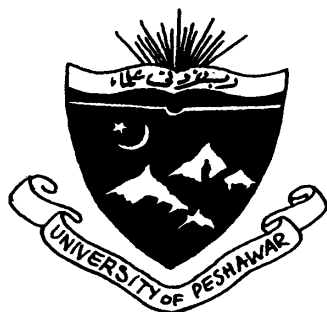


**ADVANCED SOLID PHASE EXTRACTION METHODS
FOR THE PRECONCENTRATION OF SELECTED
HEAVY METALS USING MAGNETIC
NANOMATERIALS**



Ph.D Thesis

By

MANSOOR KHAN

**INSTITUTE OF CHEMICAL SCIENCES
UNIVERSITY OF PESHAWAR
PAKISTAN
APRIL 2016**

**ADVANCED SOLID PHASE EXTRACTION METHODS
FOR THE PRECONCENTRATION OF SELECTED
HEAVY METALS USING MAGNETIC
NANOMATERIALS**

By

MANSOOR KHAN

DISSERTATION

**SUBMITTED TO THE UNIVERSITY OF PESHAWAR IN
PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY
IN CHEMISTRY**

**INSTITUTE OF CHEMICAL SCIENCES
UNIVERSITY OF PESHAWAR
PAKISTAN
APRIL 2016**

INSTITUTE OF CHEMICAL SCIENCES
UNIVERSITY OF PESHAWAR
PAKISTAN

Certified that **MR MANSOOR KHAN S/O SHERA JAN** has carried out his research and experimental work on the topic entitled as “**Advanced Solid Phase Extraction Methods for the Preconcentration of Selected Heavy Metals Using Magnetic Nanomaterials**” under our guidance and supervision. His research work is original and his dissertation is worthy of presentation to the University of Peshawar for the award of degree of **Doctor of Philosophy in Chemistry**.

SUPERVISOR

Meritorious Prof. Dr. Jasmin Shah
Institute of Chemical Sciences
University of Peshawar,
Khyber Pakhtunkhwa, Pakistan

CO-SUPERVISOR

Prof. Emeritus Dr. Muhammad Rasul Jan
Institute of Chemical Sciences,
University of Peshawar,
Vice Chancellor,
University of Peshawar,
Khyber Pakhtunkhwa, Pakistan

EXTERNAL EXAMINER

بِسْمِ اللَّهِ الرَّحْمَنِ الرَّحِيمِ

In the name of **ALLAH**, the most **B**eneficent, the most **M**erciful.

To My

Parents

With Prayers and Love

ACKNOWLEDGEMENTS

In the name of ALLAH, the most Gracious, the most Compassionate, Who is the Creator of the heavens and the earth and He, Who guides us in oceans of darkness and difficulties. I would like to express my gratitude to Allah for providing me the blessings to accomplish this work. May Allah accept this work as Sadqa-e-Jaria for helping the environment and His creation, and reward us the highest level in Jannah. During my PhD a number of people contributed, to whom my words are insufficient to acknowledge.

First, I submit my highest appreciation to my primary supervisor, meritorious professor **Dr. Jasmin Shah**, whose institution elevated me to the stature I am today, who have been my parent, my mentor, my confidant, my colleague, and a never-ending fount of moral support. Whose guidance, stimulation, valuable suggestions, constant encouragement and affectionate behavior helped me to complete this work. She encouraged me to not only grow as a researcher and as a chemist, but also as an instructor and an independent thinker. She is an excellent example of a good and successful women chemist.

I am also obliged to my co-supervisor professor emeritus **Dr. Muhammad Rasul Jan**, whose thought provoking attitude, skilled discussions, highly specialized guidance, constant support and continuous feedback enabled me to complete this thesis. I am thankful to him and acknowledge his devotion and precious time.

In fact, I am truly thankful to both of them and find myself lucky to have such teachers, who cared so much about me and my work. I pray, may Allah shower His endless blessing upon them and reward them according to His Generosity.

I would also like to mention my foreign advisor **Mustafa Soylak** Professor, Department of Chemistry, Erciyes University, Kaysery, Turkey. I am thankful to him for providing me the opportunity to work as a visiting researcher in his lab. I learned much more from his company. I am also thankful to **Erkan Yelmiz**, Research Assistant, Erciyes University, Kaysery, Turkey for his help and guidance in research.

I acknowledge **TUBITAK, 2216** for financial support and to providing me research opportunity in Turkey. I am also thankful to the Director and all the faculty of Institute of Chemical Sciences, University of Peshawar for providing me help, facilities and encouragement in pursuing my higher education in chemistry.

I am thankful to the teaching faculty of our section **Assistant Prof. Dr. Kashif Gul, Dr. Sajjadullah** and **Mrs. Saima Sohni**.

I am obliged to **Mr. Iftikhar Ahmad, Mr. Zia ur Rehman, Mr. Hamid Ali, Mr. Asmat Ali, Mr. Muhammad Ali**, other clerical and para teaching staff.

In my PhD lab. work, my lab. colleagues have a major role and they have to be mentioned individually. I am thankful to **Dr. Atta ul Haq** for extreme sincerity, **Dr. Mian Muhammad** for his constant encouragement and boost up, **Dr. Behisht Ara** for kind guide and gentle handling, **Dr. Maria Sadia** for creation of trust and

self-confidence, **Dr. Inayatullah** for his soft accent with kind heart, and a man of principles, **Dr. Sultan Shah** for his wise talks, advises and sea of knowledge, **Dr. Muhammad Naeem** for his friendly brother hood, moral support and working efficiency, **Dr. Adnan Rauf** for his guidance in research and constant partnership, **Ms. Salma Amir** for her companionship and enhancing quench of knowledge, **Mr. Mansoor Ahmed** and **Mr. Wali Muhammad** for their joyful company, **Ms. Tasmia** for her believes and approach toward gaining knowledge, **Mr. Aamir Iqbal** for his good attitude toward research and social work, **Mr. Ibadat ur Rehman** for his learning techniques **Mr. Muhammad Zada** as co-worker.

At the end, I have to mention my family; my father, my mother, my wife, my brothers, my sisters, my late grandmother (May Allah keep her soul in rest and peace) and other relatives, whose prayers and continuous moral support enabled me to achieve this hard task done.

Mansoor

Khan

TABLE OF CONTENTS

S. No.	Title	Page No.
	LIST OF FIGURES	x
	LIST OF TABLES	xiv
	ABBREVIATIONS	xvii
	SUMMARY	xxiv
CHAPTER 1. INTRODUCTION		
1.1	Solid phase extraction	1
1.2	Solid phase adsorbent	2
1.3	Modified solid phase material	2
1.4	Magnetic nanoparticles and magnetic modified nanomaterial	3
1.5	Magnetic graphene nanocomposite	4
1.6	Magnetic carbon nanotubes	4
1.7	Magnetic nanoparticle impregnated biosorbent	5
1.8	Advantages of magnetic nanoparticles and magnetic modified nanomaterials	5
1.9	Aims and objectives	6
	References	7
CHAPTER 2. LITERATURE REVIEW		
	References	35

CHAPTER 3. EXPERIMENTAL

3.1	Preparation of adsorbent	42
3.1.1	Preparation of magnetic nanoparticles (MNPs)	42
3.1.2	Preparation of silica coated magnetic nanoparticles (SiMNPs)	42
3.1.3	Preparation of magnetic nanoparticle impregnated banana peels (MNPs-BP)	42
3.1.4	Synthesis of magnetic carbon nanotubes (MCNTs)	43
3.1.5	Synthesis of silica coated magnetic carbon nanotubes (SiMCNTs)	43
3.1.6	Synthesis of 1-(2-Pyridylazo)-2-naphthol (PAN) impregnated SiMCNTs (SiMCNTs-PAN)	43
3.1.7	Synthesis of graphene oxide (GO)	44
3.1.8	Synthesis of allylamine modified graphene oxide	44
3.1.9	Synthesis of Magnetic modified graphene oxide-DVB-VA	44
3.2	Characterization of adsorbent	45
3.2.1	Characterization by using FT-IR	45
3.2.2	SEM and EDX analysis	45
3.2.3	XRD analysis	46
3.2.4	Surface area, pore volume and pore size analysis	46

3.3	Sample preparation	46
3.3.1	Preparation of water samples	46
3.3.2	Preparation food samples	47
3.3.3	Preparation of soil samples	47
3.4	Determination of heavy metals in the samples	48

CHAPTER 4. RESULTS AND DISCUSSIONS

Part 1: Magnetic solid phase extraction of Cd(II) using magnetic nanoparticles (MNPs) and silica coated magnetic nanoparticles (SiMNPs)		50
4.1	Result and discussion	50
4.1.1	Characterization of adsorbent	50
4.1.2	Magnetic solid phase extraction procedure	54
4.1.3	Optimization of the parameter of magnetic solid phase extraction	54
4.1.3.1	Effect of pH	54
4.1.3.2	Effect of adsorbent dose	56
4.1.3.3	Effect of sample volume	58
4.1.3.4	Desorption condition	59

4.1.3.5	Matrix effect	61
4.1.4	Kinetic studies	63
4.1.5	Isotherm studies	66
4.1.6	Thermodynamic studies	71
4.1.7	Application to real samples	73
Part 2	Solid phase extraction of Pb(II) using magnetic nanoparticles (MNPs) and magnetic nanoparticles impregnated banana Peels (MNPs-BP)	74
4.2	Result and discussion	74
4.2.1	Characterization	74
4.2.2	Magnetic solid phase extraction procedure	78
4.2.3	Optimization of the parameter related with magnetic solid phase extraction procedure	79
4.2.3.1	Effect of pH	79
4.2.3.2	Effect of adsorbent dose	80
4.2.3.3	Effect of sample volume	81
4.2.3.4	Desorption studies	82
4.2.3.5	Matrix effect	84

4.2.4	Kinetic studies	86
4.2.5	Isotherm studies	87
4.2.6	Thermodynamic studies	90
4.2.7	Validation of the proposed magnetic solid phase extraction method	90
Part 3:	Application of response surface methodology to the magnetic nanoparticle impregnated orange peels for the removal of Ni(II)	92
4.3	Result and discussion	92
4.3.1	Characterization of adsorbents	92
4.3.2	Experimental design and optimization	94
4.3.2.1	Statistical analysis	96
4.3.3	Kinetic studies	99
4.3.4	Isotherm studies	103
4.3.5	Thermodynamic studies	107
4.3.6	Effect of coexisting cations	108

4.3.7	Application to real samples	109
-------	-----------------------------	-----

Part 4: Vortex assisted magnetic solid phase extraction of lead(II) and cobalt(II) on silica coated magnetic carbon nanotubes impregnated 1-(2-Pyridylazo)-2-naphthol (SiMCNTs-PAN)	111
--	------------

4.4	Result and discussion	111
-----	-----------------------	-----

4.4.1	Characterization of SiMCNTs-PAN	111
-------	---------------------------------	-----

4.4.2	Optimization	113
-------	--------------	-----

4.4.2.1	Effect of pH	113
---------	--------------	-----

4.4.2.2	Amount of adsorbent	115
---------	---------------------	-----

4.4.2.3	Effect of sample volume	115
---------	-------------------------	-----

4.4.2.4	Desorption studies	116
---------	--------------------	-----

4.4.2.5	Matrix effect	118
---------	---------------	-----

4.4.2.6	Kinetic study	120
---------	---------------	-----

4.4.2.7	Thermodynamic studies	122
---------	-----------------------	-----

4.4.2.8	Validation of the proposed method	123
---------	-----------------------------------	-----

Conclusions	126
-------------	-----

Part 5: Published Work	128
-------------------------------	------------

LIST OF FIGURES

Fig. No.	Caption	Page No.
3.1	Standard calibration curve for determination of Cd(II) using FAAS.	48
3.2	Standard calibration curve for determination of Pb(II) using FAAS.	49
4.1	FT-IR spectra of MNPs (a) and SiMNPs (b).	50
4.2	SEM micrographs of SiMNPs(a) and MNPs(b).	52
4.3	EDX mapping of SiMNPs(a) and MNPs(b).	53
4.4	Effect of pH on % recovery of Cd(II) using MNPs and SiMNPs (Volume of sample: 10 mL, amount of adsorbent: 0.1 g, final volume: 10 mL, N=3).	56
4.5	Effect of adsorbent dose on % recovery of Cd (II) using MNPs and SiMNPs (pH: 7, Volume of sample: 10 mL, final volume: 10 mL, (N=3).	57
4.6	Effect of volume of sample on % recovery of Cd (II) using MNPs and SiMNPs (pH: 7, Volume of eluent: 10 mL, amount of adsorbent: 0.1 g, (N=3).	59
4.7	Effect of volume of eluent on % recovery of Cd (II) using MNPs and SiMNPs (pH: 7, Volume of sample: 10 mL, amount of adsorbent: 0.1 g, (N=3).	61
4.8a	Pseudo second order kinetic model for the adsorption of Cd(II) on SiMNPs and MNPs.	64
4.8b	Intraparticle diffusion model for the adsorption of Cd(II) using	65

	SiMNPs and MNPs.	
4.9	Langmuir adsorption isotherm for the adsorption of Cd(II) using SiMNPs and MNPs.	67
4.10	Freundlich isotherm model for the adsorption of Cd(II) using SiMNPs and MNPs.	68
4.11	Plot of $\ln K_D$ versus $1/T$ for estimation of thermodynamic parameters for Cd(II) adsorption on SiMNPs and MNPs.	72
4.12	SEM micrographs of BP(a), MNPs-BP(b) and MNPs (c).	75
4.13	EDX spectrum of BP, MNPs(a) and MNPs-BP(b), BP(c)	77
4.14	Schematic representation of the solid phase extraction method.	78
4.15	Effect of pH on % recovery Pb(II) using MNPs and MNPs-BP (Volume of sample: 10 mL, amount of adsorbent: 0.1 g, final volume: 10 mL N=3).	80
4.16	Effect of adsorbent dose on % recovery Pb(II) using MNPs and MNPs-BP (pH of solution: 7, volume of sample: 10 mL, final volume: 10 mL, N=3).	81
4.17	Effect of sample volume on % recovery of Pb(II) using MNPs and MNPs-BP (pH of solution: 7, adsorbent dose: 0.1 g, final volume: 10 mL, N=3).	82
4.18	Effect of volume of 2 mol L ⁻¹ HCl on % recovery Pb(II) using MNPs and MNPs-BP (pH of solution: 7, volume of sample: 10 mL, final volume: 10 mL N=3).	84
4.19	Pseudo-second order kinetics for the adsorption of Pb(II) on MNPs and MNPs-BP.	87

4.20a	Freundlich isotherm model for the adsorption of Pb(II) using MNPs-BP and MNPs.	88
4.20b	Pseudo-second order kinetics for the adsorption of Pb(II) using MNPs-BP and MNPs.	89
4.21	FT-IR spectra of OP and MNP-OP.	92
4.22	SEM micrograph of OP(a) and MNPs-OP(b).	93
4.23	Cube model graph of the 2 ⁵ factorial designs.	99
4.24a	Pseudo-first-order kinetics of Ni(II) uptake using MNPs-OP	100
4.24b	Pseudo-second-order kinetics of Ni(II) uptake using MNPs-OP.	101
4.24c	Intraparticle diffusion model of Ni (II) uptake using MNPs-OP.	101
4.24d	Elovich kinetic model of Ni(II) uptake using MNPs-OP.	102
4.25a	Langmuir adsorption isotherm.	104
4.25b	Freundlich adsorption isotherm.	105
4.25c	Temkin adsorption isotherm.	105
4.25d	Dubinin–Radushkevich (D–R) adsorption isotherm.	106
4.26	Effect of coexisting cations on adsorption capacity of Ni(II) by using MNPs-OP.	109
4.27	FT-IR spectra of SiMCTNTs-PAN.	111
4.28	XRD patterns of SiMCNTs-PAN.	112
4.29	SEM micrograph of SiMCNTs-PAN.	113
4.30	Effect of pH on % recovery of Pb (II) and Co (II) using SiMCNTs-PAN (sample volume: 10 mL, adsorbent dose: 0.1 g,	

	final volume: 2 mL, N=3)	114
4.31	Effect of adsorbent dose on percent recovery of Pb (II) and Co (II) using SiMCNTs-PAN (pH: 6.6, sample volume: 10 mL, final volume: 2 mL, N=3).	115
4.32	Effect of sample volume on % recovery of Pb (II) and Co (II) using SiMCNTs-PAN (pH: 6.5, sorbent dose: 0.1 g, final volume: 2 mL, N=3)	116
4.33	Effect of volume of 2 mol L ⁻¹ on % recovery of Pb (II) and Co (II) using SiMCNTs-PAN.	118
4.34a	Pseudo-second-order kinetics for the adsorption of Pb(II) and Co(II) using SiMCNTs-PAN.	121
4.34b	Intraparticle diffusion model for the adsorption of Pb(II) and Co(II) using SiMNCNTs-PAN.	122

LIST OF TABLES

Table No.	Caption	Page No.
4.1	Surface area, pore volume and pore size by BET and BJH methods	53
4.2	Effect of pH on % recovery of Cd(II) using MNPs and SiMNPs	55
4.3	Effect of adsorbent dose on % recovery of Cd(II) using MNPs and SiMNPs	57
4.4	Effect of sample volume on % recovery of Cd(II) using MNPs and SiMNPs	58
4.5	Effect of type and concentration of eluent on % recovery of Cd(II) using MNPs and SiMNPs as adsorbents (N=3)	60
4.6	Effect of coexisting ions on % recoveries of Cd (II) using SiMNPs and MNPs, pH: 7, amount of adsorbent: 0.1 g, volume of sample solution: 10 mL (N=3)	62
4.7	Kinetic parameters for the adsorption of Cd(II) on MNPs and SiMNPs using different kinetic model	66
4.8	Comparison of the parameter of different isotherm model	70
4.9	Thermodynamic parameter for the adsorption of Cd (II) on MNPs and SiMNPs	72
4.10	Addition recovery results for Cd (II) using application of the proposed solid phase extraction method for the recovery of Cd(II) from real samples (pH: 7, amount of adsorbent: 0.1 g, volume of sample: 15 mL, final volume: 2 mL (N=3)	73
4.11	Surface area, pore volume and pore size by BET and BJH methods	77

4.12	Effect of type and concentration of eluent on percent recovery of Pb (II) using MNPs and MNPs-BP as adsorbents, pH: 7, amount of adsorbents: 0.1 g, volume of sample solution: 10 mL (N=3)	83
4.13	Effect of coexisting ions on % recoveries of Pb (II) using MNPs and MNPs-BP as adsorbents, pH: 7, amount of adsorbents: 0.1 g, volume of sample solution: 10 mL (N=3)	85
4.14	Kinetic parameter for the adsorption of Pb (II) using MNPs and MNPs-BP as adsorbents	87
4.15	Comparison of parameters of Freundlich and Langmuir adsorption isotherm models	89
4.16	Thermodynamic parameter for the adsorption of Pb (II) using MNPs and MNPs-BP as adsorbents	90
4.17	Addition recovery results for Pb (II) using the proposed solid phase extraction method (pH: 7, amount of adsorbent: 0.1 g, volume of sample: 15 mL, final volume: 2 mL (N=3)	91
4.18	Factorial 25 experimental design	94
4.19	Effect list of main factors and their interactions	96
4.20	Analysis of variance	98
4.21	Kinetic parameters of Ni(II) sorption on MNPs-OP	103
4.22	Comparison of various isotherm constants for the sorption of Ni(II) on MNPs-OP	107
4.23	Thermodynamic parameters for the adsorption of Ni(II) on MNPs-OP	108
4.24	Application of the proposed method to real water samples	110

4.25	Effect of type and concentration of eluent on percent recovery of Pb (II) and Co (II) on SiMCNTs-PAN (N=3)	117
4.26	Effect of coexisting ions on % recoveries of Pb (II) and Co (II) using SiMCNTs-PAN, pH: 7, amount of SiMCNTs-PAN: 0.1 g, volume of sample solution: 10 mL (N=3)	119
4.27	Kinetic parameter of the adsorption of Pb(II) and Co(II) on the surface of SiMCNTs-PAN core shell	122
4.28	Thermodynamic parameter for the adsorption of Pb(II) and Co(II) on SiMCNTs-PAN	123
4.29	Validation of the proposed solid phase microextraction of Pb and Co at trace level using certified water reference material (pH: 6, Amount of adsorbent: 0.1 g, Volume of sample: 15 mL, Final volume: 2mL)	124
4.30	Real samples recovery results for Pb (II) and Co (II) using the proposed solid phase micro extraction method (pH: 6, amount of SiMCNTs-PAN: 0.1 g, volume of sample: 15 mL, Final volume: 2 mL (N=3)	125

ABBREVIATIONS

Abbreviation	Full name
%	Percent
(c-MWCNT)-Fe ₃ O ₄	carboxylated multi-wall carbon nanotube
°C	Degree centigrade
µm	Micrometer (unit of length)
Å	Angstrom
ACMNP _s	Agarose coated magnetic nanoparticles
ACN	Acetonitrile
AIBN	Azobisisobutyronitrile
a _L	Langmuir constant related adsorbate –adsorbent binding force
As	Arsenic
A _T	Equilibrium binding constant
BDL	Below detection limit
BET	Brunauer, Emmett and Teller method
BJH	Barrett, Joyner and Halenda method
BP	Banana peels
C _o	Initial concentration
Cd	Cadmium
C _e	Final concentration
CNT _s	Carbon nanotubes
Co	Cobalt
-COOH	Carboxyl group

Cr	Chromium
Cu	Copper
DDTC	Diethyldithiocarbamate
DLLE	Dispersive liquid–liquid extraction
DOP	Dioctyl phthalate
DTA	Differential thermal analysis
DVB	Divinylbenzene
EDX	Energy dispersive X-ray
EF	Enrichment factor
Eu	Europium
FAAS	Flame atomic absorption spectrometry
Fe	Iron
Fe ₂ O ₃	Ferric oxide
Fe ₃ O ₄	Magnetite
Fe ₃ O ₄ /SiO ₂ -GO	Silica coated magnetic nanoparticle-graphene oxide
FT-IR	Fourier transform-infra red
g	Gram (unit of mass)
g/ml	Gram per milli liter (unit of density)
g/mol	Gram per mole (unit of molar mass)
GC-MS	Gas chromatography-Mass spectrometry
GC-MS	Gas chromatography-mass spectrometry
GO	Graphene oxide
H	Hydrogen
h	Hour
H ⁺	Hydrogen ion

H2Dz-SCMNPs	Dithizone modified silica-coated magnetic nanoparticles
H ₂ O ₂	Hydrogen per oxide
Hg	Mercury
HNO ₃	Nitric acid
HSLPE	Headspace liquid phase extraction
ICP-MS	Inductively coupled plasma-Mass spectrometry
ISFE	In-situ 3 solvent formation extraction
K	Kelvin
K ₁	Rate constant for pseudo-first-order kinetics
K ₂	Rate constant for pseudo-Second-order kinetics
K _D	Equilibrium constant
k _F	Relative adsorption capacity
K _{int}	Intraparticle diffusion rate constant
KJ/mol	Kilo joule per mol (Unit of energy per amount of material)
K _L	Langmuir constant related to the adsorption energy
KV	Kilo volt (major unit of electric potential)
La	Lanthanum
LOD	Limit of detection
LOQ	Limit of quantification
m/s	meter per second (unit of velocity)
m ² g ⁻¹	Meter square per gram (Unit of surface area)
mA	Milli ampere (sub unit of electric current)
MCNTs	Magnetic carbon nanotubes

MeHg	Methyl mercury
MFA	Magnetic field agitation
mg g ⁻¹	Milligram per gram (Unit of adsorption capacity)
mg L ⁻¹	Milligram per liter (unit of concentration)
mg ² /g	Milligram square per gram (unit of surface area)
MGCB	Malachite green carbinol green
MIBK	Methyl isobutyl ketone
min	Minute
mL	Milliliter
mm	Millimeter (sub unit of length measurement)
MNCS	Magnetic nanocomposites surface
MNP	Magnetic nanoparticle
MNPs-BP	Magnetic nanoparticle impregnated banana peels
mol	Mole (unit for the expression of amounts of a chemical substance)
mol L ⁻¹	Mole per liter
MPANI-GO	Fe ₃ O ₄ @SiO ₂ @polyaniline-graphene oxide
MWCNT	Multi walled carbon nanotube
N ₂	Molecular nitrogen
NaOH	Sodium hydroxide
ng L ⁻¹	Nomogram per liter
ng mL ⁻¹	Nano gram per milli liter
-NH ₂	Ammine
Ni	Nickel
nm	Nano meter (sub unit of length)

OP	Orange peels
PAN	1-(2-Pyridylazo)-2-naphthol
PANI	polyaniline
Pb	Lead
Pd	Palladium
pH	Negative log of hydrogen concentration
PPy	Polypyrrole
q_e	Adsorption capacity
$q_{\max}$	Maximum adsorption capacity
Q^o	Theoretical monolayer adsorption capacity
q_t	Adsorption capacity at time t
R	Universal gas constant
r^2	Correlation coefficient
REEs	Rare earth elements
RSD	Relative standard deviation
SAA	Surface area analysis
SD	Saw dust
SD	Standard deviation
SDS	Sodium dodecyl sulfate
SEM	Scanning electron microscopy
SiMCNTs	Silica coated magnetic carbon nanotube
SiMCNTs-PAN	1-(2-Pyridylazo)-2-naphthol impregnated silica coated magnetic carbon nanotube
SiMNPs	Silica coated magnetic nanoparticles
SiO ₂	Silica

SPE	Solid phase extraction
TEM	Transmission Electron Microscopy
TEPA-NMPs	Tetraethylenepentamin-Functional Fe ₃ O ₄ magnetic polymer
TETA	Triethylenetetramine
TG	Thermogravimetry
TPED	N-[3-(trimethoxysilyl)propyl]-ethylenediamine
TW	Tea waste
U	Uranium
UAEE	Ultrasound-assisted emulsification extraction
USA	United States of America
V	Volume
V-Pic	N-(pyridine-2-ylmethyl)ethenamine
W _f	Concentration in reference
W _o	Concentration in sample
wt. %	Weight percent
XRD	X-ray diffraction
Zn	Zinc
α	Elovich coefficient
α	Alpha
β	Desorption constant
β	Beta
γ	Specific refraction
γ -Fe ₂ O ₃	Magemite nanoparticle
$\Delta^\circ G$	Gibbs free energy

$\Delta^{\circ}H$	Enthalpy
$\Delta^{\circ}S$	Entropy
θ	Theta
λ	Lambda
σ	Sigma
σ_s	Specific saturation magnetization
ϵ	Polanyi potential

SUMMARY

Excessive industrialization apart from normal natural activities discharge large amount of heavy metals into the water streams which is the main cause of environmental pollution. This has received considerable attention of the scientists in the last few decades due to health consequences for human beings and other living organism even at very low level concentration. Due to nonbiodegradable and nonthermodegradable nature, high enrichment factor and slow removal rate, heavy metals accumulate in various tissues especially in aquatic organisms to toxic level and can cause severe health risks for human beings like kidney failure, liver damage, cancer, nausea, high blood pressure, pulmonary fibrosis, skin dermatitis, renal edema, diarrhea and vomiting. In most cases, the concentration of these heavy metals in real sample is lower than the analytical detection system. Therefore, for the accurate determination of these metals in the real samples, preconcentration prior to its determination is needed. The aim of the present work was to develop advanced magnetic solid phase extraction methods for the preconcentration of trace heavy metals. Also the magnetic nanomaterial was used for solid phase extraction of trace heavy metals and applied the developed methods to certified reference materials for heavy metal analysis.

The first chapter of this dissertation based on brief introduction to solid phase extraction, advantages of solid phase extraction, the adsorbents used in solid phase extraction, modified solid phase material, magnetic nanoparticle and magnetic modified nanomaterial, magnetic graphene nanocomposites, magnetic

carbon nanotube, magnetic nanoparticle impregnated biosorbent and advantages of magnetic nanoparticles and magnetic modified nanomaterials. The aim and objectives of the work is also included in first chapter.

The second chapter covers a thorough review of relevant literature reported for the solid phase extraction of toxic heavy metals using magnetic nanomaterial. The literature included the use of magnetic nanoparticle like Fe_3O_4 and advanced magnetic nanomaterial like Fe_3O_4 coated polypyrrole (PPy) magnetic nanocomposite, Fe_3O_4 /polyaniline nanoparticles (core shells), dithizone modified silica-coated magnetic nanoparticles (H2Dz-SCMNPs), magnetic graphene oxide nanocomposite and graphene oxide/chitosane/ FeOOH (GO/Ch/ FeOOH) etc for the solid phase extraction of heavy metals and its determination by using analytical detection system.

The third chapter consists of experimental procedure used for the stepwise preparation of magnetic nanoparticle, silica coated magnetic nanoparticles, magnetic carbon nanotube and magnetic modified graphene oxide-DVB-VA. This chapter also includes characterization procedure and different instrument used for the characterization of the adsorbent. Various sample preparation procedures used for environmental samples, soil samples and food samples are also include in this chapter. Batch adsorption procedure and determination of heavy metals in the samples using analytical detection system like Uv-Vis Spectrometry and FAAS are also given in chapter third.

The fourth chapter includes results and discussions of the experimental data. This includes characterization of the adsorbents using FT-IR, XRD, SAA, SEM and EDX analysis. It also include optimization of various factors effecting solid phase extraction like pH, adsorbent dose, contact and shaking time, sample volume, desorption condition, temperature, matrix effect and initial metal concentrations. Equilibrium adsorption data were fitted into two most common isotherm models i.e. Freundlich and Langmuir. The kinetics of the adsorption processes were described using four common kinetic models i.e. pseudo-first, pseudo-second, intraparticle diffusion and Elovich models. For validation, the methods were applied to various environmental samples like water samples, soil samples and food samples with satisfactory results. The develop methods were also applied to certified reference material like fortified water (TMDA 64-2), wastewater (SPS-WW2), Oriental Basma Tobacco Leaves (INCT-OBTL-5) and Tomato Leaves (1573a) for trace metal analysis.

Part 1 of the chapter fourth consist of comparative study of the solid phase extraction of Cd (II) using magnetic nanoparticles (MNPs) and silica coated magnetic nanoparticle (SiMNPs). It was observed that maximum % recoveries of Cd(II) (99 ± 4 % and 100 ± 1 %) on MNPs and SiMNPs, respectively was achieved at pH 7 with 0.1 g of adsorbent dose. The proposed method was successfully applied to 40 mL of sample volume and the method is highly selective with no significant interferences from the matrix ions. kinetic data fit to pseudo second order kinetics while the thermodynamic data shows that the method feasible in nature. Desorption studies shows that 2 mL of HCl (2 mol L^{-1}) in acetone was the

optimum desorption condition for quantitative % recoveries. The method was successfully applied to environmental water samples like Tap water, River water for % recoveries using standard addition procedure.

Part 2 of the chapter fourth composed of Solid phase extraction of Pb(II) using magnetic nanoparticles (MNPs) and magnetic nanoparticles impregnated banana Peels (MNPs-BP). pH 7 was the optimum pH at which maximum % recovery was achieved. The method was applicable up to 40 mL of sample. The developed method is highly selective with significant interferences from the matrix ion. Kinetic data shows that this adsorption study follows pseudo second order kinetics and the equilibrium data fit to Langmuir adsorption isotherm. The positive values of ΔH° , ΔS° and negative values of ΔG° show that the adsorption process is endothermic, feasible and spontaneous in nature. The method was successfully applied to real water samples with satisfactory recovery results.

Part 3 of the chapter fourth comprises of application of response surface methodology to the magnetic nanoparticles impregnated orange peel for the removal of Ni(II). The adsorption experiments using five variables on MNP–OP adsorbent were conducted according to the experimental design. Analysis of variance was carried out for statistical confirmation of these results which indicate that the equation and the actual relationship presented by the equation between the response and significant variable are accurate. The significance of the coefficient term is calculated by F and p values, the larger F value and the smaller p value, shows that the results are more significant. Result indicates that the adsorption of Ni (II) on Fe₃O₄-OP depends on pH and maximum Ni (II) was achieved at pH 7.

Adsorption rate was higher in the beginning and then remain constant. The kinetic models shows that the data fit to the pseudo-second order kinetics. The experimental data fit to the Langmuir adsorption isotherm with monolayer adsorption capacity of (1110.12 mg g⁻¹). The thermodynamic parameter shows that the adsorption process is endothermic and spontaneous in nature. The effect of coexisting metal ions were studied which showed that the presence of these metals has negligible effect on the removal efficiency Ni (II) from the aqueous solution. The new adsorbent (MNPs-OP) not only showed high adsorption capacity and rapid kinetics but also showed simple inexpensive adsorbent method of adsorbent preparation, which is and environment friendly.

Part 4 of the chapter fourth include vortex assisted magnetic solid phase extraction of lead(II) and cobalt(II) on silica coated magnetic carbon nanotubes impregnated 1-(2-Pyridylazo)-2-naphthol (SiMCNTs-PAN). The adsorbent was characterized using FT-IR, SEM and XRD. Kinetic models show that the data fit to pseudo first order kinetics. The method is highly selective as there are no significant interferences from matrix cations and anions even at high concentration. Thermodynamic studies show that the method is highly feasible and spontaneous in nature. Low values of RSD of Pb (II) (3.3 %) and a Co (II) (2.5 %) show that's the method is reproducible. The method was successfully applied to TMDA 64.2 environmental water, TMDA 62.2 environmental water and SPS-WW2 waste water certified water reference materials for trace metal determination. The method was also successfully applied to real water samples for heavy metal analysis.

