

**SYNTHESIS OF OPEN-SHELL IRON
OXIDE-POLYELECTROLYTE-SILICA
NANOCOMPOSITE FOR WATER
TREATMENT APPLICATION**

CHE HUI XIN

**UNIVERSITI SAINS MALAYSIA
2017**

**SYNTHESIS OF OPEN-SHELL IRON OXIDE-POLYELECTROLYTE-
SILICA NANOCOMPOSITE FOR WATER TREATMENT APPLICATION**

by

CHE HUI XIN

**Thesis submitted in fulfillment of the
requirements for the degree of
Doctor of Philosophy**

May 2017

ACKNOWLEDGEMENTS

This PhD dissertation is the culmination of over five years of research at School of Chemical Engineering, Universiti Sains Malaysia. It is truly amazing and unbelievable that I successfully have gone through this miserable time. Finally, let me take this precious opportunity to acknowledge a number of persons who have contributed in diverse ways and influenced me greatly in accomplishing my research and thesis.

The first person I would like to convey my deepest appreciation is my main supervisor, Professor Madya Lim Jit Kang. I know him since my second year of undergraduate who requires us to design an experiment to remove oil spillage, in conjunction with the Gulf of Mexico, oil spill 2010. I admire his creativity and teaching style since that project. Besides his research area is interesting, his passion in work has driven me to choose him as my main advisor without a second thought. He is the driving force behind all the research works. He emphasizes quality (instead of quantity) of work and great science, and has never compromised on it. He requires every student working with him to achieve scientific maturity as the main criteria to graduate. He keeps pushing up my top limit with force, stress, encouragement and motivation where I don't believe I can achieve it. Thanks for his great effort and constructive suggestions along the years. He is an extremely smart and hardworking advisor. I am proud and lucky to have him as my advisor. To me, he is not only my mentor, but also a big brother. His great patience, unconditional guidance and hearty advice have led me through the obstacles. Secondly, I need to thank my co-advisor Professor Ahmad Abdul Latif for giving me the huge freedom in doing research over the years. I feel glad to

have the enthusiastic assistance from technicians during my lab works. I am blessed to have sincere help from administrative staffs when dealing with all the research related documents.

Secondly, I must thank my beloved family for their unflagging love and spiritual support throughout the years in my research and my life, keeping me harmonious and well taken care, especially my dad for his great consideration and patience, although from time to time, he keeps asking for the date I graduate and start to work. Thanks for raising me up. You are my pillar of strength. Without you, I will never be who I am today. I love you, dad.

Next, I would like to thank all my friends and colleagues who have gone through ups and downs in my research life. I need to convey my gratitude to my senior Swee Pin for his guidance during my premature stage of research. From him, I learn to be strong and determined. My other colleagues, Syazwan, Sim Siong, Chuan Chun, Wei Ming, Foo Kean, Shang Jun, Mun Jun, Yee Ling, Wei Mei, and Huzaifah who work close to me and have been a source of assistance in my research. I wish to record my appreciation to Qi Hwa, Huey Ping, Pey Yi, Li Peng, Jing Yao, Guat Wei, Qian Yee and others who I am not able to address here. Their invaluable and selfless discussion is much appreciated. I need specifically mentioning Pei Teng, Yong Yi, Choon Gek, Yee Jie, Mei Kee and Siong Voon who always care about me and send me warmest regards. Not to mentioning Roy, who initiates me for choosing this research path. His presence, contribution and influence have deeply imprinted in my life. Special appreciation must be expressed to H.L. Lye who has been a source of motivation and inspiration. He unconditionally supports me through the last stage in finishing this

thesis, patiently walks me through the rough times and leads me out of dark. There is no word can precisely express my gratitude to him. Without each of them, my experience would not be so wonderful and I will cherish the memories for the rest of my life. Their support and care will always be remembered. Thanks to all of you. I am eternally grateful for those who have involved in this process towards the completion in reality.

