Kirkendall effect, a similar step was observed in the urchin-like hierarchical $\alpha$-FeOOH spheres$^{150}$; in this case, the aggregates of amorphous intermediary first grows concentric nanorods in the surface, until eventually the center is hollow and the surface heavily populated with nanorods. The same is observed in the herein reported clusters, the aggregates of intermediary first crystallize nanoparticles in
the surface, until eventually the center is hollow and the surface densely covered with well-packed nanoparticles. Despite some experiments are required to confirm this proposed mechanism, the experiments discussed in this chapter provide good supporting evidence for the above mechanism.

5.9. Applications in arsenic removal

Finally, to get a general idea of the performance of the clusters for arsenic removal, the study of the arsenic removal efficiency was analyzed in batch experiments. Two main parameters were expected to have a big effect in the arsenic removal, the size of the cluster and the size of the nanoparticles. For that reason, the arsenic removal efficiencies were measured when clusters with different size, keeping the unit size constant; and the nanoparticle size was changed, keeping the cluster size constant.

Figure 5.25 shows the TEM images of the clusters selected to study the effect of the cluster size. The nanoparticle size was 5±1nm for all of them, and average sizes selected were: 107±22nm, 207±51nm, 277±66nm and 390±115nm. The corresponding histograms are shown below the TEM images. In addition, the BET areas are also measured; it was surprising to observe that despite the big change in the clusters size, the surface area is very similar. The arsenic removal efficiencies of each of them for an [As]=100μg/L solution at pH and Salamanca groundwater are shown in Figure 5.26.i and Figure 5.26.ii, respectively.
Figure 5.25 Clusters used for arsenic adsorption with the same unit size
Four sizes of clusters were selected to observed the effect of the cluster size. All of the had an unit size of 5±1nm. TEM images of clusters with average cluster sizes (CS) of 107nm (i), 207nm (ii), 277nm (iii), and 390nm (iv) are shown. Histograms are displayed below each image to show the size distribution; the BET are is also reported and it is similar for all samples.

Figure 5.26 Effect of the cluster size in arsenic adsorption performance
Four sizes of clusters (107nm, 207nm, 277nm, and 390nm) were selected to observed the effect of the cluster size in arsenic adsorption. When only arsenic ([As]=100μg/L, pH 7) is present in solution (i), the size seems to have not effect. A similar result is observed with Salamanca groundwater (ii); as expected, a decreasing in the removal efficiencies is also seen.
The same kind of experiment was used to evaluate the effect of the nanoparticles size. Figure 5.27 shows the clusters with unit sizes of: 5±1nm, 9±2nm and 12.5±3nm; the three samples had average clusters size close to 110nm. The corresponding histograms are shown below the TEM images. In addition, the BET areas are also measured. Surprisingly, the surface area decreases as the unit size increases. Figure 5.28.i and Figure 5.28.ii show the arsenic removal efficiencies of each of them for an [As]=100μg/L solution at pH and Salamanca groundwater, respectively.

![Figure 5.27](image)

**Figure 5.27  Clusters used for arsenic adsorption with the same cluster size**

Three samples were selected to observed the effect of the unit size. All of the had a cluster size close to 110nm. TEM images of clusters with average unit sizes of 5nm (i), 9nm (ii), and 12.5nm (iii) are shown. Histograms are displayed below each image to show the size distribution; the BET are is also reported and it decreases as the unit size increases.
Figure 5.28  Effect of the unit size in arsenic adsorption performance
Clusters with three different average unit sizes (5nm, 9nm, and 12.5nm) were selected to observed its effect in arsenic adsorption. When only arsenic ([As]₀=100μg/L, pH 7) is present in solution (i), contrary to expected, the efficiency increases with the unit size. However, the opposite happens with Salamanca groundwater (ii); the typical decreasing in the removal efficiencies is higher in the clusters with bigger unit size.

The arsenic removal performance observed in both studies was significantly lower than expected and not meaningful trend was observed. For example, in Figure 5.26.i, the adsorption efficiency shows a significant increase when cluster size is bigger than 200nm, when only arsenic is present in solution; being the maximum observed with the cluster size of 277nm, when the particle size is kept at 5nm. However, when Salamanca groundwater is used (Figure 5.26.ii), the performance decreases at least to half the observed when in contact with the same concentration of Arsenic without any interference present. On the other hand, a surprising trend is observed when the cluster size is kept constant and the unit size varies: the arsenic removal efficiency increases when the unit size is larger. This is observed when only arsenic was present in solution (Figure 5.28.i); however, when Salamanca groundwater is used (Figure 5.28.ii) the trend is opposite. In this case, the clusters
that showed the biggest removal efficiency with only arsenic is present do not show any removal in natural groundwater. It was evident that in both experiments the negative surface coating has an adverse effect with arsenic adsorption, as observed when analyzing the effect of different surface coating in nanoparticles on arsenic removal performance discussed in section 4.3; however, this was mistakenly not considered when designing the experiments. Also, as the observed trends and not completely clear and are not kept when changing conditions, it is suspected that the clusters have different amount of polymer covering their surface. For that reason, the complete removal of the coating is recommended for future studies.

Despite the unsuccessful results obtained in batch experiments, a column experiment was carried out to verify the feasibility of the use of clusters in this set up; as this is one of the biggest challenges observed for nanoparticles. (Figure 5.29.i used for assembly the cluster column ((Figure 5.29.ii).

