SYNTHESIS, CHARACTERIZATION AND OPTIMIZATION OF MAGNETIC NANOSTRUCTURES BY SOL-GEL TECHNIQUE AND APPLICATION IN WATER PURIFICATION

SYED FARHAN HASANY

Thesis submitted in fulfillment of the requirements for the award of the degree of
Doctor of Philosophy in Chemical Engineering (Advanced materials)

Faculty of Chemical Engineering & Natural Resource
UNIVERSITI MALAYSIA PAHANG

February 2014

ABSTRACT

Tailored maghemite nanoparticles with improved thermo-physical properties have attracted vast interest in current years. The design and synthesis of these particles have generated innovative magnetic, optical and other physical properties that arise from quantum size effect and enhanced surface to volume ratio with huge application significance. Tailored magnetic nanoparticles are prepared either by wet chemical methods such as colloidal chemistry or by dry processes such as vapor deposition techniques. This PhD project, aimed to develop novel vanadium doped maghemite ($Fe_{2-x}V_xO_3$) particles with novel properties of ~ 5 nm and nanohybrids of maghemite size ranges from 13-15 nm decorated multiwalled carbon nanotubes (MWCNTs) by wet methods. Tailored maghemite – MWCNTs nanohybrid was later, applied in efficient Lead removal application from aqueous solutions. The synthesis involved a facile Sol-gel route, with control over the size, morphology and the magnetic properties. Tailored maghemite particles were synthesized from a metal precursors and MWCNTs in a single pot reactor assembly, with forced nucleation in slight basic medium at pH ~ 9, yields crystalline, pure phase and thermally stable particles and nanohybrids. The synthesized particles and nanohybrids were characterized for different physical properties; crystallinity, phase purity and transformations, morphology, hydrodynamic particle size, polydispersity, magnetic properties, surface area studies, elemental and oxidation states of iron and vanadium, thermal stability, colloidal stability, zeta potential values and elemental ratios of iron, oxygen and carbon in tailored maghemite – MWCNT nanohybrids. The comparative changes in structural, magnetic, surface area and colloidal properties of the nanoparticles were found significant for future applications in nano devices, magnetic coatings, magnetic separations and other applications. Tailored maghemite – MWCNT nanohybrids were applied for efficient removal of Lead from aqueous solutions in batches magnetically. Lead adsorption mechanism was studied with Kinetics rate, adsorption isotherms. The effects of pH, contact time, adsorbent dosage, and agitation speed on the Pb (II) removal were scrutinized. Repeated adsorption–desorption cycles were studied to investigate the prolonged use of nanohybrids. The maximum removal achieved was ~ 94 % in less than 2 h in a pH range of 6–7, which is very good yield with respect to previous studies. A mathematical model (Minitab version 15) was studied to validate the experimental method for the removal of Lead.

ABSTRAK

Nanopartikel maghemite disesuaikan dengan baik sifat termo-fizikal telah menarik minat yang besar dalam tahun-tahun semasa. Reka bentuk dan sintesis zarah ini telah menjana magnet, optik dan lain-lain ciri-ciri fizikal yang inovatif yang timbul daripada kesan saiz kuantum dan permukaan dipertingkatkan kepada nisbah jumlah permohonan dengan kepentingan yang besar. Nanopartikel magnetik disesuaikan disediakan sama ada dengan kaedah kimia basah seperti kimia koloid atau oleh proses kering seperti teknik pemendapan wap. Projek PhD, bertujuan untuk membangunkan vanadium novel maghemite didopkan ($Fe_{2-x}V_xO_3$) zarah dengan ciri-ciri novel ~ 5 nm dan nanohybrids saiz maghemite antara 13-15 nm dihiasi nanotube karbon multiwalled (MWCNTs) dengan kaedah basah. Maghemite disesuaikan - MWCNTs nanohybrid kemudiannya, digunakan dalam cekap Lead penyingkiran permohonan daripada penyelesaian berair. Sintesis melibatkan facile Sol-gel laluan, dengan kawalan ke atas saiz, morfologi dan sifat-sifat magnet. Zarah maghemite disesuaikan telah disintesis daripada prekursor logam dan MWCNTs dalam periuk pemasangan reaktor tunggal, dengan penukleusan terpaksa dalam medium asas sedikit pada pH ~ 9, hasil kristal, fasa tulen dan zarah nanohybrids dan haba stabil. Zarah disintesis dan nanohybrids telah disifatkan dengan sifat-sifat yang berbeza fizikal; penghabluran, kesucian dan perubahan fasa, morfologi, saiz zarah hidrodinamik, polydispersity, sifat magnet, kajian kawasan permukaan, unsur dan pengoksidaan besi dan vanadium, kestabilan terma, kestabilan koloid, zeta nilai-nilai yang berpotensi dan nisbah unsur besi, oksigen dan karbon dalam maghemite disesuaikan - nanohybrids MWCNT. Perubahan perbandingan struktur, magnet, kawasan permukaan dan sifat-sifat koloid nanopartikel didapati penting bagi aplikasi masa depan dalam peranti nano, lapisan magnet, pemisahan magnet dan aplikasi lain. Maghemite disesuaikan - nanohybrids MWCNT telah digunakan untuk penyingkiran cekap Lead daripada penyelesaian akueus dalam kumpulan magnet. Utama mekanisme penjerapan telah dikaji dengan kadar Kinetics, isoterma penjerapan. Kesan pH, masa sentuhan, dos bahan penjerap, dan kelajuan pergolakan di Pb (II) penyingkiran telah diteliti. Berulang kitaran penjerapan-desorption dikaji untuk menyiasat penggunaan berpanjangan nanohybrids. Penyingkiran maksimum dicapai adalah ~ 94% dalam masa kurang daripada 2 jam dalam pelbagai pH 6-7, yang merupakan hasil yang sangat baik berkenaan dengan kajian sebelum ini. Model matematik (Minitab versi 15) telah dikaji untuk mengesahkan kaedah eksperimen bagi penyingkiran Lead.