Chapter 1

INTRODUCTION

1.1. Solid phase extraction (SPE)

In the recent past extraction technique has been used largely for the preconcentration of trace metal prior to its determinations. The extraction techniques used mainly for preconcentration of heavy metals are headspace liquid phase extraction (HSLPE), ultrasound-assisted emulsification extraction (UAEE), in-situ 3 solvent formation extraction (ISFE), dispersive liquid–liquid extraction (DLLE) and solid phase extraction (SPE) [1-8]. Due to significant inadequacies like high running cost, long time of extraction and high amount of toxic reagents as a waste during liquid-liquid extraction, SPE is the preferred method for the extraction of heavy metals due to its environmental friendliness and use of minimum solvent and reagents. SPE is a pretreatment method in which the analyte is separated from the sample solution by

using solid phase adsorbent. In combination with other techniques like filtration, homogenization, digestion and solubilization, the sample obtained is well-suited for its analytical measurement. SPE can be coupled with other analytical techniques or methods in order to achieve its application of that particular purpose [9-12]. The advantages of the solid phase include:

(i) low running cost, (ii) high percent recovery for the analyte (iii) short extraction time (iv) environmental friendly (v) high preconcentration factor (vi) high selectivity and sensitivity and low cost of the adsorbent [13-15].

1.2. Solid phase adsorbent

In the SPE, the adsorbent has key role and the selection of proper adsorbent is of immense importance. Researcher have used different solid phases for adsorption and preconcentration of trace elements which can be divided into four categories ie materials of high surface area like silica gel [16], amberlite [17], and activated carbon [18], adsorbing material derived from biological material (biosorbents) like spent animal bones [19], crab shell [20], activated carbon prepared from rice husk [21], and seaweeds [22], polymeric substances like ionic imprinted polymer [23], molecularly imprinted polymer [24] and nanometer size materials such as graphene oxide [25], silica nanoparticle [26], carbon nano tubes [15] and nanodiamonds etc. were used by many scientist in the recent past. The nanometer size materials are preferable adsorbent over ordinary adsorbent because, it has smaller particle size and high surface area and can be used as an excellent adsorbing materials for the SPE of heavy metals. However due to low surface functional groups, lack of selectivity and aggregation in aqueous solution the applications of the CNTs, graphene and other advanced nanomaterial for SPE of heavy metals are not 100 % efficient [27, 28].

1.3. Modified solid phase material

The use of nanometer size material without any modification like CNTs and graphene has major drawback as it resist the flow of water especially in samples having suspended particles. Therefore, larger volume of the sample cannot be used and thus high preconcentration factor cannot be achieved [29]. In order to make the adsorbent more specific and to avoid agglomeration, different surface modified nanomaterial like chitosan-grafted multi-walled carbon nanotubes [13], diamine modified

mesoporous silica multi-walled carbon nanotube [30], molecularly imprinted coated multi-walled carbon nanotube [31], ethylenediamine modified multi walled carbon nanotube [14], 2-aminobenzothiazole modified carbon nanotube [32], reduced graphene oxide metal-metal oxide composite [33], graphene oxide/ferric hydroxide composite [34] and polystyrene/graphene oxide composite [35] have been used for the SPE of heavy metals. However, due to the enormously small particle size and high dispersibility and high water holding capacity, ordinary centrifugation and filtration failed to separate nanomaterial from aqueous solution that limit its application in the field of SPE. Therefore in the recent past magnetic nanoparticles and magnetic modified materials are mostly used in order to use external magnetic field for separation of nanomaterial from aqueous solution instead of centrifugation and filtration during solid phase experiments [36-38].

1.4. Magnetic nanoparticles and magnetic modified nanomaterial

Magnetic nanoparticle has large surface-to-volume ratio and thus having large adsorption capacity. Iron-oxide magnetic nanoparticles, Fe_3O_4 and Fe_2O_3 have been the focus of a wide-reaching research interest as they have unique size-dependent characteristics that strongly differ from the properties of the corresponding bulk material and enable them to be used for numerous applications [39]. Moreover magnetic nanoparticles can be separated by using external magnetic field without agglomeration to avoid the sample loss during filtration [40, 41]. The size of magnetic nanoparticles ranges from 1 nm to 100 nm in diameter, having large surface area and with wide range of applications including catalysis, chromatographic separation and drug delivery [38]. Magnetic nanoparticles can be successfully used

for the removal of heavy metal ions like Cr(III), As(V) and Cd(II) from the aqueous solution [42-44]. To overcome the drawbacks of nanometer size material like carbon nanotube, graphene and also other biosorbents (saw dust, orange peels, banana peels) modification particularly with magnetic material is preferred. In the last few years magnetic particles and magnetic nanocomposite is largely used as solid phase by researches in the field of SPE of heavy metals [45].

1.5. Magnetic graphene nanocomposite

Geim et al have synthesized a new kind of carbon-based nanomaterial called graphene in 2004, owning unique thermal, electronic and mechanical properties [46]. In a single layer of graphene, each carbon possesses sp^2 -hybridization with carbon lattice honeycomb in geometry [47]. Due to extremely large surface area and high adsorption capacity, graphene can be used as an excellent adsorbent for trace metals [45]. In order to make it more efficient, different hybrid material of graphene with magnetic nanoparticle were used for the SPE like Fe_3O_4 grafted graphene oxide [45], zero-valent iron/iron oxide-oxyhydroxide/graphene [48], magnetic Fe_3O_4 -graphene oxide/polystyrene [49], silica coated magnetic nanoparticle-graphene oxide Fe_3O_4/SiO_2 -GO nanocomposite [47] in the field of SPE of heavy metals.

1.6. Magnetic carbon nanotubes

Carbon nanotubes (CNTs) having graphite sheets with hexagonal arrangement of carbon atoms on its surface were discovered in 1991. Due to large surface area and strong surface interaction with heavy metals make it efficient materials for the SPE of heavy metals [50]. The extraction efficiency of the CNTs can be increased by surface

modification with magnetic iron oxide nanoparticles (Fe_3O_4). The magnetic modified carbon nanotube is more dispersed and can be easily separated by external magnetic field [29].

1.7. Magnetic nanoparticle impregnated biosorbent

Biosorbent obtained from spent animal bones, crab shell, activated carbon prepared from rice husk, seaweeds, orange peels, banana peels and saw dust have been used as solid phase extracting material by many researchers [51]. Biosorbent consists of cellulose, hemi-cellulose, pectin substances, chlorophyll pigments and low molecular weight compounds like limonene are also present. Hydroxyl and carboxyl functional groups in the cellulose are the active sites for binding the heavy metals. However the extraction efficiency of these biosorbent can be improved by modifying its surface with magnetic nanoparticles. Magnetic impregnated biosorbent has greater surface area and magnetic property. Therefore the magnetic nanoparticle impregnated biosorbent can be used as an excellent solid phase extracting material for heavy metals [52].

1.8. Advantages of magnetic nanoparticles and magnetic modified nanomaterials

The use of magnetic nanoparticles and magnetic modified nanomaterial as solid phase extracting material has substantial advantages over other adsorbing material like:

- i. small particle size and large surface area.
- ii. large surface to volume ratio with high adsorption capacity can be obtained by using it as adsorbents.
- iii. greater dispersibility in aqueous solutions.

- iv. ability can be separated by using external magnetic field.
- v. easy to operate with short extraction time.
- vi. good chemical and physical stability [53-55].

1.9. Aims and objectives of the present work

The aims of the present work was synthesize and characterization of novel magnetic nanomaterial like, magnetic nanoparticles ($\text{Fe}_3\text{O}_4/\text{Fe}_2\text{O}_3$), magnetic impregnated biosorbent, magnetic nanocomposite of allylamine modified graphene oxide, magnetic nanodiamonds and silica coated magnetic carbon nano tube (core shell). The synthesized material was used as solid phase extractant for the preconcentration and determination of trace heavy metals with aim to propose new methods based on these extractant. The developed methods was applied to certified reference material like (TMDA 64-2), fortified water, (SPS-WW2) waste water, Oriental Basma Tobacco Leaves (INCT-OBTL-5) and Tomato Leaves (1573a) for trace metal analysis and real environmental water samples like sea water, river water and tap water for heavy metal analysis.

References

- [1] E. Z. Jahromi, A. Bidari, Y. Assadi, M. R. M. Hosseini, M. R. Jamali, Dispersive liquid–liquid microextraction combined with graphite furnace atomic absorption spectrometry: Ultra trace determination of cadmium in water samples, *Analytica Chimica Acta* 585 (2) 305-311 (2007).
- [2] M. A. Bezerra, M. A. Z. Arruda, S. L. C. Ferreira, Cloud point extraction as a procedure of separation and pre-concentration for metal determination using spectroanalytical techniques: a review, *Applied Spectroscopy Reviews* 40 (4) 269-299 (2005).
- [3] N. Shokoufi, F. Shemirani, Y. Assadi, Fiber optic-linear array detection spectrophotometry in combination with dispersive liquid–liquid microextraction for simultaneous preconcentration and determination of palladium and cobalt, *Analytica chimica acta* 597 (2) 349-356 (2007).
- [4] L. Moens, T. De Smaele, R. Dams, P. Van Den Broeck, P. Sandra, Sensitive, simultaneous determination of organomercury, lead, and tin compounds with headspace solid phase microextraction capillary gas chromatography combined with inductively coupled plasma mass spectrometry, *Analytical Chemistry* 69 (8) 1604-1611 (1997).
- [5] H. Sereshti, Y. E. Heravi, S. Samadi, Optimized ultrasound-assisted emulsification microextraction for simultaneous trace multielement determination of heavy metals in real water samples by ICP-OES, *Talanta* 97 235-241 (2012).
- [6] B. Majidi, F. Shemirani, In situ solvent formation microextraction in the presence of ionic liquid for preconcentration and speciation of arsenic in saline samples and

- total arsenic in biological samples by electrothermal atomic absorption spectrometry, *Biological Trace Element Research* 143 (1) 579-590 (2011).
- [7] M. Mirzaei, M. Behzadi, N. M. Abadi, A. Beizaei, Simultaneous separation/preconcentration of ultra-trace heavy metals in industrial wastewaters by dispersive liquid–liquid microextraction based on solidification of floating organic drop prior to determination by graphite furnace atomic absorption spectrometry, *Journal of Hazardous Materials* 186 (2) 1739-1743 (2011).
- [8] Z. Es’haghi, M. Khalili, A. Khazaeifar, G. H. Rounaghi, Simultaneous extraction and determination of lead, cadmium and copper in rice samples by a new pre-concentration technique: Hollow fiber solid phase microextraction combined with differential pulse anodic stripping voltammetry, *Electrochimica Acta* 56 (9) 3139-3146 (2011).
- [9] N. J. Simpson, *Solid-phase extraction: principles, techniques, and applications*, CRC press, 2000.
- [10] M.-C. Hennion, Solid-phase extraction: method development, sorbents, and coupling with liquid chromatography, *Journal of Chromatography A* 856 (1) 3-54 (1999).
- [11] M. Falahnejad, H. Zavvar Mousavi, H. Shirkhanloo, A. M. Rashidi, Preconcentration and separation of ultra-trace amounts of lead using ultrasound-assisted cloud point-micro solid phase extraction based on amine functionalized silica aerogel nanoadsorbent, *Microchemical Journal* 125 (236-241 (2016)).

- [12] E. Yavuz, Ş. Tokalıoğlu, H. Şahan, Ş. Patat, Nanosized spongelike Mn_3O_4 as an adsorbent for preconcentration by vortex assisted solid phase extraction of copper and lead in various food and herb samples, *Food Chemistry* 194 (463-469 (2016).
- [13] M. Soylak, O. Ercan, Selective separation and preconcentration of copper (II) in environmental samples by the solid phase extraction on multi-walled carbon nanotubes, *Journal of Hazardous Materials* 168 (2) 1527-1531 (2009).
- [14] Z. Zang, Z. Hu, Z. Li, Q. He, X. Chang, Synthesis, characterization and application of ethylenediamine-modified multiwalled carbon nanotubes for selective solid-phase extraction and preconcentration of metal ions, *Journal of Hazardous Materials* 172 (2) 958-963 (2009).
- [15] B. Dai, M. Cao, G. Fang, B. Liu, X. Dong, M. Pan, S. Wang, Schiff base-chitosan grafted multiwalled carbon nanotubes as a novel solid-phase extraction adsorbent for determination of heavy metal by ICP-MS, *Journal of Hazardous Materials* 219 (103-110 (2012).
- [16] F. Xie, X. Lin, X. Wu, Z. Xie, Solid phase extraction of lead (II), copper (II), cadmium (II) and nickel (II) using gallic acid-modified silica gel prior to determination by flame atomic absorption spectrometry, *Talanta* 74 (4) 836-843 (2008).
- [17] V. M. Akhmedov, S. Alfadul, A. M. Maharramov, A. A. Azizov, R. M. Alosmanov, I. A. Buniyad-Zadeh, Modification of industrial divinyl rubber by oxidative chlorophosphorylation and assessment of metal ion removal efficiency of obtained polymer sorbent, *Polish Journal of Chemical Technology* 17 (2) 112-118 (2015).

- [18] M. Soylak, L. Elci, M. Dogan, Determination of some trace metal impurities in refined and unrefined salts after preconcentration onto activated carbon, *Fresenius Environmental Bulletin* 5 (3-4) 148-155 (1996).
- [19] K. Chojnacka, I. Michalak, Using wood and bone ash to remove metal ions from solutions, *Global NEST Journal* 11 (2) 205-217 (2009).
- [20] H. K. An, B. Y. Park, D. S. Kim, Crab shell for the removal of heavy metals from aqueous solution, *Water Research* 35 (15) 3551-3556 (2001).
- [21] I. Nhapi, N. Banadda, R. Murenzi, C. Sekomo, U. Wali, Removal of heavy metals from industrial wastewater using rice husks, *Open Environmental Engineering Journal* 4 (170-180 (2011).
- [22] J. Shah, M. R. Jan, A. u. Haq, M. Zeeshan, Equilibrium, kinetic and thermodynamic studies for sorption of Ni (II) from aqueous solution using formaldehyde treated waste tea leaves, *Journal of Saudi Chemical Society* 19, 301-310 (2015).
- [23] T. P. Rao, S. Daniel, J. M. Gladis, Tailored materials for preconcentration or separation of metals by ion-imprinted polymers for solid-phase extraction (IIP-SPE), *TrAC Trends in Analytical Chemistry* 23 (1) 28-35 (2004).
- [24] E. Birlik, A. Ersöz, A. Denizli, R. Say, Preconcentration of copper using double-imprinted polymer via solid phase extraction, *Analytica Chimica Acta* 565 (2) 145-151 (2006).
- [25] V. Chandra, J. Park, Y. Chun, J. W. Lee, I.-C. Hwang, K. S. Kim, Water-dispersible magnetite-reduced graphene oxide composites for arsenic removal, *ACS Nano* 4 (7) 3979-3986 (2010).

- [26] P. Jal, S. Patel, B. Mishra, Chemical modification of silica surface by immobilization of functional groups for extractive concentration of metal ions, *Talanta* 62 (5) 1005-1028 (2004).
- [27] M. Tuzen, K. O. Saygi, C. Usta, M. Soylak, *Pseudomonas aeruginosa* immobilized multiwalled carbon nanotubes as biosorbent for heavy metal ions, *Bioresource Technology* 99 (6) 1563-1570 (2008).
- [28] A. H. El-Sheikh, J. A. Sweileh, Y. S. Al-Degs, Effect of dimensions of multi-walled carbon nanotubes on its enrichment efficiency of metal ions from environmental waters, *Analytica Chimica Acta* 604 (2) 119-126 (2007).
- [29] D. Pardasani, P. K. Kanaujia, A. K. Purohit, A. R. Shrivastava, D. Dubey, Magnetic multi-walled carbon nanotubes assisted dispersive solid phase extraction of nerve agents and their markers from muddy water, *Talanta* 86, 248-255 (2011).
- [30] W. Yang, P. Ding, L. Zhou, J. Yu, X. Chen, F. Jiao, Preparation of diamine modified mesoporous silica on multi-walled carbon nanotubes for the adsorption of heavy metals in aqueous solution, *Applied Surface Science* 282, 38-45 (2013).
- [31] Z. Zhang, H. Zhang, Y. Hu, X. Yang, S. Yao, Novel surface molecularly imprinted material modified multi-walled carbon nanotubes as solid-phase extraction sorbent for selective extraction gallium ion from fly ash, *Talanta* 82 (1) 304-311 (2010).

- [32] R. Li, X. Chang, Z. Li, Z. Zang, Z. Hu, D. Li, Z. Tu, Multiwalled carbon nanotubes modified with 2-aminobenzothiazole modified for uniquely selective solid-phase extraction and determination of Pb (II) ion in water samples, *Microchimica Acta* 172 (3-4) 269-276 (2011).
- [33] T. S. Sreeprasad, S. M. Maliyekkal, K. P. Lisha, T. Pradeep, Reduced graphene oxide–metal/metal oxide composites: Facile synthesis and application in water purification, *Journal of Hazardous Materials* 186 (1) 921-931 (2011).
- [34] K. Zhang, V. Dwivedi, C. Chi, J. Wu, Graphene oxide/ferric hydroxide composites for efficient arsenate removal from drinking water, *Journal of Hazardous Materials* 182 (1–3) 162-168 (2010).
- [35] J. Yang, M. Wu, F. Chen, Z. Fei, M. Zhong, Preparation, characterization, and supercritical carbon dioxide foaming of polystyrene/graphene oxide composites, *The Journal of Supercritical Fluids* 56 (2) 201-207 (2011).
- [36] Y.-P. Chang, C.-L. Ren, J.-C. Qu, X.-G. Chen, Preparation and characterization of Fe₃O₄/graphene nanocomposite and investigation of its adsorption performance for aniline and p-chloroaniline, *Applied Surface Science* 261, 504-509 (2012).
- [37] M. Zhang, M. Jia, Y. Jin, Fe₃O₄/reduced graphene oxide nanocomposite as high performance anode for lithium ion batteries, *Applied Surface Science* 261, 298-305 (2012).

- [38] M. Zhang, B. L. Cushing, C. J. O'Connor, Synthesis and characterization of monodisperse ultra-thin silica-coated magnetic nanoparticles, *Nanotechnology* 19 (8) 085601 (2008).
- [39] Y.-H. Deng, C.-C. Wang, J.-H. Hu, W.-L. Yang, S.-K. Fu, Investigation of formation of silica-coated magnetite nanoparticles via sol–gel approach, *Colloids and Surfaces A: Physicochemical and Engineering Aspects* 262 (1–3) 87-93 (2005).
- [40] M. Adeli, Y. Yamini, M. Faraji, Removal of copper, nickel and zinc by sodium dodecyl sulphate coated magnetite nanoparticles from water and wastewater samples, *Arabian Journal of Chemistry* 2012).
- [41] C. Huang, B. Hu, Silica-coated magnetic nanoparticles modified with γ -mercaptopropyltrimethoxysilane for fast and selective solid phase extraction of trace amounts of Cd, Cu, Hg, and Pb in environmental and biological samples prior to their determination by inductively coupled plasma mass spectrometry, *Spectrochimica Acta Part B: Atomic Spectroscopy* 63 (3) 437-444 (2008).
- [42] G. Cheng, M. He, H. Peng, B. Hu, Dithizone modified magnetic nanoparticles for fast and selective solid phase extraction of trace elements in environmental and biological samples prior to their determination by ICP-OES, *Talanta* 88, 507-515 (2012).
- [43] T. Tuutijärvi, J. Lu, M. Sillanpää, G. Chen, As (V) adsorption on maghemite nanoparticles, *Journal of Hazardous Materials* 166 (2) 1415-1420 (2009).

- [44] Y. Feng, J.-L. Gong, G.-M. Zeng, Q.-Y. Niu, H.-Y. Zhang, C.-G. Niu, J.-H. Deng, M. Yan, Adsorption of Cd (II) and Zn (II) from aqueous solutions using magnetic hydroxyapatite nanoparticles as adsorbents, *Chemical Engineering Journal* 162 (2) 487-494 (2010).
- [45] S. Zeng, N. Gan, R. Weideman-Mera, Y. Cao, T. Li, W. Sang, Enrichment of polychlorinated biphenyl 28 from aqueous solutions using Fe₃O₄ grafted graphene oxide, *Chemical Engineering Journal* 218, 108-115 (2013).
- [46] Q. Han, Z. Wang, J. Xia, S. Chen, X. Zhang, M. Ding, Facile and tunable fabrication of Fe₃O₄/graphene oxide nanocomposites and their application in the magnetic solid-phase extraction of polycyclic aromatic hydrocarbons from environmental water samples, *Talanta* 101, 388-395 (2012).
- [47] Y. Yao, S. Miao, S. Yu, L. Ping Ma, H. Sun, S. Wang, Fabrication of Fe₃O₄/SiO₂ core/shell nanoparticles attached to graphene oxide and its use as an adsorbent, *Journal of Colloid and Interface Science* 379 (1) 20-26 (2012).
- [48] A. A. Karamani, A. P. Douvalis, C. D. Stalikas, Zero-valent iron/iron oxide-oxyhydroxide/graphene as a magnetic sorbent for the enrichment of polychlorinated biphenyls, polyaromatic hydrocarbons and phthalates prior to gas chromatography–mass spectrometry, *Journal of Chromatography A* 1271 (1) 1-9 (2013).
- [49] M. Z. Kassaei, E. Motamedi, M. Majdi, Magnetic Fe₃O₄-graphene oxide/polystyrene: Fabrication and characterization of a promising nanocomposite, *Chemical Engineering Journal* 172 (1) 540-549 (2011).

- [50] A. Duran, M. Tuzen, M. Soylak, Preconcentration of some trace elements via using multiwalled carbon nanotubes as solid phase extraction adsorbent, *Journal of Hazardous Materials* 169 (1) 466-471 (2009).
- [51] M. Rafatullah, O. Sulaiman, R. Hashim, A. Ahmad, Adsorption of copper (II), chromium (III), nickel (II) and lead (II) ions from aqueous solutions by meranti sawdust, *Journal of Hazardous Materials* 170 (2–3) 969-977 (2009).
- [52] V. Gupta, A. Nayak, Cadmium removal and recovery from aqueous solutions by novel adsorbents prepared from orange peel and Fe₂O₃ nanoparticles, *Chemical Engineering Journal* 180 (81-90 (2012).
- [53] F. Marahel, M. Ghaedi, M. Montazerzohori, M. N. Biyareh, S. N. Kokhdan, M. Soylak, Solid-phase extraction and determination of trace amount of some metal ions on Duolite XAD 761 modified with a new Schiff base as chelating agent in some food samples, *Food and Chemical Toxicology* 49 (1) 208-214 (2011).
- [54] N. Jalbani, M. Soylak, Ligandless ultrasonic-assisted and ionic liquid-based dispersive liquid–liquid microextraction of copper, nickel and lead in different food samples, *Food Chemistry* 167, 433-437 (2015).
- [55] E. Yilmaz, M. Soylak, Ionic liquid-linked dual magnetic microextraction of lead (II) from environmental samples prior to its micro-sampling flame atomic absorption spectrometric determination, *Talanta* 116, 882-886 (2013).

Chapter 2

LITERATURE REVIEW

Panneeerselvam et al., [1] reported removal of Ni(II) from aqueous solution using magnetic nanoparticles prepared and impregnated onto tea waste (Fe_3O_4 -TW) from agriculture biomass. Chemical precipitation method was used for the preparation of magnetic nanoparticles (Fe_3O_4). Adsorption parameters such as solution pH, contact time, concentration, adsorbent dosage and temperature were investigated. The adsorption kinetics shows that the adsorption of Ni(II) on Fe_3O_4 -TW followed first order kinetics and the value of rate constant was calculated as $1.90 \times 10^{-2} \text{ min}^{-1}$ at 100 mg L^{-1} and 303 K. Thermodynamic studies shows that this adsorption process is endothermic and spontaneous in nature. The equilibrium data can be best explained by using Langmuir and Freundlich isotherm models. The results showed that nanoparticle impregnated onto tea waste can be an excellent adsorbent for heavy metal removal from industrial effluent.

Karatapanis et al., [2] investigated magnetic solid phase microextraction method for the preconcentration of heavy metals like Cu(II), Ni(II), Cd(II), Pb(II), Co(II) and Mn(II) from environmental water samples using silica-modified magnetic nanoparticle coated with cationic surfactant; a cetylpyridinium bromide. Due to strong hydrophobic interaction between hydrophobic hemimicelles and complexed metal make this new microextraction method more efficient. Another advantage this method is that, the solid phase can be easily separated from the sample solution by using external magnetic field to avoid sample loss during filtration. Parameter like limit of detection (LOD) and relative standard deviation shows that the method is highly sensitive and reproducible. Recovery results were in the range of 93-113%.

Lin et al., [3] synthesized new amine-functionalized silica magnetite using N-[3-(trimethoxysilyl)propyl]-ethylenediamine (TPED) as a surface modification agent. The synthesized magnetic amine adsorbent was used for the adsorption of copper ions and the maximum adsorption was achieved at $\text{pH } 5.5 \pm 0.1$. The equilibrium data shows that the adsorption of Cu(II) on amine-functionalized silica magnetite using N-[3-(trimethoxysilyl)propyl]-ethylenediamine (TPED) follow Langmuir adsorption isotherm with maximum adsorption capacity of 10.41 mg g^{-1} . Kinetic data best fitted to pseudo second-order model and the activation energy was found to be $26.92 \text{ kJ mol}^{-1}$. The optimum condition for the desorption of Cu(II) from $\text{NH}_2/\text{SiO}_2/\text{Fe}_3\text{O}_4$ was achieved using $0.1 \text{ mol L}^{-1} \text{ HNO}_3$ solution.

Bhaumik et al., [4] reported a new magnetic solid phase extraction method based on Fe_3O_4 coated polypyrrole (PPy) magnetic nanocomposite for the removal of Cr(VI). The optimum pH was 2, at which, about 100 % adsorption of Cr(VI) in aqueous solution was achieved. XPS studies suggested that, ion exchange and reduction on the surface of the nanocomposite may be the possible mechanism for the adsorption of Cr(VI) on the surface of PPy/ Fe_3O_4 nanocomposite. Adsorption kinetics was best explained by pseudo-second-order rate model, while equilibrium data fitted well to the Langmuir isotherm model. Thermodynamic study shows that the adsorption of Cr(VI) on Fe_3O_4 coated polypyrrole (PPy) magnetic nanocomposite is endothermic and spontaneous in nature. Desorption experiment showed that the adsorbent can be reused successfully for two successive adsorption–desorption cycles without significant loss in its original adsorption capacity.

Mashhadizadeh and Karami [5] reported a fast, sensitive and simple magnetic solid phase extraction method for the extraction, preconcentration of trace metal like Ag, Cd, Cu and Zn from environmental samples by using magnetic nanoparticle coated by 3-(trimethoxysilyl)-1-propanol and modified with 2-amino-5-mercapto-1,3,4-thiadiazole prior to its determination by ICP-OES. FT-IR and SEM were used for determination of functional group and surface morphology, respectively. Factors affecting extraction efficiency like solution pH, eluent condition, sample volume, ultrasonication time and matrix effect were optimized. The proposed method also applied for the preconcentration and extraction of trace amount of Ag, Cd, Cu and Zn in real environmental water samples.

Huang et al., [6] developed displacement solid phase extraction method for trace noble elements like Ru, Rh, Pd, Pt, Ir and Au using mercapto functionalized magnetite microspheres on to the inner wall of the knotted reactor coupled with inductively coupled mass spectrometry (ICP-MS). The method is highly sensitive with low detection limit values of 2.1 ng L^{-1} for Ru, 1.9 ng L^{-1} for Rh, 2.5 ng L^{-1} for Pd, 1.8 ng L^{-1} for Ir, 1.9 ng L^{-1} for Pt and 1.5 ng L^{-1} for Au with high enrichment factors in the range of 32-46 for 2.5 mL sample volume. The developed method is fast with high throughput of 20 samples per hour. The method is highly reproducible with low relative standard deviation values of (% RSD) 1.2 % to 2.1 % of 30 ng L^{-1} concentration. Quantitative % recoveries (> 90 %) confirmed that the proposed magnetic solid phase extraction method is highly sensitive, selective and efficient for trace noble metal analysis.

Singh et al., [7] synthesized new surface engineered magnetic nanoparticles by using facile soft-chemical approach. The magnetic nanoparticles were functionalized with

carboxyl (succinic acid), amine (ethylenediamine) and thiol (2,3-dimercaptosuccinic acid) and used for the solid phase extraction of selected heavy metals. TEM micrograph shows that there is no significant difference in the sizes of functionalized and non-functionalized magnetic nanoparticles 6 nm and 10 nm, respectively, while amine functionalized magnetic nanoparticles have size of 40 nm. Surface functional group like COOH, NH₂ and SH were responsible for the interactions with analyte followed chelate or complex formation, ion exchange or electrostatic interaction mechanisms. Experimental results show that magnetic nanoparticles are selective and reusable for trace metal extraction.

Mehdinia et al., [8] developed rapid magnetic solid phase extraction method with in-situ derivitization for methyl mercury in water samples using Fe₃O₄/polyaniline nanoparticles (core shells) as adsorbent, prior to its quantification by gas chromatography/mass spectrometry (GC-MS). The developed magnetic solid phase extraction method involve three steps like dispersion of Fe₃O₄-PANI in the water samples, magnetic retrieval of the adsorbent and then, desorption of the extracted MeHg for GC-MS analysis using appropriate solvent (hexane). The method obey Beers law in the concentration range of 0.5-300 ng mL⁻¹ (R²>0.993) with limit of detection value of 0.1 ng mL⁻¹ (n=3), while the reusability of the method was (4.1 %). The accuracy of the method was determined by analyzing different spiked sample of sea water with satisfactory recovery (>98 %) results.

Cheng et al., [9] has investigated magnetic solid phase extraction method for the preconcentration of selected heavy metals like Cr(III), Cu(II), Zn(II) and Pb(II) using dithizone modified silica-coated magnetic nanoparticles (H2Dz-SCMNPs). Limit of detection values of Cr(III), Cu(II), Zn(II) and Pb(II) were found to be 35 ng L⁻¹, 11 ng L⁻¹

¹, 8 ng L⁻¹ and 62 ng L⁻¹, respectively, under optimized experimental condition using ICP-OES with preconcentration factor of 100. The relative standard deviation values were in the range of 1.7-3.1 % for seven repeated determination of 10 µg L⁻¹ concentrations. The method was validated by applying to certified reference material (GSBZ50009-88 environmental water samples and GBW07601 human hair samples). The method was also applied to real water and human hair samples for spiked samples. The good agreement between determined and certified values and quantitative percent recoveries in the range of 85 % to 110 % shows the applicability to real samples.

Ngomsik et al., [10] reported magnetic solid-liquid extraction of Eu(III), La(III), Ni(II) and Co(II) by using magemite nanoparticle (magemite, γ -Fe₂O₃) modified with citrate ions. The prepared adsorbent was characterized using TEM and SAA. High surface area 170 m² g⁻¹ of the material shows that the modified magemite nanoparticles have high adsorption capacity. The equilibrium data fit to Langmuir adsorption isotherm and the kinetic data shows that equilibrium was established within 15 min. Maximum adsorption takes place at pH 3.5 and there is no significant change in % adsorption of the selected heavy metals above this pH. The proposed solid phase extraction method was then successfully applied to real water samples for heavy metal analysis.

Gupta and Nayak [11] successfully impregnated agricultural waste orange peel powder (OPP) with magnetic nanoparticle (MNP) using co-precipitation method and successfully used it for Cd(II) removal from the aqueous solutions. The adsorbent MNP-OPP was characterized using FTIR, SEM, XRD, TEM and VSM and confirmed that the covalent binding of hydroxyl group of MNPs and carboxyl group of OPP and its other physico-chemical properties enable the adsorbent for metal binding. The kinetic data can be well

explained by pseudo-second order kinetics and the adsorption equilibrium data fit in to Langmuir adsorption isotherm. The thermodynamic study shows that the adsorption process is feasible and endothermic in nature. The column experiment for desorption study shows that MNP-OPP can be reused without significant change in the adsorption efficiency of the adsorbent. The method was successfully applied for removal and recovery of Cd(II) from waste water of electroplating industry.

Bagheri et al., [12] synthesized Schiff base/silica/magnetite nanocomposite ($\text{Fe}_3\text{O}_4/\text{SiO}_2/\text{L}$) and employed it for the solid phase extraction of some heavy metals from environmental, biological and food samples. Extracted metals ions were then analyzed using Flame atomic absorption spectrometry. The synthesized product was characterized using FT-IR, XRD and TEM. The synthesized solid phase was observed and have high surface area and can be retrieved by external magnetic field was employed for the preconcentration of selected heavy metals like Pb(II), Cd(II) and Cu(II) in environmental, biological and food samples. All parameters that effect extraction of heavy metals were optimized. Detection at optimum condition was investigated for Pb(II), Cd(II) and Cu(II) and was $0.14 \mu\text{g L}^{-1}$, $0.19 \mu\text{g L}^{-1}$ and $0.12 \mu\text{g L}^{-1}$, respectively. The proposed method has been successfully applied to environmental, biological and food samples with good quantitative results.