(Figure 5.29 Clusters used for the column experiment
Clusters with a size of 290±80nm were used for the column (i). They were mixed with PMMA beads; the media was 20%wt in clusters. The media was added to a small column for an active bed of 3cm (ii). After treatment with NaOH, leaching of the small clusters was observed (iii).
For the assembly of the small cluster column ((Figure 5.29.ii), a similar sample to the one that showed the highest arsenic removal in batch experiments (Figure 5.25.iii) was selected ((Figure 5.29.i)); with a unit size of 5±1nm and an average clusters size of 290±80nm. Figure 5.30.i shows the arsenic breakthrough of the column.

![Figure 5.30](image)

**Figure 5.30** Column breakthrough curves of arsenic and vanadium in groundwater

The breakthrough for arsenic happens almost immediately after the experiment started but stabilize at around \([\text{As}]/[\text{As}]_0=0.8\) (i). Same behavior is observed with vanadium (ii), stabilization occurs at around \([\text{V}]/[\text{AV}]_0=0.55\).

As expected, no treatment zone was observed and the arsenic concentration in the outlet almost immediately reached 80% of the initial concentration. Surprisingly, after 100BVs, the normalized arsenic concentration does no reach 1. This shows there is adsorption of arsenic after the mass transfer zone of the experiment, this kind of behavior is only observed in ionic exchange fixed bed columns. The same effect is observed in the vanadium breakthrough curve.
(Figure 5.30.ii). This suggests the PAA chains anchored to the clusters surface are exchanged for the vanadate and arsenate ions in solution; this confirms the negative effect of the polymer in the batch experiments. For that reason, the column was in situ treated with NaOH 1M, to try to remove the excess PAA; however, the leaching of particles was observed during treatment. (Figure 5.29.iii shows that the leached clusters are the smallest ones; these tend to aggregate which suggest that PAA coating is removed.

Despite the arsenic removal studies with clusters did not show the expected performance, it was determinate that the factor was the negative charged coating. It is imperative that clusters without coating or with neutral or positive charged coatings are studied for arsenic removal applications. The column experiment confirms that the implementation of clusters of nanoparticles are feasible to solve the technical issues that using nanoparticles generates, as not problem was observed with a cluster loading of 20%. It is suggested that columns studies with higher clusters loading are carried out as it is expected columns with packed with only clusters, when cluster size is higher than 200nm, in the active media shall perform without any technical issues.

5.10. Conclusions

This chapter focused in the formation of hollow clusters of iron oxide nanoparticles. Studies to corroborate the reproducibility and the repeatability were performed. The effect of the parameters involved in their synthesis was studied,
including the concentration of polymer and urea, temperature and time. For each study, TEM and SEM images for morphological and size characterization were taken; and XRD, Raman, and XPS were used for structural characterization.

Strong correlations between the concentration of urea and the cluster size, and the concentration of polymer and the unit size were found. Also it was observed that size of the nanoparticles decreases with the presence of water; and the formation of the clusters is also affected. Also it was observed that as reaction evolves and the temperature increases inside the reactor, the dissolved iron (III) chloride evolves from FeOCl to $\alpha$-FeOOH, to a mixture of $\alpha$-FeOOH/$\gamma$-Fe$_2$O$_3$, and then to Fe$_3$O$_4$.

By understanding the effect each parameter, a grasp of what happens inside the autoclave during the solvothermal synthesis and a mechanism was proposed. The is includes the formation of huge aggregates that changes to smaller and homogenous spheres, composed of an intermediary embedded in an organic amorphous matrix. As the temperature increases, the crystallization of nanoparticles in the surface starts, usually at times longer than 16h. The formation of the hollow structure is a result of a Kirkendall effect, which makes the remaining intermediary inside the particle to dissolve to generate a thicker layer of nanoparticles until the clusters is hollow. Finally, depending on the cooling conditions, clusters could contract its size.

Additional experiments are required to corroborate the proposed mechanism, but the knowledge obtained by this work gives the tools to modify the reaction to further control the reaction. So far, a control in cluster size and unit sizes
was obtained, but it is expected that the reaction could also be fined to control factor as chemical composition and pinholes in the structure.

Finally, the application of the clusters of iron oxides nanoparticles for arsenic removal was explored. Removal efficiencies were measured for clusters with different cluster and nanoparticles were measured under two punctual conditions: a solution 100μg/L As and Salamanca groundwater. The results were much lower than expected and trends could not be determined. It was determinate that the poor results were because the coating of the used clusters, it was clear that the use of the proposed clusters could solve the technical difficulties that implementation of nanoparticles in remediation technologies has, keeping the advantages that use of nanomaterials provide.
Chapter 6