Here, I would like to express my greatest appreciation to Ministry of Higher Education, MyBrain15 MyPhD scholarship for financially supporting me in this academy. Without MyBrain15, I can hardly survive through the expenses. I wish to acknowledge Universiti Sains Malaysia (Grant No. 1001/PJKIMIA/811219), Exploratory Research Grants Scheme (ERGS) with (Grant No. 203/PJKIMIA/6730012), FRGS grant from MOHE (Grant No. 203/PJKIMIA/6071269), International Foundation for Science (IFS) (Grant No. 304/PJKIMIA/ 6050232), International Foundation for Science (IFS) (Grant No. 304/PJKIMIA/6050324) co-financed by the Organization for the Prohibition of Chemical Weapon (OPCW), and Membrane Science and Technology Cluster of USM for providing me financial support throughout my research.

Sincerely, Hui Xin

TABLE OF CONTENTS

	Page
ACKNOWLEDGEMENT	ii
TABLE OF CONTENTS	v
LIST OF TABLES	xi
LIST OF FIGURES	xiii
LIST OF PLATES	xix
LIST OF ABBREVIATIONS	xx
LIST OF SYMBOLS	xxiii
ABSTRAK	xxvii
ABSTRACT	xxix
CHAPTER ONE: INTRODUCTION	
1.1 Iron oxide nanoparticles	1
1.2 Problem Statement	2
1.3 Research Objectives	5
1.4 Research Scope	5
1.5 Organization of Thesis	7
CHAPTER TWO: LITERATURE REVIEW	
2.1 Building blocks of nanocomposite	8
2.1.1 Iron oxide nanoparticles	8
2.1.1(a) IONPs synthesis by co-precipitation	9
2.1.1(b) Unique property of IONPs in magnetic behaviour	11

	2.1.1(c) Unique property of IONPs in catalytic behavior	15
	2.1.2 Silica	17
	2.1.3 Polyelectrolyte	19
	2.1.3(a) Poly(diallyldimethylammonium) choride)	20
	2.1.3(b) Poly(ethyleneimine)	21
2.2	Formation of core-shell structure of nanocomposite	22
	2.2.1 Layer-by-layer assembly	22
	2.2.2 Adsorption of polyelectrolyte	26
	2.2.3 Theoretical description of adsorption layer	28
	2.2.3(a) Mean field approximation	28
	2.2.3(b) Scaling approximation	29
	2.2.3(c) The combination of mean field and scaling approximations	29
	2.2.3(d) Deposition of IONPs with DLVO theory	30
	2.2.4 Mechanism of core-shell formation	31
	2.2.5 Constraints and future outlook on IONPs deposition	33
2.3	Magnetic nanocomposite	34
	2.3.1 Advantages of magnetic nanocomposite	35
	2.3.2 Morphology of magnetic nanocomposite	37
	2.3.3 Advantages of silica-polyelectrolyte-IONPs nanocomposite	41
2.4	Environmental engineering application	43
	2.4.1 Current stage of magnetic nanocomposite	43
	2.4.1(a) Dye removal	45
	2.4.1(b) Amoxicillin antibiotic removal	46

2.4.2	Mechanism of pollutant removal	47
CHAPTER THREE: MATERIALS AND METHODS		
3.1	Materials and chemicals list	50
3.2	The flow of experiments	52
3.3	Synthesis of nanoparticles	53
3.3.1	Synthesis of silica nanoparticles	53
3.3.2	Synthesis of iron oxide nanoparticles	54
3.3.3	Synthesis of magnetic nanocomposite	54
3.4	Characterization of nanoparticles	56
3.4.1	Sizing information	56
	3.4.1(a) Dynamic light scattering	56
	3.4.1(b) Transmission Electron Microscope	57
3.4.2	Surface charge determination	57
3.4.3	Surface topology	58
	3.4.3(a) Transmission Electron Microscope	58
	3.4.3(b) Atomic Force Microscope (AFM)	58
3.4.4	Colloidal stability assessment	59
3.4.5	Determination for stability ratio	59
3.5	Interfacial phenomena by QCM-D	61
3.5.1	Working principal	61
3.5.2	Substrate preparation	63
3.6	Performance test of synthesized magnetic nanocomposite	64
3.6.1	Measurement of pollutant concentration	66
3.6.2	Leaching test of IONPs	68