Idris et al., [13] synthesized magnetic alginate beads by including ferrofluids based on magemite nanoparticles ($\gamma\text{-Fe}_2\text{O}_3$) and sodium alginate and used it for removal of Pb(II) from aqueous solutions. The specific saturation magnetization (σ_s) value of uncoated particles was found to be greater than the coated particles and zero coercivity of the magnetization curve indicated that the particles were superparamagnetic in nature. The

results indicate that equilibrium was established in 2 h with maximum percent removal (95.2%) of Pb(II) at pH 7. The equilibrium data shows that the adsorption of Pb(II) followed Langmuir adsorption isotherm with $q_{\max}$ of 50 mg/g. The isolated beads were used as a regenerated sorbent in repeated sorption–desorption cycles in order to determine the reusability potential of the adsorbent. Results revealed that the modified magnetic beads can be successfully used for the waste water treatment and can be regenerated at least five times before significant change in there adsorbing efficiency.

Yao et al., [14] synthesized a new solid phase extractant based on tetraethylenepentamin-Functional Fe_3O_4 magnetic polymer (TEPA-NMPs) for the preconcentration of ultra-trace Cr(VI) in water samples prior to its determination by using flame atomic absorption spectrometry (FAAS). Various optimization studies like solution pH, shaking time, adsorption temperature, sample volume, desorption condition and matrix effect were investigated and optimized. Kinetic date fit to pseudo-first order kinetics, while the thermodynamic study shows that the adsorption of Cr(VI) on TEPA-NMPs is endothermic and entropy favored process. Under optimized experimental condition the values of detection limit (LOD), enrichment factor (EF) and relative standard deviations were $0.16 \mu\text{g L}^{-1}$, 125 and 1.9 % ($n=7$), respectively. The method was successfully validated by applying it to real water samples like river and tap water with satisfactory results.

Jiang et al., [15] offered a new protocol for the separation and preconcentration of trace Pb(II) in water samples using silica-coated magnetic Fe_3O_4 nanoparticle (Zincon-Si-MNPs) as sold phase. Parameters like solution pH, eluent, sample volume and interference affect that influence the extraction efficiency of the adsorbent were

investigated. The limit of detection (LOD) value of the proposed method for Pb(II) with 200 enrichment factor was 10 ng L^{-1} . This method has been successfully applied for the preconcentration of Pb(II) in real water samples with quantitative % recoveries ranging from 84 % to 104 %.

Zhang et al., [16] investigated high-magnetization $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{TiO}_2$ nanoparticle based solid phase extraction for the preconcentration of Cd(II), Cr(III), Cu(II) and Mn(II) in environmental samples. pH of the solution was adjusted by using light induced hydroxide ion emitter, malachite green carbinol green (MGCB) for quantitative adsorption instead of conventional buffer solution. Based on high-magnetization $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{TiO}_2$ with MGCB, a convenient separation and preconcentration method for Cd(II), Cr(III), Cu(II) and Mn(II) in environmental water has been developed. Limit of detection for Cd(II), Cr(II), Mn(II) and Cu(II) were calculated 4.0 , 2.6 , 1.6 and 2.3 ng L^{-1} , respectively and the relative standard deviation values were calculated as (RSDs, $C=1 \text{ } \mu\text{g L}^{-1}$, $n=7$) 3.6 %, 4.5 %, 4.0 % and 4.1 % . The method was applied to certified reference material and environmental water samples with satisfactory results.

Wang et al., [17] reported the synthesis of aminated- $\text{CoFe}_2\text{O}_4/\text{SiO}_2$ nanoparticles (core shell) and used it as solid phase adsorbent for the extraction of cadmium from environmental water samples prior to its quantification by hydride generation atomic fluorescence spectrometry. The limit of detection value (3σ) is 3.15 ng L^{-1} while the relative standard deviation value is 4.9 % for ($n=11$) repeated determination of $1.0 \text{ } \mu\text{g L}^{-1}$ Cd (II) concentration. For 50 mL of sample the enrichment factor is 50 and the adsorbent can be reused for at least 45 cycles of preconcentration and elution experiments. The method was successfully applied for the determination of cadmium in spiked samples in

environmental water samples. The method was validated by analyzing two certified reference materials.

Safdarian et al., [18] investigated magnetic solid phase extraction for the preconcentration of Pd(II) by using agarose coated magnetic nanoparticles (ACMNPs) as adsorbent coupled to a new magnetic field agitation (MFA) device. The formation of the nanoparticles and their encapsulation in agarose micro-flakes was carried out in a single step which was reported for the first time in this work. For this purpose, preparation of the magnetic iron oxide nanoparticles was performed in an alkaline agarose solution. The synthesized nonmagnetic agarose particles were treated with iminodiacetic acid for functionalization under the influence of magnetic field agitation in the MFA device. Analytical parameters like limit of detection (LOD) and relative standard deviation (RSD) were determined as 47 ng L^{-1} and 5.2 %, respectively with 94.1 % recovery of Pd(II). The method was successfully validated by applying the method to natural water samples for determination of Pd(II).

Tarigh et al., [19] reported magnetic solid phase extraction for the preconcentration and determination of Pb(II) and Mn(II) using magnetic multi-wall carbon nanotube (MMWCNT) as an adsorbent. The concentration of the analytes were determined using flame atomic absorption spectrometry FAAS. Analytical parameters like detection limits and enhancement factors of the proposed method for Pb and Mn were determined as ($1.0 \text{ } \mu\text{g L}^{-1}$, $0.6 \text{ } \mu\text{g L}^{-1}$) and (390 and 697), respectively. The proposed magnetic solid phase extraction method was successfully applied for determination of Pb(II) and Mn(II) contents in lipstick and rice samples. The accuracy was evaluated by analyzing a certified reference material SeronormTM Urine LOT NO2525.

Li et al., [20] synthesized amino-functionalized magnetic nanoparticle ($\text{NH}_2\text{-MNP}$) by a sol-gel approach and used it for the adsorption of Cu(II) ions from environmental water samples. Kinetic data shows that the pseudo-second-order model can be successfully employed, and pseudo-first-order model verified that Cu(II) adsorption on $\text{NH}_2\text{-MNP}$ was a diffusion-based process. Equilibrium data shows, that Langmuir model and Dubinin-Radushkevich model ($R^2 > 0.99$) were more paralleled with the adsorption isotherm data of Cu(II) ions than Freundlich model. The prepared adsorbent can be reused after five adsorption and desorption cycles. Ion exchange-surface complexation mechanism was confirmed from adsorption activation energy and thermodynamic studies. The method was successfully validated by applying it to real environmental water samples with satisfactory results.

Najafi et al., [21] reported solid phase extraction of Hg(II) using magnetic nanoparticles (Fe_3O_4) functionalized with novel ion imprinted polymer based on N-(pyridine-2-ylmethyl)ethenamine (V-Pic). The adsorbent was characterized by using thermogravimetric and differential thermal analysis (TG/DTA), SEM, FT-IR and EDX. The proposed method was applied for rapid extraction, preconcentration and determination of Hg(II) by inductively coupled plasma-optical emission spectrometry (ICP-OES). Analytical parameter like limit of detection and relative standard deviation were determined as 0.03 ng mL^{-1} and 1.47 %, respectively. The method was validated by analyzing trace Hg(II) in standard reference materials. The method was also applied to spiked fish samples with quantitative percent recoveries.

Giakisikli and Anthemidis [22] used automated magnetic solid phase extraction approach for preconcentration of trace Cd(II) in natural water samples using octadecylsilane

functionalized magemite magnetic nanoparticles in sequential injection system prior to its determination by electrothermal atomic absorption spectrometry. Two neodymium iron boron (NdFeB) magnets across the micro-column in which octadecylsilane functionalized magemite magnetic nanoparticles were used as sorbent. Diethyldithiocarbamate (DDTC) was used as complexing agent form online complex with Cd(II), adsorption of Cd-DDTC and elution by using methyl isobutyl ketone (MIBK). The column was remained stable for about 600 cycle without any significant loss in its extraction efficiency. The method was validated by applying it to certified reference materials.

Zhu et al., [23] designed a new 1-8 naphthalimide-functionalized $\text{Fe}_3\text{O}_4@\text{SiO}_2$ core/shell magnetic fluorescent nanoparticle based adsorption of trace Hg(II). Characterization of the adsorbent was carried out using FT-IR, TEM and XRD. Adsorption experiments were conducted at different solution pH, Hg(II) concentration, temperature and time for finding best condition to obtain maximum adsorption of the analyte. Maximum adsorption capacity of 30 mg g^{-1} was obtained over a temperature range of (0 °C, 25 °C and 50 °C) and pH (4-10). Under optimized experimental condition the detection limit was calculated as 3.4 nM. The adsorbent is highly specific and can be reused without substantial decrease in its adsorption capacity. The method was used for adsorption of trace Hg(II) in environmental samples.

Liu et al., [24] investigated solid phase extraction of Cu(II) using EDTA functionalized magnetic nanoparticles (MNPs-EDTA). The adsorbent was characterized using TGA, SEM, FT-IR and XRD. Different parameters influencing the adsorption of Cu(II) on MNPs-EDTA like pH, contact time, salinity, temperature and initial metal ion concentration were optimized. Kinetic data shows that the adsorption equilibrium is

established in 5 min and the adsorption of Cu(II) on MNPs-EDTA follow pseudo second order kinetics. Equilibrium data was best fitted to Langmuir adsorption isotherm with maximum adsorption capacity of 46.27 mg g⁻¹ at pH 7 and 298 K. Various thermodynamic parameters like $\Delta^{\circ}H$, $\Delta^{\circ}G$ and $\Delta^{\circ}S$ shows that the adsorption of Cu(II) on MNPs-EDTA is endothermic and spontaneous in nature. The prepared adsorbent has good stability and reusability.

Ziaei et al., [25] reported new solid phase extraction method for the preconcentration of Hg(II) using novel mercapto-grafted graphene oxide-magnetic chitosan nanocomposite (mercapto/GO-MC) as biosorbent. Continuous flow cold vapor atomic absorption spectrometry technique was used for the Hg(II) analysis in the sample solution. The optimum values of various parameters at which maximum extraction of Hg(II) takes place were; pH 6.5, 10 min contact time, 3 mL HCl (0.1 mol L⁻¹)/thiourea (2% w/v) as eluent and 250 mL breakthrough volume. Analytical parameters like limit of detection 0.03 ng mL⁻¹, preconcentration factor of 80 and relative standard deviation of 4.7 % were investigated under optimized experimental condition. The method was successfully applied to real water samples with quantitative percent recoveries in the range of 95-100 %.

Li et al., [26] used surface sulfhydryl-functionalized magnetic mesoporous silica nanoparticles for the solid phase extraction of trace alkyl mercury from aqueous solution. Non-sulfhydryl-functionalized Fe₃O₄@SiO₂ and sulfhydryl-functionalized Fe₃O₄@SiO₂ were carried out for the extraction of CH₃Hg⁺ and CH₃CH₂Hg⁺. The results indicate that sulfhydryl-functionalized Fe₃O₄@SiO₂ exhibited high adsorption affinity as compared to non-sulfhydryl-functionalized Fe₃O₄@SiO₂. The chelating interaction CH₃Hg⁺ and CH₃CH₂Hg⁺ with surface sulfhydryl group was not significantly influenced

by pH within the range of 3.5–9.0. Adsorption equilibrium was established in 2 min. More than 80 % recoveries were obtained by using acetonitrile and L-cysteine aqueous solution or HCl solution. It can be concluded that $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-RSH}$ magnetic nanoparticles can be an excellent, effective and reusable adsorbents for extraction of ultra-trace alkylmercury from environmental water samples.

Guo et al., [27] synthesized graphene magnetic material ($\text{Fe}_3\text{O}_4\text{-GS}$) was prepared by introducing ferroferric oxide (Fe_3O_4) into graphene sheet and used it for the removal of Cr(VI), Pb(II), Hg(II), Cd(II) and Ni(II) ions from aqueous solution. $\text{Fe}_3\text{O}_4\text{-GS}$ can be simply recovered from the sample solution with magnetic separation at low magnetic field. The adsorption capacities of the metals were determined as 17.29, 27.95, 23.03, 27.83 and 22.07 mg g^{-1} for Cr(VI), Pb(II), Hg(II), Cd(II) and Ni(II), respectively. Kinetic data can be best explained by using pseudo-second-order equation and for the explanation of equilibrium data, Freundlich model was found to be more suitable. It was found that metal chelation ion exchange mechanisms are involved in metals sorption. The thermodynamic data supported that the adsorption process was endothermic and spontaneous in nature.

Xiao et al., [28] prepared new carboxylated multi-wall carbon nanotube (c-MWCNT)- Fe_3O_4 magnetic hybrids (c-MWCNTMCs) by mixing $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, sodium acetate, ethylene glycol and diethylene glycol with c-MWCNTs, under the influence of sonication and heat treatment at 200 °C for 10 h. The c-MWCNTMCs showed high dispersion stability and magnetic property and can be used as adsorbents for Cu(II) removal. The c-MWCNTMCs could be easily retrieved from water by a magnet to avoid sample loss in filtration and showed a high adsorption capacity for Cu(II). The adsorbent can be

successfully renewed at pH (>2). The adsorption of Cu(II) on the c-MWCNTMCs was quick, follow pseudo-second-order model and the reaction of chemical nature.

Mashhadizadeh et al., [29] examined Fe₃O₄ nanoparticles coated with 3-(trimethoxysilyl)-1-propanethiol and modified with ethylene glycol bis-mercaptoacetate based extraction, pre-concentration, and determination of trace amounts of Ag, Cd, Cu, Hg, and Pd from some food samples. Concentrations of the metal ions were determined by using ICP-OES and for mercury CV-AAS method was used. Various parameter affecting the extraction and desorption of target metal ions were optimized. For desorption of the target metal ion eluent (1 mL of 1 mol/L HCl and 5% thiourea) was used. The detection limits of 0.07, 0.06, 0.09, 0.01, and 0.08 ng/mL for Ag, Cd, Cu, Hg, and Pb with enrichment factors of 240, 294, 297, 291, and 236, respectively were found under optimized experimental condition. The develop method was used for the determination of target metal ions in food samples like rice, canned tuna fish, and tea leaves.

Zong and Gou [30] developed new rapid and economical solid phase extraction method for the preconcentration of U(VI) by using magnetic multi walled carbon nanotube/iron oxide nano composite (Fe₃O₄/MCNTs) prior to its determination by flame atomic absorption spectrometry (FAAS). It was observed that pH 7 is the most suitable pH at which maximum adsorption of U(VI) takes place. Kinetic data can be well explained by using pseudo first order kinetics, while the equilibrium data follow Langmuir adsorption isotherm. The experimental data shows that the adsorption of U(VI) on the Fe₃O₄/MCNTs favored at higher environmental temperature. The proposed adsorbent was successfully applied to real environmental samples with satisfactory adsorption results.

Su et al., [31] synthesized novel $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{polyaniline-graphene oxide}$ composite (MPANI-GO) through noncovalent method and used it for the magnetic solid phase extraction (MSPE) of trace rare earth elements (REEs) followed by inductively coupled mass spectrometry (ICP-MS) determination. The synthesized MPANI-GO was characterized by using TEM and vibrating sample magnetometer. Factors effecting MSPE of REEs on MPANI-GO was investigated. Under optimized experimental condition limit of detection were in the range of $0.04\text{--}1.49\text{ ng L}^{-1}$ and the relative standard deviation (RSD, $C = 20\text{ ng L}^{-1}$, $n=7$) was 1.7–6.5%. The accuracy of the proposed method was investigated by analyzing certified reference material GBW 07605 tea leaves. The method was also applied for trace REEs determination in tea leaves and environmental samples.

Khan et al., [32] reported innovative ionic liquid based ultrasound assisted dual magnetic microextraction (IL-UA-DMME) technique for the preconcentration of Cd(II) from environmental and biological samples followed by flame atomic absorption spectrometric (FAAS) determination. The combination of magnetic solid phase extraction (MSPE) with dispersive liquid-liquid extraction (DLLE) microextraction has significant advantages like low amount of organic and other chemical sludge's are discharge into the waste and also high extraction of the analyte metal is achieved. The method was validated by analyzing certified reference material like fortified lake water TMDA-54.4, SPS-WW2 waste water and spinach leaves 1570a.

Omidi et al., [33] studied trace separation/preconcentration of cadmium ions using pyridine-functionalized magnetic nonporous silica material (called $\text{Py-Fe}_3\text{O}_4@\text{MCM-41}$) as a new magnetic sorbent. Flame atomic absorption spectrometry (FAAS) was used for

determination of Cd(II). The Py-Fe₃O₄@MCM-41 was characterized by TG/DTA, TEM, FT-IR and XRD. Extraction parameter like pH of solution, amount of functionalized Fe₃O₄@MCM-41, extraction time, type and concentration of eluent, desorption time, and matrix effect were investigated. Detection limit and relative standard deviation was determined as 0.04 µg L⁻¹ and 2.9%, respectively. The maximum adsorption capacity of Py-Fe₃O₄@MCM-41 for cadmium ions was 154 mg g⁻¹. The proposed method has been successfully applied to the determination of Cd ions at trace levels in food and water samples with satisfactory recovery results.

Banazadeh et al., [34] investigated new solid phase extraction method for Cd(II) from environmental samples using cysteine functionalized magnetic graphene oxide nanosheets. The functionalized graphene oxide nanosheets are efficient and selective sorbent for the extraction of trace Cd(II) from food samples. The adsorption capacities for Cd(II) were 24.39-30.30 mg g⁻¹ at 298 K and 328 K, respectively. The adsorption equilibrium established within 5 min and the kinetics of the adsorption followed pseudo second order model. The equilibrium can be best interpreted by Langmuir adsorption isotherm and the thermodynamic data shows the adsorption process is endothermic, spontaneous and chemical in nature.

Mahmoud et al., [35] reported simple and solvent-free method for synthesis of novel magnetic nano-sorbents functionalized with dioctyl phthalate (DOP) to produce a nano-Fe₃O₄-DOP sorbent. The synthesized nano-Fe₃O₄-DOP was then treated with triethylenetetramine (TETA) in another solvent-free procedure for the establishment of a novel nano-Fe₃O₄-DOP-TETA. Both a nano-Fe₃O₄-DOP and nano-Fe₃O₄-DOP-TETA were characterized by FT-IR, TGA, SEM and HR-TEM (3.0–12.0 nm). The optimization

parameters of magnetic solid phase were investigated and optimized. The proposed magnetic solid phase extraction procedure was applied for the preconcentration of Ni(II), Cd(II) and Pb(II) in drinking tap water, industrial wastewater and sea water samples.

Mahmoudi et al., [36] synthesized magnetic nano-sorbent through direct surface impregnation of dioctyl phthalate (Dop) on magnetic nano-iron oxide (nano-Fe₃O₄) for the establishment of (nano-Fe₃O₄-Dop). Novel magnetic nano-sorbent (nano-Fe₃O₄-Dop-HA) was prepared from nano-Fe₃O₄-Dop after its functionalization with nitrogen and oxygen donor atoms by surface immobilization of hydroxylamine. SEM, HR-TEM, TGA, FT-IR and surface area analysis were carried out for its characterization. According to HR-TEM analysis, the average particle size was found in the range of 5–16 nm. The unified selectivity was studied for removal of Cd(II), Hg(II) and Pb(II) from aqueous solutions using static and dynamic techniques. Nano-Fe₃O₄-Dop-HA was found to have high uptake values of 1433.3–1633.3 $\mu\text{mol g}^{-1}$ at pH 1.0–7.0 for Hg(II) as compared to Cd(II) and Pb(II). The potential applications of nano-Fe₃O₄-Dop-HA for the extraction of Cd(II), Hg(II) and Pb(II) from industrial wastewater, sea water and drinking tap water samples were successfully investigated.

Sun et al., [37] reported one step synthesis magnetic graphene oxide nanocomposite by one-step coprecipitation method and use it for the solid phase extraction of Co(II), Ni(II), Cu(II), Cd(II), and Pb(II) from biological samples. The adsorbent can be reused more than 20 times without significant change in its extraction efficiency. The limits of detection values of 0.016, 0.046, 0.395, 0.038, 0.157 $\mu\text{g L}^{-1}$ for Co(II), Ni(II), Cu(II), Cd(II), and Pb(II), respectively, were found under optimized experimental condition. The low values of intra-day relative standard deviations ($n=5$), in the range of 1.8–5.5% at

10 $\mu\text{g L}^{-1}$ shows that the method is repeatable. The proposed solid phase extraction method was successfully applied to biological sample with satisfactory recoveries of 81 % to 113 % without the interferences of complex matrix nature of the samples.

Sheshmani et al., [38] established new protocol for the removal of trace Pb(II) in water samples by using graphene oxide/chitosane/FeOOH (GO/Ch/FeOOH) as an adsorbent. Parameters like solution pH, eluent, sample volume and interference affect that influence the extraction efficiency of the adsorbent were optimized. The surface of the prepared adsorbent (GO/Ch/FeOOH) has amino and hydroxyl functional group which make it selective for the extraction of Pb(II) from the aqueous solution. Both Langmuir and Freundlich isotherm were used to explain the equilibrium data but Langmuir isotherm model has high correlation coefficient (r^2) value.

Tadjarodi et al., [39] investigated magnetic solid phase extraction method for the preconcentration of Cd(II) and Pb(II) ions by using novel $\text{Fe}_3\text{O}_4@\text{SiO}_2$ core-shell nanoparticles functionalized with phenyl isothiocyanate as an adsorbent. Box–Behnken design through response surface methodology was used to optimize various parameters, influencing preconcentration procedure. The analyte ions were quantified after preconcentration by FAAS. The limit of detection was found as 0.05 ng mL^{-1} for Cd(II) and 0.9 ng mL^{-1} for Pb(II). The relative standard deviations were less than 6.4% and the adsorption capacity (in mg g^{-1}) of the new adsorbent was found as 179 and 156 for Cd(II) and Pb(II), respectively. The prepared nanocomposite was successfully applied for the rapid extraction of trace amount of heavy metal ions from food, soil and water samples.

Mirabi et al., [40] investigated new magnetic solid phase extraction method for the preconcentration of Cu(II) by using magnetic nanocomposites surface (MNCS), which has anionic surfactant sodium dodecyl sulfate (SDS) coating and functionalized with dithiooxamide sorbent. The pre-concentrated copper ions were determined by flame atomic absorption spectrometry (FAAS). The effect of the experimental parameters such as the pH of the sample, the type and concentration of the eluent, concentration of dithiooxamide, amount of sorbent and matrix effect were optimized. Linear calibration graph in the range of 2–600 ng ml⁻¹ was obtained with detection limit of 0.2 ng ml⁻¹ and relative standard deviation (RSD) for (n=6) was 1.8%. This method was applied for the determination of Cu ions in food and water samples satisfactory results.

References

- [1] P. Panneerselvam, N. Morad, K. A. Tan, Magnetic nanoparticle (Fe_3O_4) impregnated onto tea waste for the removal of nickel(II) from aqueous solution, *Journal of Hazardous Materials* 186 (1) 160-168 (2011).
- [2] A. E. Karatapanis, Y. Fiamegos, C. D. Stalikas, Silica-modified magnetic nanoparticles functionalized with cetylpyridinium bromide for the preconcentration of metals after complexation with 8-hydroxyquinoline, *Talanta* 84 (3) 834-839 (2011).
- [3] Y. Lin, H. Chen, K. Lin, B. Chen, C. Chiou, Application of magnetic particles modified with amino groups to adsorb copper ions in aqueous solution, *Journal of Environmental Sciences* 23 (1) 44-50 (2011).
- [4] M. Bhaumik, A. Maity, V. V. Srinivasu, M. S. Onyango, Enhanced removal of Cr(VI) from aqueous solution using polypyrrole/ Fe_3O_4 magnetic nanocomposite, *Journal of Hazardous Materials* 190 (1–3) 381-390 (2011).
- [5] M. H. Mashhadizadeh, Z. Karami, Solid phase extraction of trace amounts of Ag, Cd, Cu, and Zn in environmental samples using magnetic nanoparticles coated by 3-(trimethoxysilyl)-1-propanthiol and modified with 2-amino-5-mercapto-1,3,4-thiadiazole and their determination by ICP-OES, *Journal of Hazardous Materials* 190 (1–3) 1023-1029 (2011).
- [6] Y. Li, Y.-F. Huang, Y. Jiang, B.-l. Tian, F. Han, X.-P. Yan, Displacement solid-phase extraction on mercapto-functionalized magnetite microspheres for inductively coupled plasma mass spectrometric determination of trace noble metals, *Analytica Chimica Acta* 692 (1–2) 42-49 (2011).

-
- [7] S. Singh, K. C. Barick, D. Bahadur, Surface engineered magnetic nanoparticles for removal of toxic metal ions and bacterial pathogens, *Journal of Hazardous Materials* 192 (3) 1539-1547 (2011).
- [8] A. Mehdinia, F. Roohi, A. Jabbari, Rapid magnetic solid phase extraction with in situ derivatization of methylmercury in seawater by Fe₃O₄/polyaniline nanoparticle, *Journal of Chromatography A* 1218 (28) 4269-4274 (2011).
- [9] G. Cheng, M. He, H. Peng, B. Hu, Dithizone modified magnetic nanoparticles for fast and selective solid phase extraction of trace elements in environmental and biological samples prior to their determination by ICP-OES, *Talanta* 88, 507-515 (2012).
- [10] A.-F. Ngomsik, A. Bee, D. Talbot, G. Cote, Magnetic solid–liquid extraction of Eu (III), La (III), Ni (II) and Co (II) with maghemite nanoparticles, *Separation and Purification Technology* 86, 1-8 (2012).
- [11] V. Gupta, A. Nayak, Cadmium removal and recovery from aqueous solutions by novel adsorbents prepared from orange peel and Fe₂O₃ nanoparticles, *Chemical Engineering Journal* 180, 81-90 (2012).
- [12] H. Bagheri, A. Afkhami, M. Saber-Tehrani, H. Khoshsafar, Preparation and characterization of magnetic nanocomposite of Schiff base/silica/magnetite as a preconcentration phase for the trace determination of heavy metal ions in water, food and biological samples using atomic absorption spectrometry, *Talanta* 97, 87-95 (2012).

-
- [13] A. Idris, N. S. M. Ismail, N. Hassan, E. Misran, A.-F. Ngomsik, Synthesis of magnetic alginate beads based on maghemite nanoparticles for Pb(II) removal in aqueous solution, *Journal of Industrial and Engineering Chemistry* 18 (5) 1582-1589 (2012).
- [14] X.-P. Yao, Z.-J. Fu, Y.-G. Zhao, L. Wang, L.-Y. Fang, H.-Y. Shen, Use of tetraethylenepentamine-functional Fe₃O₄ magnetic polymers for matrix solid phase dispersion extraction and preconcentration of Cr (VI) in water samples at ultratrace levels, *Talanta* 97, 124-130 (2012).
- [15] H.-m. Jiang, Z.-p. Yan, Y. Zhao, X. Hu, H.-z. Lian, Zincon-immobilized silica-coated magnetic Fe₃O₄ nanoparticles for solid-phase extraction and determination of trace lead in natural and drinking waters by graphite furnace atomic absorption spectrometry, *Talanta* 94, 251-256 (2012).
- [16] N. Zhang, H. Peng, B. Hu, Light-induced pH change and its application to solid phase extraction of trace heavy metals by high-magnetization Fe₃O₄@SiO₂@TiO₂ nanoparticles followed by inductively coupled plasma mass spectrometry detection, *Talanta* 94, 278-283 (2012).
- [17] Y. Wang, T. Tian, L. Wang, X. Hu, Solid-phase preconcentration of cadmium (II) using amino-functionalized magnetic-core silica-shell nanoparticles, and its determination by hydride generation atomic fluorescence spectrometry, *Microchimica Acta* 180 (3-4) 235-242 (2013).
- [18] M. Safdarian, P. Hashemi, M. Adeli, One-step synthesis of agarose coated magnetic nanoparticles and their application in the solid phase extraction of Pd(II) using a new magnetic field agitation device, *Analytica Chimica Acta* 774, 44-50 (2013).

-
- [19] G. Daneshvar Tarigh, F. Shemirani, Magnetic multi-wall carbon nanotube nanocomposite as an adsorbent for preconcentration and determination of lead (II) and manganese (II) in various matrices, *Talanta* 115, 744-750 (2013).
- [20] L. Hui, D.-l. Xiao, H. Hua, L. Rui, P.-l. Zuo, Adsorption behavior and adsorption mechanism of Cu (II) ions on amino-functionalized magnetic nanoparticles, *Transactions of Nonferrous Metals Society of China* 23 (9) 2657-2665 (2013).
- [21] E. Najafi, F. Aboufazeli, H. R. L. Z. Zhad, O. Sadeghi, V. Amani, A novel magnetic ion imprinted nano-polymer for selective separation and determination of low levels of mercury (II) ions in fish samples, *Food chemistry* 141 (4) 4040-4045 (2013).
- [22] G. Giakissikli, A. N. Anthemidis, Automated magnetic sorbent extraction based on octadecylsilane functionalized maghemite magnetic particles in a sequential injection system coupled with electrothermal atomic absorption spectrometry for metal determination, *Talanta* 110, 229-235 (2013).
- [23] B. Zhu, J. Zhao, H. Yu, L. Yan, Q. Wei, B. Du, Naphthalimide-functionalized Fe₃O₄@SiO₂ core/shell nanoparticles for selective and sensitive adsorption and detection of Hg²⁺, *Chemical Engineering Journal* 219, 411-418 (2013).
- [24] Y. Liu, M. Chen, H. Yongmei, Study on the adsorption of Cu(II) by EDTA functionalized Fe₃O₄ magnetic nano-particles, *Chemical Engineering Journal* 218, 46-54 (2013).
- [25] E. Ziaei, A. Mehdinia, A. Jabbari, A novel hierarchical nanobiocomposite of graphene oxide–magnetic chitosan grafted with mercapto as a solid phase extraction sorbent for the determination of mercury ions in environmental water samples, *Analytica Chimica Acta* 850, 49-56 (2014).

-
- [26] G. Li, M. Liu, Z. Zhang, C. Geng, Z. Wu, X. Zhao, Extraction of methylmercury and ethylmercury from aqueous solution using surface sulfhydryl-functionalized magnetic mesoporous silica nanoparticles, *Journal of Colloid and Interface Science* 424, 124-131 (2014).
- [27] X. Guo, B. Du, Q. Wei, J. Yang, L. Hu, L. Yan, W. Xu, Synthesis of amino functionalized magnetic graphenes composite material and its application to remove Cr(VI), Pb(II), Hg(II), Cd(II) and Ni(II) from contaminated water, *Journal of Hazardous Materials* 278, 211-220 (2014).
- [28] D.-l. Xiao, H. Li, H. He, R. Lin, P.-l. Zuo, Adsorption performance of carboxylated multi-wall carbon nanotube-Fe₃O₄ magnetic hybrids for Cu(II) in water, *New Carbon Materials* 29 (1) 15-25 (2014).
- [29] M. H. Mashhadizadeh, M. Amoli-Diva, M. R. Shapouri, H. Afruzi, Solid phase extraction of trace amounts of silver, cadmium, copper, mercury, and lead in various food samples based on ethylene glycol bis-mercaptoacetate modified 3-(trimethoxysilyl)-1-propanethiol coated Fe₃O₄ nanoparticles, *Food Chemistry* 151, 300-305 (2014).
- [30] P. Zong, J. Gou, Rapid and economical synthesis of magnetic multiwalled carbon nanotube/iron oxide composite and its application in preconcentration of U (VI), *Journal of Molecular Liquids* 195, 92-98 (2014).
- [31] S. Su, B. Chen, M. He, B. Hu, Z. Xiao, Determination of trace/ultratrace rare earth elements in environmental samples by ICP-MS after magnetic solid phase extraction with Fe₃O₄@SiO₂@ polyaniline-graphene oxide composite, *Talanta* 119, 458-466 (2014).

-
- [32] S. Khan, T. G. Kazi, M. Soylak, Rapid ionic liquid-based ultrasound assisted dual magnetic microextraction to preconcentrate and separate cadmium-4-(2-thiazolylazo)-resorcinol complex from environmental and biological samples, *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy* 123, 194-199 (2014).
- [33] F. Omid, M. Behbahani, M. Kalate Bojdi, S. J. Shahtaheri, Solid phase extraction and trace monitoring of cadmium ions in environmental water and food samples based on modified magnetic nanoporous silica, *Journal of Magnetism and Magnetic Materials* 395, 213-220 (2015).
- [34] A. Banazadeh, S. Mozaffari, B. Osoli, Facile synthesis of cysteine functionalized magnetic graphene oxide nanosheets: Application in solid phase extraction of cadmium from environmental sample, *Journal of Environmental Chemical Engineering* 3 (4) 2801-2808 (2015).
- [35] M. E. Mahmoud, A. A. Yakout, K. H. Hamza, M. M. Osman, Novel nano-Fe₃O₄-encapsulated-dioctylphthalate and linked-triethylenetetramine sorbents for magnetic solid phase removal of heavy metals, *Journal of Industrial and Engineering Chemistry* 25, 207-215 (2015).
- [36] M. E. Mahmoud, A. A. Yakout, K. H. Hussein, M. M. Osman, Magnetic accumulation and extraction of Cd(II), Hg(II) and Pb(II) by a novel nano-Fe₃O₄-coated-dioctylphthalate-immobilized-hydroxylamine, *Journal of Environmental Chemical Engineering* 3 (2) 843-851 (2015).
- [37] J. Sun, Q. Liang, Q. Han, X. Zhang, M. Ding, One-step synthesis of magnetic graphene oxide nanocomposite and its application in magnetic solid phase extraction of heavy metal ions from biological samples, *Talanta* 132, 557-563 (2015).