The synthesis of iron oxide nanoparticles from everyday ingredients

6.1. Introduction

Iron oxide nanoparticles (IO-NPs) can be prepared in many ways, including co-precipitation, microemulsion, hydrothermal synthesis, solvothermal synthesis, sonolysis, sol-gel reactions, microwave-assisted synthesis, aerosol methods, and electrochemical methods. However, thermal decomposition is the preferred method for producing homogeneous and well-dispersed IO-NPs. This is an expensive methodology, difficult to scale up, that produces only a small amount (e.g. milligrams) of material. In 2004, Park et al. achieved a large-scale synthesis of IO-NPs by separating the preparation of the precursor from the formation of nanocrystals during thermal decomposition. In 2010, the Colvin group developed a
simple and inexpensive method for synthesizing IO-NPs. Known as a “kitchen synthesis,” the technique used everyday ingredients such as olive oil and rust as starting materials to produce magnetite nanoparticles.\textsuperscript{77} More recently, similar procedures have been reported using canola oil.\textsuperscript{159,160} While these approaches using widely available ingredients are interesting, and potentially practical for large-scale applications in low-infrastructure environments, the utility of these nanoparticles for water treatment and other environmental applications has never been assessed. In this chapter, we describe a synthetic method that yields high-quality nanomaterials from everyday ingredients and then quantify the nanomaterials’ performance in arsenic removal.

### 6.2. Optimizing synthesis using everyday ingredients

The original kitchen synthesis reported by Yavuz \textit{et al.}\textsuperscript{77} in 2010. This method made an important modification to the thermal decomposition strategy for nanocrystal production in that it changed the iron precursor and the surfactant to everyday ingredients. Many other features of the reaction were kept unchanged; Figure 6.1 summarizes these changes. In the thermal decomposition (Figure 6.1.i), iron oleate is the iron source and oleic acid (OA) is the surfactant; 1-octadecene (ODE) is used as the solvent. In the original kitchen synthesis, rust served as the iron source and a mixture of fatty acids derived from edible oils served as the solvent (Figure 6.1.ii). This synthesis produces large nanoparticles due to the high concentration of iron precursor in the reaction. In our proposed modification
(Figure 6.1.iii)—referred to as the Modified Kitchen Synthesis (MKS)—we selected olive oil as the surfactant. Olive oil was chosen because of its high concentration of oleic acid (58%-79%)\textsuperscript{161}; it was used in large amounts as well as to dilute the concentration of precursors to obtain smaller nanoparticles.

![Figure 6.1 Modifying the synthesis of nMag](image)

The TEM images above show IO-NPs prepared by thermal decomposition (i), the original kitchen synthesis (ii), and the modified kitchen synthesis (iii). Using the same conditions (time and temperature) but varying the iron precursor, the carboxylate source, and the solvent, nanoparticles are still obtained. The middle image (ii) is reprinted with permission from Yavuz et al.\textsuperscript{77}.

The modifications were made in steps to determine the optimal conditions and iron precursor to use. TEM images of the particles obtained with each change are shown in Figure 6.2; the images also include the corresponding histograms characterizing the diameter distributions of the products. The first modification made was the exchange of oleic acid and ODE for olive oil (Figure 6.2.i); as a result, smaller particles were obtained and the uniformity of the nanoparticle decreased.
The second modification was to exchange the iron oleate for iron (III) chloride (Figure 6.2.ii); smaller particles are obtained and the dispersity of the nanoparticle sizes slightly increases. The second modification was to exchange the iron oleate for iron (III) chloride (Figure 6.2.iii); the nanoparticles produced were even smaller. Finally, in order to make the process as inexpensive as possible, the iron precursor was changed to rust (Figure 6.2.iv). This change yielded larger nanocrystals with less uniformity. Note that the reactions were carried out on larger scale; Figure 6.3 shows the results.

**Figure 6.2**  **Varying the Fe precursor in the modified kitchen synthesis**
The TEM images above present IO-NPs prepared using Fe oleate in the presence of oleic acid and 1-octadecene (i), only olive oil (ii), iron (III) chloride in olive oil (iii), and rust in olive oil (iv). Reaction time and temperature were the same for all experiments. Histograms are displayed below each image to show the size distribution. Reactions were carried out for 2h.
Figure 6.3 Scale up of the modified kitchen synthesis

TEM images show IO-NPs prepared using rust in only olive oil at different scales: 1x (i), 5x(ii), and 5x (iii). Histograms are displayed below each image to show the size distribution. The dispersion in the size increases with the bigger reactions. Reactions were carried out for 6h.

In Figure 6.3.i, the TEM image includes the nanoparticles obtained in the original reaction; the corresponding histogram appears below the image Figure 6.3.ii and Figure 6.3.iii the nanoparticles obtained when the reaction is scaled up 5 and 10 times. Because of the increase in the average nanoparticle size, and more importantly the large spread in the diameters at large scale, the reaction using iron (III) chloride (Figure 6.2.iii) was selected for further study. NPs prepared from MKS will be referred as MKS-NPs henceforth.

To better understand this reaction, a differential scanning calorimeter (DSC) was used to evaluate the chemical changes that occurred at high temperatures. This
data is shown in Figure 6.4. All experiments were performed under air atmosphere to mimic the reaction conditions.

![DSC plots for thermal decomposition and modified kitchen synthesis reactions](image)

**Figure 6.4** DSC plots for thermal decomposition and modified kitchen synthesis reactions

The heat flow over the reaction time is shown for the iron precursors, the solvent and the reaction mixture for thermal decomposition (i) and the modified kitchen synthesis (ii). The temperature variation is shown in the left axes and are represented with dashed lines for each measurement; with some small variations, they are almost identical.