CHAPTER FOUR: RESULTS AND DISCUSSION

4.1	Outline	69
4.2	Synthesis and characterization of nanomaterials	69
4.2.1	Synthesis of silica colloids	69
4.2.2	Synthesis of iron oxide nanoparticles	70
4.2.3	Synthesis of magnetic nanocomposite	71
4.3	Evaluation ‘soft matter’ properties of magnetic nanocomposite	73
4.3.1	Particle concentration effect	73
4.3.2	Ionic species effect	81
	4.3.2(a) Experimental determination for stability ratio	90
	4.3.2(b) DLVO prediction for stability ratio	91
	4.3.2(c) Analysis on the experimental and theoretical outcomes	93
4.3.3	Summary	99
4.4	Advanced surface engineering of magnetic nanocomposite	99
4.4.1	Multilayers polyelectrolyte	100
	4.4.1(a) Evolution of nanocomposite	100
	4.4.1(b) Conformational change of particles-polymeric structure	102
	4.4.1(c) Performance test of synthesized nanocomposite	103
	4.4.1(d) Summary	105
4.4.2	Effect of polyelectrolyte’s molecular weight	106
	4.4.2(a) Evolution of nanocomposite	107
	4.4.2(b) Unique features from DLS, QCM-D, TEM and AFM	112
	4.4.2(c) Ionic species effect	116

4.4.2(d)	Performance test of synthesized nanocomposite	121
4.4.2(e)	Leaching study	125
4.4.2(f)	Summary	126
4.4.3	Linear and branched of polyelectrolyte	126
4.4.3(a)	Evolution of nanocomposite	127
4.4.3(b)	Interfacial phenomena	133
4.4.3(c)	Mean field and scaling approaches	139
4.4.3(d)	Performance test of synthesized nanocomposite	148
4.4.3(e)	Summary	152
4.5	Engineering feasibility study	153
4.5.1	Evolution of nanocomposite	153
4.5.2	Removal of MB and MO dyes from aqueous environment	157
4.5.2(a)	Langmuir and Freundlich adsorption analysis	163
4.5.2(b)	Pseudo-first-order and pseudo-second-order kinetic study	170
4.5.3	Summary	174
 CHAPTER FIVE: CONCLUSION AND RECOMMENDATIONS		
5.1	Conclusion	175
5.2	Recommendations	179
 REFERENCES		181

APPENDICES

- Appendix A: Estimation of particles involved in nanocomposite synthesis
- Appendix B: Calculation on collision frequency of IONPs
- Appendix C: M-file for DLVO calculation
- Appendix D: Calculation on PDDA and PEI deposited on QCM-D quartz crystal
- Appendix E: Calibration curves for pollutants
- Appendix F: Dyes removal by nanocomposite of different polyelectrolyte layer
- Appendix G: AMX removal by co-precipitated IONPs and nanocomposite of different polyelectrolyte molecular weight
- Appendix H: Dyes removal by co-precipitated IONPs, silica, and nanocomposite of linear or branched polyelectrolyte
- Appendix I: Dyes removal by silica, silica-PDDA, and nanocomposite of commercial IONPs
- Appendix J: Separation of used nanoparticles after dyes removal
- Appendix K: Recyclability test using nanocomposite after 6 months of storage