-
- [38] S. Sheshmani, M. A. Nematzadeh, S. Shokrollahzadeh, A. Ashori, Preparation of graphene oxide/chitosan/FeOOH nanocomposite for the removal of Pb (II) from aqueous solution, *International Journal of Biological Macromolecules* 80, 475-480 (2015).
- [39] A. Tadjarodi, A. Abbaszadeh, M. Taghizadeh, N. Shekari, A. A. Asgharinezhad, Solid phase extraction of Cd(II) and Pb(II) ions based on a novel functionalized Fe₃O₄@ SiO₂ core-shell nanoparticles with the aid of multivariate optimization methodology, *Materials Science and Engineering: C* 49, 416-421 (2015).
- [40] A. Mirabi, A. Shokuhi Rad, H. Khodadad, Modified surface based on magnetic nanocomposite of dithiooxamide/Fe₃O₄ as a sorbent for preconcentration and determination of trace amounts of copper, *Journal of Magnetism and Magnetic Materials* 389, 130-135 (2015).

Chapter – 3

EXPERIMENTAL

3.1. Preparation of adsorbents

3.1.1. Preparation of magnetic nanoparticles (MNPs)

Chemical precipitation method is one of the most reliable methods used for the preparation of magnetic nanoparticles and was followed. For this salts of Fe(II) (4.2 g $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) and salt of Fe(III) (6.3 g of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$) were mixed in 200 mL of distilled water with vigorous stirring at 80 °C under nitrogen atmosphere. Black precipitates of Fe_3O_4 were formed when 20 mL of 25 % ammonia solution was added. The precipitate was washed twice with distilled water and three times with ethanol and dried in oven at 100°C.

3.1.2. Preparation of silica coated magnetic nanoparticles (SiMNPs)

The magnetic nanoparticle obtained through the process above was re-dispersed in 150 mL of ethanol and 50 mL of distilled water. To obtain pH 9, NH_3 solution was added with vigorous stirring. To this, 8 mL of tetraethyl orthosilicate (TEOS) was added and allowed the reaction for 24 h. The resultant SiMNPs were separated by using external magnetic field and dried in the oven at 100°C to obtain the powder.

3.1.3. Preparation of magnetic nanoparticle impregnated banana peels (MNPs-BP)

Banana peels (BP) were collected from juice shops, washed with distilled water and dried it in sun light. The dried banana peels were grinded in grinder and passed through the sieve to obtain uniform particle size of 355 μm . The powder banana peels were washed

several time with distilled water and ethanol in order to completely remove the dust particles.

For impregnation of banana peel, 5 g of BP was added to the solution of MNPs at 80°C for 2 h under vigorous stirring. The resultant MNPs–BP was filtered, washed twice with distilled water and dried in oven at 100°C.

3.1.4. Synthesis of magnetic carbon nanotube (MCNTs)

CNT (1g) was added to the solution of MNPs (Fe_3O_4) at 60°C, at basic pH of 9.4 in ethanol solution and allowed the reaction for about 5h under the influence of ultrasonication and under argon atmosphere so as the reaction is complete. The resultant MCNTs were washed three time with distilled and redispersed in ethanol.

3.1.5. Synthesis of silica coated magnetic carbon nanotube (SiMCNTs)

Tetraethyl orthosilicate (TEOS) (10 mL) was added to the MCNTs solution at basic pH of 9.4 at 80°C and allowed the reaction for about 24 h under the influence of ultrasonication. After 24 h, the SiMCNTs were separated using external magnetic field and washed three times with ultra-pure water and dry in oven at 100°C.

3.1.6. Synthesis of 1-(2-Pyridylazo)-2-naphthol (PAN) impregnated SiMCNTs (SiMCNTs-PAN)

For synthesis of SiMCNTs-PAN, SiMCNTs was taken and 50 mL of 0.5 % PAN solution added to it and incubated for 6 h with continuous shaking. The resultant product SMCNTs-PAN was washed with ethanol and ultra-pure water, followed by drying in oven at 100°C.

3.1.7. Synthesis of graphene oxide (GO)

Graphite powder (3 g) was slowly added to 70 mL of H_2SO_4 in a flask, cooled to 0°C in ice bath. Under the influence of vigorous stirring, KMnO_4 (9 g) was added to this reaction mixture and the reaction temperature was kept around 20°C for 30 min. The reaction mixture was then stirred at 40°C for 30 min. Deionized water (150 mL) was added to the mixture and the reaction temperature was raised to 95°C . After refluxing the reaction mixture at 95°C for 15 min, 500 mL deionized water and 15 mL of 30% H_2O_2 were added to it, and reaction was refluxed again for 10 min. After that the reaction mixture was cooled down to room temperature. Brown-yellow colored product was filtered, and washed with 10% HCl to remove unreacted reagents, following by drying in oven at 50°C for 24 h.

3.1.8. Synthesis of allylamine modified graphene oxide

Graphene oxide (250 mg) in a round bottom flask was dispersed in 5 mL of acetonitrile (ACN), and cooled down to 0°C in ice bath. Thionyl chloride (2 mL) was added to the reaction mixture dropwise under nitrogen atmosphere. Reaction temperature was 70°C , and refluxed for 24 h. After 24 h, the reaction mixture was filtered and washed with water and ethanol. The resulted product formed was dried in oven at 60°C for 12 h. The product was then dispersed in acetonitrile. Allylamine (3 mL) was added to this solution and reaction mixture was stirred at room temperature for 24 h. The product was then filtered and washed with water and ethanol and dried in oven at 60°C for 24 h.

3.1.9. Synthesis of magnetic modified graphene oxide-DVB-VA

A mixture of Azobisisobutyronitrile (AIBN) 0.1mol vinyl acetate (VA), 0.1 mol divinylbenzene (DVB) and 65 mg allylamine modified graphene oxide (Mod. GO) were

stirred in a 100 mL round bottom flask. Nitrogen gas was passed through the reaction mixture and heated at 65°C. After the reaction was completed, the product was washed with water and dried in oven at 60°C.

Modified GO-DVB-VA (600 mg), 80 mg of FeSO₄, 157 mg of FeCl₃ and 50 mL of water was mixed in 250 mL round bottom flask and stirred in sonicator for 20 min. Then, the reaction mixture was heated at 70°C under nitrogen atmosphere for 30 min. The mixture was cooled down to room temperature and 0.5 M NaOH was added dropwise to the reaction mixture until pH=11 obtained. After that, the reaction mixture was refluxed for 5 h. The prepared product was washed with water, ethanol and dried in oven at 100°C for 24 h.

3.2. Characterization of the adsorbents

The adsorbents were characterized step by step during its preparation using FT-IR, SEM, EDX, XRD and SAA.

3.2.1. Characterization using FT-IR

IR Prestigue-21 SHIMADZU, UK and Perkin-Elmer Spectrum 400 FT-IR spectrometer (Waltham, MA, USA) in the range of 4000 cm⁻¹ to 400 cm⁻¹ were used in order to record the FT-IR spectra of the adsorbents.

3.2.2. SEM and EDX analysis

Surface morphology and physical nature of the adsorbent can be examined by studying SEM micrograph. For this purpose small amount of adsorbent particles were taken on stubs with adhesive carbon taps (1.15 cm × 0.9 cm) and SEM images of the adsorbent

were taken using 30 KV SEM and EDX (JSM5910, JEOL, Tokyo, Japan). For elemental analysis the EDX mapping of the adsorbents were obtained using EDX-INCA 200, UK Oxford Instrument.

3.2.3. XRD analysis

JDX-3532 JEOL (Tokyo, Japan) diffractometer with monochromatic Cu-K α radiation ($\lambda=1.5418\text{\AA}$) at 40 KV and 30 mA in the 2θ range of $10-80^\circ$ with 1.03° per minute were used to obtain X-ray diffraction (XRD) designs of the adsorbents.

3.2.4. Surface area, pore volume and pore size analysis

Brunauer-Emmett-Teller (BET) and Barrett-Joyner-Halenda (BJH) method were used for surface area, pore volume and pore size determination using Surface Area Analyzer “NOVA2200e Quantachrome, USA” with nitrogen adsorption/desorption at 77.4 K. The sample analyses were carried out in a vacuum at 120°C in order to remove all adsorbed moisture from the adsorbent surface.

3.3. Sample preparation

3.3.1. Preparation of water samples

Certified water samples like TMDA 64.2 fortified water, TMDA 62.2 environmental water and SPS WW2 wastewater were directly subjected to the proposed solid phase extraction methods without further purification. Environmental water samples like sea water, river water, dam water and wastewater were filtered through a cellulose membrane filter having $0.45\text{ }\mu\text{m}$ pore size (Millipore Corporation, Bedford, MA, USA) to remove the solid suspended particles. After this the real environmental samples were subjected to the proposed solid phase extraction methods

3.3.2. Preparation of food samples

Certified reference material (Tomato Leaves, 1573a) and Oriental Basma Tobacco Leaves (INCT-OBTL-5) and Food samples (Chili, Black pepper, Hemp) collected from the local market were used. A wet ashing procedure was adopted for digestion of food sample and certified reference material. In this procedure, known amount of the food and certified reference materials were weighed into beakers and digested with 10 mL concentrated HNO_3 for 10 min at room temperature and then to 95 °C on hot plate till residue was obtained. After cooling, the residues was again digested with mixtures of 24 mL $\text{HNO}_3\text{-H}_2\text{O}_2$ (2:1 v/v) until dryness. The residues obtained was dissolved with 15 mL of distilled water and filtered with Whatman filter paper to obtain clear solution.

3.3.3. Preparation of soil samples

Aqua-regia was used for wet digestion of real soil sample and certified reference material, in which 24 mL of aqua-regia were added to each beaker having 1g of soil sample (replicate) and 1g of certified reference material GBW07424 (GSS-10) (replicate). All the samples were kept at room temperature for 30 min, and then on hot plate at 95°C till dry residue was obtained. The residue was again digested with 24 mL of aqua-regia at room temperature for 30 min and then heated on hot plate at 95°C until dry residue obtained. Final residues were dissolved in 15 mL of distilled water and filtered. The clear solutions of the samples were subjected to the proposed solid phase extraction method.

3.4. Determination of heavy metals in the samples

A Perkin-Elmer flame atomic absorption spectrometer (FAAS) Model 3110 (Norwalk, CT, USA) and Perkin Elmer model AA200, USA with air–acetylene flame having 10 cm long-slot burner head was used for absorbance measurements. The measurements were performed with the continuous aspiration mode of FAAS. For standard calibration curves, working standards of Cd(II) and Pb(II) in the range of 5-25 $\mu\text{g g}^{-1}$, 2-14 $\mu\text{g mL}^{-1}$, respectively were prepared from stock solution of 100 $\mu\text{g g}^{-1}$ purchased from (Merck, Darmstadt Germany). The standard calibration curve of Cd(II) and Pb(II) are given in Fig. 3.1 and 3.2, respectively.

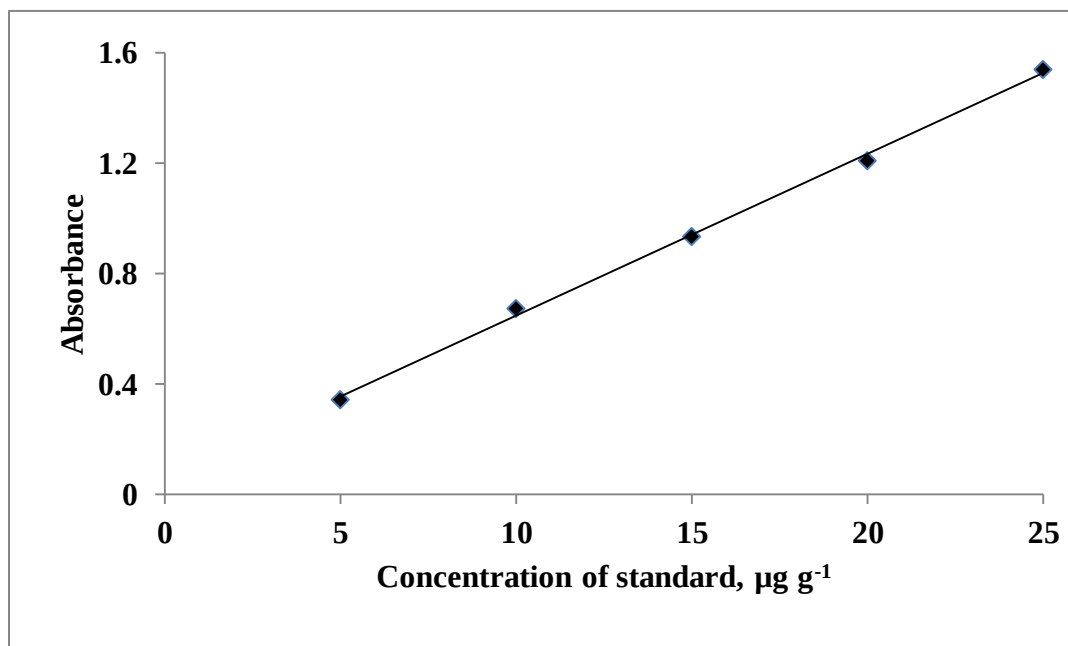


Fig. 3.1: Standard calibration curve for determination of Cd(II) using FAAS.

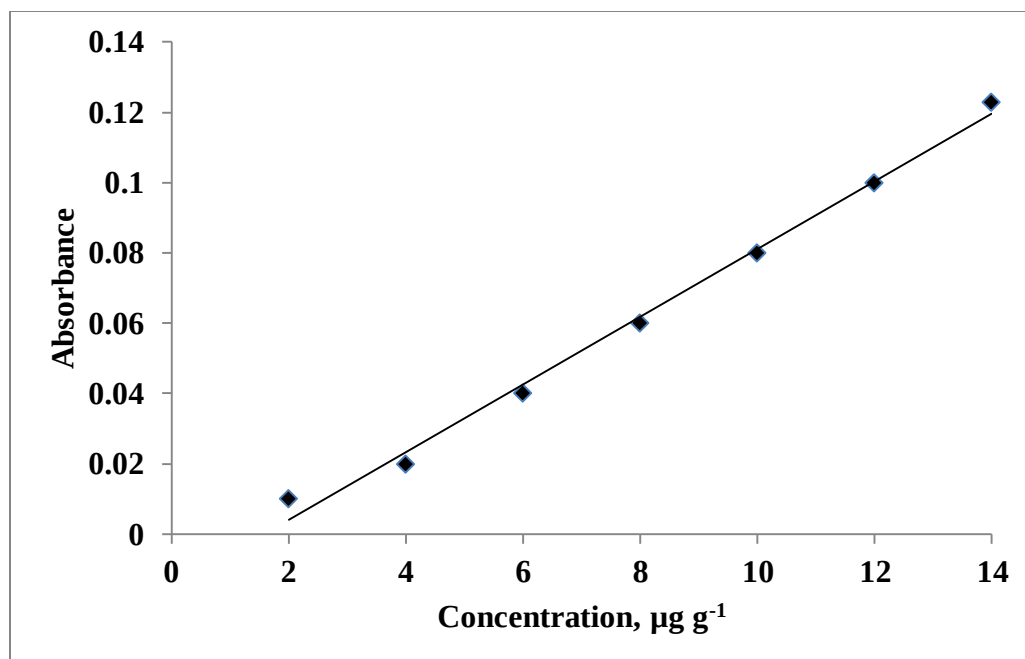


Fig. 3.2: Standard calibration curve for determination of Pb(II) using FAAS.

The following equations were employed for the calculation of adsorption capacity and % recovery.

$$\text{Adsorption capacity (q}_e\text{)} = (C_o - C_e)V/m \quad (1)$$

$$\text{Recovery, \%} = (W_o/W_f) \times 100 \quad (2)$$

Where q_e is the adsorption capacity (mg g^{-1}), C_o and C_e express the initial and equilibrium concentrations of metal ions, respectively; V is the volume of metal ions solution (mL) and m is the amount of sorbent (g). Where W_o and W_f are the amount of analyte (μg) in sample and reference solution, respectively.

Part 1: Magnetic solid phase extraction of Cd(II) using magnetic nanoparticles (MNPs) and silica coated magnetic nanoparticles (SiMNPs)

4.1. Result and Discussion

4.1.1. Characterization of Adsorbent

The adsorbents SiMNPs and MNPs were characterized using FTIR, SEM, EDX and SAA. Comparing FT-IR spectra of MNPs (a) and SiMNPs (b) in the (Figure. 4.1) the presence of a strong absorption band at 1069.65 cm^{-1} (b) that correspond to Si-OH and Si-O-Si that confirms that the surface of SiMNPs covered by Si-OH functional group, while such kind of peak is missing in case of MNPs.

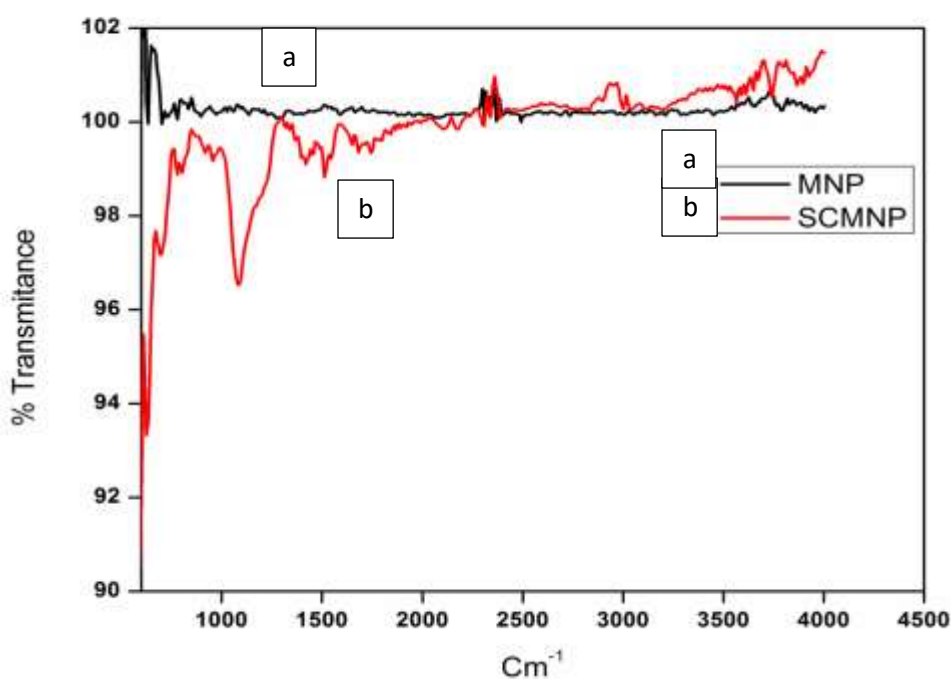
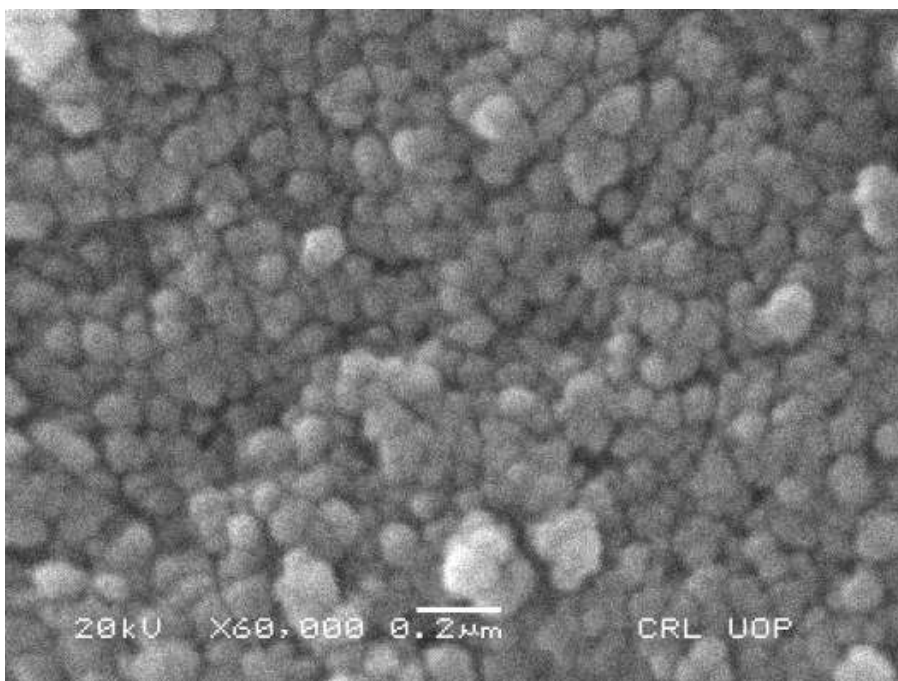
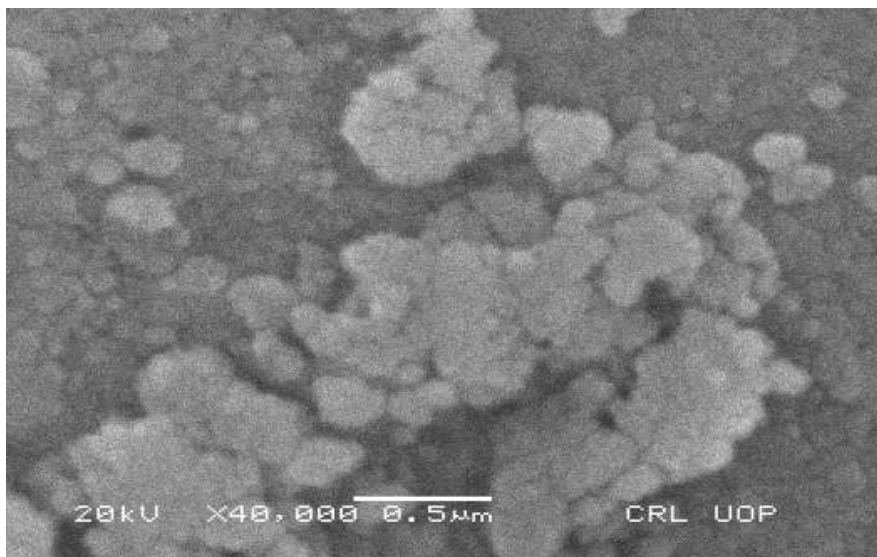


Figure 4.1: FT-IR spectra of MNPs (a) and SiMNPs (b).

The physical nature and surface morphology of SiMNPs and MNPs can be viewed from SEM micrograph given in the Figure 4.2 a and 4.2 b More spherical and dispersed nature of SiMNPs (Fig.4.2) as compared to MNPs (Fig.4.2b) shows that silica core shell avoid SiMNPs from agglomeration in aqueous solution. Thus the problem of self-aggregation of MNPs in aqueous solution can be overcome by coating Si-OH functional group on the surface of MNPs.



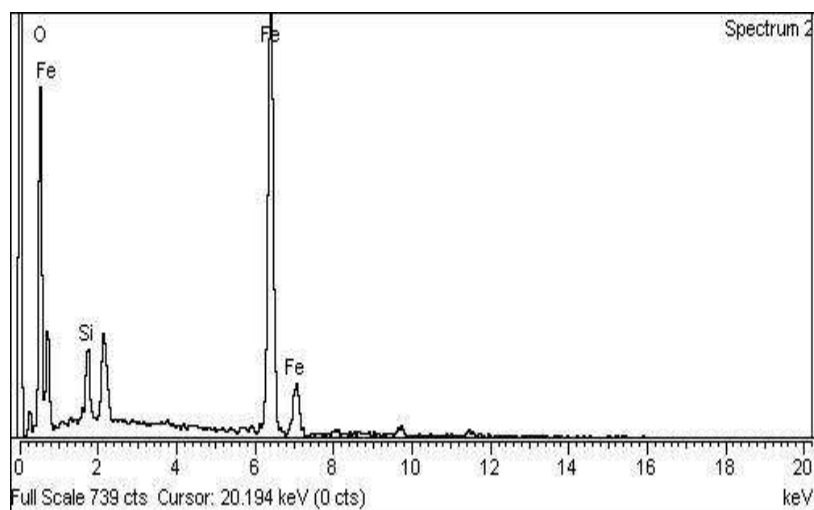
SiMNPs



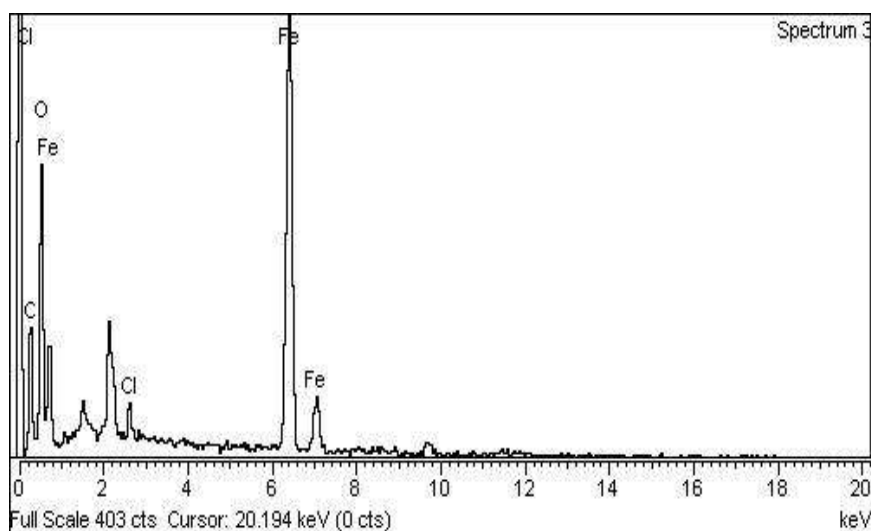
MNPs

Figure. 4.2: SEM micrographs of SiMNPs(a) and MNPs(b).

The Electron dispersive X-ray (EDX) mapping of SiMNPs and MNPs are shown in the Figure 4.3a and 4.3b, respectively. High concentration of Si and Fe in case of SiMNPs, while high concentration of Fe is present in MNPs confirms successful coating of Si on MNPs which avoid the MNPs from agglomeration and acid decomposition during elution.



SiMNPs



MNPs

Figure. 4.3: EDX mapping of SiMNPs(a) and MNPs(b).

Surface area, pore size and pore volume of adsorbent were calculated by BET and BJH methods. According to BET result, the cumulative surface area of the MNPs and SiMNPs were determined as 80.18 mg²/g and 81.35 mg²/g respectively, while the BJH cumulative surface area of MNPs and SiMNPs were calculated as 104.8 m²/g and 105.43 mg²/g, respectively. The average pore volume and pore size of MNPs are 0.21 ccg⁻¹ and 44.23 Å° respectively, while for SiMNPs the values are 0.27 ccg⁻¹ and 46.41 Å°, respectively. The results are given in the Table 4.1.

Table 4.1: Surface area, pore volume and pore size by BET and BJH methods.

Sample	Method	Surface area (mg ² g ⁻¹)	Pore volume (cm ⁻³ g ⁻¹)	Pore size (Å°)
SiMNPs	BET	81.35	0.27	46.41
	BJH	105.43		
MNPs	BET	80.18	0.21	44.23
	BJH	104.8		

4.1.2. Magnetic solid phase extraction procedure

Magnetic solid phase extraction experiments were carried out in 50 mL of centrifuge tubes, containing 2 µg/mL Cd(II) at pH 7. The sample solutions were then added to another tube containing MNPs (0.1 g) and SiMNPs (0.1 g) and the solutions were allowed for 4 min under the influence of vortex (10×40 rpm). When the adsorption was complete, MNPs and SiMNPs were separated using external magnetic field and the liquid phase was separated using pipette. For quantitative recoveries of analyte, HCl (2 mL, 1.0 mol L⁻¹) in acetone was added to the adsorbent. The solutions were again subjected to vortex for 4 min and MNPs and SiMNPs were separated using external magnetic field. The eluent was analyzed by FAAS.

4.1.3. Optimization of the parameter of magnetic solid phase extraction

Optimization studies were performed using model solution containing known amount of analyte. The parameters like solution pH, sorbent dose, sample volume, desorption condition and matrix effect were investigated.

4.1.3.1 Effect of pH

The effect of pH on % recovery of Cd(II) on MNPs and SiMNPs were investigated in the range of 2 to 9 (Figure 4.4 and Table 4.2). The results indicate that % recoveries of Cd(II) increases with increase in pH and reach to its maximum value of (99±4 % and 100±1 %) at pH 7 on MNPs and SiMNPs, respectively. It can be explained that at lower pH, concentration of H⁺ is high which compete with Cd(II) for the vacant sites on the adsorbent leading to the decrease of % recovery of Cd(II). It can also be explained that at lower pH the surface of adsorbent become positively charged and it is difficult to adsorb

positively charged Cd(II) on positively charged adsorbent. The surface of adsorbent is neutral in the range of pH 6 to 8 and is suitable for quantitative % recovery of Cd(II). At higher pH insoluble metal hydroxide formation takes place which causes decrease in the % recoveries.

Table 4.2: Effect of pH on % recovery of Cd(II) using MNPs and SiMNPs.

pH	% Recovery	
	SiMNPs	MNPs
2	82 $\pm$ 3	55 $\pm$ 5
3	92 $\pm$ 4	69 $\pm$ 5
4	94 $\pm$ 5	78 $\pm$ 6
5	95 $\pm$ 6	85 $\pm$ 2
6	97 $\pm$ 5	94 $\pm$ 1
7	100 $\pm$ 4	98 $\pm$ 1
8	97 $\pm$ 3	99 $\pm$ 4
9	86 $\pm$ 6	89 $\pm$ 5

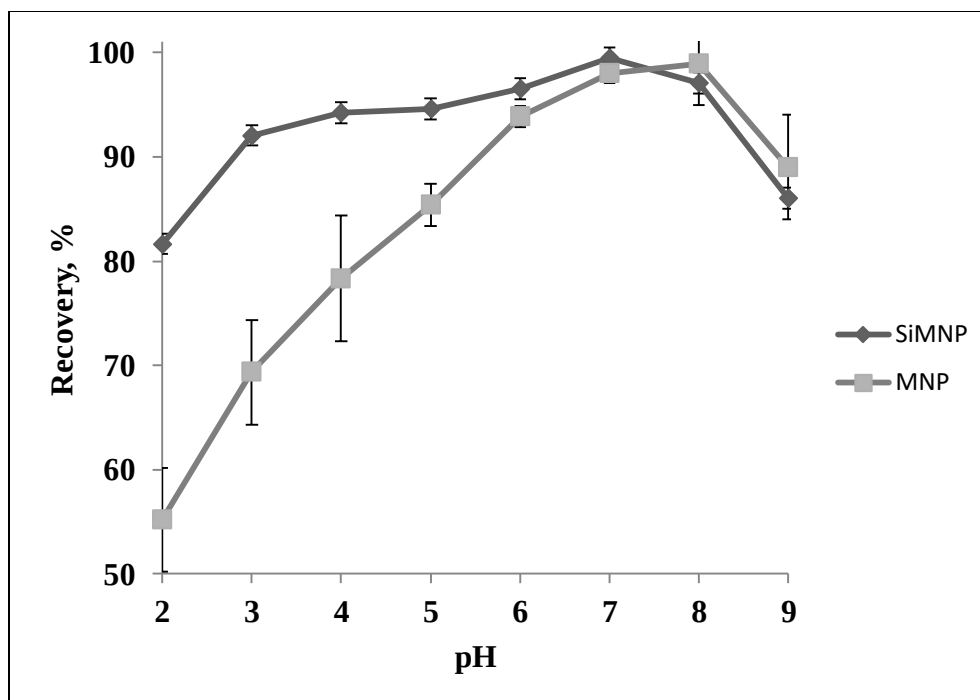


Figure 4.4: Effect of pH on % recovery of Cd(II) using MNPs and SiMNPs (Volume of sample: 10 mL, amount of adsorbent: 0.1 g, final volume: 10 mL, N=3).

4.1.3.2. Effect of adsorbent dose

The effect of adsorbent dose on % recovery is an important parameter as it determines the maximum adsorption capacity of the adsorbent for constant adsorbate concentration. Therefore the solid phase extractions studies were carried out at different adsorbent doses ranging from 0.02 g to 0.14 g (Figure 4.5). It can be concluded from the Figure 4.7 that % recovery of Cd(II) increases with increases in amount of MNPs and SiMNPs and reach to its maximum values of 97 ± 3 % and 100 ± 6 %, respectively with 0.14 g of adsorbent. It can be explained that with increase in amount of adsorbent the number of vacant sites also increases that increase % recovery of Cd(II).

Table 4.3: Effect of adsorbent dose on % recovery of Cd(II) using MNPs and SiMNPs.

Adsorbent dose, g	% Recovery	
	SiMNPs	MNPs
0.02	49±2	47±3
0.04	58±2	58±5
0.06	75±4	61±3
0.08	86±5	71±5
0.1	96±1	97±6
0.12	99±4	97±4
0.14	100±6	97±3

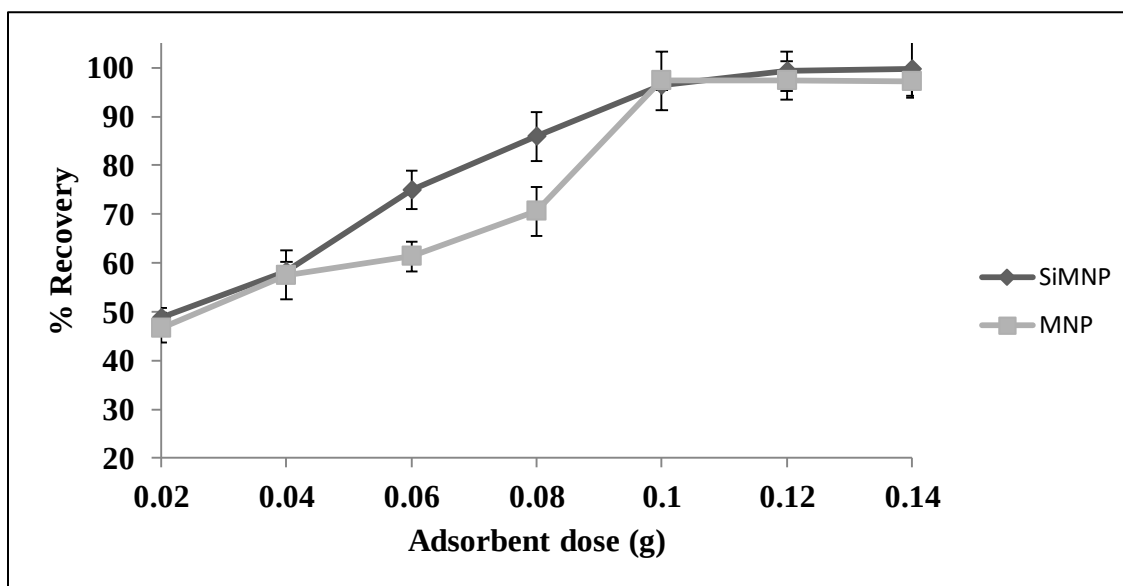


Figure. 4.5: Effect of adsorbent dose on % recovery of Cd (II) using MNPs and SiMNPs (pH: 7, Volume of sample: 10 mL, final volume: 10 mL, (N=3).