In Figure 6.4.i, heat flow for the Fe oleate (dark orange line), the mixture of oleic acid and ODE (blue line), and the reaction mixture for thermal decomposition (black line) are plotted against time. The corresponding temperature is displayed on the left axis and is represented by dashed lines. Similar plots are displayed in Figure 6.4.ii for the MKS: FeCl$_3$·6H$_2$O (orange line), olive oil (blue line), and the reaction mixture for MKS (green line).

These mixtures evolve in a similar way as a function of temperature. First, the iron precursors show a transformation at 315°C. The main difference is that both the reactions and the solvent (OA+ODE or olive oil) show endothermic peaks at
different temperatures prior to this decomposition. For the thermal decomposition, the peak is observed at around 270°C and for the MKS at 315°C. This peak is related to the temperature at which white vapor appears in the reaction vessel. Generally this is thought to signal the start of nucleation. The fact that this occurs at a higher temperature in the MKS, in contrast to the conventional thermal decomposition study, indicates that the growth of nanoparticles is already occurring in the thermal decomposition when 315°C is reached, while in the MKS the nucleation process is just starting.

As our primary interest in this synthesis was the use of the materials to remove arsenic from water, we evaluated the MKS-NPs for this purpose using batch isotherms (see Chapter 1, p.20). Figure 6.5.i and Figure 6.5.ii show the isotherms of a solution of arsenic in the absence and presence of silica ([SiO₂]=85mg/L), respectively. In both cases, the experimental data was described using a Langmuir isotherm model with \( q_{\text{max}} \) and \( k_L \) adjustable parameters. The fitted curves for nMag isotherms, calculated in section 4.4 are shown with a purple line for comparison. In both cases, the performance is significantly better than the particles produced with more conventional methods. Additionally, the presence of added silica had a minimal effect on this sorption process in contrast to the results reported in Chapter 3 for commercial arsenic sorbents.
Figure 6.5  Arsenic adsorption isotherms for the MKS-NPs
The nanoparticles prepared by modified kitchen synthesis showed an outstanding arsenic removal in both absence (i) and presence of silica, [SiO$_2$]=85g/L, (ii). The isotherm of nMag (purple line) is shown for comparison.

6.1. Forming larger quantities of nanoparticles

Reactions ten times larger than the initial one were carried out over longer time periods, and the general appearance of the products and reaction progress was similar to that seen with smaller scale reactions. Purification, however, presented a significant challenge. Figure 6.6.i illustrates the typical purification process for these materials. The thick black liquid formed as a product is transferred to 50mL centrifuge tubes and precipitated with a 1:1 mixture of acetone and ethanol, after centrifugation the supernatant is discarded and the black solid is re-dissolved in 10mL of hexanes and then re-precipitated with acetone and hexane. This step is repeated until the supernatant is clear; in a small reaction, the process usually requires three repetitions. The nanoparticles are then re-dispersed in hexanes and
saved for later use. The whole process for a thermal decomposition reaction usually takes one day; for a small-scale kitchen synthesis, the process can take up to a week due to the excess of organics present in the reaction mixture.

Figure 6.6  The purification of MKS-NPs is the limiting step
The black liquid is collected from the reaction flask and purified to obtain the clean nanoparticles. In (i), the scheme for a typical purification is shown. In small reactions, a negligible amount of solid is left in the flask; nanoparticles are extracted from the solid with hexanes until it is no longer black (ii). When scaling up, the amount of black solid is significant and is easily separated (iii).

The challenge is that the use of olive oil rather than saponified fatty acids as in the original kitchen synthesis leads to thermal decomposition of the oil in addition to some formation of fatty acids. This left a residue in the reaction vessels, present as a small amount of black solid observed in the bottom of the reaction flask. This was usually washed until the color was no longer black, as nanoparticles were extracted from the flask. Figure 6.6.ii shows the remaining washed solids. The
amount of black solid remaining in the reaction flask was significant for the large-scale reaction; for that reason, the solid was separated from the liquid as shown in Figure 6.6.iii. After washing it once with hexanes, the solid was dried and stored. The large-scale reaction was repeated several times, and in every replicate, the amount of solid was significant; for that reason, the solid was characterized, and it will be referred to as MKS-s henceforth.

Because MKS-s is responsive to a magnet, it was hypothesized that nanoparticles were embedded in a carbon matrix. This was confirmed when nanoparticles were observed in TEM images (Figure 6.7.i); MKS-s was sonicated in ethanol, and this solution was used to prepare the TEM grid. In some samples, spindle-like structures were observed. Figure 6.7.ii shows an area of MKS-s that is highly populated with spindle-like structures; however, this is observed in only a few areas, and most of the sample shows morphology similar to amorphous carbon.