LIST OF PUBLICATIONS

LIST OF TABLES

		Page
Table 2.1	IONPs core with different material(s) acted as shell for different water treatment purposes.	39
Table 2.2	Maximum adsorption capacity for different pollutants by different iron oxide adsorbents.	44
Table 3.1	List of chemicals and materials.	50
Table 4.1	Characteristic rate constant, k_{obs} and equilibrium deposited mass, $q_{e,fitted}$ after the fitting from the experimental data of IONPs deposited onto PDDA pre-adsorbed silica surface as a function of IONPs concentration.	78
Table 4.2	Debye length and the deposited mass and thickness of PDDA and IONPs assembled layers on silica quartz crystal surface evaluated by Voigt-model when ionic strength is increased.	86
Table 4.3	Hydrodynamic diameter with polydispersity index (PDI) for all the building blocks and nanocomposite as measured by DLS, and their associated electrophoretic mobility and zeta potential. All measurements were made by Malvern Instruments, Zetasizer Nano-ZS. The solution pH was in the range of 6.3 – 6.8.	101
Table 4.4	Hydrodynamic diameter, polydispersity index (PDI), electrophoretic mobility and zeta potential for all the building blocks and nanocomposite.	108
Table 4.5	Diameters of nanoparticles determined by TEM and DLS. The size of nanoparticles in TEM was determined using Image J by performing image analysis on 100 nanoparticles.	109
Table 4.6	Film thickness increment for different combination of PDDA molecular weight and IONPs with respect to silica.	113
Table 4.7	AFM result of root-mean-square roughness of assembled films on silica-coated quartz crystal.	116
Table 4.8	Total iron content leached out from nanocomposite after five consecutive runs of AMX removal.	126
Table 4.9	Hydrodynamic diameter, polydispersity index (PDI), electrophoretic mobility and zeta potential for silica, IONPs, polyelectrolyte (PDDA and PEI), silica-polyelectrolyte and silica-polyelectrolyte-IONPs.	129

Table 4.10	Diameters of nanoparticles determined by TEM. The size of nanoparticles in TEM was determined using Image J by performing image analysis on 100 nanoparticles.	130
Table 4.11	Compilation of the raw data (frequency and dissipation shifts), thickness and mass evaluated from Voigt-model.	134
Table 4.12	Zeta potential and hydrodynamic diameter of different nanoparticles measured by Zetasizer Nano-ZS (Malvern Instruments).	154
Table 4.13	Langmuir, Freundlich isotherm model constants with regression coefficient, separation factor, adsorption intensity and favourability.	169
Table 4.14	Comparison of the pseudo-first-order, pseudo-second-order adsorption rate constants and calculated and experimental q_e values with regression coefficient and nonlinear regression chi-square.	173

LIST OF FIGURES

		Page
Figure 2.1	Schematic representation of LBL self-assembly film of polyanion and polycation on a planar charged surface.	24
Figure 2.2	Schematic representation of the segments of a randomly adsorbed polyelectrolyte showing tail, loop and train.	26
Figure 2.3	Different morphologies of magnetic nanocomposite with IONPs are assumed always to be the core.	38
Figure 2.4	The structural formula for (a) positively charged Methylene Blue (MB) and (b) negatively charged Methyl Orange (MO).	46
Figure 2.5	Amoxicillin (AMX) molecular structure.	46
Figure 3.1	Schematic flow of conducting overall experiments.	52
Figure 3.2	Schematic diagram showing the major steps involved in directed assembly of silica-polyelectrolyte-IONPs nanocomposite. Negatively charged silica colloid is surface functionalized with cationic polyelectrolyte first and later subjected to the attachment of negatively charged iron oxide nanoparticles (IONPs).	53
Figure 4.1	TEM image of silica colloids synthesized by <i>Stöber</i> process.	70
Figure 4.2	TEM image of IONPs synthesized by co-precipitation method.	71
Figure 4.3	Schematic diagram showing major steps involved in layer-by-layer assembly of nanocomposite by commercial IONPs.	71
Figure 4.4	TEM image of silica-PDDA-IONPs nanocomposite in core-shell structure.	73
Figure 4.5	Time dependence of frequency and dissipation shift for 6 mM PDDA and IONPs concentration of (a) 20 ppm and (b) 500 ppm onto a QCM-D silica quartz crystal.	75
Figure 4.6	Changes of deposited mass of IONPs at 20 ppm and 500 ppm over time by evaluating both frequency and dissipation shifts simultaneously with Voigt-model QCM-D.	76