4.1.3.3. Effect of sample volume

Investigation of highest preconcentration factor has significant importance as it determines the efficiency of the proposed magnetic solid phase extraction method. Therefore, for determination of highest preconcentration factor the magnetic solid phase extraction studies were conducted at different sample volume ranging from 5 mL to 50 mL as shown in the Figure 4.6 and Table 4.4. Recovery results indicate that the proposed method can be successfully applied up to 40 mL of sample volume. Above 40 mL there is significant decrease in the percent recoveries of Cd(II). Therefore, preconcentration factor of 20 was achieved using 40 mL of sample and 2 mL of elution volume.

Table 4.4: Effect of sample volume on % recovery of Cd(II) using MNPs and SiMNPs.

Sample volume, mL	% Recovery	
	SiMNPs	MNPs
5	97±4	94±3
10	95±5	97±2
15	97±6	96±3
20	99±2	100±1
25	97±1	98±5
30	96±6	97±3
35	97±7	95±2
40	98±3	97±4
45	90±2	88±5
50	83±1	80±6

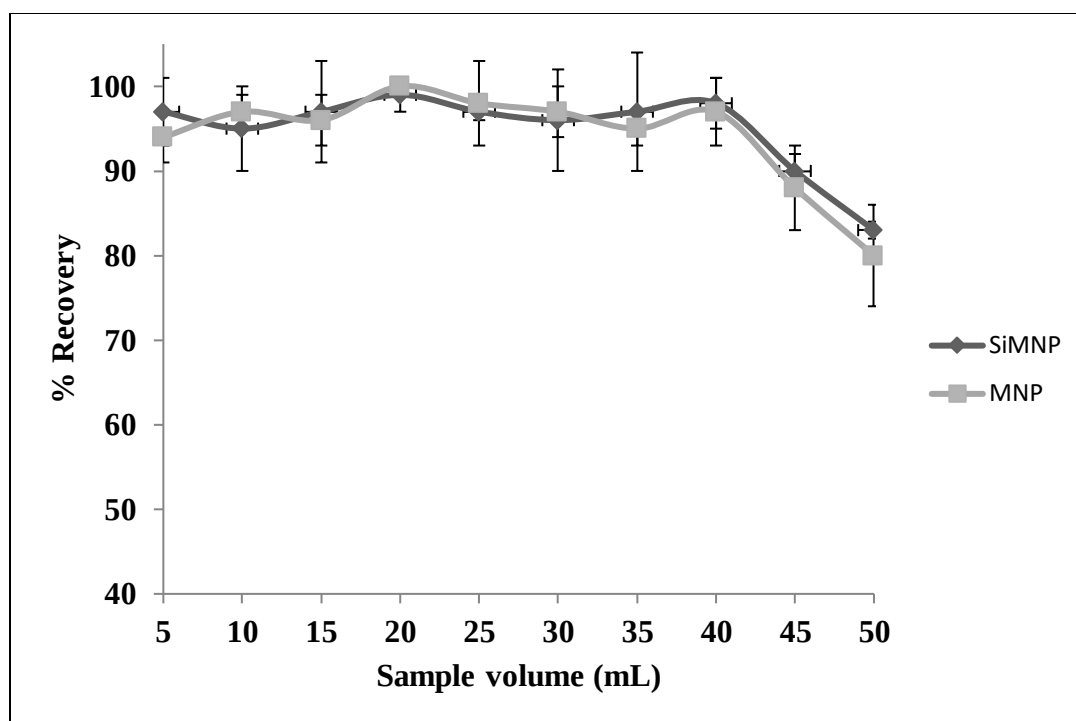


Figure 4.6: Effect of volume of sample on % recovery of Cd (II) using MNPs and SiMNPs (pH: 7, Volume of eluent: 10 mL, amount of adsorbent: 0.1 g, (N=3).

4.1.3.4. Desorption condition

For quantitative percent recovery the proper type and concentration of eluting agent is of immense important. For this purpose mineral acids like HCl and HNO₃ were used at different concentration like 0.25 mol L⁻¹, 0.5 mol L⁻¹ and 1.00 mol L⁻¹ both in water and acetone (Table 4.5). Recovery results obtained shows that HCl in acetone (1 mol L⁻¹) is the best choice for complete desorption of Cd (II) from the surface of MNPs and SiMNPs to obtain quantitative recoveries.

Table 4. 5: Effect of type and concentration of eluent on % recovery of Cd(II) using MNPs and SiMNPs as adsorbents (N=3).

Type and concentration of eluent	% Recovery	
	MNPs	SiMNPs
0.25 mol L⁻¹ HCl in water	45±6	34±4
0.5 mol L⁻¹ HCl in Water	67±7	52±4
1 mol L⁻¹ HCl in Water	86±5	65±3
0.25 mol L⁻¹ HNO₃ in water	37±4	32±4
0.5 mol L⁻¹ HNO₃ in Water	54±4	47±7
1 mol L⁻¹ HNO₃ in Water	83±3	59±6
0.25 mol L⁻¹ HCl in Acetone	59±2	57±6
0.5 mol L⁻¹ HCl in Acetone	89±6	80±5
1 mol L⁻¹ HCl in Acetone	97±4	94±5

After selecting proper type and concentration, volume of eluting agent was optimized. Different volume (1-10 mL) of HCl (1 mol L⁻¹) in acetone was used for Cd(II) elution and the % recovery results are given in the Figure 4.7. It can be evaluated from Figure 4.7 that 2 mL of HCl (2 mol L⁻¹) HCl in acetone was enough volume for quantitative % recoveries.

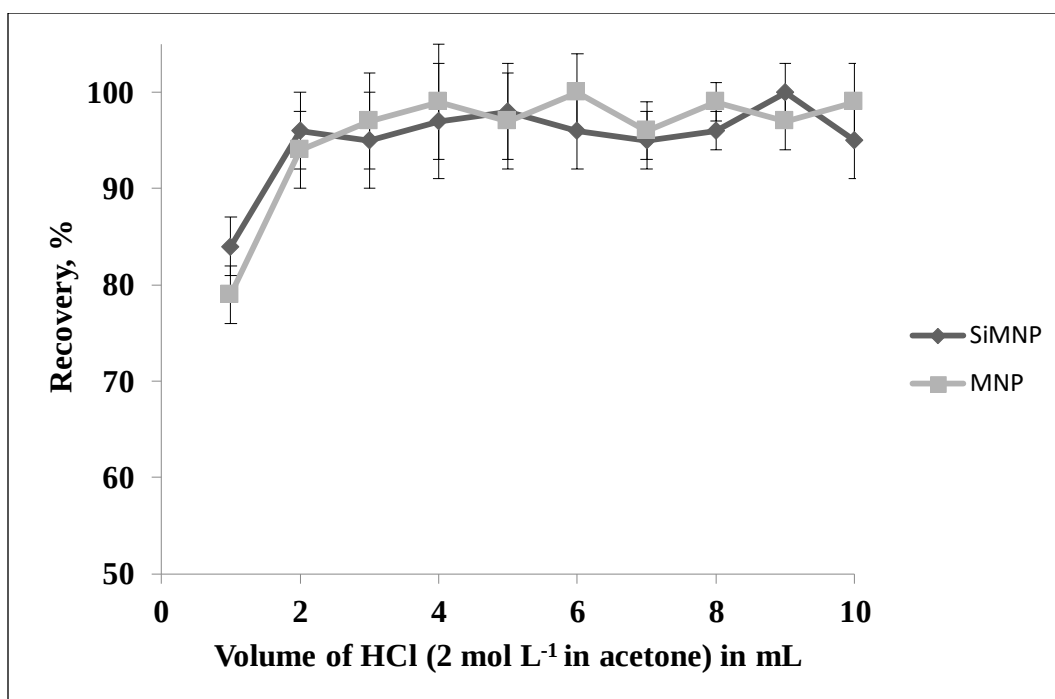


Figure 4.7: Effect of volume of eluent on % recovery of Cd (II) using MNPs and SiMNPs (pH: 7, Volume of sample: 10 mL, amount of adsorbent: 0.1 g, (N=3).

4.1.3.5. Matrix effect

The effects of different interfering ions which are coexisting with analyte metal in matrices of complex sample were studied and % recovery results are given in the Table 4.6. Recovery results shows that the divalent metal ions such as Zn(II), Cu(II), Fe(II), Ni(II), Mn(II) and trivalent ion Al(III) can be tolerated up to 10 µg. While Ca(II) and Mg(II) can be tolerated up to 100 µg. Due to the presence of trace level concentration in water samples these metals ions have relatively negligible effect on % recovery of Cd(II) using MNPs and SiMNPs as adsorbents. Therefore it can be conclude that the proposed magnetic solid phase extraction method is relatively selective.

Table 4.6: Effect of coexisting ions on % recoveries of Cd (II) using SiMNPs and MNPs, pH: 7, amount of adsorbent: 0.1 g, volume of sample solution: 10 mL (N=3).

Interfering ions	Added as	Concentration, $\mu\text{g mL}^{-1}$	Recovery, %	
			MNPs	SiMNPs
Na⁺	NaCl	1000	96 $\pm$ 2	95 $\pm$ 4
K⁺	KCl	1000	98 $\pm$ 1	97 $\pm$ 6
Ca⁺⁺	Ca(NO ₃) ₂ .4H ₂ O	100	99 $\pm$ 4	97 $\pm$ 1
Mg⁺⁺	Mg(NO ₃) ₂ .6H ₂ O	100	96 $\pm$ 4	94 $\pm$ 8
Al⁺⁺⁺	Al(NO ₃) ₃ .7H ₂ O	10	96 $\pm$ 3	95 $\pm$ 10
Zn⁺⁺	Zn(NO ₃) ₂ .6H ₂ O	10	97 $\pm$ 1	96 $\pm$ 4
Fe⁺⁺	Fe(NO ₃) ₂ .6H ₂ O	10	95 $\pm$ 6	95 $\pm$ 4
Cu⁺⁺	Cu(NO ₃) ₂ .6H ₂ O	10	95 $\pm$ 2	97 $\pm$ 1
Ni⁺⁺	Ni(NO ₃) ₂ .6H ₂ O	10	94 $\pm$ 9	96 $\pm$ 1
Mn⁺⁺	Mn(NO ₃) ₂ .6H ₂ O	10	99 $\pm$ 4	95 $\pm$ 1
SO₄⁻⁻	Na ₂ SO ₄	500	94 $\pm$ 2	98 $\pm$ 4
CO₃⁻⁻	Na ₂ CO ₃	500	93 $\pm$ 0	95 $\pm$ 4
F⁻	NaF	1000	100 $\pm$ 5	96 $\pm$ 1

4.1.4. Kinetic study

To evaluate the kinetic studies, pseudo-first order, pseudo-second order, intraparticle diffusion model and elovich kinetic model were employed to obtain useful information about adsorption efficiency of the adsorbate. For the pseudo-first order kinetics the equation is given as under:

$$\log (q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \quad (3)$$

Where q_t and q_e are the adsorption capacities at time t (min) and at equilibrium, respectively; k_1 is the rate constant for pseudo-first-order kinetics of the adsorption process. The values of q_e and k_1 were calculated from the pseudo-first-order model and are given in the Table 4.7. The calculated adsorption capacities from pseudo-first order kinetics did not agree with experimental adsorption capacity. Therefore the adsorption of Cd(II) on SiMNPs and MNPs cannot follow pseudo-first order kinetics.

For the pseudo – second order kinetics the following equation was used:

$$\frac{t}{q_t} = \frac{t}{q_e} + \frac{1}{k_2 q_e^2} \quad (4)$$

Where q_e and q_t are the adsorption capacity at equilibrium and at time t , respectively; k_2 is the rate constant for pseudo - second order kinetics. The values of K_2 and q_e were calculated from pseudo – second order model (Fig. 4.8a) and are given in the Table 4.7. The calculated adsorption capacities from pseudo-second order kinetics are in close agreement with experimental adsorption capacities therefore the adsorption of Cd(II) on SiMNPs and MNPs follows pseudo-second order kinetics.

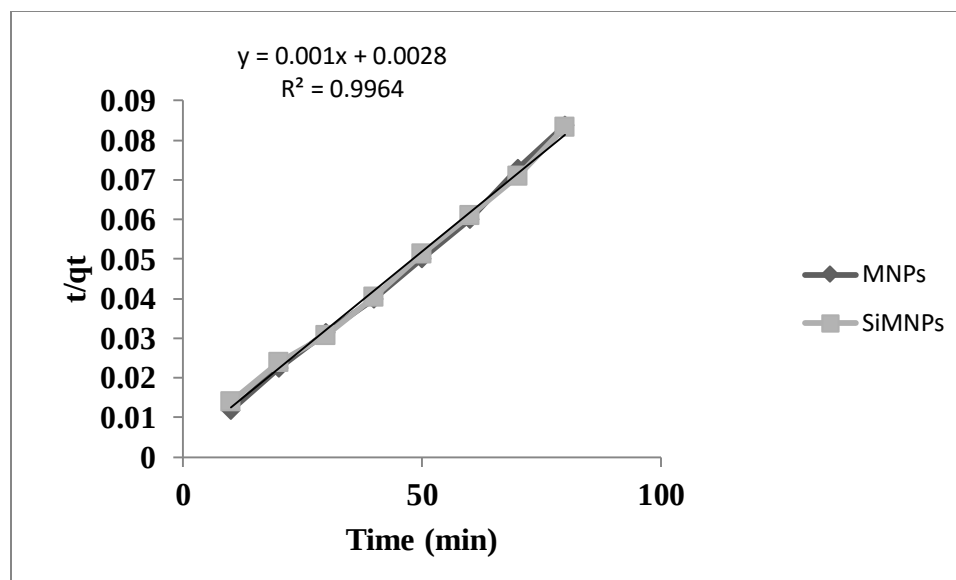


Figure 4.8a. Pseudo-second order kinetic model for the adsorption of Cd(II) on SiMNPs and MNPs.

For the calculation of intraparticle diffusion in the adsorption process of Cd (II) on MNPs and SiMNPs, the following equation was used to describe the intra particle diffusion model:

$$q_t = k_{int} t^{1/2} + c \quad (5)$$

Where q_t is the sorption capacity at time t , K_{int} is the intraparticle diffusion rate constant, t is the time (min). The values of K_{int} , C and R^2 were calculated from intraparticle diffusion model and are given in the Table 4.7.

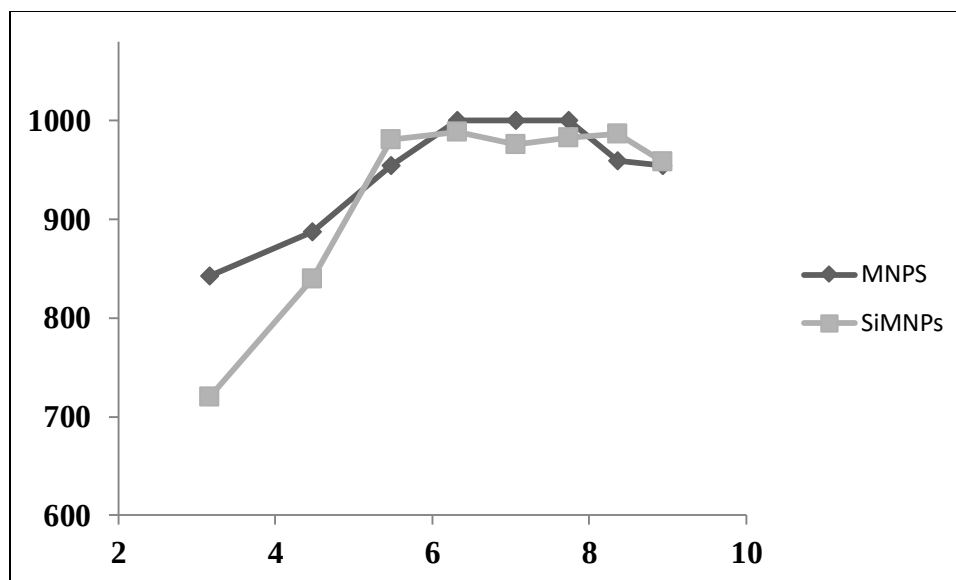


Figure 4.8b: Intraparticle diffusion model for the adsorption of Cd(II) using SiMNPs and MNPs.

The kinetics of chemisorption on heterogeneous surface was also calculated and explained by using elovich kinetic model which can be described by the following equation:

$$q_t = \frac{1}{\beta} \ln(\alpha \beta) + \frac{1}{\beta} \ln t \quad (6)$$

Where q_t is the sorption capacity (mg g^{-1}) at time t , α and β represent the elovich coefficient. Where α is the initial rate of adsorption ($\text{mg g}^{-1} \text{min}^{-1}$), β (desorption constant) related to the extent of surface coverage. The values of α , β and R^2 for adsorption of Cd (II) on MNP and SiMNPs were calculated from elovich kinetic model and are given in Table 4.7. The high α values shows that initial rate of adsorption of Cd (II) on MNPs and SiMNPs is high.

Table 4.7. Kinetic parameters for the adsorption of Cd(II) on MNPs and SiMNPs using different kinetic model.

Kinetic model	Parameters	SiMNPs	MNPs
	$Q_e \text{ (exp) (mg/g)}$	22.39	21.812
Pseudo-First order model	$k_1 \text{ (min)}^{-1}$	0.062	0.0481
	$Q_e \text{ (mg/g)}$	8.48	0.8077
	R^2	0.027	0.734
Pseudo-second order model	$k_2 \text{ (min)}^{-1}$	0.247	0.13
	$Q_e \text{ (mg/g)}$	22.17	21.92
	R^2	0.9999	1
Inraparticlr diffusion model	$k_{\text{int}} \text{ (min)}^{-1}$	0.0129	0.147
	C	22.389	20.749
	R^2	0.0478	0.779
Elovich kinetic model	$\alpha \text{ (mgg}^{-1} \text{ min}^{-1})$	6.91×10^{85}	5.6×10^{21}
	$\beta \text{ (gmg)}^{-1}$	8.69	2.522
	R^2	0.746	0.8615

4.1.5. Isotherm studies

Four adsorption isotherms Langmuir, Freundlich, Dubinin-Redushkviech (D-R), and Temkin were applied to the adsorption data of Cd(II) on SiMNPs and MNPs to express adsorption equilibrium.

Monolayer adsorption on homogenous surfaces can be best explained by using Langmuir adsorption isotherm. Linear form of the Langmuir adsorption isotherm is given as under:

$$\frac{C_e}{q_e} = \frac{1}{k_L} + \frac{a_L}{k_L} C_e \quad (6)$$

Where q_e is the adsorption capacity in (mg g^{-1}), C_e is the equilibrium concentration of the metal ion in (mg L^{-1}), a_L and k_L are Langmuir constant related to the adsorption energy and adsorbate –adsorbent binding force, respectively. The values of these parameters were calculated from Langmuir model (Fig. 4.9a), correlation co-efficient (r^2) and the theoretical monolayer adsorption capacity (Q^0) for the adsorption of Cd (II) on SiMNPs and MNPs was calculated and shown in the Table 4.8.

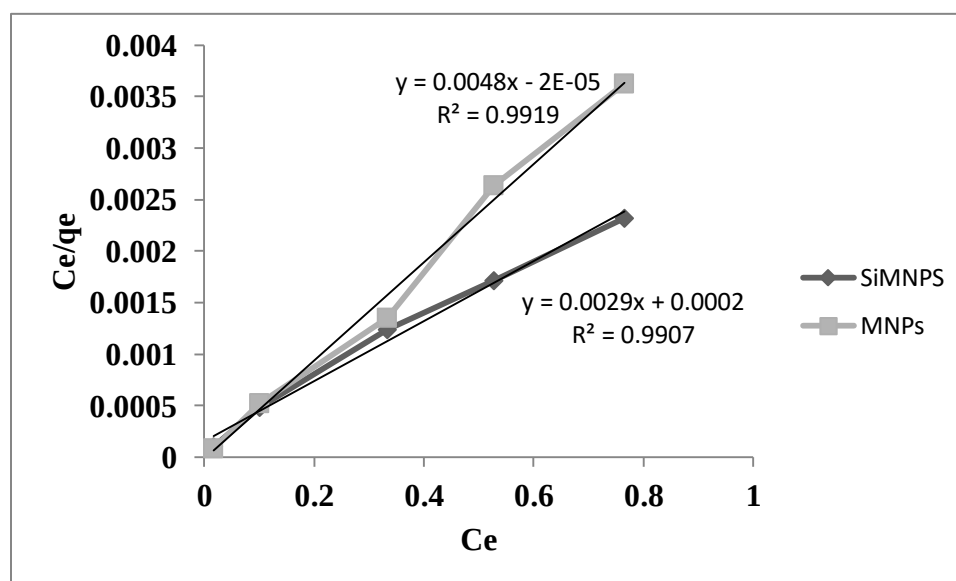


Figure 4.9: Langmuir adsorption isotherm for the adsorption of Cd(II) using SiMNPs and MNPs.

Freundlich adsorption isotherm is used to explain metal adsorption on heterogeneous surfaces. The linear and non-linear form of Freundlich adsorption isotherm can be expressed by using the following two equations:

$$q_e = k_F C_e^{1/n} \quad (7)$$

$$\log q_e = \log k_F + \frac{1}{n} \log C_e \quad (8)$$

Where k_F is the relative adsorption capacity and $1/n$ indicates the intensity of adsorption process. The value of n , $1/n$, k_F and correlation coefficient (r^2) for the adsorption of Cd (II) and MNPs and SiMNP's were calculated from Freundlich model (Fig. 4.9b) and shown in the Table 4.8.

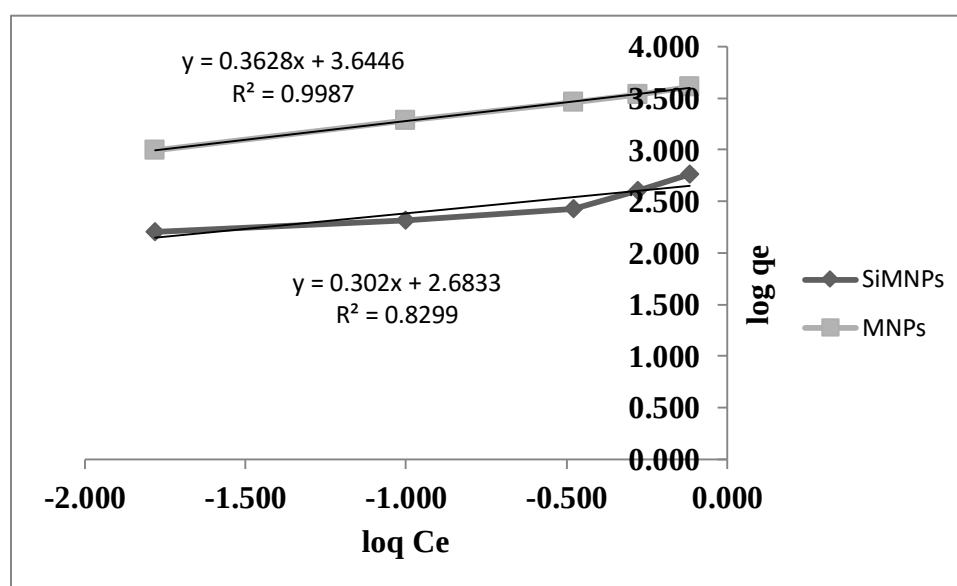


Figure 4.10: Freundlich isotherm model for the adsorption of Cd(II) using SiMNP's and MNPs.

The correlation coefficient value of Langmuir isotherm model is higher than Freundlich isotherm model, the adsorption process follow monolayer adsorption with adsorption capacity of 625.33 mg g⁻¹.

The non-linear and linear forms of Temkin model are given below:

$$q_e = \frac{RT}{b_T} \ln (A_T C_e) \quad (9)$$

$$q_e = B_T \ln A_T + B_T \ln C_e \quad (10)$$

Where $B_T = \frac{RT}{b_t}$, T is the absolute temperature in Kelvin (K) and R is the universal gas constant (8.314 Jmol⁻¹ K⁻¹). The constant b_T is related to the heat of adsorption, A_T is another constant called equilibrium binding constant (Lmin⁻¹) related to the binding energy. The value of A_T and b_T for the adsorption of Cd (II) on SiMNPs and MNPs were calculated and are given in the Table 4.8.

D-R adsorption isotherm can be used to distinguish between chemical and physical adsorption process. The linear form of the equation is given as following:

$$\ln q_e = \ln q_m - K\epsilon^2 \quad (11)$$

Where q_e and q_m are the equilibrium and the maximum adsorption capacities of Cd(II) on MNPs and SiMNPs respectively, K is a constant related to the adsorption energy (E), ϵ is the Polanyi potential which is described by the following equation:

$$E = \frac{1}{\sqrt{2k}} \quad (12)$$

$$\epsilon = RT \ln \left(1 + \frac{1}{C_e}\right) \quad (13)$$

Where C_e is the equilibrium concentration in mg L⁻¹, and T is the absolute temperature in Kelvin (K). The values of K and q_m , for the adsorption of Cd(II) on SiMNPs and MNPs were calculated and shown in the Table 4.8. E is a parameter that shows whether the

adsorption is chemical or physical in nature. The value of E calculated from the model for the adsorption of Cd(II) on SiMNPs and MNPs are $7.142 \text{ KJ mol}^{-1}$ and $0.877 \text{ KJ mol}^{-1}$, respectively (Table 4.8), which indicate physical adsorption phenomenon on SiMNPs and MNPs.

Table 4.8: Comparison of the parameter of different isotherm models.

Isotherm	Parameters	SiMNPs	MNPs
Freundlich	$K_F (\text{mgg}^{-1})$	481.95	354.8
	n	3.31	5.68
	$1/n$	0.30	0.18
	R^2	0.83	0.998
Langmuir	$a_L (\text{Lmg}^{-1})$	5.33	1.06
	$k_L (\text{Lg}^{-1})$	3333.33	625
	$Q^o (\text{mgg}^{-1})$	625.33	588.51
	R^2	0.990	0.991
Temkin	A_T	186.20	1348.9
	B_T	91.02	53.43
	b_T	27.20	46.28
	R^2	0.69	0.81
D-R	$q_m (\text{mgg}^{-1})$	398.10	398.1
	k	1×10^{-8}	1×10^{-8}
	$E (\text{KJmol}^{-1})$	7.14	0.88
	R^2	0.65	0.87

4.1.6. Thermodynamic studies

For thermodynamic study the adsorption of Cd(II) on SiMNPs and MNPs were studied at different temperature. Various thermodynamic parameters like enthalpy (ΔH°), Gibbs free energy (ΔG°) and entropy (ΔS°) were calculated using the following equations.

$$K_D = \frac{q_e}{C_e} \quad (14)$$

$$\Delta G^\circ = -RT \ln K_c \quad (15)$$

$$\Delta H^\circ = R \frac{T_2 T_1}{T_2 - T_1} \ln \frac{K_2}{K_1} \quad (16)$$

$$\Delta S^\circ = \frac{\Delta H^\circ - \Delta G^\circ}{T} \quad (17)$$

Where K_c is the equilibrium constant, q_e and C_e are the equilibrium concentration of the metal ion on the adsorbent (mg g^{-1}) and the concentration of the metal ion in the solution (mg L^{-1}) respectively. It can be seen from Table 4.9, that the value of K_D increase with increase in temperature and also the value of ΔH° is positive which shows that the adsorption of Cd (II) on SiMNPs and MNPs is endothermic in nature. The positive values of ΔS° shows that these adsorption process is spontaneous in nature.

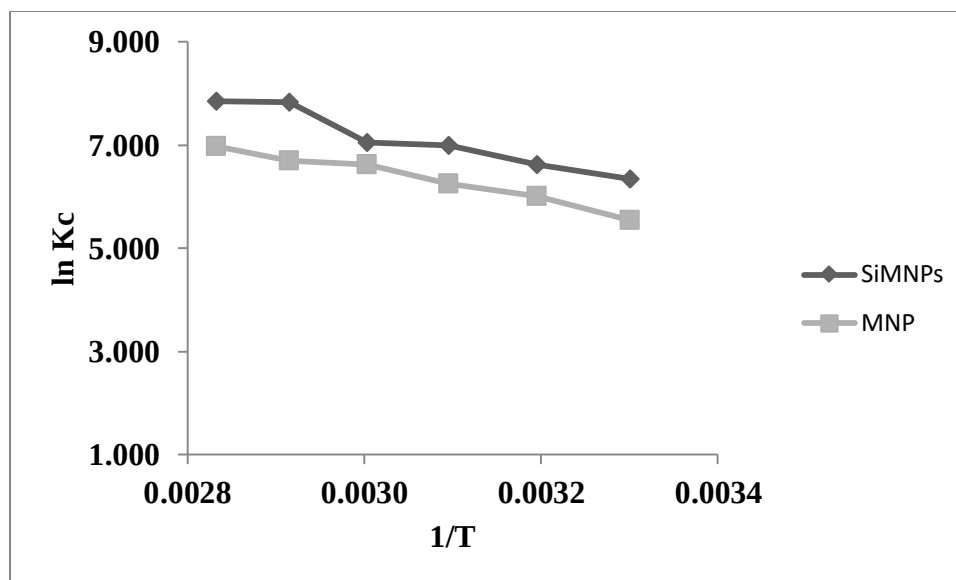


Figure 4.11: Plot of $\ln K_c$ versus $1/T$ for estimation of thermodynamic parameters for Cd(II) adsorption on SiMNPs and MNPs.

Table 4.9: Thermodynamic parameter for the adsorption of Cd (II) on MNPs and SiMNPs.

	SiMNPs			MNPs		
Temperature, K	ΔG° KJ mol ⁻¹	ΔH° KJ mol ⁻¹	ΔS° KJ mol ⁻¹	ΔG° KJ mol ⁻¹	ΔH° KJ mol ⁻¹	ΔS° KJ mol ⁻¹
303	-16.0	28.24	0.15	-12.7	62.48	0.35
313	-17.2			-18.4		
323	-18.8			-20.9		
333	-19.5			-22.0		
343	-22.3			-24.6		
353	-23.0			-26.4		

4.1.7. Application to the real sample

The proposed solid phase extraction method was applied for preconcentration of Cd(II) in tap water and river water samples. The % recovery results (Table 4.10) shows that the proposed solid phase extraction method can be successfully applied to real water samples.

Table 4.10. Standard addition method for % recovery of Cd (II) using the proposed solid phase extraction method from real samples (pH: 7, amount of adsorbent: 0.1 g, volume of sample: 15 mL, final volume: 2 mL (N=3)).

