DEVELOPMENT OF METHODS FOR THE CHARACTERISATION OF ENGINEERED NANOPARTICLES USED FOR SOIL AND GROUNDWATER REMEDIATION

by

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A Thesis submitted in fulfilment for the degree of

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February 2015

CERTIFICATE OF AUTHORSHIP/ORIGINALITY

I certify that this thesis has not previously been submitted for a degree nor has it been submitted as part of requirements for a degree except as fully acknowledge within the text.

I also certify that the thesis has been written by me. Any help that I have received in my research work and the preparation of the thesis itself has been acknowledged. In addition, I certify that all information sources and literature used are indicated in the thesis.

Signature of candidate:

………………………..

Date:

I dedicate this thesis to my parents

Thierry and Nathalie Chekli

ACKNOWLEDGEMENTS

First of all, I would like to express my deepest gratitude to my principal supervisor, A/Prof. Hokyong Shon for his excellent advices, contagious passion for research and never-ending support throughout the course of my PhD. I thank you for guiding me on how to become a bright researcher. I also would like to thank my external supervisors from UniSA, Prof. Enzo Lombi and Dr. Erica Donner as I have always felt welcome every time I was coming to Adelaide. You have been wonderful supervisors and I thank you for all your support and advices during my PhD. Many thanks as well to my co-supervisors, Dr. Sherub Phuntsho and Dr. Leonard Tijing for your continuous help and support.

I also want to acknowledge the contribution I received from my colleagues and friends Dr. Gianluca Brunetti, Dr. Yanxia Zhao, Bita Bayatsarmadi and Adi Maoz Shen and external collaborator and friend Dr. Maitreyee Roy from the National Measurement Institute who helped me to design and carry out some of my experimental works.

I would like also to acknowledge Prof. Hu Hao Ngo, Rami Hadad and Johir for their support in the laboratories as well as Katie McBean and Mark Berkahn for their valuable help and knowledge in SEM analysis. I also acknowledge the administrative support from Phyllis, Craig, Van and Viona during my three years at UTS.

Special thanks as well to all my dear friends Fouzy Lofti, Jung Eun Kim, Mohammad Shahid, Soleyman Memesahebi, Kanupriya Khurana, Sotos Vasileiadis as well as Julie, Laure, Delphine, Simon and Thomas for their constant support, encouragement and friendship.

Finally, I would like to express my profound gratitude to my family, especially my parents who have always supported me and encouraged me during my study. Without their support, I would not have been able to come to Australia. I also would like to thank my dearest friend Charlotte for her patience, comfort and continuous moral support during these three years.

Last but not least, I would like to acknowledge CRC CARE and the University of Technology, Sydney for providing full financial support through scholarship for the completion of this research thesis.

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**Publications made during the PhD candidature including articles not entirely related to the Thesis. *Articles related to the Thesis.