Figure 4.7	Specific amount of IONPs deposited on a 14 mm diameter of silica surface as a function of initial IONPs concentration. This result is obtained from the Voigt-model based upon the QCM-D measurement.	77
Figure 4.8	The resulted conformation of the PDDA matrix in low (top) and high (below) concentration of introduced IONPs on QCM-D silica quartz crystal. It was noticed that a stiff layer of PDDA/IONPs (image below) prohibited further registration of incoming IONPs into the particles-polymeric matrix. Hence, this layer accommodated lesser amount of IONPs.	79
Figure 4.9	Stiffness of the PDDA/IONPs assembled layers on silica quartz crystal surface (denoted by D/f relationship) as a function of IONPs concentration.	81
Figure 4.10	Time variation of frequency and dissipation shift for 6 mM PDDA and 100 ppm IONPs onto a QCM-D silica quartz crystal at ionic strength of (a) 0.1 and (b) 5.0 mM NaCl.	83
Figure 4.11	Dissipation versus frequency shift of the PDDA/IONPs assembled layers on QCM-D silica quartz crystal from solution of (a) 0, (b) 1 and (c) 10 mM NaCl.	84
Figure 4.12	(a) The deposition of IONPs on QCM-D silica quartz crystal surface pre-coated with PDDA over time from solution of (i) 0, (ii) 1 and (iii) 10 mM NaCl with the deposited mass estimated by using Voigt-model. (b) Kinetic rate constant of IONPs deposition as a function of solution ionic strength based on result presented in (a) by fitting through first order kinetic equation.	85
Figure 4.13	Typical tapping-mode of AFM 3D images ($3 \times 3 \mu\text{m}$) of PDDA/IONPs assembled films on QCM-D silica quartz crystal, from 0 mM (left) and 1.0 mM (right) NaCl solution.	89
Figure 4.14	Aggregation profile of IONPs in the presence of different concentration of NaCl.	91
Figure 4.15	Aggregation attachment efficiency of IONPs as function of NaCl (M) at pH 8.5. The critical coagulation concentration (CCC) based on DLS (●) and DLVO (□) measurements was found at 50 mM NaCl.	94
Figure 4.16	IONPs (a) deposition rate (Hz/sec) and (b) deposition efficiency onto silica (○) and PDDA-coated silica (●) surface as function of NaCl.	95