Figure 6.7  SEM and TEM of the MKS-s.
The MKS solid is mostly formed of nanoparticles trapped in amorphous carbon, but some areas show the presence of spindle-like fiber carbon structures. These structures are observed by SEM (i) and TEM (ii).
In order to fully characterize MKS-s, two samples were analyzed using XRD (Figure 6.8), Raman (Figure 6.9) and XPS (Figure 6.10). In Figure 6.8, the presence of magnetite is confirmed; however, it is not the predominant phase. Peaks that agree with the pattern of FeCl$_2$·4H$_2$O are observed in both samples. To corroborate its presence, sample B was washed with ethanol and acetone several times; its XRD spectrum is labeled as C. The peaks corresponding to FeCl$_2$·4H$_2$O disappear. Also, it is important to point out that sample B shows the presence of spindle-like structures, and it shows peaks in the area where graphite typically has its main peak. These spindle-like structures could be the result of the carbon exfoliation produced by the presence of the intercalated iron chloride.$^{162}$ The corresponding peaks from magnetite to maghemite usually occur under laser radiation during collection—(500, 665, and 730 cm$^{-1}$)$^{149}$, are shown in Figure 6.9.i and marked with an asterisk (*). The wider peaks and the extra ones correspond to those reported for FeCl$_2$·4H$_2$O (310, 482, and 552 cm$^{-1}$)$^{163}$ and are marked with a plus symbol (+). Also, the characteristic water bending peaks of FeCl$_2$·4H$_2$O (around 1680 cm$^{-1}$) can be observed in Figure 6.9.ii.
XRD diffractograms were taken for two samples (replicates of the synthesis), A and B. Both of them show peaks that agree with the pattern for magnetite (PDF 03-065-3107), shown in black, and for FeCl$_2$·4H$_2$O (PDF 01-071-0917), shown in orange. After sample B is washed several times (C), the peaks that agreed with FeCl$_2$·4H$_2$O disappear.

In Figure 6.9.ii, the typical wide band for amorphous carbon is present, around 1300cm$^{-1}$. However, the G band at 1680cm$^{-1}$ is well defined; as the G peak is directly proportional to the degree of disorder, it indicates that some graphite, or nano crystalline graphite structures are present. This corroborates that the spindle-like nanostructures observed in Figure 6.7 are made of graphite-like carbon.
Figure 6.9  Raman of the MKS-s

Raman spectra were taken for two samples (replicates of the synthesis), A and B. In (i), the typical peaks of maghemite (*; 500, 665, and 730cm$^{-1}$) are present; in addition, peaks for FeCl$_2$·4H$_2$O (+; 310, 482 and 552cm$^{-1}$) widen the typical iron oxide peaks. In (ii), the characteristic water bending peaks of FeCl$_2$·4H$_2$O (+, around 1680cm$^{-1}$) are barely noticed in comparison with the typical peaks for amorphous carbon; the G band is also marked.

Finally, elemental XPS scans were performed for two samples (Figure 6.10), A and B, where B was washed with ethanol and acetone several times to ensure FeCl$_2$·4H$_2$O was rinsed out of sample B. As expected, the Fe2p, O1s, and Cl2p spectra are different. Fe$_3$O$_4$, FeCl$_2$·4H$_2$O, activated carbon, and graphite were measured and their spectra are displayed to facilitate the comparison. In Figure 6.10.i, the Fe2p region is shown. The difference between the iron present in each sample is evident. For A, where FeCl$_2$·4H$_2$O was rinsed out, the spectrum fully coincides with the magnetite. On the other hand, for sample B, the peaks are wider, but the presence of magnetite and FeCl$_2$·4H$_2$O is confirmed for the peak maximum at 724eV for Fe2p$_{1/2}$ and the satellite Fe2p$_{3/2}$ observed around 716eV, respectively.$^{166}$
Figure 6.10  XPS elemental scans of the MKS-s

Fe2p (i), O1s (ii), Cl2p (iii) and C1s(iv) spectra were taken for two samples (replicates of the synthesis), A and B. Spectra of Fe3O4, FeCl2·4H2O, activated carbon and graphite were taken for comparison. Sample B was washed several times, therefore Fe2p and O1s spectra agree better with Fe3O4 (i), and the Cl2p signal is minimal (iii); as opposite as shown by sample A, where spectra agree better with the FeCl2·4H2O binding energies. Both of them have similar C1s spectra; which is closer to the graphite one.

Figure 6.10.ii, shows the O1s region. For A, the main peak for magnetite is observed. For sample B, the peak is mainly for the water present in FeCl2·4H2O. In Figure 6.10.iii, the Cl2p region is shown. Some remaining Cl is observed for sample
B, but it is minimal in comparison with sample A. In Figure 6.10.iv, the C1s region is shown; both spectra are similar to that of graphite.

Because the process of washing the MKS-s resulted in different predominant iron structures, a study of the effect of washing on its composition was carried out. The quantification of composition was done by TGA (Figure 6.11), ICP and relative intensities in XPS. The results are summarized in Table 6.1.

![TGA plot](image)

**Figure 6.11  TGA the MKS-s after washing process.**
The TGA plot for the MKS solid before and after two, three, and five washing cycles is shown. With the exception of the original product, the shape of the curves is similar for all of them, and the final remaining weight increases with the number of washings.

Figure 6.11 shows the TGA plot for the original sample and after two, three, and five washing cycles. The original sample shows a different shape than the other ones because some remaining reagents from the product might be present. After the
first washing, a trend is observed in the remaining weight increases. This is what was expected, and in addition to wash out the FeCl$_2$·4H$_2$O, the excess of organic molecules was removed. The numeric values are displayed in Table 6.1.