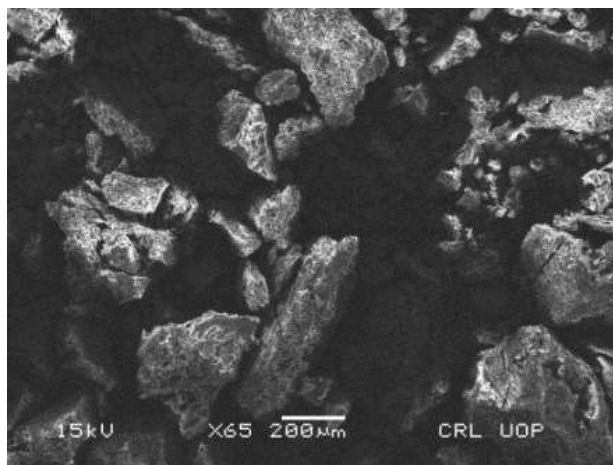
		MNPs		SiMNPs	
Sample	Added ($\mu\text{g mL}^{-1}$)	Found ($\mu\text{g mL}^{-1}$)	% Recovery	Found ($\mu\text{g mL}^{-1}$)	% Recovery
Tap water	0	BDL	---	BDL	---
	10	9.4 $\pm$ 0.8	94	9.6 $\pm$ 0.7	96
	20	18.9 $\pm$ 1.2	95	18.3 $\pm$ 1.2	92
River Kurram, Bannu	0	0.5 $\pm$ 0.04	---	0.6 $\pm$ 0.04	---
	10	10.0 $\pm$ 1.4	95	11.0 $\pm$ 2.8	104
	20	20.8 $\pm$ 0.9	102	20.0 $\pm$ 1.9	97
River Tochi, NWA	0	0.8 $\pm$ 0.02	---	0.68 $\pm$ 0.02	---
	10	10.7 $\pm$ 0.5	99	9.9 $\pm$ 0.5	92
	20	20.4 $\pm$ 1.4	98	20.7 $\pm$ 1.4	100

Part 2: Solid phase extraction of Pb(II) using magnetic nanoparticles (MNPs) and magnetic nanoparticles impregnated banana Peels (MNPs-BP)

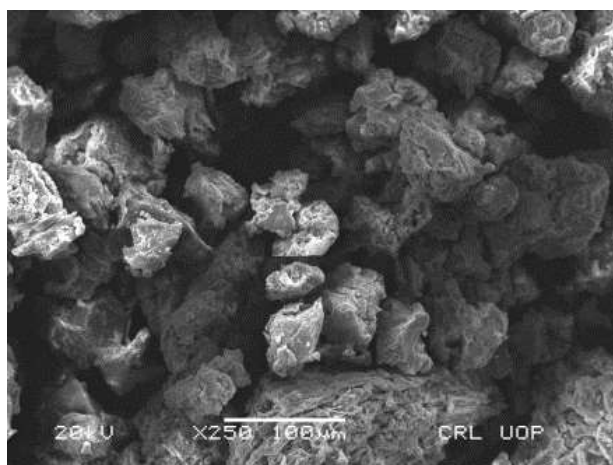
4.2. Result and discussion

4.2.1. Characterization

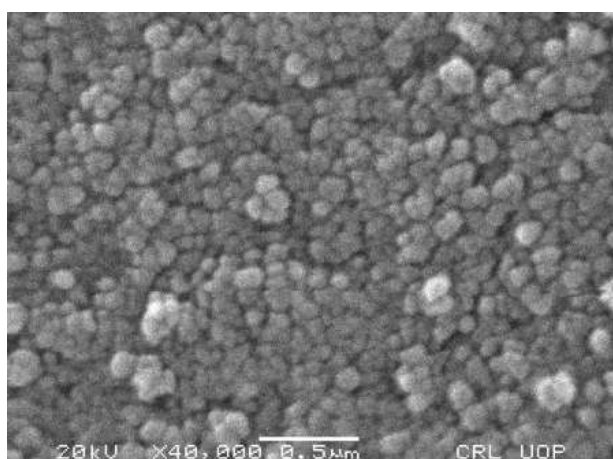
Surface morphology, can be best examined by studying SEM micrograph of the adsorbent. SEM micrograph of banana peels (BP), banana peels impregnated with magnetic nanoparticle (MNPs-BP) and magnetic nanoparticle (MNPs) are shown in Figures 4.12a, 4.12b and 4.12c, respectively. Porous surface morphology of (BP) with average pore size of 18 μm can be seen from Figure 4.12a. SEM micrographs of MNPs-BP shows that the surface of MNPs-BP is covered with MNPs and all the MNPs aggregated on the surface of BP (Figure 4.12b). Surface morphology of MNPs having particle size below 100 nm was observed from the Figure 4.12c.



BP.



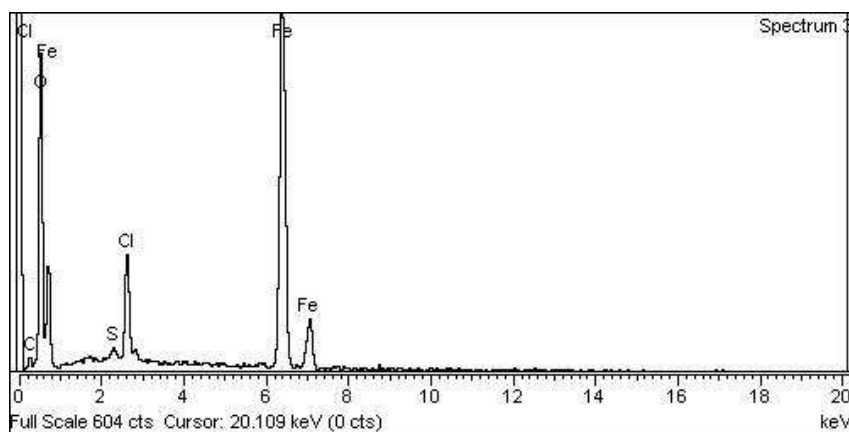
MNPs-BP.



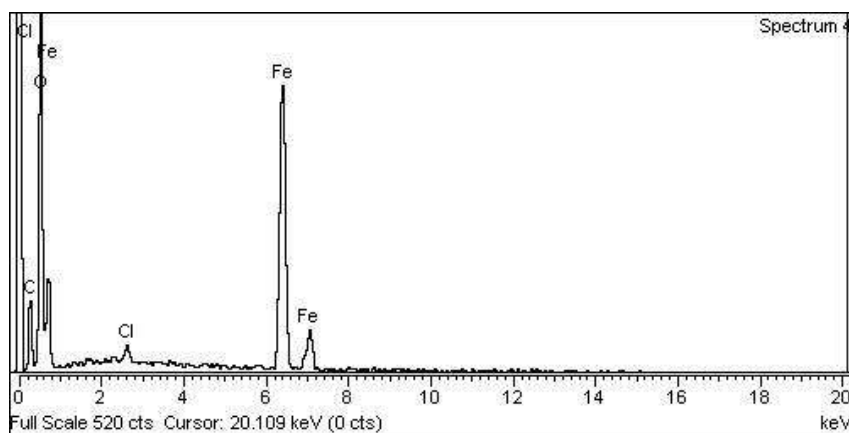
MNPs.

Figure 4.12: SEM micrographs of BP(a), MNPs-BP(b) and MNPs (c).

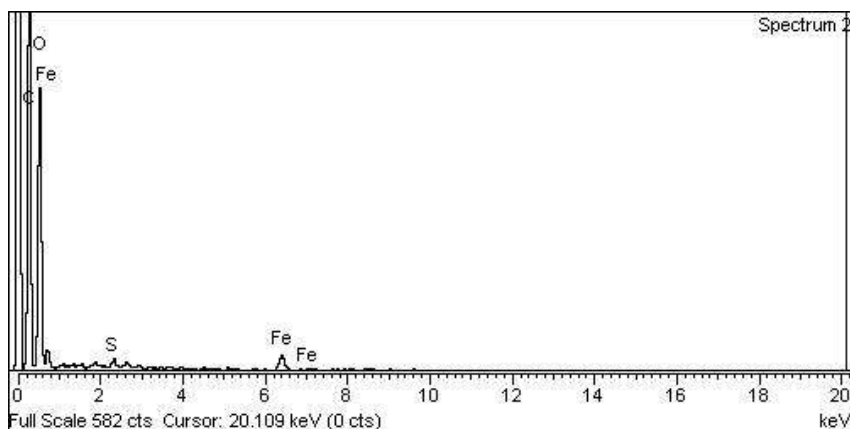
Elemental analysis of MNPs, MNPs-BP and BP can be done by analyzing the EDX mapping shown in Figures 4.13a, 4.13b and 4.13c, respectively. High concentration of Fe in MNPs (Fig. 4.13a) and MNPs-BP (Fig. 4.13b) confirm the impregnation of MNPs on the surface of BP. Fe concentration is almost negligible in case BP (Fig. 4.13c).



MNPs.



MNPs-BP.

**BP.****Figure 4.13: EDX spectrum of BP, MNPs(a) and MNPs-BP(b), BP(c)**

BET and BJH Surface area, pore volume and pore size of MNPs, MNPs-BP and BP were determined by using N₂ adsorption/desorption methods and the results are given in the Table 4.11. Increase in BET surface area of BP occur from 28.92 to 49.71 mg² g⁻¹ after modification with MNPs. Increase was also observed in the case of pore volume and pore size from 0.11 to 0.14 ccg⁻¹ and 139.43 to 142.23 A °, respectively.

Table 4.11. Surface area, pore volume and pore size by BET and BJH methods.

Sample	Method	Surface area (mg ² g ⁻¹)	Pore size (cm ⁻³ g ⁻¹)	Pore volume, (A °)
MNPs	BET	80.14	0.21	44.32
	BJH	104.9		
MNPs-BP	BET	49.71	0.14	142.23
	BJH	58.67		
BP	BET	28.92	0.11	139.43
	BJH	41.53		

4.2.2. Magnetic solid phase extraction procedure

Magnetic solid phase extraction studies were carried out by taking MNPs and MNPs-BP (0.1g) and surfactant cetyl triammonium bromide (CTAB) (0.06 g) in 50 mL of centrifuge. To this, Britton and Robinson buffer solution (pH: 7, 5 mL) were added to the centrifuge tube to completely soak the adsorbents. Sample solution (5 mL) having 100 μg of Pb(II) were added to the flask and allowed the adsorption reaction for 5 min under the influence of ultrasonication. MNPs and MNPs-BP were separated by using Nd magnetic and the liquid phase was transferred to another tube carefully. To the solid phase, HCl (1 mL, 2 mol L⁻¹) solution in acetone was added to elute the adsorbed Pb (II) from the surface of MNPs and MNPs-BP (Fig. 4.14).

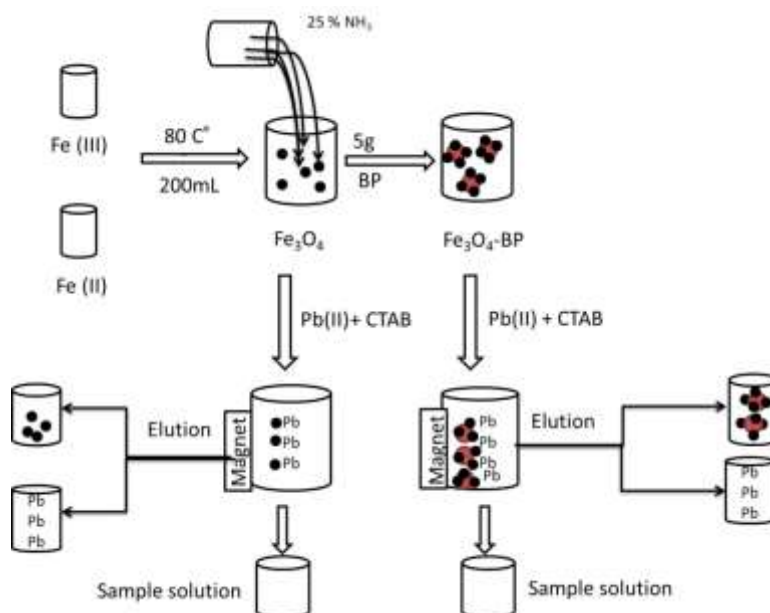


Figure 4.14: Schematic representation of the solid phase extraction method.

4.2.3. Optimization of the parameter related with magnetic solid phase extraction procedure

All the optimization studies were performed using model solution containing known amount of analyte. The parameters like solution pH, sorbent dose, sample volume, desorption conditions and matrix effects were optimized.

4.2.3.1. Effect of pH

Due to high tendency of hydrogen (H^+) and hydroxyl (OH^-) ion towards the surface of adsorbent, the pH of the solution greatly influence the % recovery of Pb(II). Change in pH also changes the adsorptive capacity of the adsorbent through the dissociation of the surface functional group of the adsorbent. Therefore, the effect of pH on % recovery of Pb(II) was studied over the pH range of 3-9 using MNP and MNP-BP (Figure 4.15). The % recovery of Pb(II) increases as the pH of the solution increases from 3 to 7. After that a significant decrease occur in % recovery of Pb(II). It can be explained that, as the pH of the solution increases the electrostatic attraction between Pb(II), and negatively charged surface of the adsorbent increases and thus increase the % recovery. It can also be explained that at low pH the H^+ ion concentration is high and occupies most of the vacant sites of the adsorbent and thus decrease the % recovery of Pb(II). Above pH 7 metal hydroxide formation takes place that decrease the % recovery of Pb(II).

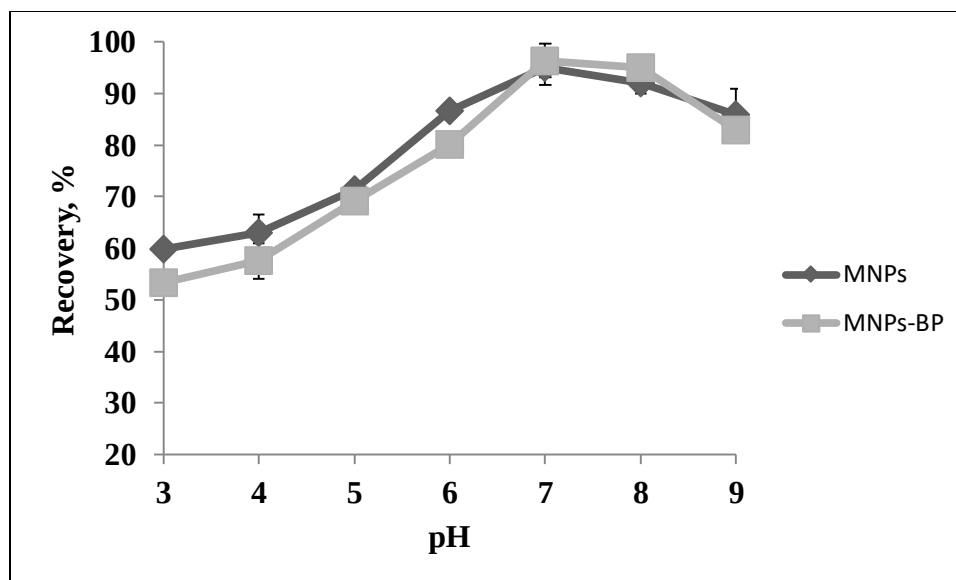


Figure 4.15: Effect of pH on % recovery Pb(II) using MNPs and MNPs-BP (Volume of sample: 10 mL, amount of adsorbent: 0.1 g, final volume: 10 mL N=3).

4.2.3.2. Effect of adsorbent dose

The effect of adsorbent dose is an important parameter because it determines the adsorption capacity of the adsorbent for constant initial adsorbate concentration. Therefore, the magnetic solid phase extraction studies were carried out at different adsorbent doses ranging from 20 to 140 mg (Figure 4.16). It can be concluded that the % recovery of Pb(II) increases rapidly with increase in the amount of MNPs and MNPs-BP, and after the critical dose of 100 mg the % recovery of Pb(II) reached to a constant value. Therefore, 100 mg was the optimized adsorbent dose used in further preconcentration studies.

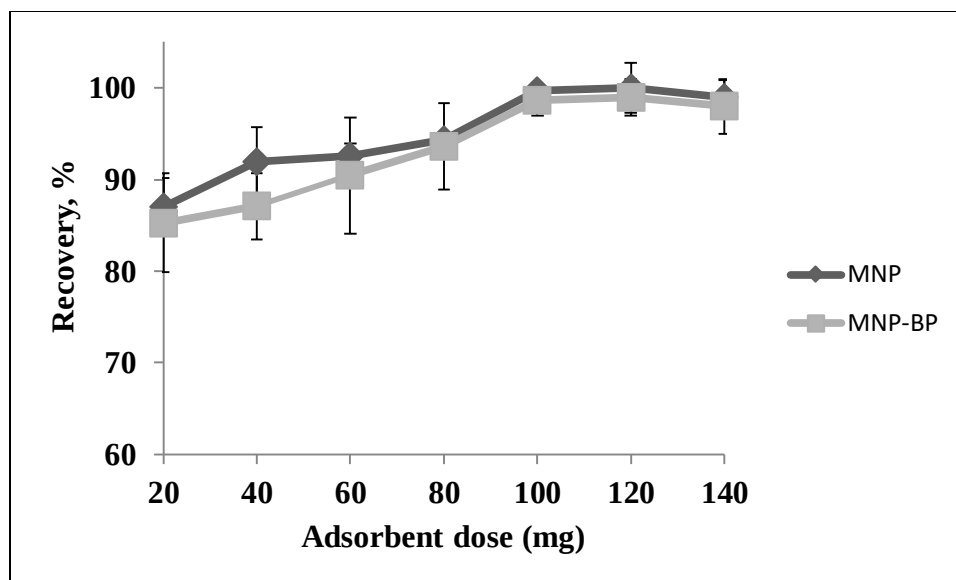


Figure 4.16: Effect of adsorbent dose on % recovery Pb(II) using MNPs and MNPs-BP (pH of solution: 7, volume of sample: 10 mL, final volume: 10 mL, N=3).

4.2.3.3. Effect of sample volume

For the highest preconcentration factor, the proposed solid phase extraction studies were carried out at different sample volume ranging from 5 to 50 mL (Figure 4.17). The % recoveries of Pb(II) show that the proposed magnetic solid phase extraction can be successfully applied up to 40 mL. Therefore, preconcentration factors of 20 can be achieved by using 40 mL of sample volume and 2 mL of elution volume.

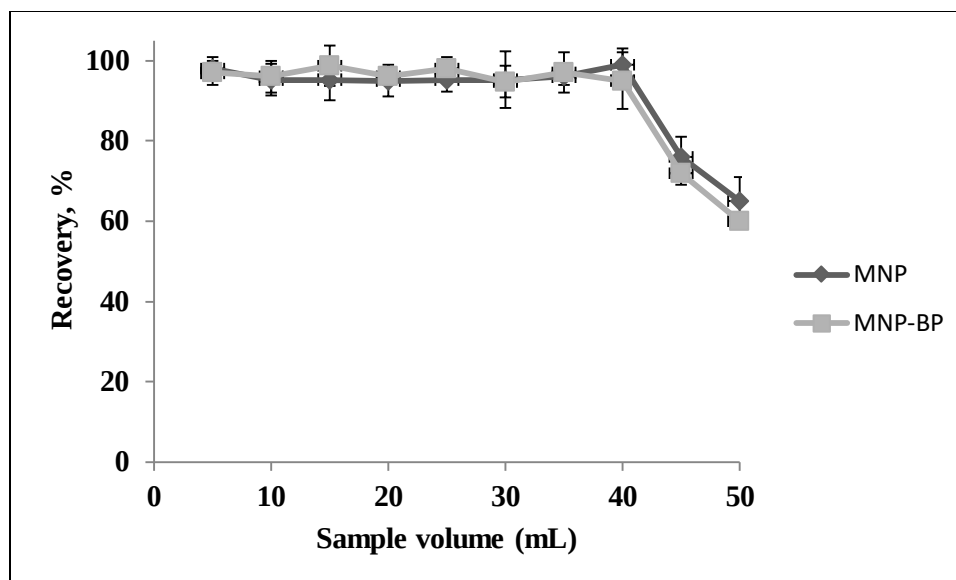


Figure 4.17: Effect of sample volume on % recovery of Pb(II) using MNPs and MNPs-BP (pH of solution: 7, adsorbent dose: 0.1 g, final volume: 10 mL, N=3).

4.2.3.4. Desorption studies

For quantitative % recovery of Pb(II) HCl and HNO₃ were used as eluents in the concentration range of 1 to 3 mol L⁻¹ using water as solvents and the % recovery results are given in the Table 4.12. Recovery results shows that 2 mol L⁻¹ of HCl is the best choice to obtained quantitative % recovery.

Table 4.12. Effect of type and concentration of eluent on percent recovery of Pb (II) using MNPs and MNPs-BP as adsorbents, pH: 7, amount of adsorbents: 0.1 g, volume of sample solution: 10 mL (N=3).

Type and concentration of Eluent	% Recovery	
	MNPs	MNPs-BP
1 mol L⁻¹ HCl	56±5	67±3
2 mol L⁻¹ HCl	98±1	96±2
3 mol L⁻¹ HCl	68±0	64±3
1 mol L⁻¹ HNO₃	76±2	93±1
2 mol L⁻¹ HNO₃	85±1	94±3
3 mol L⁻¹ HNO₃	82±1	81±3

After selecting type and concentration of eluent, optimization of volume of eluting agent is important. Therefore, the desorption studies were carried out at different volume ranging from 1 to 8 mL of HCl (1.0 mol L⁻¹). The % recovery results are given in the Figure 4.18 and shows that 2 mL of HCl (2 mol L⁻¹) HCl is enough to obtain quantitative percent recoveries.

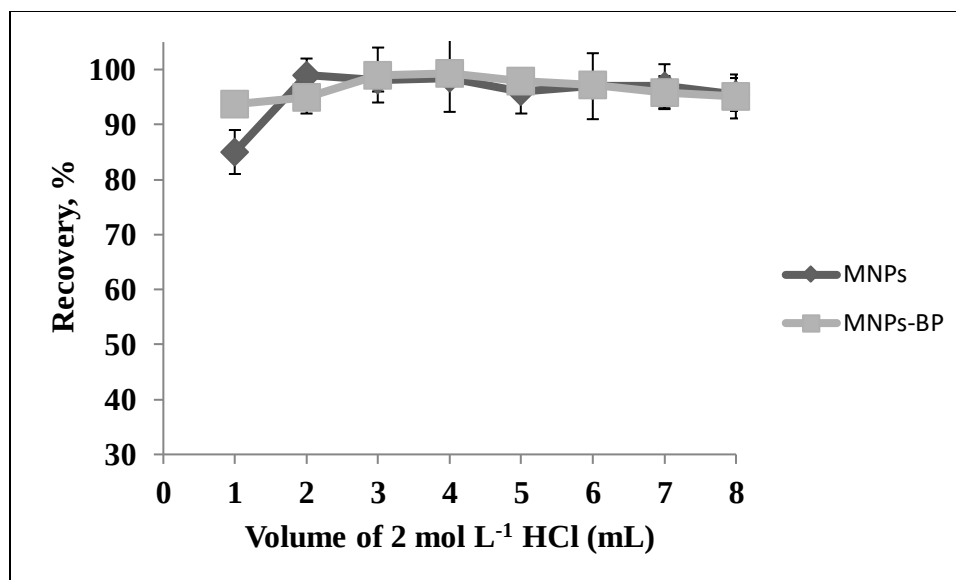


Figure 4.18: Effect of volume of 2 mol L⁻¹ HCl on % recovery Pb(II) using MNPs and MNPs-BP (pH of solution: 7, volume of sample: 10 mL, final volume: 10 mL N=3).

4.2.3.5. Matrix effect

The selectivity and specificity of the method can be investigated by studying the effect of different ions, which are coexisting with analyte ions especially in the samples of complex matrix nature. For this purpose the solid phase extraction studies of Pb(II) on MNPs and MNPs-BP were carried out in the presence of different interfering ions. % recovery results are given in the Table 4.13. The results show that divalent transition metal are competitive with Pb(II) SPE. The studied metal ions like Cd(II), Zn(II), Fe(II), Cu(II), Ni(II) and Mn(II) are tolerable up to 2.5 $\mu\text{g g}^{-1}$ to 5 $\mu\text{g g}^{-1}$ while Al(III) up to 10 $\mu\text{g g}^{-1}$ shows that the solid phase extraction of Pb(II) on MNPs and MNPs-BP is selective at lower concentration of interfering ions.

Table 4.13: Effect of coexisting ions on % recoveries of Pb (II) using MNPs and MNPs-BP as adsorbents, pH: 7, amount of adsorbents: 0.1 g, volume of sample solution: 10 mL (N=3).

Interfering ions	Added as	Concentration, $\mu\text{g g}^{-1}$	Recovery, %	
			MNPs	MNPs-BP
Na⁺	NaCl	5000	97±7	98±8
K⁺	KCl	5000	95±5	96±3
Ca⁺⁺	Ca(NO ₃) ₂ .4H ₂ O	100	94±5	99±1
Mg⁺⁺	Mg(NO ₃) ₂ .6H ₂ O	100	98±2	94±8
Al⁺⁺⁺	Al(NO ₃) ₃ .7H ₂ O	10	97±7	95±8
Cd⁺⁺	Cd(NO ₃) ₂ .6H ₂ O	5	97±3	98±7
Zn⁺⁺	Zn(NO ₃) ₂ .6H ₂ O	5	95±1	99±4
Fe⁺⁺	Fe(NO ₃) ₂ .6H ₂ O	5	99±6	97±8
Cu⁺⁺	Cu(NO ₃) ₂ .6H ₂ O	2.5	95±2	96±9
Ni⁺⁺	Ni(NO ₃) ₂ .6H ₂ O	2.5	99±5	98±3
Mn⁺⁺	Mn(NO ₃) ₂ .6H ₂ O	2.5	99±4	99±1
SO₄⁻	Na ₂ SO ₄	500	97±2	98±5
CO₃⁻	Na ₂ CO ₃	500	96±8	96±4
F⁻	NaF	100	94±2	97±8

4.2.4. Kinetic study

For adsorption kinetics two kinetic models like pseudo first order kinetics and pseudo second order kinetics were employed.

For pseudo-first-order kinetics of the adsorption process, the values of q_e and k_1 were calculated from the slop and intercept of the plot of $\log (q_e - qt)$ versus t , respectively (Table 4.14). The experimental q_e values, $q_{e \text{ exp}}$ did not coincide with calculated values, $q_{e \text{ cal}}$, obtained from the linear plots. It shows that the adsorption of Pb(II) on MNPs and MNP-BP do not follow pseudo first order kinetics.

Values of q_e and k_2 for pseudo-second-order kinetics were determined from the intercept and slop and are presented in Table 4.14. The linear plot shows a good agreement between experimental and calculated q_e values (Fig.4.19). Beside this the corresponding correlation coefficient values are also high that shows that the adsorption of Pb(II) on MNPs and MNPs-BP follow pseudo-second order kinetics. It means that pseudo-second order kinetics parameter obtained could be used to determine the rate constant, equilibrium sorption capacity, percentage removal of Pb(II) and initial rate of adsorption. Since this adsorption process follow pseudo-second order kinetics, thus the solid phase extraction of Pb(II) on MNPs and MNP-BP was controlled by chemisorption.

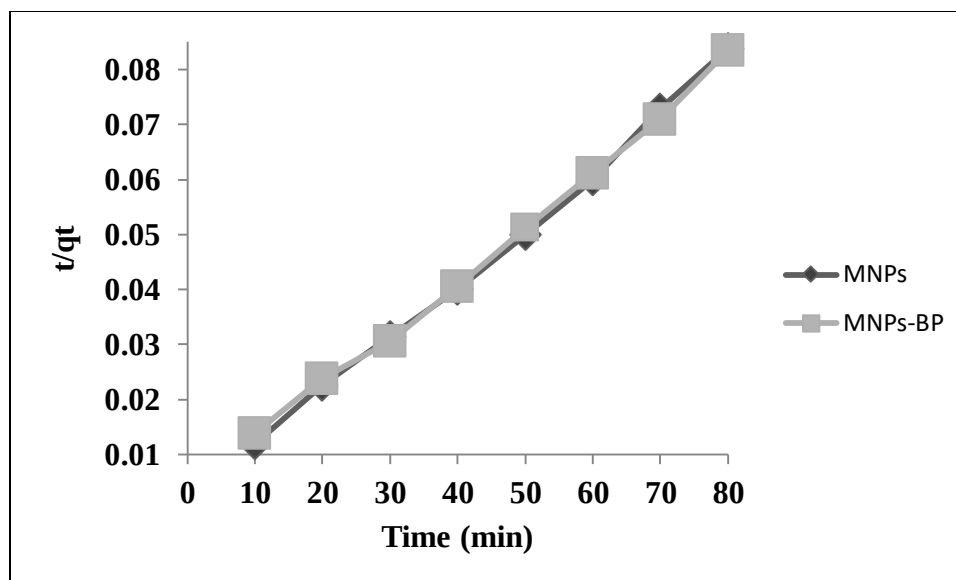


Fig.4.19: Pseudo-second order kinetics for the adsorption of Pb(II) on MNPs and MNPs-BP.

Table 4.14. Kinetic parameter for the adsorption of Pb (II) using MNPs and MNPs-BP as adsorbents.

Adsorbent	Experimental	Kinetic models					
		Pseudo first order			Pseudo second order		
		$K_1 \text{ min}^{-1}$	$q_e \text{ mgg}^{-1}$	R^2	$K_2 \text{ min}^{-1}$	$q_e \text{ mgg}^{-1}$	R^2
MNPs	1000	0.034	1.237	0.18	0.001	1000	0.997
MNPs-BP	988	0.049	96.36	0.465	0.0004	1000	0.995

4.2.5. Isotherm studies

Two adsorption isotherms Langmuir and Freundlich were employed in order to explain the interaction mechanism between the adsorbent surface and adsorbate leading to the affinity of adsorbent towards adsorbate.

The values for Langmuir adsorption isotherm K_L , a_L correlation co-efficient (R^2) and the theoretical monolayer adsorption capacity (Q^0) for the adsorption of Pb(II) on MNPs and MNPs-BP was calculated and shown in the Table 4.15 using same procedure as mentioned earlier. Similarly for Freundlich adsorption isotherm the values of n , $1/n$, k_F and correlation coefficient (R^2) for the adsorption of Pb (II) on MNPs and MNPs-BP were calculated and given in the Table 4.15. Both Freundlich and Langmuir model are shown in the Fig.4.20a and 4.20b, respectively.

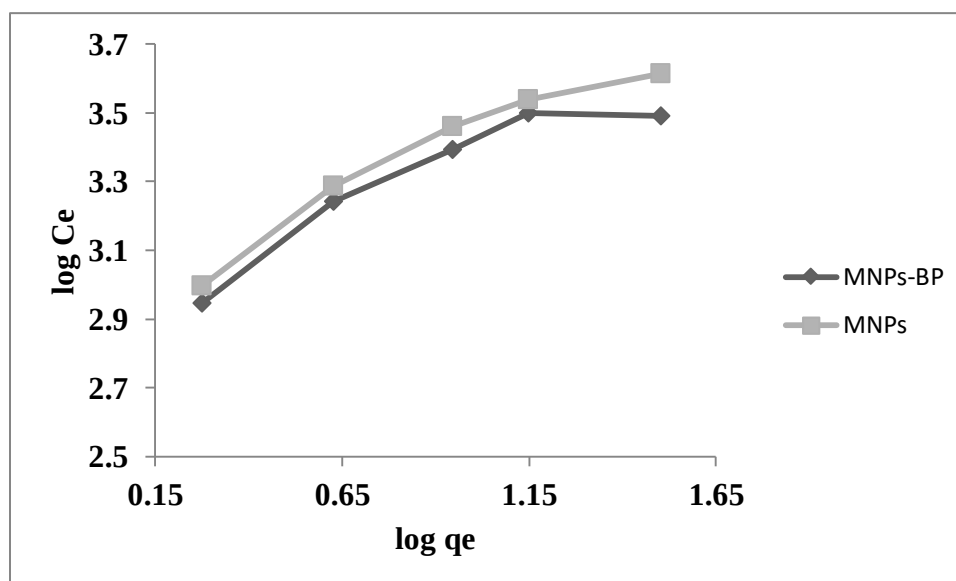


Figure 4.20a: Freundlich isotherm model for the adsorption of Pb(II) using MNPs-BP and MNPs.

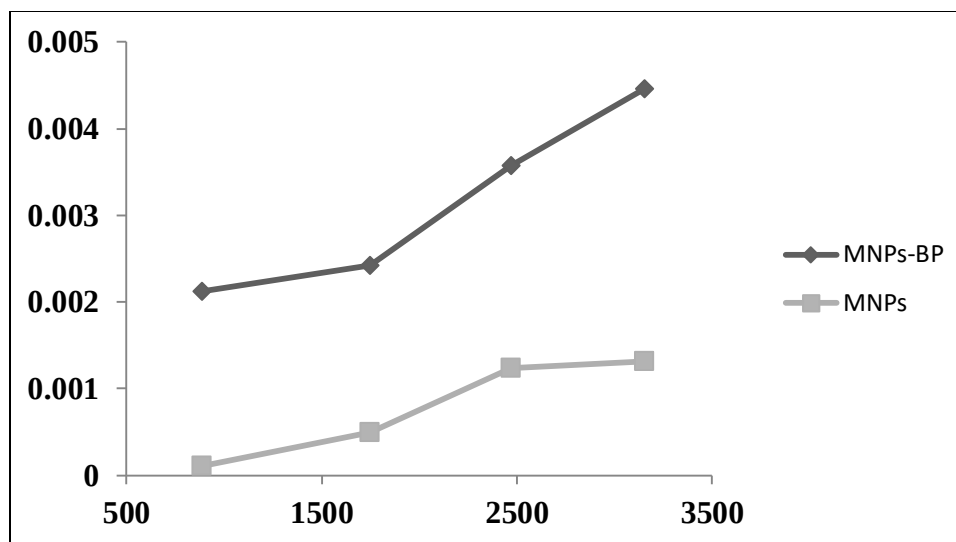


Figure 4.20b: Pseudo-second order kinetics for the adsorption of Pb(II) using MNPs-BP and MNPs.

Table 4.15: Comparison of parameters of Freundlich and Langmuir adsorption isotherm models.

Adsorbent	Isotherm Model							
	Freunlich				Langmuir			
	K_F (mg g^{-1})	n	$1/n$	R^2	K_L (L g^{-1})	a_L (L mg^{-1})	Q^o (mg g^{-1})	R^2
MNPs	1.87	3.7	0.3	0.967	5000	1	5000	0.988
MNPs-BP	2.835	2.2	0.4	0.867	833	0.25	3333	0.985

As can be seen from the Table 4.15, K_F values of MNPs-BP (2.835 mg g^{-1}) is greater than MNPs. Poor values of correlation coefficients (R^2) indicate inapplicability of Freundlich isotherm. The Langmuir isotherm model gave better fit then Freundlich as indicated by values of correlation coefficients.

4.2.6. Thermodynamic studies

Various thermodynamic parameters like enthalpy (ΔH°), Gibbs free energy (ΔG°) and entropy (ΔS°) were calculated in order to explain the spontaneity and feasibility of the adsorption of Pb(II) on MNPs and MNPs-BP and are given in the Table 4.16.

Positive values of ΔH° and ΔS° in the Table 4.16 shows that the adsorption of Pb(II) on MNPs and MNPs-BP is endothermic and spontaneous in nature.