Figure 4.17	IONPs deposition in terms of (a) D/f ratio and (b) relative increment amount onto silica (○) and PDDA-coated silica (●) surface as function of NaCl.	98
Figure 4.18	TEM images of (a) silica-PDDA-IONPs and (b) silica-PDDA-PSS-PDDA-IONPs.	102
Figure 4.19	QCM-D measurement of frequency (grey line) and dissipation (black line) shifts at the normalized third overtone in the systems of (a) PDDA and IONPs, (b) PDDA/PSS/PDDA and IONPs, and (c) the dissipation shift versus frequency shift using data from (a) and (b).	103
Figure 4.20	Dye removal of (a) MB and (b) MO by silica-PDDA-IONPs (—■—), and silica-PDDA-PSS-PDDA-IONPs (—△—) without H ₂ O ₂ (1 st cycle) and with H ₂ O ₂ (recycling run 2-5).	105
Figure 4.21	Schematic diagram shows the major steps involved in directed-assembly of silica-PDDA-IONPs nanocomposite. Negatively charged silica colloid is surface functionalized with cationic polyelectrolyte PDDA first and later subjected to the attachment of negatively charged IONPs. Low MW PDDA forms a more compact polyelectrolyte layer and high MW PDDA tends to form a more extended layer.	106
Figure 4.22	TEM images of (a) silica-low MW PDDA-IONPs and (b) silica-high MW PDDA-IONPs.	109
Figure 4.23	Colloidal stability profile of IONPs (▲), silica-low MW PDDA-IONPs (□), and silica-high MW PDDA-IONPs (●) monitored in terms of averaged hydrodynamic diameter throughout the 500 minutes measurement time using dynamic light scattering.	110
Figure 4.24	Real-time magnetophoretic separation rate of IONPs (▲), silica-low MW PDDA-IONPs (□), and silica-high MW PDDA-IONPs (●) at 100 mg/L under influence of a NdFeB magnet.	111
Figure 4.25	QCM-D measurement of frequency (grey line) and dissipation (black line) shift at third overtone in the systems of (a) low MW PDDA and IONPs, (b) high MW PDDA and IONPs, as well as the (c) dissipation shift versus frequency shift using data from (a) and (b).	114

Figure 4.26	AFM images in 2D mode (3×3μm) of the low MW PDDA/IONPs (left) and high MW PDDA/IONPs (right) assembled films deposited on silica quartz crystal.	116
Figure 4.27	Averaged hydrodynamic diameter decrement of (a) silica-low MW PDDA(▲) and (b) silica-high MW PDDA(●) by varying ionic strength of MgCl ₂ ranging from 0 to 10 mM.	117
Figure 4.28	Schematic diagram for the interaction of low MW PDDA and high MW PDDA with the silica colloid of same dimension. The radius of curvature effect is more pronounced for high MW PDDA.	120
Figure 4.29	Changes in dissipation as function of time of (a) low MW PDDA (black line) and (b) high MW PDDA (grey line) on silica-coated quartz crystal by changing the background medium from deionized water to 10 mM MgCl ₂ solution at 1800 seconds.	121
Figure 4.30	The Amoxicillin antibiotic removal by IONPs (▲), silica-low MW PDDA (+), silica-high MW PDDA (×), silica-low MW PDDA-IONPs (○) and silica-high MW PDDA-IONPs (□) in the experiment condition without H ₂ O ₂ (1 st cycle) and in the presence of H ₂ O ₂ (recycling run 2-5), with all particle concentration of 0.01 g/ml.	125
Figure 4.31	Directed-assembly scheme of silica-polyelectrolyte-IONPs by using either PDDA or PEI.	127
Figure 4.32	TEM micrographs of (a) silica-low MW PDDA-IONPs and (b) silica-PEI-IONPs.	130
Figure 4.33	Colloidal stability profile of IONPs (▲), silica-PDDA-IONPs (□), and silica-PEI-IONPs (●) monitored via the averaged hydrodynamic diameter over 500 minutes time interval using dynamic light scattering, where every single data was collected with 15 runs per measurement of total 3 measurements.	132
Figure 4.34	Real-time magnetophoretic separation rate of IONPs (—▲—) at $3.44 \times 10^{-4} \text{ sec}^{-1}$, silica-PDDA-IONPs (—□—) at $3.57 \times 10^{-4} \text{ sec}^{-1}$, and silica-PEI-IONPs (—●—) at $3.72 \times 10^{-4} \text{ sec}^{-1}$. All experiments were conducted at the particle concentration of 1000 mg/L under influence of a NdFeB magnet, where the data were collected over 2000 seconds by using a UV-vis spectrophotometer (Agilent, Cary-60). A sample of nanocomposite or IONPs was placed in a cuvette exposed to a NdFeB magnet which was placed at the side wall.	133