CONTENTS

APPENDICES

LIST OF TABLES

LIST OF FIGURES

NOMENCLATURES

List of Symbols

Symbol	Meaning
K	Kelvin
^{o}C	Degree Celsius
TN	Neel Temperature
K/s	Cooling rate
XM	Magnetic susceptibility
CM	Curie constant
CT	Curie Temperature
hv	photon energy
T	Absolute temperature (K)
TB	Blocking temperature
eg	Unpaired electrons
Keff	Anisotropy constant
Ek	Kinetic energy
B.E	Binding energy
Pa	Pascal
Ti	Lowest temperature when mass change is detected (TGA)
Tf	Lowest temperature when the mass change is completed
V	Voltage (emf)
n	Turns of cross-sectional area
B	flux
M	Magnetization
H_0	Measuring field

VT	Potential energy function
VS	Potential energy due to the solvent
VA	Potential energy due to attractive forces
VR	Potential due to repulsive forces
A	Hamaker constant
D	Particle separation
a	Particle radius
d	diffractional spacings
a^0	Lattice parameters
eV	Electron volt
Ms	Magnetic saturation
Oe	Oersted
Mr	Magnetic remanence
r2	correlation coefficients
pHiep	pH of zero potential
P/Po	Relative pressure
k	Rate constant of sorption (g/mgh-1)
qeq	Amount of Pb (II) ions adsorbed at equilibrium (mg/g)
Ce	Equilibrium Lead ions concentration in solution (mg/L)
qmax	Maximum capacity of adsorbent (mg/g)
K	Langmuir adsorption constant(L/mg)
xi	The factor
b_0	The constant
bi	is the linear effect of the factor xi
bii	Quadratic effect of the factor xi

bij	The interaction effects between the input factors xi and xj
R2	Coefficient of determination
Bhf	Magnetic hyperfine field
qt	The amount of Pb (II) ions adsorbed at any time (mg/g)
y	The response

Greek Symbols

Symbol	**Meaning**
	height of the energy barrier
λ	Wavelength
Φ	Work function of spectrophotometer
δ	Path difference
ω	Frequency domain
υ	Frequency
π	Solvent permeability
κ	Function of the ionic composition
ζ	Zeta potential
θ	Angle
ε	The residual term.