Table 4.16: Thermodynamic parameter for the adsorption of Pb (II) using MNPs and MNPs-BP as adsorbents.

Temperature, K	MNPs			MNPs-BP		
	ΔG° KJ mol ⁻¹	ΔH° KJ mol ⁻¹	ΔS° KJ mol ⁻¹	ΔG° KJ mol ⁻¹	ΔH° KJ mol ⁻¹	ΔS° KJ mol ⁻¹
303	-13.95	24.55	0.127	-13.27	17.32	0.103
313	-15.61			-15.09		
323	-16.80			-15.71		
333	-18.35			-16.37		
343	-19.08			-17.50		
353	-20.46			-18.91		

4.2.7. Validation of the proposed magnetic solid phase extraction method

For validation, the proposed solid phase extraction method was applied to three real water sample like tap water (Analytical chemistry lab), river water (River Tochi, NWA) and dam water (Baran dam, Bannu) and the % recovery results are given in the Table 4.17. It can be concluded that all the % recovery results of Pb(II) are quantitative and the

proposed solid phase extraction method can be successfully applied for extraction of Pb(II) from real water samples.

Table 4.17: Standard addition method for % recovery of Pb (II) using the proposed solid phase extraction method (pH: 7, amount of adsorbent: 0.1 g, volume of sample: 15 mL, final volume: 2 mL (N=3).

Sample	Added ($\mu\text{g mL}^{-1}$)	MNPs		MNPs-BP	
		Found ($\mu\text{g mL}^{-1}$)	% Recovery	Found ($\mu\text{g mL}^{-1}$)	% Recovery
Tap water	0.0	BDL	---	BDL	---
	3.33	3.20 ± 0.2	96	3.1 ± 0.3	94
	10.0	9.2 ± 1.2	92	9.7 ± 0.9	97
Dam water	0.0	0.5 ± 0.04	---	0.6 ± 0.04	---
	3.33	3.7 ± 0.5	97	3.7 ± 0.8	98
	10	10.3 ± 0.4	98	10.0 ± 0.6	94
River Tochi, NWA	0	0.8 ± 0.02	---	0.7 ± 0.02	---
	3.33	3.9 ± 0.5	98	9.9 ± 0.5	92
	10	10.4 ± 0.7	96	20.7 ± 0.8	100

Part 3: Application of response surface methodology to the magnetic nanoparticles impregnated orange peel for the removal of Ni(II)**4.3. Result and discussion****4.3.1. Characterization of the adsorbent**

FT-IR spectra were recorded (Figure 4.21) in order to identify the functional groups on the surface of orange peel (OP) and magnetic nanoparticles orange peels (MNPs-OP). The comparison of FT-IR spectrum of OP and MNPs-OP shows the appearance, disappearance and shifting of some peaks. Band shifting from 3327 cm^{-1} , 2923 cm^{-1} and 1640 cm^{-1} on OP to 3325 cm^{-1} , 2921 cm^{-1} and 1623 cm^{-1} on MNPs-OP correspond to the bonded -OH , -CH stretching and -C=O stretching in carboxyl group which indicates that the MNPs are successfully bonded to OP. The disappearance of peak at 1730 cm^{-1} on MNP-OP (present in OP due to stretching vibration of carboxyl group -COOH) shows the binding of Fe with the -OH of the carboxyl group. The strong band at 1014 cm^{-1} in both OP and MNP-OP is due to -OCH_3 groups which confirms the presence of lignin in OP.

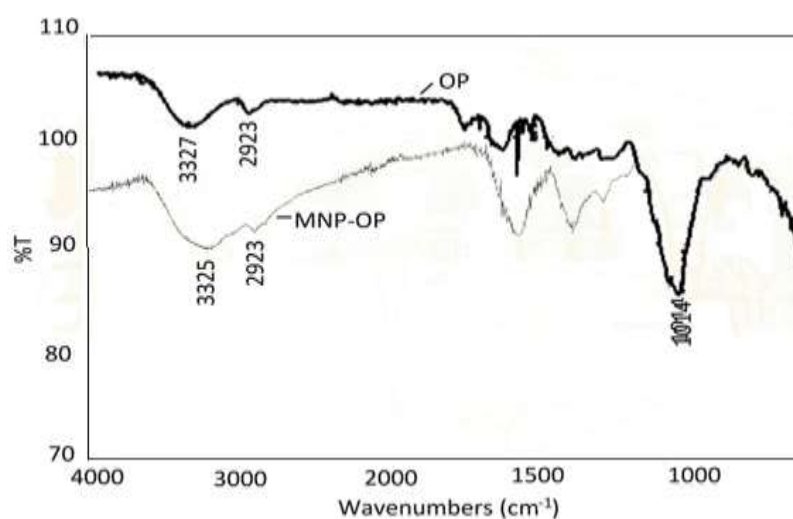
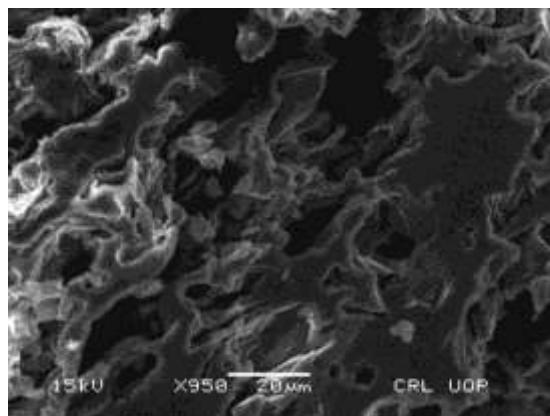
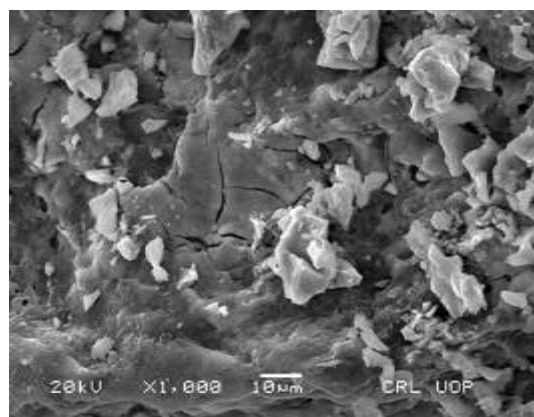


Figure 4.21: FT-IR spectra of OP and MNP-OP.

SEM micrograph of orange peel (OP) and orange peel impregnated with magnetic nanoparticle (MNPs-OP) shows the morphological characteristic of the adsorbent. (Figure 4.22a) Porous surface morphology for OP with average pore size of 20 μm was observed. The SEM images for the MNPs-OP (Fig. 4.22b) shows that OP is covered with MNPs and all the MNP aggregated on the surface of OP.



OP.



MNPs-OP

Figure 4.22: SEM micrograph of OP(a) and MNPs-OP(b).

Surface area, pore size and pore volume of MNPs-OP were calculated by BET and BJH method. The surface area was found to be 40.98 $\text{m}^2 \text{g}^{-1}$ with 1.43 cc/g pore volume and 129.02 $\text{\AA}$ pore size.

4.3.2. Experimental design and optimization

The response surface methodology (RSM) is a set of statistical methods used for designing experiments, evaluation of the effects of different variables and looking for optimum conditions of variables to achieve the target response. RSM has greater application in experimental situation where large number of variables are effecting the process.

The factorial design 2^5 level was performed with five factors affecting the experimental design based on the adsorption of Ni(II) response on MNPs – OP. A total of 32 runs were performed in replicate to optimize the level of selected variables like pH, time, adsorbent dose, temperature, and initial metal ion concentration. The experimental design 2^5 is given in the Table 4.18.

Table 4.18: Factorial 2^5 experimental design.

<i>Std</i>	Run	Factor A (pH)	Factor B (Time)	Factor C (Ni (II) Conc)	Factor D (S. Dose)	Factor E (Temp)	Response Adsorption (%)
6	2	7	20	30	0.02	303	85.658
30	3	7	20	30	0.22	363	88.792
17	4	2	20	5	0.02	363	84.811
2	5	7	20	5	0.02	303	86.685
27	6	2	60	5	0.22	363	87.574
21	7	2	20	30	0.02	363	81.854
8	8	7	60	30	0.02	303	84.12
7	9	2	60	30	0.02	303	64.288
4	10	7	60	5	0.02	303	84.879

31	11	2	60	30	0.22	363	82.744
23	12	2	60	30	0.02	363	82.603
26	13	7	20	5	0.22	363	91.563
22	14	7	20	30	0.02	363	85.00
29	15	2	20	30	0.22	363	85.243
3	16	2	60	5	0.02	303	82.435
11	17	2	60	5	0.22	303	86.432
13	18	2	20	30	0.22	303	82.342
1	19	2	20	5	0.02	303	82.342
28	20	7	60	5	0.22	363	92.312
19	21	2	60	5	0.02	363	85.339
16	22	7	60	30	0.22	303	87.00
18	23	7	20	5	0.02	363	88.123
9	24	2	20	5	0.22	303	82.342
15	25	2	60	30	0.22	303	83.123
25	26	2	20	5	0.22	363	87.865
14	27	7	20	30	0.22	303	86.432
24	28	7	60	30	0.02	363	86.324
5	29	2	20	30	0.02	303	79.411
10	30	7	20	5	0.22	303	88.923
20	31	7	60	5	0.02	363	90.00
12	32	7	60	5	0.22	303	90.00

4.3.2.1. Statistical analysis

The adsorption experiments using five variables on MNPs–OP adsorbent were conducted according to the experimental design and the result are given in the Table 4.19.

Table 4.19: Effect list of main factors and their interactions.

Error / included	Term intercept	Effect	Sum sqr	% Contribution
Model	A-pH	5.28275	223.26	29.9259
Error	B-Time	-0.547	2.39367	0.32085
Model	C-Initial metal	-3.57688	102.352	13.7194
Model	D-sorbent dose	3.64225	106.128	14.2255
Model	E-Temperature	3.32475	88.4317	11.8535
Error	AB	0.912	6.65395	0.891902
Error	AC	1.11463	9.93911	1.33225
Error	AD	-0.6805	3.70464	0.496573
Error	AE	-1.090	9.5048	1.27403
Error	BC	-1.33662	14.2925	1.91578
Error	BD	1.190	11.3288	1.51852
Error	BE	0.93525	6.99754	0.937956
Error	CD	0.842625	5.68014	0.76137
Error	CE	0.381125	1.16205	0.155762
Error	DE	-0.95475	7.29238	0.977477
Error	ABC	1.22737	12.0516	1.61541
Error	ABD	-0.78925	4.98332	0.667969

Error	ABE	-0.1455	0.169362	0.0227014
Error	ACD	-1.15863	10.7393	1.4395
Error	ACE	-1.02413	8.39066	1.12469
Error	ADE	1.16325	10.8252	1.45102
Error	BCD	0.573375	2.63007	0.352537
Error	BCE	1.00912	8.14667	1.09199
Error	BDE	-1.92125	29.5296	3.95818
Error	CDE	-0.915375	6.70329	0.898515
Error	ABCD	-0.611375	2.99024	0.400814
Error	ABCE	-1.05812	8.95703	1.20061
Error	ABDE	1.07475	9.2407	1.23863
Error	ACDE	1.52563	18.6203	2.49588
Error	BCDE	-0.817875	5.35136	0.7173
Error	ABCDE	0.974125	7.59136	1.01755
	Lenth's ME	3.38297		
	Lenth's SME	6.43213		

Analysis of variance was carried out for statistical confirmation of these results which indicate that the equation and the actual relationship presented by the equation between the response and significant variable are accurate. The significance of the coefficient term is calculated by F and p values, the larger F value and the smaller p value, shows that the results are more significant. The model is considered to be statistically significant with p value less than 0.01 as shown in the Table 4.20.

Table 4.20: Analysis of variance.

Source	Sum of Squares	df	Mean squares	F-value	P-value	
Model	520.17	4	130.04	15.55	< 0.0001	significant
A-pH	223.26	1	223.26	26.69	< 0.0001	
C-Initial metal ion	102.35	1	102.35	12.23	0.0016	
D-sorbent dose	106.13	1	106.13	12.69	0.0014	
E-Temperature	88.43	1	88.43	10.57	0.0031	
Residual	225.87	27	8.37			
Cor Total	746.04	31				

The ANOVA results for the adsorption of Ni(II) ion on MNPs-OP indicated the F-value for the model is 15.55 and the $p < 0.0001$, suggesting that the model is significant. The results obtained shows that factor A (pH) is more significant (223.26) as compared to the other factors like C (initial metal ion concentration), D (sorbent dose) and E (temperature) having values 102.35, 106.13 and 88.43 respectively. The ANOVA results for the adsorption of Ni(II) on MNPs-OP indicated that F-value for the model is 15.55 and $p < 0.0001$, suggesting that the model is significant.

The cube model graph of the 2^5 factorial design for Ni(II) % adsorption on MNPs-OP is shown in Figure 4.23. As can be seen from the cube model that pH of solution, initial metal ion concentration and adsorbent dose are the important variables which influence the %adsorption of Ni(II). The cube model shows that maximum % adsorption of 91.439% was obtained at pH 7 with 0.22 g of adsorbent dose.

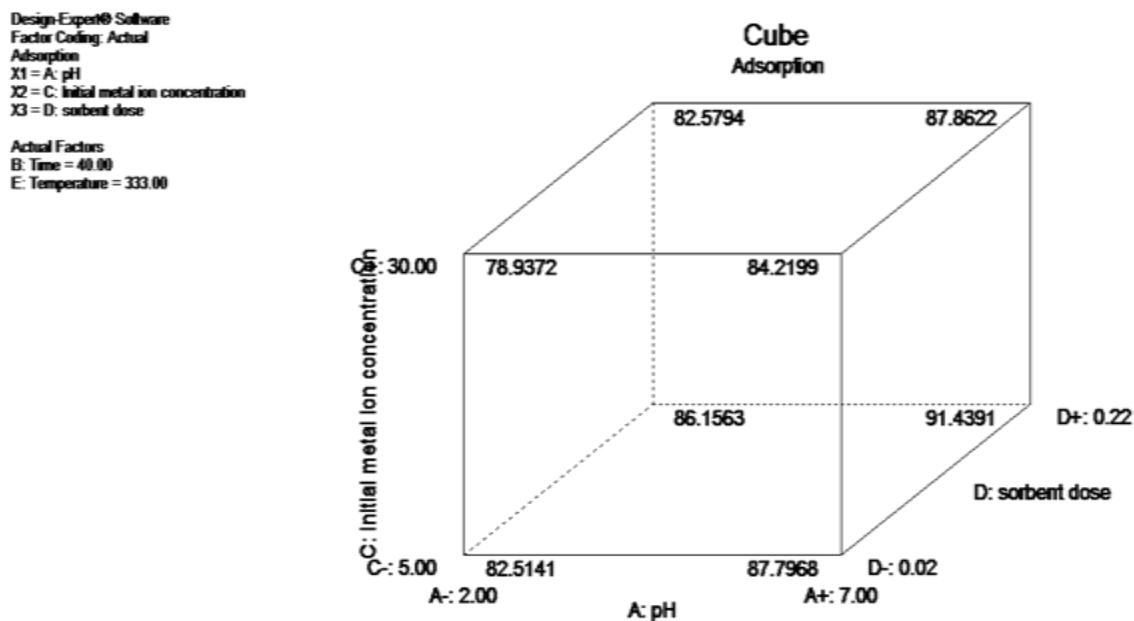


Figure 4.23: Cube model graph of the 2^5 factorial designs.

4.3.3. Kinetic studies

For pseudo- first order kinetics a plot of $\log (q_e - q_t)$ against time t was constructed and is shown in Figure 4.24a. The values of q_e and k_1 were calculated from the slope and intercept and are given in the Table 4.21. It can be seen that the value of adsorption capacity calculated from the model is not in agreement with experimental sorption capacity.

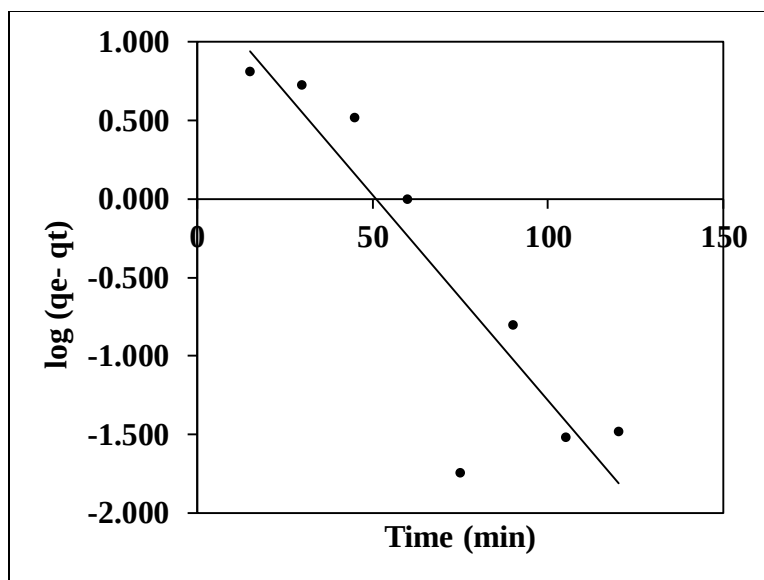


Figure 4.24a: Pseudo-first-order kinetics of Ni(II) uptake using MNPs-OP

For the pseudo – second order kinetics a plot of $\frac{t}{q_t}$ against t was constructed and shown in Figure 4.24b. The values of K_2 and q_e were calculated from the slope and intercept of the model and are given in the Table 4.21. As compared to pseudo-first order kinetics, the calculated adsorption capacity's value is closer to the experimental adsorption capacity's value as well as the model has high correlation co-efficient. Therefore the data follows pseudo-second order kinetic equation.

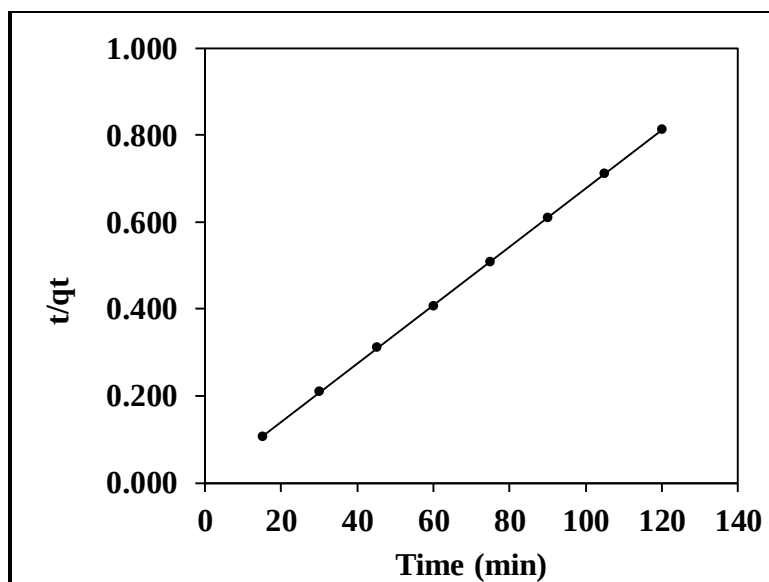


Figure 4.24b: Pseudo-second-order kinetics of Ni(II) uptake using MNPs-OP.

For the evaluation of intraparticle diffusion in the adsorption process of Ni(II) on MNPs-OP, a plot of the q_t to $t_{1/2}$ is shown in Figure 4.24c. If the line passes through the origin then the adsorption process must follow intraparticle diffusion model, but the Figure 4.28 shows that the adsorption process follows some other kinetic models.

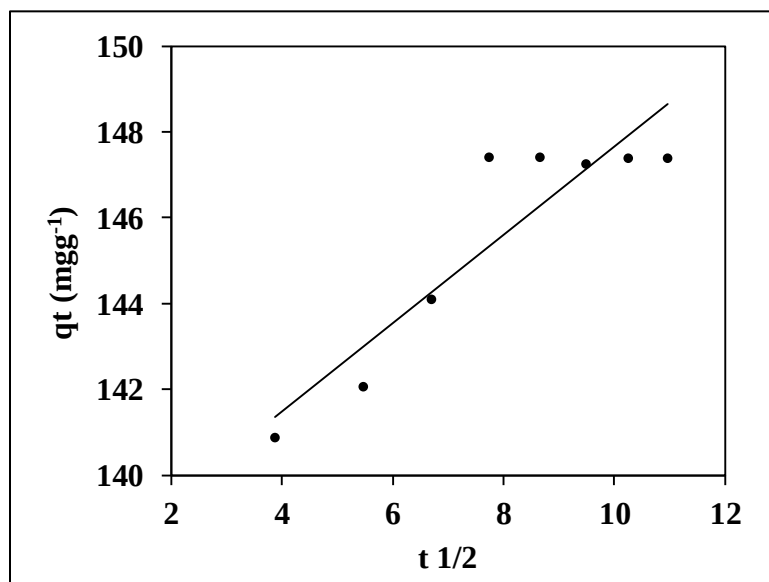


Figure 4.24c: Intraparticle diffusion model of Ni (II) uptake using MNPs-OP.

The kinetics of chemisorption on heterogeneous surface is also calculated and explained by using Elovich kinetic model. A plot of $\ln t$ vs q_t was plotted and the values of α and β were calculated from the slope and intercept of the plot (Figure 4.24d) and are given in the Table 4.21.

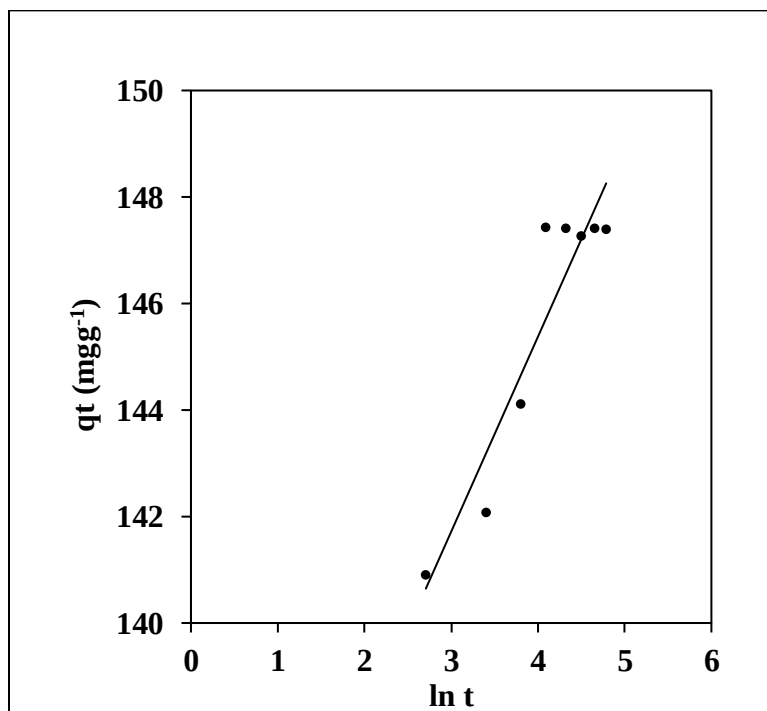


Figure 4.24d: Elovich kinetic model of Ni(II) uptake using MNPs-OP.

A comparison of the parameters calculated from pseudo first order, pseudo second order, intraparticle diffusion and Elovich kinetic model is given in Table 4.21.

Table 4.21: Kinetic parameters of Ni(II) sorption on MNPs-OP.

Kinetic model	Parameters	Value
	q_{exp} (mg g ⁻¹)	147.428
Pseudo-First Order Model	K_1 (min ⁻¹)	0.060
	q_e (mg g ⁻¹)	21.55
	R^2	0.797
Pseudo-Second Order Model	K_2 (mg g ⁻¹)	0.00614
	q_e (mg g ⁻¹)	149.25
	R^2	0.999
Intraparticle Diffusion Model	K_{Int} (min ⁻¹)	1.030
	C	137.37
	R^2	0.837
Elovich Kinetic Model	α (mg g ⁻¹ min ⁻¹)	4.2×10^{14}
	β (g mg ⁻¹)	0.273
	R^2	0.883

4.3.4. Isotherms studies

Four adsorption isotherms were applied to analyze the adsorption equilibrium between Ni(II) and MNPs-OP. These isotherms are Langmuir, Freundlich, Dubinin-Redushkviech (D-R), and Temkin. The parameter of these isotherms expresses the surface characteristics and the affinity of adsorbent towards adsorbate. The concentration of the Ni(II) on the surface of the MNPs-OP and dissolved Ni(II) in the liquid at equilibrium

was expressed by using these isotherms. The comparison of the correlation coefficient values of the isotherms expressed the isotherm that best applicable to the adsorption process.

in case of Langmuir adsorption isotherm the plot of C_e/q_e to the C_e is a straight line as shows in Figure 4.25a. The high value of correlation co-efficient ($r^2= 0.999$) revealed that the equilibrium data followed the Langmuir isotherm with (Q°) 1110.12 mg g⁻¹.

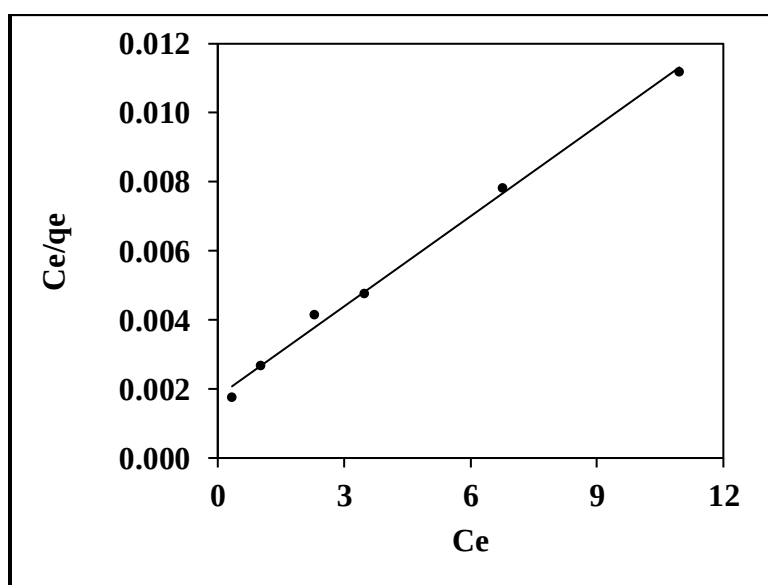


Figure 4.25a: Langmuir adsorption isotherm.

For checking the heterogeneity of the adsorption surface Freundlich isotherm was investigated as mentioned earlier. The plot between $\log q_e$ and $\log C_e$ gives straight line as shown in Figure 4.25b. The value of $1/n$ and k_F were calculated from the slop and intercept. The value of correlation coefficient was also high indicating that the adsorption also follows Freundlich adsorption isotherms. The value of n lies in between 1 and 10 indicate that the adsorption process is favorable.

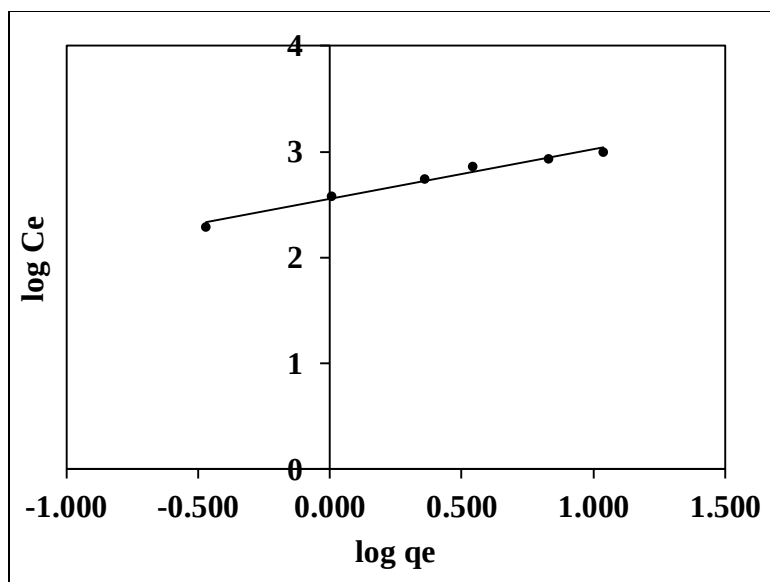


Figure 4.25b: Freundlich adsorption isotherm.

For the application of temkin adsorption model a plot of q_e against $\ln C_e$ was drawn as shown in the Figure 4.25c. The value of A_T and b_T were calculated from the slope and intercept given in the Table 4.22. The value of Temkin adsorption potential ($B_T \ln A_T$) is $410.89 \text{ kJ mol}^{-1}$ which is greater than 8 KJ mol^{-1} indicating strong bond between Ni(II) and MNPs-OP.

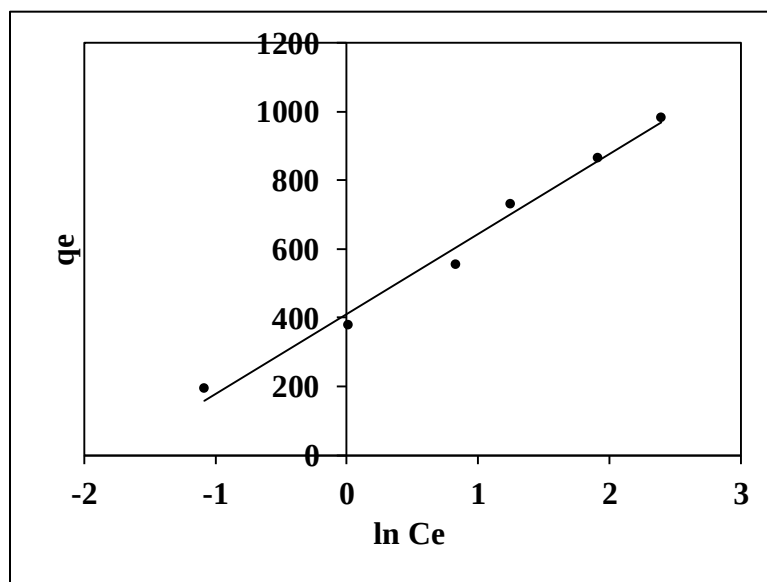


Figure 4.25c: Temkin adsorption isotherm.

For investigation of nature of adsorption process D-R adsorption isotherm was applied. For this a plot of $\ln q_e$ against ϵ^2 was drawn and shown in the Figure 4.25d. The values of K and q_m were calculated from the intercept and slope respectively. Similarly the value of E was calculated using equation 11 and the results are given in the Table 4.22. It can be seen that the value of E calculated from the model is 2.27 KJ mol^{-1} which is less than 8 KJ mol^{-1} . Therefore, the adsorption process is physical in nature.

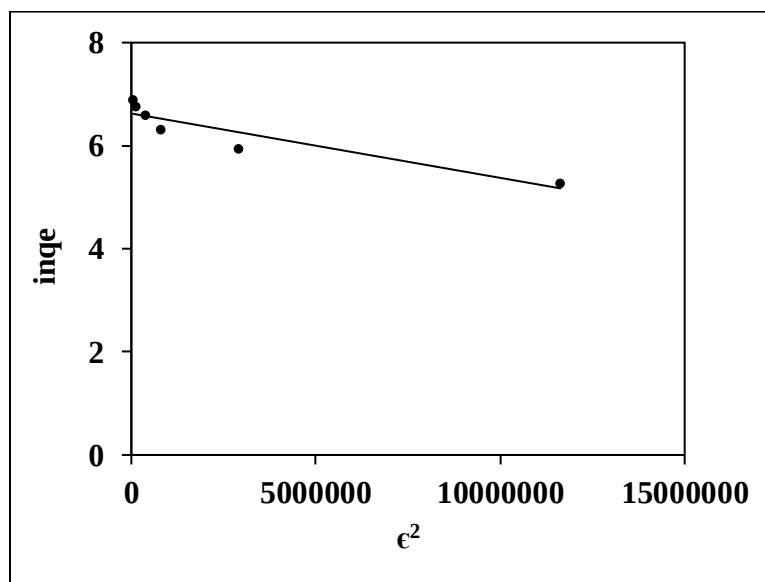


Figure 4.25d: Dubinin–Radushkevich (D–R) adsorption isotherm.

The Freundlich, Langmuir, Temkin and D-R for Ni(II) adsorption on MNPs-OP are summarized in Table 4.22. The result show that the Langmuir isotherm fitted to the adsorption data based on correlation coefficient value and adsorption capacity (Q°). The value of E in the Table 4.22 is less than 8 KJmol^{-1} so the adsorption process is physical in nature.

Table 4.22: Comparison of various isotherm constants for the sorption of Ni(II) on MNPs-OP.

Isotherm model	Constants	Value
Freundlich	KF (mg g ⁻¹)	356.615
	N	2.12
	1/n	0.471
	R ²	0.975
Langmuir	a _L (mg g ⁻¹)	0.5
	k _L (L g ⁻¹)	555.55
	Q ^o (mg g ⁻¹)	1110.12
	R ²	0.995
Temkin	A _T	5.792
	B _T	233.08
	b _T	24.43
	R ²	0.9865
D-R	q _m (mg g ⁻¹)	741.31
	E KJ mol ⁻¹	2.27
	R ²	0.863

4.3.5. Thermodynamic studies

The different process in the adsorption could be explained by thermodynamic study. The thermodynamic parameters like enthalpy (ΔH°), Gibbs free energy (ΔG°) and entropy (ΔS°) for the adsorption of Ni(II) on MNPs-OP was studied at different temperature. These parameters, were calculated in the same manner as mentioned before and the

results are given in the Table 4.23. The positive values of (ΔS°) and (ΔH°) in the Table 4.23 also shows that the process is endothermic. It was also observed that value of (ΔG°) decreased with increase in temperature. This shows that the uptake of metal ion increased with increase of temperature.