Figure 4.35	QCM-D measurement of frequency (grey line) and dissipation (black line) shifts at the normalized third overtone in the systems of (a) PDDA and IONPs, (b) PEI and IONPs, and (c) the dissipation shift versus frequency shift using data from (a) and (b).	134
Figure 4.36	Three-dimensional AFM topographic images showing the morphology of IONPs deposited on (a) PDDA-coated and (b) PEI-coated silica quartz crystal surface. AFM images were all $3\ \mu\text{m} \times 3\ \mu\text{m}$ scans for samples that were being compared, accompanied with the z-scales as shown.	139
Figure 4.37	Schematic diagram showing the attachment and the possible orientation of PDDA (left) and PEI (right) with the silica surface, with an adsorbing backbone (λ). PDDA adsorbed mainly as train segments (left). Side chains of branched PEI conserved the tail segments upon adsorption, denoted as “brush” regime with thickness (L) in the blob model of size D_b of scaling law (right).	147
Figure 4.38	(a) MB and (b) MO dyes removal by silica ($\text{---}\times\text{---}$), silica-PDDA ($\text{---}\square\text{---}$), silica-PEI ($\text{---}\blacktriangle\text{---}$), IONPs ($\text{---}\ominus\text{---}$), silica-PDDA-IONPs ($\text{---}\blacksquare\text{---}$), and silica-PEI-IONPs ($\text{---}\blacktriangle\text{---}$) in the experiment without H_2O_2 (1st cycle) and in the presence of H_2O_2 (recycling run 2–5), with all particle concentrations of 0.01 g/mL.	152
Figure 4.39	TEM micrographs of (a) commercial IONPs obtained from Nanostructured & Amorphous Materials Inc., commercial IONPs covered on (b) one and (c) four PDDA-coated silica colloids	155
Figure 4.40	Colloidal stability is conducted by studying the changing of averaged hydrodynamic diameter of commercial IONPs (\bullet) and silica-PDDA-IONPs (\blacktriangle) over predetermined time where the data were collected every 3 minutes for total 5 hours run.	156
Figure 4.41	Dye removal percentage in (a) MB and (b) MO by silica (\bullet), silica-PDDA (\blacklozenge) and silica-PDDA-IONPs (\blacktriangleleft).	158

Figure 4.42	Schematic diagram showing the electrostatic interactions and mechanisms involved for MB and MO removal by (a) silica colloid, (b) silica-PDDA, and (c) silica-PDDA-IONPs. For processes which are mainly driven by adsorption, such as (a) and (b), electrostatic plays an important role to either promote or suppress the MB and MO removal depends on the charges of adsorbate (here dye molecules) and adsorbent (silica colloid and silica-PDDA). For silica-PDDA-IONPs process (c), the influence of electrostatic interaction is negligible as Fenton-reaction dominates the removal mechanism.	161
Figure 4.43	Dye removal percentage of silica-PDDA-IONPs used in (a) MB and (b) MO.	162
Figure 4.44	Removal of (a) MB and (b) MO by using 6 months old silica-PDDA-IONPs compared with silica in MB removal and silica-PDDA in MO removal respectively.	163
Figure 4.45	Langmuir adsorption isotherm plots of silica (●), silica-PDDA (◆) and silica-PDDA-IONPs (▲) in MB and MO dyes removal.	167
Figure 4.46	Freundlich adsorption isotherm plots of silica (●), silica-PDDA (◆) and silica-PDDA-IONPs (▲) in MB and MO dyes removal.	168
Figure 4.47	Pseudo-first-order and pseudo-second-order kinetic plots of silica (●), silica-PDDA (◆) and silica-PDDA-IONPs (▲) in MB and MO dyes removal.	172