<table>
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<tr>
<th>Remaining mass</th>
<th>TGA</th>
<th>ICP</th>
<th>XPS</th>
</tr>
</thead>
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<td>m/m$_{\text{raw material}}$</td>
<td>Fe + O + C</td>
<td>Fe</td>
<td>C</td>
</tr>
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<td>After washing 3x</td>
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<td>After washing 5x</td>
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<td>12.0</td>
<td>5.9</td>
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</table>

Table 6.1  **Elemental quantification after washing cycles.**
The amount of material left was quantified in the raw material and after two, three, and five cycles of washing. In the *remaining mass* column, the weight after washing and drying is reported normalized by the initial raw material mass. In the *TGA* column, the material left after heating at 800°C is reported. Using *ICP*, the iron content of the sample was measured. Using *XPS*, an approximation of the superficial concentrations of Fe, C, O, and Cl is reported. All values reported in columns *TGA*, *ICP*, and *XPS* are percent values based on the initial weight of the corresponding sample.

Table 6.1 illustrates the effect of the washing process. After two washing cycles, the remaining mass decreases to 82% of the original. With an extra cycle, the remaining mass falls to 78% of the original. The mass reduction becomes minor with a larger amount of washing cycles; after five washing cycles, the remaining mass is 76% of the original. On the other hand, the iron concentration was measured by ICP-EOS. As expected, the concentration decreases as the FeCl$_2$·4H$_2$O is rinsed out. The similarity between the iron percent values from ICP and XPS are very similar when washing is more intense. Furthermore, the total iron
concentration decreases (ICP) with the washing cycles, but the superficial iron concentration increases (XPS). This could be explained by the intercalation of the FeCl$_2$·4H$_2$O in the carbon composite.$^{167}$

Because carbon composites with embedded iron nanomaterials with low oxidation states have been reported to have enhancement properties for water treatment applications$^{168}$, MKS-s, after only one washing cycle, was evaluated for its arsenic removal characteristics.

6.2. Environmental applications

The use of magnetic composites for water applications has gained popularity because the composites can be easily removed from the reaction medium using a simple magnet.$^{169}$ Specifically a magnetic carbon composite using an inexpensive technology could be of particular interest in water treatment. We explored this opportunity using MKS-s for arsenic removal and dye remediation.

6.2.1. Arsenic adsorption

In Figure 6.12, the arsenic adsorption isotherm of the MKS-s is displayed when only arsenic is present at pH 7. Even though is the maximum capacity is not as impressed as the one shown by MKS-NPs (Figure 6.5.i), it is very good. The fitted curve the Bayoxide commercial sorbent, calculated in section 3.4, is shown with a dark red line for comparison; the behaviors are very similar, but the MKS-s show higher maximum capacities. For that reason, the next step for the characterization
of it arsenic removal performance was a column experiment with Salamanca groundwater (Figure 6.13).

![Graph showing arsenic adsorption for the MKS-s.](image)

**Figure 6.12  Arsenic adsorption for the MKS-s.**

The solid recovered from the modified kitchen synthesis showed an arsenic removal performance similar to the commercial arsenic sorbent Bayoxide E33 (dark red line) under ideal conditions, using arsenic only at pH 7.

Figure 6.13.i displays the assembled column with MKS-s; the solid material was packed between beds of PMMA beads as described in section 2.4.2.1. Figure 6.13.ii shows the arsenic breakthrough curve. The experimental data fits the advection dispersion equation (ADE) (see Chapter 1, p. 21) almost perfectly, and the $D$ value is very low, which indicates no issues are observed with the mass transfer; this is remarkable for a nanomaterial. Though no technical issues (back pressure, changes in the flow rate) were observed, a higher amount of BVs for the water treatment area was expected, based on the batch experiments. Figure 6.13.iii shows
the vanadium breakthrough curve; however, no increase in the outlet concentration was observed during the experiment. Since vanadium is present in Salamanca water in concentrations 10 times lower than As (Table A. 4), this suggests that this material’s water treatment performance would be greater when the arsenic concentration is lower. Iron concentration was also monitored during the experiment, but the concentrations detected were lower than the initial iron concentration of Salamanca water.

![Graph](image)

**Figure 6.13 Column of MKS-s with Salamanca groundwater.**
The solid recovered from the modified kitchen synthesis was assembled in a small column (i). The breakthrough curves of arsenic and vanadium are shown in (ii) and (iii), respectively.

**6.2.2. Dye remediation studies**

Four dyes were selected for this study because of their chemical structure (Figure 6.14): rose bengal, congo red, orange II, and methyl blue. Orange II and congo read are mono and di azo dyes. Rose bengal and methyl blue have chloro and sulfonic groups.
Figure 6.14 Chemical structure of selected dyes
Four dyes were selected for remediation studies because of their chemical structure: rose bengal (i), congo red (ii), orange II (iii) and methyl blue (iv).

The remediation efficiency of MKS-s is displayed in Figure 6.15. P25 (a TiO$_2$ nanomaterial) was selected for comparison for this study because it the nanomaterial that is the more widely used for degradation of organic dyes.$^{170}$
Figure 6.15  Dye remediation performance of MKS-s and TiO$_2$.

(i) The remediation of four different dyes was measured when using MKS-s and TiO$_2$; dye concentration was 50mg/L and the treatment dosage was 10L/g. (ii) The effect of the concentration was measured in two dyes for both the MKS solid and TiO$_2$. The MKS solid shows greater removal efficiency with all the dyes, except for methyl blue, in which case the performance is similar for both materials.