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LIST OF ABBREVIATIONS

AFM: **A**tomic **F**orce **M**icroscopy

BTC: **B**reakthrough **C**urve

CCA: **C**hromated-**C**opper-**A**rsenate

CCC: **C**ritical **C**oagulation **C**oncentration

CE: **C**apillary **E**lectrophoresis

CMC: **C**arboxymethyl **C**ellulose

CNTs: **C**arbon **N**anotubes

CPM: **C**ount **P**er **M**inute

DLA: **D**iffusion-**L**imited **A**ggregation

DLS: **D**ynamic **L**ight **S**cattering

DLVO: **D**erjaguin–**L**andau–**V**erwey–**O**verbeek

DO: **D**issolved **O**xygen

DOC: **D**issolved **O**rganic **C**arbon

DOM: **D**issolved **O**rganic **M**atter

EC: **E**lectrical **C**onductivity

EXAFS: **X**-ray **A**dsorption **F**ine **S**tructure

ENPs: **E**ngineered **N**anoparticles

FD: **F**ractal **D**imension

FFF: **F**ield-**F**low **F**ractionation

FlFFF: **F**low **F**ield-**F**low **F**ractionation

sFlFFF: **S**ymmetrical **F**low **F**ield-**F**low **F**ractionation

AsFlFFF: **As**ymmetrical **F**low **F**ield-**F**low **F**ractionation

FTIR: **F**ourier **T**ransform **I**nfrared **S**pectroscopy

GZVI: **G**ranular **Z**ero **V**alent **I**ron

HA: **H**umic **A**cid

HMW: **H**igh **M**olecular **W**eight

IC: **I**on **C**hromatography

ICP-MS: **I**nductively **C**oupled **P**lasma **M**ass **S**pectrometry

IS: **I**onic **S**trength

LIBD: **L**aser-**i**nduced **B**reakdown **D**etection

MA(L)LS: **M**ulti **A**ngle (**L**aser) **L**ight **S**cattering

MWCNTs: **M**ulti-**w**alled **C**arbon **N**anotubes

NOM: **N**atural **O**rganic **M**atter

NTU: **N**ephelometric **T**urbidity

nZVI: **n**anoscale **Z**ero **V**alent **I**ron

ORP: **O**xydo-**r**eduction **P**otential

PAA: **P**olyacrylic **A**cid

PRBs: **P**ermeable **R**eactive **B**arriers

PSS: **P**olystyrene **S**ulfonate

PZC: **P**oint of **Z**ero **C**harge

QELS: **Q**uasi-**e**lastic **L**ight **S**cattering

RF: **R**ecovery **F**actor

RLA: **R**eaction-**l**imited **A**ggregation

RPs: **R**etention **P**rofiles

SAXS: **S**mall **A**ngle **X**-ray **S**cattering

SDBS: **S**odium **D**odecyl**b**enzene**s**ulfonate

(HP)SEC: (**H**igh **P**erformance) **S**ize-**E**xclusion **C**hromatography

SEM: **S**canning **E**lectron **M**icroscopy

SF: **S**trength **F**actor

SLS: **S**tatic **L**ight **S**cattering

SPM: **S**canning **P**robe **M**icroscopy

SRNOM: **S**uwannee **R**iver **N**atural **O**rganic **M**atter

SWCNTs: **S**ingle-**w**alled **C**arbon **N**anotubes

TCE: **T**ri**c**hloro**e**thylene

(S)TEM: (**S**canning) **T**ransmission **E**lectron **M**icroscopy

TOC: **T**otal **O**rganic **C**arbon

WWTPs: **W**astewater **T**reatment **P**lants

XANES: **X**-ray **A**dsorption **N**ear-**e**dge **S**tructure

XAS: **X**-ray **A**dsorption **S**pectroscopy

XEDS: **X**-ray **E**nergy **D**ispersive **S**pectroscopy

XPS: **X**-ray **P**hotoelectron **S**pectroscopy

XRD: **X-r**ay **D**iffraction

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ABSTRACT

In the past two decades, extremely rapid progress in the nanotechnology R&D sector has been met by equally rapid commercialisation of this new technology. As a consequence, engineered nanoparticles (ENPs) are increasingly released into the environment. For the purpose of soil and groundwater remediation, large amounts of nanomaterials are intentionally discharged to the environment. Risk assessment of these novel technologies is therefore required due to the uncertainties regarding their potential side effects. To support this, research into the environmental fate of ENPs is urgently needed but has been so far hindered by significant analytical challenges. Developing novel methodologies to better understand the ENPs behaviour in the environment is therefore crucial to assessing their potential risk.

Iron nanoparticles, and more specifically nanoscale zero-valent iron (nZVI), are becoming increasingly popular for the treatment of contaminated soil and groundwater; however, their mobility and reactivity in subsurface environments are significantly affected by their tendency to aggregate. Assessing their stability under environmental conditions is crucial for determining their environmental fate. A multi-method approach (including different size-measurement techniques and the DLVO theory) has been developed to thoroughly characterise the behaviour of iron oxide nanoparticles (Fe_2O_3NPs – used as a surrogate for nZVI) under environmentally relevant conditions. Although recent studies have demonstrated the importance of using a multi-method approach when characterising nanoparticles, the majority of current studies continue to use a single-method approach.

Under some soil conditions (i.e. pH 7, 10 mM NaCl and 2 mM $CaCl_2$) and increasing particle concentration, Fe_2O_3NPs underwent extensive aggregation to form large aggregates (> 1 µm). Coating the nanoparticles with dissolved organic matter (DOM) was investigated as an alternative “green” solution to overcoming the aggregation issue instead of using the

more commonly proposed polyelectrolytes. At high concentrations, DOM effectively covered the surface of the Fe_2O_3NPs, thereby conferring negative surface charge on the particles across a wide range of pH values. This provided electrostatic stabilisation and considerably reduced the particle aggregation effect. DOM-coated Fe_2O_3NPs also proved to be more stable under high ionic strength conditions. The presence of $CaCl_2$, however, even at low concentrations, induced the aggregation of DOM-coated Fe_2O_3NPs, mainly via charge neutralisation and bridging. This has significant implications in regards to the reactivity and fate of these materials in the environment.