LIST OF PLATES

	Page
Plate 4.1	112
Temporal evolution of suspension opacity for (top) bare IONPs and silica-PDDA-IONPs constructed by either (middle) low or (bottom) high MW PDDA under the influence of a NdFeB cylindrical magnet with surface magnetization at around 5300 gauss. Iron oxide nanoparticles content for all three suspensions was maintained at 0.01 g/ml.	
Plate 4.2	132
Time dependent magnetophoretic behavior of bare IONPs, silica-PDDA-IONPs, and silica-PEI-IONPs under the influence of a NdFeB magnet. All the samples were prepared in 1000 mg/L.	
Plate 4.3	157
Comparison the collection rate of bare IONPs (left) and silica-PDDA-IONPs (right) by a NdFeB magnet within 4 minutes. Both suspensions were prepared with concentration at 500 mg/L. The crystal clear solution formed at the end of magnetic collection for silica-PDDA-IONPs suspension also directly proved that both silica colloid and IONPs have been integrated into one unified structure.	

LIST OF ABBREVIATIONS

AFM	Atomic force microscopy
AMX	Amoxicillin
As	Arsenic
Au	Gold
B	Boron
CCC	Critical coagulation concentration
CeO ₂	Cerium (IV) oxide
Cd	Cadmium
Co	Cobalt
Cr	Chromium
Cu	Copper
DLS	Dynamic light scattering
DLVO	Derjaguin-Landau-Verwey-Overbeek
Fe	Iron
FeO	Wüstite
Fe ₃ O ₄	Magnetite
γ -Fe ₂ O ₃	Maghemite
α -Fe ₂ O ₃	Hematite
GNS	Graphene nanosheets
Hg	Mercury
HGMS	High-gradient magnetic separation
HNT	Halloysite nanotubes
H ₂ O ₂	Hydrogen peroxide
H ₂ O	Water

ICP-OES	Inductively coupled plasma-optical emission spectrometry
IONPs	Iron oxide nanoparticles
LBL	Layer-by-layer
LGMS	Low-gradient magnetic separation
MB	Methylene Blue
Mg	Magnesium
MIH	Magnetic inductive heating
Mn	Manganase
MO	Methyl Orange
MRI	Magnetic resonance imaging
Ms	Saturation magnetization
MW	Molecular weight
NaOH	Sodium hydroxide
NdFeB	Neodymium boron ferrite
NH ₂	Amidogen
NH ₃	Ammonia
Pb	Lead
PCP	Pentachlorophenol
Pd	Palladium
PDI	Polydispersity index
PDDA	Poly(diallyldimethylammonium chloride)
PEI	Poly(ethyleneimine)
PSS	Poly(styrenesulfonate)
QCM-D	Quartz crystal microbalance with dissipation
RhB	Rhodamine B

RMS	Root-mean-square
SDS	Sodium dodecyl sulphate
Se	Selenium
SFA	Surface Force Apparatus
SiO ₂	Silica
Te	Tellurium
TEM	Transmission electron microscopy
TEOS	Tetraethoxyorthosilicate
Ti	Titanium
U	Uranium
XPS	X-ray Photoelectron Spectroscopy
XRD	X-ray powder diffraction
ZnO	Zinc oxide
ZnS	Zinc sulphide

LIST OF SYMBOLS

<i>cm</i>	Centrimeter
<i>D</i>	Dissipation
<i>f</i>	Frequency
<i>g</i>	Gram
<i>G</i>	Gauss
<i>Hz</i>	Hertz
<i>L</i>	Litre
<i>m</i>	Meter
<i>mg</i>	Milligram
<i>mM</i>	Millimolar
<i>mL</i>	Millilitre
<i>min</i>	Minutes
<i>ng</i>	Nanogram
<i>nm</i>	Nanometer
μm	Micrometre
<i>ppb</i>	Part per billion
<i>ppm</i>	Part per million
<i>rpm</i>	Revolutions per minute
<i>s</i>	Second
<i>n</i>	Overtone number
<i>t</i>	Time
<i>T</i>	Tesla
<i>I</i>	Ionic strength
<i>L</i>	Thickness of the brush