Figure 6.15.i shows the removal efficiency of the four dyes using both MKS-s and TiO$_2$, when the dye concentration is 50mg/L and the treatment dosage is 10L of water per gram of material. Experiments with UV radiation were also performed as it increases the efficiency of TiO$_2$. MKS-s was more efficient in removing all of the dyes despite their chemical structure. This is promising as the efficiency in photocatalytic processes diminish with the presence of some functional groups such as chloro or sulfonic substituents.$^{170}$ In Figure 6.15, two concentrations were selected for methyl blue and orange II, 10mg/L and 50mg/L. As expected, at lower concentrations, dye removal efficiency was higher for both MKS-s and TiO$_2$. However, in the case of orange II, the greater increase in efficiency produced by the MKS-s suggests that the removal mechanisms are different: the dye absorbs over
MKS-s, opposed to the photochemical degradation promoted by TiO$_2$. More detailed studies will be required to corroborate this hypothesis.

6.3. Conclusions

We explored the modification of the kitchen synthesis method in this chapter and the efficacies of its products for two water treatment applications. The modification was successful, in part, because it produces nanoparticles capable of adsorbing arsenic. Also, when completed on a large scale, it generates a solid material that can be used without further treatment for environmental applications.

In order to better understand this material, TEM and SEM images for morphological characterization were taken; XRD, Raman, and XPS were used for chemical and structural characterization. This solid material, herein referred as MKS-s, is composed of IO-NPs and FeCl$_2$·4H$_2$O embedded in a carbon matrix. This combination makes it a promising material for arsenic removal as it can be directly used in a column with additional support media. This material also showed significant potential for remediation of organic compounds perhaps because of its similarity to activated carbon.
Appendix A

Tables complementing Chapter 3 are presented in this appendix.
Table A. 1    Elemental analysis of several Salamanca wells during 2011

<table>
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<th>Element</th>
<th>EPA MCLG (μg/L)</th>
<th>EPA MCL (μg/L)</th>
<th>Mexico MCL (μg/L)</th>
<th>Well 2 (μg/L)</th>
<th>Well 5 (μg/L)</th>
<th>Well 12 (μg/L)</th>
<th>Well 18 (μg/L)</th>
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a) Treatment technique, TT; b) Action Level, AL; c) secondary standard; d) units=mg/L; e) less than Limit of Detection, LOD or Limit of Quantification, LOQ; f) measurement made by an external laboratory (CEMAPAS employee); g) normativity in discussion; h) N=number of measurement done, the average is presented, if standard deviation is larger than 5%, a range between parenthesis is given. When value is not given, the measurement was not made. All values are average of triplicate measurements by the instrument; standard deviation is less than 5% in all of them.
Table A.2: Elemental analysis of several Salamanca wells during November 2012

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<th>U (μg/L)</th>
<th>Be (μg/L)</th>
<th>Cd (μg/L)</th>
<th>Mn (μg/L)</th>
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<th>Al (μg/L)</th>
<th>As (μg/L)</th>
<th>Pb (μg/L)</th>
<th>V (μg/L)</th>
<th>Fe (μg/L)</th>
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Limit of Detection, LOD; Limit of Quantification, LOQ. All values are average of triplicate measurements by the instrument; standard deviation is less than 5% in all of them.
Table A. 3 Elemental analysis of several Salamanca wells during June 2013