LIST OF ABBREVIATIONS

MWCNTs	Multiwalled carbon nanotubes
nm	Nanometer
Pb	Lead
PDI	Polydispersity
HGMS	High gradient magnetic separations
CNTs	Carbon nanotubes
PEGPEI	Poly (ethylene imine) -g-poly (ethylene glycol)
ANOVA	Analysis of Variance
FTIR	Fourier transform infrared spectroscopy
AOT	Aerosol-OT anionic Surfactant
TEM	Transform electron microscope
RM	Reverse microemulsion
NaDDBS	Sodium benzene sulfonate
TEOS	Tetraethoxysilane
3D	Three dimensional
FKSSA	Faculty of Chemical Engineering & Natural Resource
IP	Isopropoxide
HRTEM	High-resolution transmission electron microscopy
SPIONs	Superparamagnetic iron oxide nanoparticles
PEG	Polyethylene glycol
PVP	Polyvinyl pyrrolidone
PEI	Poly ethylene imine
CTAB	cetyl tri methyl ammonium bromide
SWNT	Single walled nanotube
VSM	Vibrating sample magnetometer
TGA	Thermo-gravimetric analysis

BET	Brunauer-Emmet-Teller
PBS	Poly butylene succinate
EDX	Energy Dispersive X-ray spectroscopy
XRD	X-ray diffraction
AAS	Atomic absorption spectroscopy
XPS	X-ray photon spectroscopy
AES	Auger electron spectroscopy
DTA	Differential thermal analysis
SEM	scanning electron microscope
FFT	Fast Fourier transform
DVLO	Derjaguin, Verwey, Landau and Overbeek theory
BJH	Barret–Joyner–Halender
RSM	Response surface method
M	Molarity
rpm	Revolutions per minute
BJH	Barret–Joyner–Halender
MCM	Meso- porous Silicate
FESEM	Field Emission Scanning Electron Microscopy
h-$REFeO_3$	Hexagonal Rare- earth- iron oxides

PUBLICATIONS

CONFERENCE PROCEEDINGS

1. Post graduate Poster competition, (April 2011), University of Malaysia Pahang, Malaysia.

2. S.F.Hasany, A. Rehman, R. Jose, I.Ahmed. Iron Oxide Magnetic Nanoparticles: A Short Review. International Conference on Nanotechnology (ICONT 2011).Sabah, Malaysia.

3. S.F.Hasany, I.Ahmed, A. Rehman, Rajan J. Comparative study of the Preparation Techniques of Iron Oxide Magnetic Nanoparticles – A Review. International Conference of Chemical Engineering and Biotechnology, (ICCEIB-SOMCHE 2011), Malaysia.

4. S.F.Hasany, N.H.Abdurahman, A.R. Sunarti, Rajan J, M.R.Kazimi. Synthesis of Hematite nanoparticles by modified sol- gel method and study of its morphology. 3rd National Conference on Postgraduate Research, Universiti Malaysia Pahang, Kuantan, 8-9 Sep 2012.

5. S.F.Hasany, N.H.Abdurahman, A.R. Sunarti, Rajan J, M.R.Kazimi. Green synthesis of nanoparticles: A review. Poster presentation of The International Conference on Biomass for Biofuels and Value-Added Products (ICBBVAP), Double Tree by Hilton Hotel, Kuala Lumpur, 23-24 Oct 2012.

6. Bronze Medal in CITREX Exhibition 2013, University of Malaysia Pahang.

7. Paper accepted in conference ICMEE, 2013 Yokohama, Japan.

8. Paper accepted in Nano Today 2013 Conference, Singapore, will be held in December 2013.

JOURNAL PAPERS

1. S. F. Hasany, I.Ahmed, Rajan J, A.Rehman. Systematic Review of the Preparation Techniques of Iron Oxide Magnetic Nanoparticles. *Nanoscience and Nanotechnology*. 2011; 1(1): 1-11.

2. S. F. Hasany, A. Rehman, R. Jose, and I. Ahmed. Iron oxide magnetic nanoparticles: A short review. American Institute of Physics. *AIP Conf. Proc.* 2012. 1502: 298-321.

3. S. F. Hasany, N. H. Abdurahman, A.R. Sunarti, R. Jose. Magnetic Iron oxide nanoparticles: Chemical Synthesis and Applications: Review. *Journal of Current nanoscience*. 2013. 9: 561-575. Bentham publications, USA.

4. S.F.Hasany, N.H.Abdurahman, A.R. Sunarti, Anuj Kumar. Noncovalent assembly of maghemite- multiwalled carbon nanotubes for efficient lead removal from aqueous solution. *Aust. J. Chem.* 2013, 66, 1440–1446.

5. S. F. Hasany, N. H. Abdurahman, A.R. Sunarti. Wet chemical synthesis of vanadium doped maghemite magnetic nanoparticles. Inorganic Chemistry Communications. Elsevier publishing (submitted).

PATENT APPLIED:

Synthesis of Vanadium (III) doped cubic ferrite (magnetic nanoparticle).
Associate Prof. Dr. Abdurahman.H.Nour, Syed Farhan Hasany, and Prof. Dr. Jose Rajan.