Humic acid (HA) and Suwannee River natural organic matter (SRNOM) were tested and compared as surrogate for DOM to stabilise Fe_2O_3 NPs. The advantages of DOM over conventional organic surface modifiers are that DOM is naturally abundant in the environment, inexpensive, non-toxic and readily adsorbed onto the surface of metal oxide nanoparticles. The DOM-coated Fe_2O_3 NPs were characterised by developing a multi-method approach including various analytical methods: flow field-flow fractionation (FlFFF), high performance size exclusion chromatography (HPSEC) and Fourier transform infrared spectroscopy (FTIR). The stability of the coated NPs was also evaluated by assessing their aggregation and disaggregation behaviour over time.

Results showed that both HA and SRNOM were rapidly and readily adsorbed on the surface of Fe_2O_3 NPs, providing electrosteric stabilisation over a wide range of pH. HPSEC results showed that the higher molecular weight components of DOM were preferentially adsorbed onto the surface of Fe_2O_3. As SRNOM consists of macromolecules with a higher molecular weight than HA, the measured size of the SRNOM-coated Fe_2O_3 NPs was 30 % larger than the HA-coated Fe_2O_3 NPs. FTIR results indicated the occurrence of hydrogen bonding arising from electrostatic interaction between the DOM and Fe_2O_3 NPs. Finally, a stability study showed that after 14 days, small agglomerates and aggregates were formed. The HA-coated Fe_2O_3 NPs formed agglomerates which were easily disaggregated using a vortex mixer, with the coated NPs returning to their initial size. However, SRNOM-coated Fe_2O_3 NPs were only partially disaggregated using the same method, which indicates that these aggregates have a more compact structure.

To date, research focusing on the development of novel surface modifiers to increase the mobility of iron-based nanoparticles has only been carried out in highly idealised systems which facilitated their detection and quantification. In fact, one of the main analytical challenges in characterising nanomaterials is related to the difficulty of quantifying nanomaterials once they are dispersed in complex environmental matrices. Finding new analytical methods to overcome this issue would significantly help in the development of effective remediation materials. A novel method based on radiolabelling has been therefore developed and enables the detection and quantification of iron-based nanoparticles in intact soil cores. The radioisotopes (i.e. ^{59}Fe) were incorporated in the core of the nanoparticles during its synthesis. The mobility of radiolabelled nanoparticles was assessed by gamma counting analysis and then compared with the mobility of commercialised nanoparticles which was determined by common ICP-MS method. Results showed limited mobility of both nanomaterials with less than 1% of the injected mass eluted from the columns. The use of specific isotopic signature allowed determining the retention profiles of radiolabelled nanoparticles which was a major advantage compared to conventional ICP-MS method. Results indicated that the majority (i.e. 80%) of the particles were retained in the first centimetres of the columns suggesting that rapid aggregation of iron-based nanoparticles after its injection was the main explanation of its limited mobility. The method was further developed by coupling gamma counting and ICP-MS measurements to evaluate both the mobility of radiolabelled nanoparticles and its potential to co-transport contaminants in contaminated soils. Results showed that, although the mobility of iron-based nanoparticles was limited, the breakthrough of both contaminants and iron-based nanoparticles occurred

simultaneously suggesting that iron-based nanoparticles has the potential to co-transport contaminants.

Adsorption of natural organic matter (NOM), aggregation and disaggregation have been identified as three of the main processes affecting the fate and behaviour of ENPs in aquatic environments. However, although several methods have been developed to study the aggregation behaviour of ENPs in natural waters, there are only a few studies focusing on the fate of such aggregates and their potential disaggregation behaviour. In this study, we developed and demonstrated a simple method, based on on-line light scattering measurement, for characterising the aggregation behaviour and aggregate structure of ENPs in different natural waters. Both the aggregate size of ENPs and their adsorption capacity for DOM were strongly related ($R^2 > 0.97$, $p < .05$) to the combined effect of initial concentration of DOM and the ionic strength of the natural waters. The structure of the formed aggregates was strongly correlated ($R^2 > 0.95$, $p < .05$) to the amount of DOM adsorbed by the ENPs during the aggregation process. Under high ionic strength conditions, aggregation is mainly governed by diffusion and the aggregates formed under these conditions showed the lowest stability and fractal dimension, forming linear, chain-like aggregates. In contrast, under low ionic strength conditions, the aggregate structure was more compact, most likely due to strong chemical binding with DOM and bridging mechanisms involving divalent cations formed during reaction-limited aggregation.

Finally, a multi-method approach combining the developed on-line light scattering method with off-line instruments such as field-flow fractionation techniques has been proposed to overcome the limitation of light scattering instruments related to the polydispersity of the samples. Results confirmed the benefits of using a multi-method approach. While the on-line light scattering method can provide information on the larger aggregates (i.e. size and structure), FlFFF proved to be a very accurate technique for characterising the smaller

particles remaining in suspension after sedimentation. When combined, these techniques can offer complementary data on the particle size distribution of the samples.