| Well | Hg (μg/L) | Cd (μg/L) | Mn (μg/L) | Cr (μg/L) | Cu (μg/L) | Ni (μg/L) | Al (μg/L) | As (μg/L) | Ba (μg/L) | Pb (μg/L) | V (μg/L) | B (μg/L) | Fe (μg/L) | Se (μg/L) | Zn (μg/L) | SiO₂ (mg/L) |
|------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|----------|-----------|-----------|-----------|-----------|-------------|
| 1    | 14.4      | LOD       | 95.3      | LOQ       | 5.9       | LOQ       | 4.2       | 38.7      | 100.3     | LOD       | 58.4      | >600     | 28.6      | LOQ       | LOQ       | 84.5       |
| 2    | LOD       | 71.3      | LOQ       | 3.0       | 4.63      | 82.7      | 82.7      | 45.5      | LOQ       | 35.5      | >600     | 68.7      | LOQ       | LOQ       | 85.8       |
| 6    | LOQ       | LOD       | >100      | LOQ       | 4.0       | 1.26      | 328.3     | 98.2      | 64.8      | LOQ       | 18.5      | >600     | 342.1     | LOQ       | LOD       | 83.8       |
| 7    | LOD       | LOD       | 23.6      | 2.36      | 3.1       | 1.27      | 3.0       | 27.2      | 21.1      | LOQ       | 94.5      | 440.3    | 13.0      | LOQ       | LOD       | 91.2       |
| 9    | LOD       | LOD       | 74.2      | 1.50      | 6.6       | 2.43      | 3.1       | 34.9      | 36.5      | LOD       | 131.3     | >600     | 19.8      | LOQ       | LOD       | 90.0       |
| 10   | LOD       | LOD       | 18.7      | LOQ       | 14.5      | 1.52      | 1.2       | 15.4      | 91.8      | LOQ       | 119.2     | >600     | 33.8      | LOQ       | LOQ       | 86.1       |
| 11   | LOQ       | LOD       | 6.0       | 3.45      | 1.9       | 1.99      | 2.2       | 40.3      | 9.0       | LOD       | 73.5      | >600     | 10.6      | LOQ       | LOD       | 78.7       |
| 12   | LOD       | LOD       | 26.1      | LOQ       | 21.9      | 1.22      | 1.1       | 30.5      | 79.2      | LOD       | 147.0     | >600     | 17.1      | 1.1       | LOD       | 88.5       |
| 13   | LOD       | LOD       | 13.0      | 1.10      | 16.7      | 1.74      | 16.0      | 22.2      | 127.2     | LOD       | 91.4      | >600     | 62.2      | 1.3       | LOD       | 90.3       |
| 14   | LOD       | LOD       | LOD       | 1.15      | 10.5      | 1.62      | 1.4       | 17.1      | 91.7      | LOD       | 119.7     | >600     | 37.1      | 1.2       | LOD       | 86.6       |
| 17   | LOD       | LOD       | 58.7      | 2.01      | 7.9       | LOQ       | 2.7       | 27.9      | 38.0      | LOD       | 84.3      | 581.6    | 22.1      | LOQ       | LOQ       | 89.3       |
| 18   | LOD       | LOD       | 2.9       | 1.38      | 7.5       | LOQ       | 5.2       | 38.5      | 53.0      | LOD       | 100.1     | 534.6    | 21.1      | LOD       | LOD       | 82.7       |
| 19   | LOD       | LOD       | >100      | LOQ       | 20.3      | 5.32      | 5.7       | 27.5      | 86.7      | LOQ       | 214.0     | 555.9    | 35.1      | LOQ       | 1.6       | 87.1       |
| 20   | LOD       | LOD       | LOQ       | 1.74      | 20.5      | 1.02      | 4.1       | 24.0      | 94.1      | LOD       | 124.9     | >600     | 21.8      | LOQ       | LOD       | 88.7       |
| 24   | LOD       | LOD       | 15.2      | 2.50      | 4.7       | 1.12      | 15.1      | 34.3      | 16.1      | LOQ       | 99.0      | >600     | 64.4      | LOQ       | LOD       | 87.9       |
| 25   | LOD       | LOD       | 2.83      | 3.1       | LOQ       | 2.5       | 24.5      | 4.7       | LOD       | 91.4      | 461.3    | 13.6      | LOQ       | LOD       | 93.7       |
| 26   | LOD       | LOD       | 36.0      | LOQ       | 31.0      | 1.37      | 2.3       | 30.1      | 103.7     | LOD       | 96.2      | >600     | 30.2      | 1.1       | LOQ       | 85.0       |
| 27 | LOD | LOD | LOD | 2.09 | 10.6 | 1.34 | 2.7 | 14.8 | 127.5 | LOD | 94.7 | >600 | 39.0 | 1.4 | LOD | 84.6 |
| 28 | LOQ | LOD | LOQ | 23.1 | 6.25 | 3.0 | 32.6 | 59.9 | LOD | 38.0 | >600 | 61.3 | LOQ | LOD | 74.5 |
| 29 | LOD | LOD | LOD | 1.9 | 17.3 | 1.42 | 1.8 | 90.6 | 166.3 | LOD | 38.0 | >600 | 36.1 | 1.5 | LOD | 85.2 |
| 33 | LOD | LOD | LOD | 1.22 | 5.0 | LOQ | 8.9 | 20.4 | 144.1 | LOD | 94.4 | 455.1 | 33.1 | 1.7 | LOD | 87.1 |
| 34 | LOQ | LOD | LOD | 66.3 | 32.1 | 1.21 | 5.1 | 62.6 | 70.1 | LOQ | 55.4 | >600 | 25.6 | 1.6 | LOD | 79.9 |
| 35 | LOD | LOD | LOD | 1.90 | 1.8 | LOQ | 1.8 | 16.5 | 6.9 | LOD | 75.2 | 308.0 | 15.5 | LOQ | LOD | 94.0 |
| 37 | LOD | LOD | >100 | LOD | 10.5 | 1.71 | 16.5 | 31.2 | 97.3 | LOQ | 108.6 | 449.8 | 43.8 | LOQ | LOD | 88.2 |

Limit of Detection, LOD; Limit of Quantification, LOQ. All values are average of triplicate measurements by the instrument; standard deviation is less than 5% in all of them.
**Table A. 4  Elemental analysis of Well 2 in Salamanca**

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<td>2.6</td>
<td>3.8</td>
</tr>
<tr>
<td>V</td>
<td>--</td>
<td>--</td>
<td>16.9</td>
<td>14.9</td>
<td>15.6</td>
</tr>
<tr>
<td>Zn(^a)</td>
<td>5000</td>
<td>5000</td>
<td>LOQ</td>
<td>41.8</td>
<td>5.1-30.3</td>
</tr>
</tbody>
</table>

a) N=number of measurement done, the average is shown, if standard devia larger than 5%, a range between parenthesis is given; b) Secondary stand Treatment technique, TT; d) units=mg/L; f) the anion concentration is between parenthesis; e) measurement made by an external laboratory (CMAPAS employee). Contaminants exceeding the EPA MCL are remarked in red.
Appendix B


72. Ogata, A.; Banks, R. B. A solution of the differential equation of longitudinal dispersion in porous media; 411A; 1961.


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