CHAPTER I

INTRODUCTION

1.1 INTRODUCTION

This thesis presents the results of an experimental study of physical properties of vanadium tailored maghemite nanoparticles and noncovalent nanohybrids of maghemite – multiwalled carbon nanotubes (MWCNTs), that are synthesized by crystallization of amorphous precursors. In addition to the synthesis, maghemite – MWCNTs nanohybrids were employed in environmental study for the efficient removal of Lead (Pb II), from aqueous solutions. A mathematical model has been studied for the optimization of Lead removal efficacy from aqueous solutions.

Magnetic nano materials are highly pursued during the last two decades because of their improved thermo-physical properties in diverse engineering applications globally (Alivisatos, 1996; Fendler, 1998; Mahmoudi et al., 2011; Schmid, 1994; and Weller, 1993). The manipulation of matter, with control at nanometer dimensions, produces new structures, materials, and devices. Nano-particles promise an unprecedented advancement in many sectors, such as medicine, energy, materials, consumer products, and manufacturing (Tari et al., 1979; Poizot et al., 2000 and Mahmoudi et al., 2010). The main areas of application to date are in electronics, photonics, pharmaceuticals, chemical synthesis and analysis, cosmetics and finishes for surfaces and textiles. The synthesis of discrete magnetic nanoparticles with sizes ranging from 2 to 20 nm is of significant importance, because of their applications in magnetic storage devices (Awschalom and DiVicenzo, 1995; Billas et al., 1994; Handley et al., 1999 and Raj and Moskowitz, 1990). The unique magnetic property of the nano-particles arises mainly due to the reduced sizes of isolated nano particles and contributions from inter particle interactions are negligible. The surfactant coating on magnetic nanoparticles prevents clustering due to steric repulsion. Dynamic adsorption and desorption of surfactant molecules on to particle surfaces during synthesis enable reactive species to be added onto the growing particles. These nanoparticles can be dispersed in many organic solvents and can be retrieved in powdered form by removing the solvent.

The preparation method plays a key role in determining the particle size and shape, size distribution, surface chemistry and therefore the applications of the material (Jeong et al., 2007).The conditions necessary for the formation of magnetic particles are essentially the same as for non-magnetic particles but some special precautions are necessary because of strong magnetic interactions among the particles. The essential parameters are:

- Separation of the nucleation process from the growing process.
- Protection of particles from aggregation.
- A controlled supply of precursor materials, and
- Temperature and pH of the solution.

1.2 PROBLEM STATEMENT

Chemical synthesis and in particular, methods from organometallic Chemicals have been widely used to produce nanomaterials. (Klabunde et al., 1998) studied used Borohydride derivatives reduction methods extensively for the synthesis. The drawback of these reductions methods is the incorporation of boron in to the particles which leads to the modification of magnetic properties of the particles. Reduction of metal carbonyls studied by (Suslick et al., 1999) was not able to synthesis size and shape controlled nanomaterials.

(Dassenoy et al., 2000) studied the Hydrocarbyl complexes, by hydrogenating organometallic complexes containing an olefinic and poly olefinic ligand decomposed to give bare metal atom which would condenses in the reaction medium. Thus the particles are super paramagnetic with blocking temperatures near 10 K and display an enhanced magnetization at saturation per cobalt atom compared to bulk cobalt. Additions of O_2, pyridine, isocyanides or CO lead to a dramatic decrease of the magnetic properties of the particles. This demonstrates that:

- The absence or low contamination of the as prepared particles, and

- The presence of a relation between the π-accepting properties of the ligand and the magnetic properties of the nanomaterials.

In general, the particle sizes, magnetic properties of magnetic nanoparticles can be controlled by systematically adjusting the reaction parameters, such as time, temperature, and the concentrations of reagents and stabilizing surfactants. Particle size increases with increasing reaction time, because more monomeric species are generated and with increasing reaction temperature because the rate of reaction is increased.

The followings key issues for magnetic nanoparticle synthesis are problem statement of this research proposal.

- To study the particle size distribution (uniformity), in the synthesized mono dispersed magnetic nano particles.

- To study the particle size control of magnetic nanoparticles in a reproducible manner.

- To study the crystallinity and desired crystal structure of magnetic nanoparticles with satisfactory level of crystalline identity.

- To study the Shape-controlled synthesis of anisotropic nanoparticles in relation to specific applications.