Table 4.23: Thermodynamic parameters for the adsorption of Ni(II) on MNPs-OP.

Temperature, K	ln KD	ΔG° , KJ mol ⁻¹	ΔH° , KJ mol ⁻¹	ΔS° , KJ mol ⁻¹
303	3.716	-9.391	24.191	0.112
318	4.294	-11.389		
333	4.842	-13.45		
348	5.145	-14.933		
363	5.251	-15.9		

4.3.6. Effect of coexisting cations

Waste water contains different cations and it is important to study the competitive adsorption of these coexisting cations. Therefore, the effect of different coexisting cations K, Na, Ca(II), Mg(II), Cr(III), Cu(II) were studied on the adsorption of Ni(II) on MNPs-OP and the results are given in the Figure 4.28. As can be seen from the result that there is no effect of coexisting cations on the adsorption capacity of Ni(II) up to 2000 μg concentration but the adsorption capacity of Ca(II), Mg(II), and Cu(II) decreases with increase of concentration from 1000 to 2000 μg . The competitive adsorptions generally varies with change in metal ion and depend on ion charges, molar mass, hydration energy of metal ion and ionic radii of hydrated metal ions. The results Figure 4.26 show that the adsorption capacity of Ni(II) did not affect due to the presence of coexisting cations.

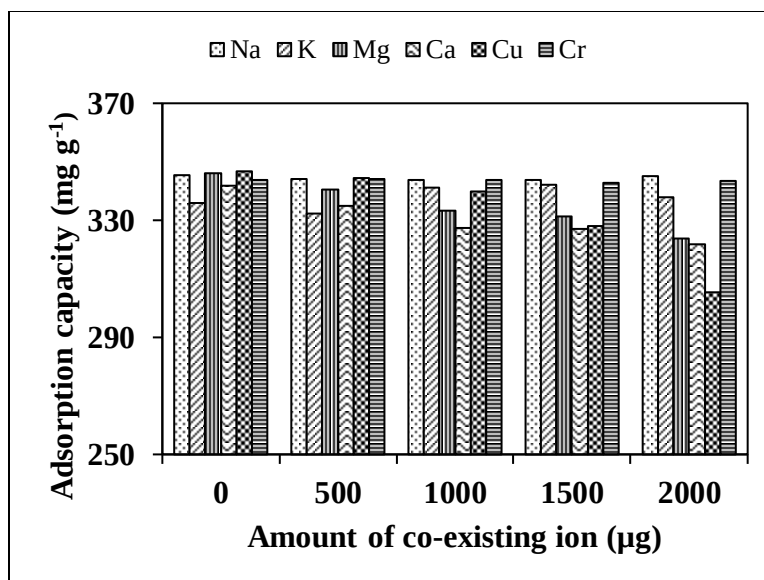


Figure 4.26: Effect of coexisting cations on adsorption capacity of Ni(II) by using MNPs-OP.

4.3.7. Application to the real sample

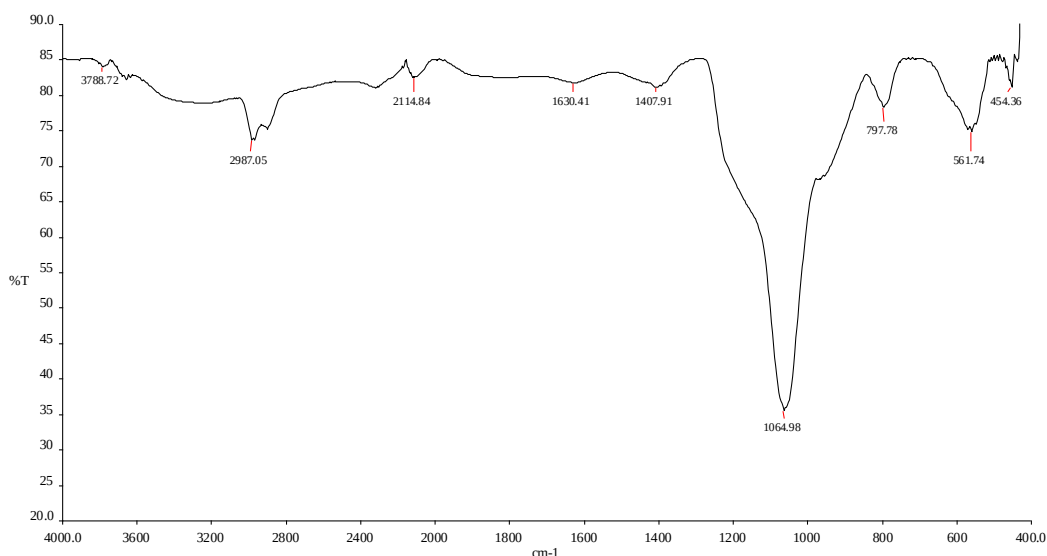
The proposed adsorption method was applied for the removal of Ni(II) from real water sample collected from various location in Pakistan. For this purpose, 10 mL of the water samples was taken, spiked with known amount of Ni(II) and the removal efficiency of Ni(II) was evaluated. The removal efficiency of Ni(II) in all type of water samples studied varies from 98 % to 100 % which shows that the method can be successfully applied to real water samples (Table 4.24).

Table 4.24: Application of the proposed method to real water samples.

Sample	Ni(II) added, μg	Ni(II) adsorption, %
Tap water,	100	99
	300	99
	500	98
Board bazar canal	100	98
	300	98
	500	97
River Kurram, Bannu	100	98
	300	98
	500	98

Part 4: Vortex assisted magnetic solid phase extraction of lead(II) and cobalt(II) on silica coated magnetic carbon nanotubes impregnated 1-(2-Pyridylazo)-2-naphthol (SiMCNTs-PAN)**4.4. Result and discussion****4.4.1. Characterization of SiMCNTs-PAN**

Core shells (SiMCNTs) were characterized by using FT-IR, XRD and SEM. In the FT-IR spectra (Figure 4.27) of SiMCNTs the absorption band at 3788.72 cm^{-1} is due to --OH stretching vibration, which is due to the PAN on the surface of the core shell. The peak at 2987.05 cm^{-1} corresponds to the C--H stretch vibration which was originally originated from the surface of MWCNTs. The weak band at 2114.84 cm^{-1} is assigned to C--C stretching vibration. Those at $1400\text{--}1650\text{ cm}^{-1}$ are due to C=N and C=C stretching vibration which is due to the PAN on the surface of the core shell. The strong absorption band at 1064.98 cm^{-1} shows the presence of Si--O--H and Si--O--Si functional group that confirm that the surface of SiMCNTs is covered by Si--O--H or Si--O--Si . The peak 561.4 cm^{-1} can be assign to either Si--O or Fe--O stretching vibration.

**Figure 4.27: FT-IR spectra of SiMCTNTs-PAN.**

The XRD pattern in Figure 4.28 indicates that the crystal structure of SiMCNTs core shells. High resolution peaks at 2θ of 36.0° , 43.3° and 63.5° confirms high crystallinity of Fe_3O_4 that impregnate at the surface of multi walled carbon nanotube (MWCNTs). The absence of SiO_2 peak in the Fig. 4.28 is due to its amorphous nature that is coated on the surface of MCNTs

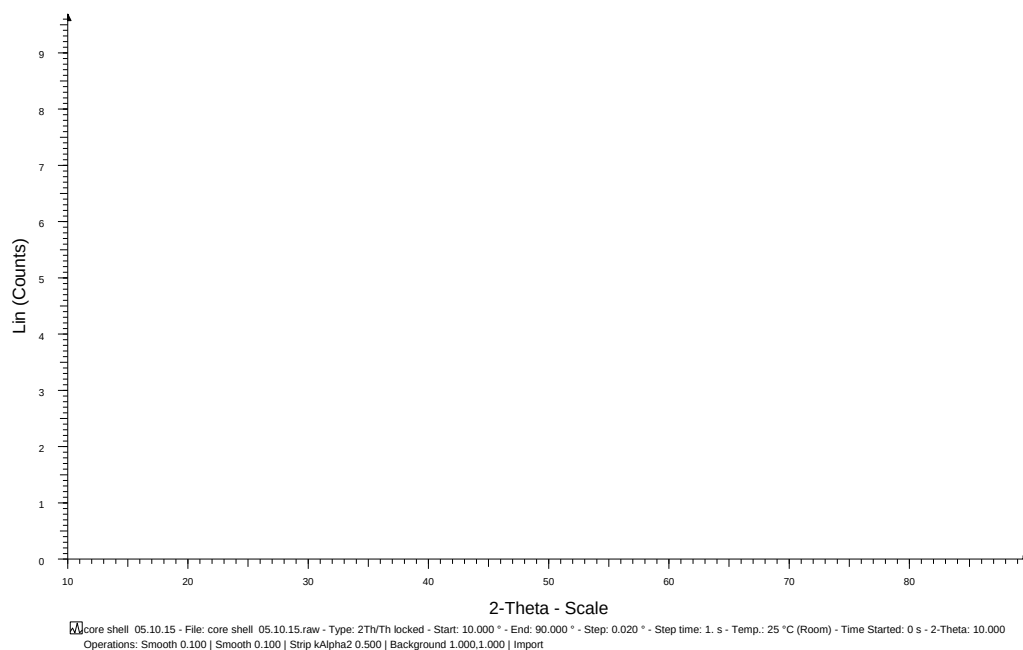


Figure 4.28: XRD patterns of SiMCNTs-PAN.

The SEM micrograph SiMCNTs (Figure 4.29) shows the rough surface of the SiMCNTs core shells, which confirm the impregnation of magnetic nanoparticle and silica coating on multi walled carbon nano tubes.

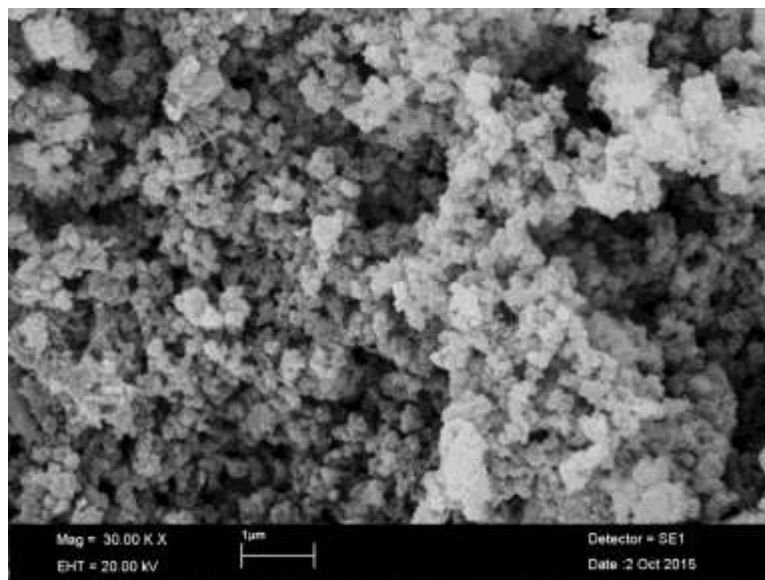


Figure 4.29: SEM micrograph of SiMCNTs-PAN.

4.4.2. Optimization

Adsorption variables like, pH, adsorbent dose, vortex time, sample volume, matrix effect, type and volume of eluent were optimized for quantitative percent recovery of Pb (II) and Co (II) using SiMCNTs-PAN. The percent recoveries values were calculated by using the following equation:

$$\text{Recovery, \%} = (w_o/w_f) \times 100 \quad (42)$$

Where w_o (μg) is amount of analyte in final solution and w_f (μg) is amount of analyte in reference solution, respectively.

4.4.2.1. Effect of pH

pH of the solution is one of the most important parameter that greatly affect the adsorption efficiency of the adsorbent. In order to optimize the most suitable pH, adsorption study was carried out at different pH ranging from 2 to 9 as shown in the Figure 4.30. It was observed that as the pH of the solution increases the percent

recoveries of Pb (II) and Co (II) also increases, till it reached to its maximum values of Pb (II) (104±4) and Co (II) (98±1) at pH 6.5. As mentioned earlier that at lower pH mobility of hydronium ion (H^+) concentration in the solution also increases which is in competition with analyte ion for the surface of the adsorbent and thus decreases the percent recoveries of the analyte ions. Another reason is that at lower pH the surface of the adsorbent is positively charged due to which electrostatic repulsion occur between positively charged surface of the adsorbent and the analyte ions which lead to the decrease in the percent recoveries of the adsorbent. At higher pH metal hydroxide formation also takes place that decrease the concentration of Pb (II) and Co (II) in the sample solution.

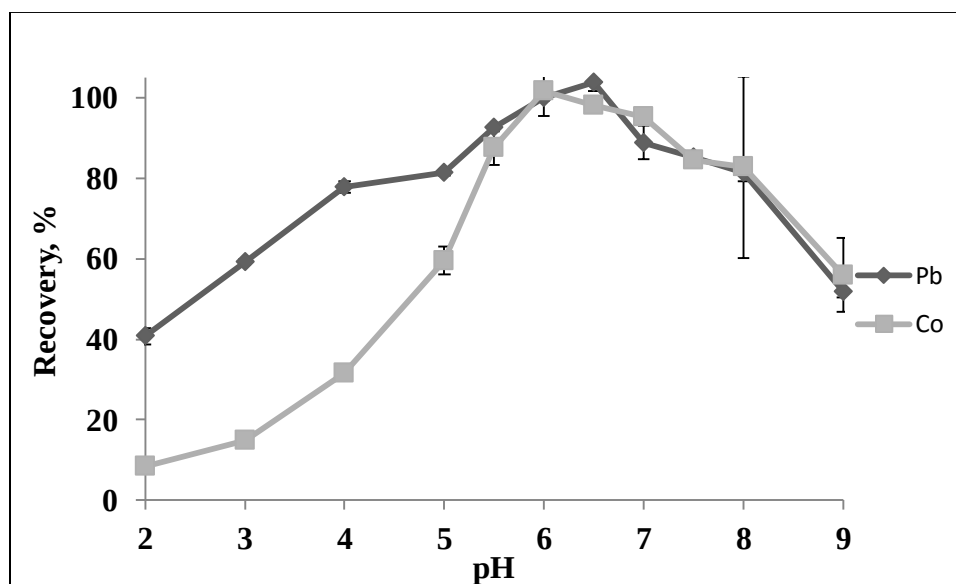


Figure 4.30: Effect of pH on % recovery of Pb (II) and Co (II) using SiMCNTs-PAN
(sample volume: 10 mL, adsorbent dose: 0.1 g, final volume: 2 mL,
N=3)

4.4.2.2. Amount of adsorbent

For finding maximum adsorption capacity of the adsorbent, it was determined by employing different adsorbent doses varied ranging from 20 mg to 150 mg at constant adsorbate concentration (Figure 4.31). As can be seen from the Figure 4.32 that as the amount of adsorbent increases the percent recovery also increases and the quantitative percent recovery of Pb (II) (99 ± 4) and Co(II) (101 ± 2) were obtained using 100 mg of adsorbent dose.

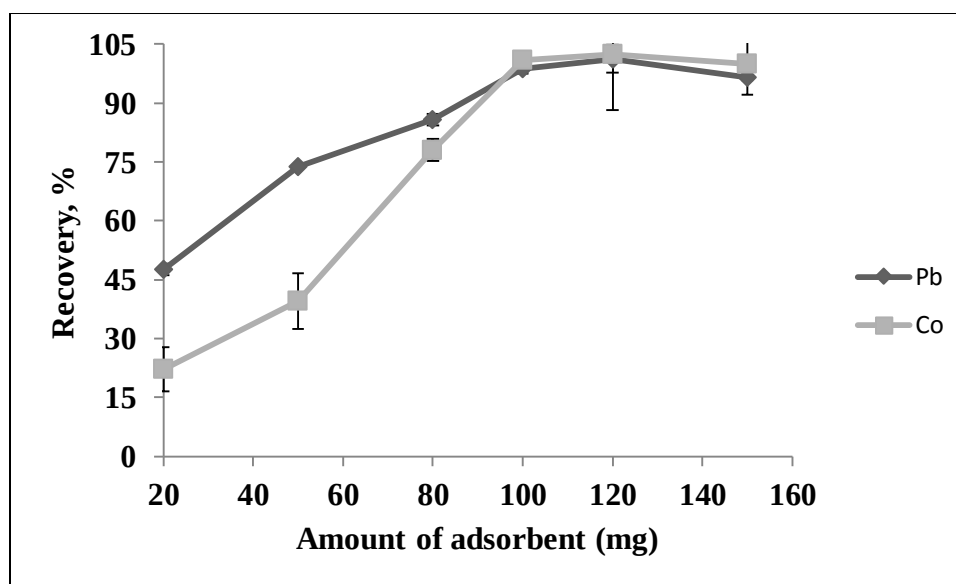


Figure 4.31: Effect of adsorbent dose on percent recovery of Pb (II) and Co (II)

using SiMCNTs-PAN (pH: 6.6, sample volume: 10 mL, final volume: 2 mL, N=3).

4.4.2.3. Effect of sample volume

Optimization of the highest possible volume to which the proposed solid phase extraction method could be successfully applied is of immense importance. It is because the efficiency of the adsorbent can be determined by calculating the highest preconcentration

factor of the proposed method. For this purpose solid phase extraction was carried out at different sample volume ranging from 5 mL to 50 mL and the results are shown in the Figure 4.32. It can be concluded from the Figure 4.32 that quantitative percent recovery can be achieved by using sample volume in the range of 5-30 mL. Therefore, highest preconcentration factor of 15 can be achieved by using sample volume of 30 mL with final elution volume of 2 mL.

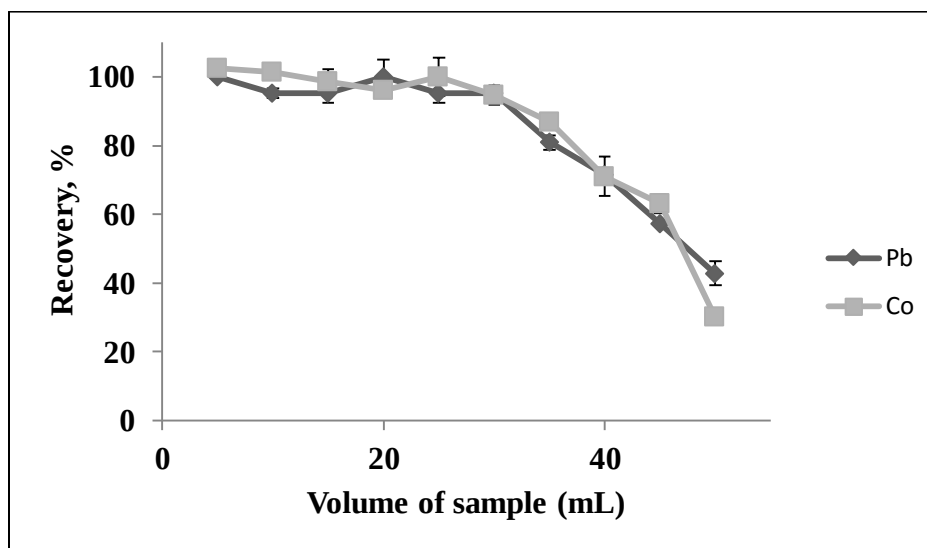


Figure 4.32: Effect of sample volume on % recovery of Pb (II) and Co (II) using SiMCNTs-PAN (pH: 6.5, sorbent dose: 0.1 g, final volume: 2 mL, N=3)

4.4.2.4. Desorption studies

Desorption of Pb (II) and Co (II) from the surface of SiMCNT-PAN can be achieved by using dilute solution of mineral acids like HCl and HNO₃. Therefore, for quantitative recovery of Pb (II) and Co (II) ions, the desorption studies were conducted by using 1-3 M of HCl and HNO₃ solutions both in distilled water and acetone (Table 4.25). It was observed that quantitative recoveries of Pb (II) and Co (II) can be achieved by using 2 M HNO₃ in acetone.

Table 4.25. Effect of type and concentration of eluent on percent recovery of Pb (II) and Co (II) on SiMCNTs-PAN (N=3).

Type and concentration of eluent	Recovery, %	
	Pb (II)	Co (II)
HCl (1 mol L ⁻¹)	47±1	67±2
HCl (2 mol L ⁻¹)	76±1	81±2
HCl (3 mol L ⁻¹)	68±0	64±3
HNO ₃ (1 mol L ⁻¹)	76±2	93±1
HNO ₃ (2 mol L ⁻¹)	85±1	94±3
HNO ₃ (3 mol L ⁻¹)	82±1	81±3
1 M HNO ₃ in acetone	92±1	83±9
2 M HNO ₃ in acetone	102±4	96±1
3 M HNO ₃ in acetone	79±1	87±1
1 M HCl in acetone	71±1	78±1
2 M HCl in acetone	76±0	79±5
3 M HCl in acetone	71±4	81±1

In order to achieve the smallest possible volume, the adsorption study was carried at different volume ranging from 1 mL to 10 mL using 2 M of HNO₃ in acetone (Figure 4.33). It can be seen that 2 mL of 2 M HNO₃ in acetone is enough to obtain the quantitative recovery Pb (II) and Co (II) using SiMCNTs-PAN.

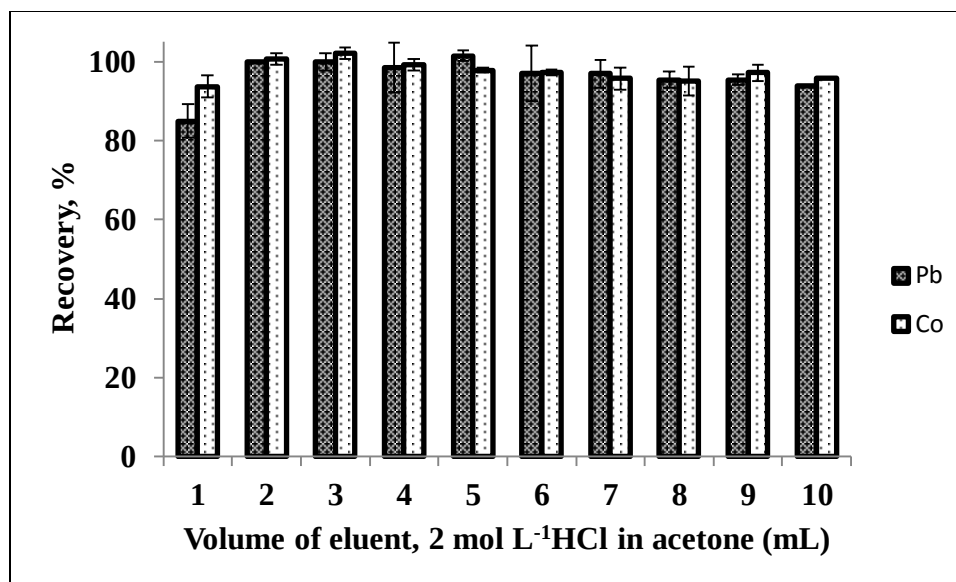


Figure 4.33: Effect of volume of 2 mol L⁻¹ on % recovery of Pb (II) and Co (II) using SiMCNTs-PAN.

Another important factor that affects the efficiency of adsorbent is the number of cycle of the adsorbent using for adsorption studies. It was found that each adsorbent can be used four times for the adsorption studies beyond that there is a great decrease in the percent adsorption capacity of Pb (II) and Co (II). It is because of corrosion of Fe₃O₄. Therefore, SiMCNTs-PAN was used four times in rest of the other adsorption studies with 2 mL of 2 M HNO₃ in acetone.

4.4.2.5. Matrix effect

The effect of different ions, which are coexisting with analyte ions especially in the samples of complex matrix nature were studied on percent recovery of Pb (II) and Co (II) as shown in the Table 2.26 It can be seen from the Table 4.26 that there is negligible effect of these ions except Cu(II), Ni(II) and Mn(II) on percent recovery of Pb (II) and Co (II). These three metal ions can be tolerated up to 10 µg g⁻¹ along with analyte ions. The

study shows that the solid phase extraction of Pb (II) and Co (II) on SiMCNTs-PAN is highly selective.

Table 4.26. Effect of coexisting ions on % recoveries of Pb (II) and Co (II) using SiMCNTs-PAN, pH: 7, amount of SiMCNTs-PAN: 0.1 g, volume of sample solution: 10 mL (N=3).

Interfering ions	Added as	Concentration, $\mu\text{g g}^{-1}$	% Recovery	
			Pb (II)	Co (II)
Na⁺	NaCl	5000	95 $\pm$ 2	93 $\pm$ 4
K⁺	KCl	5000	97 $\pm$ 1	97 $\pm$ 6
Ca⁺⁺	Ca(NO ₃) ₂ .4H ₂ O	1000	97 $\pm$ 4	99 $\pm$ 1
Mg⁺⁺	Mg(NO ₃) ₂ .6H ₂ O	1000	96 $\pm$ 4	94 $\pm$ 8
Al⁺⁺⁺	Al(NO ₃) ₃ .7H ₂ O	100	96 $\pm$ 3	95 $\pm$ 10
Cd⁺⁺	Cd(NO ₃) ₂ . 6H ₂ O	100	103 $\pm$ 1	94 $\pm$ 1
Zn⁺⁺	Zn(NO ₃) ₂ . 6H ₂ O	100	93 $\pm$ 1	96 $\pm$ 4
Fe⁺⁺	Fe(NO ₃) ₂ . 6H ₂ O	100	98 $\pm$ 6	97 $\pm$ 4
Cu⁺⁺	Cu(NO ₃) ₂ . 6H ₂ O	10	95 $\pm$ 2	97 $\pm$ 1
Ni⁺⁺	Ni(NO ₃) ₂ . 6H ₂ O	10	99 $\pm$ 9	99 $\pm$ 1
Mn⁺⁺	Mn(NO ₃) ₂ . 6H ₂ O	10	99 $\pm$ 4	95 $\pm$ 1
SO₄⁻	Na ₂ SO ₄	500	95 $\pm$ 2	98 $\pm$ 4
CO₃⁻	Na ₂ CO ₃	500	96 $\pm$ 0	96 $\pm$ 4
F⁻	NaF	1000	99 $\pm$ 5	95 $\pm$ 1

4.4.2.6. Kinetic studies

SiMCNTs-PAN (100 mg) was added to sample solution (10 mL) containing Pb (II) (20 µg) and Co (II) (10 µg). The mixture was agitated at 400×100 rpm for 4 min. For the mechanism of adsorption kinetics, the pseudo-first-order, pseudo-second-order kinetics and intraparticle diffusion model were used in order to explain the kinetic behaviour of adsorption of Pb (II) and Co (II) on SiMCNTs-PAN.

The values of k_1 and q_e for Pb (II) and Co (II) were calculated from pseudo-second-order model and are specified in the Table 4.4.3. Due to smaller values of correlation coefficient (R^2) of 0.307 and 0.636 for Pb (II) and Co (II), respectively shows that these adsorption studies do not follow pseudo-first-order kinetics. Moreover, smaller calculated values of adsorption capacities than the experimental adsorption capacities confirmed that pseudo-first-order kinetics is not applicable to the adsorption process.

In order to evaluate, that the rate limiting step is chemisorption the adsorption data were analyzed by using pseudo-second-order kinetics.

The values of q_e , k_2 and R^2 were calculated from the linear plot of pseudo-second-order model expressed by Figure 4.34a. These values are given in the Table 4.27. Higher values of correlation coefficient and close agreement between calculated adsorption capacity and experimental adsorption confirmed that the adsorption of Pb (II) and Co (II) on SiMCNTs-PAN followed pseudo-second-order kinetics.

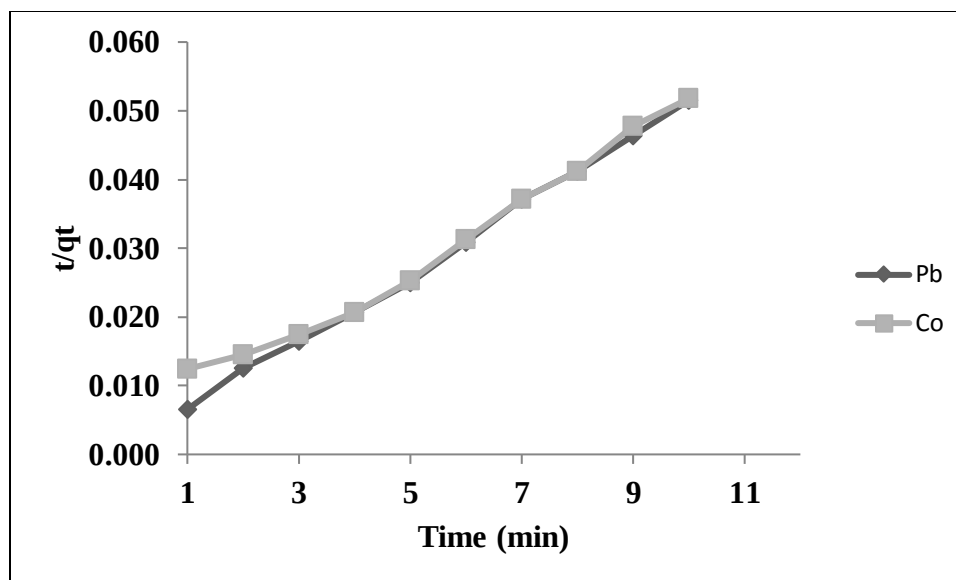


Figure 4.34a: Pseudo-second-order kinetics for the adsorption of Pb(II) and Co(II) using SiMCNTs-PAN.

For intraparticle diffusion model the intraparticle diffusion rate constant and there values were calculated directly from the intercept and slope of intraparticle diffusion model Figure 4.34b and given in the Table 4.27 The plot of q_t (mg g^{-1}) and $t^{1/2}$ shows that the adsorption of Pb (II) and Co (II) on SiMCNTs-PAN is three step adsorption processes mainly due to surface diffusion and intraparticle diffusion, while the positive value of C is mainly due to the boundary layer diffusion. The multistep adsorption process confirmed some other adsorption mechanism such as ion exchange or complexation may control the rate of adsorption.

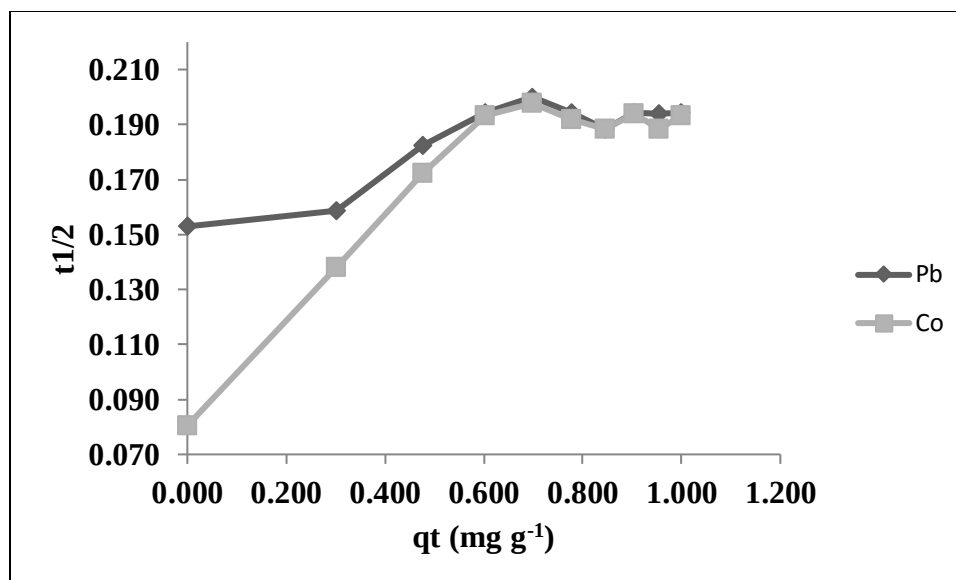


Figure 4.34b: Intraparticle diffusion model for the adsorption of Pb(II) and Co(II) using SiMNCNTs-PAN.

Table 4.27: Kinetic parameter of the adsorption of Pb(II) and Co(II) on the surface of SiMNCNTs-PAN core shell.

Metal ion	Experimental	Kinetic models								
		Pseudo first order			Pseudo second order			Intra particle diffusion		
	$q_e \mu\text{gg}^{-1}$	$K_1 \text{ min}^{-1}$	$q_e \mu\text{gg}^{-1}$	R^2	$K_2 \text{ min}^{-1}$	$q_e \mu\text{gg}^{-1}$	R^2	$K_{\text{int}} \text{ min}^{-1}$	C	R^2
Co (II)	0.198	0.301	0.06	0.636	4.62	0.198	0.984	0.104	0.105	0.795
Pb (II)	0.2	0.204	0.03	0.307	5	0.2	0.997	0.045	0.156	0.768

4.4.2.7. Thermodynamic studies

Thermodynamic studies were carried out for the adsorption of Pb(II) and Co(II) on SiMNCNTs-PAN in order to explain the spontaneity and feasibility of the adsorption process. For this purpose, adsorption studies were carried out at different temperature

(273 K-373 K and the values of enthalpy (ΔH°), Gibbs free energy (ΔG°) and entropy (ΔS°) were calculated in the same manner as mention before and are given in the Table 4.28.

The positive values of (ΔS°) and (ΔH°) in (Table 4.28) also indicate that the adsorption process is endothermic. The decrease in ΔG° values with increase in temperature confirms that metal uptake increase with increase in temperature.

Table 4.28: Thermodynamic parameter for the adsorption of Pb(II) and Co(II) on SiMCNTs-PAN.

Temperature, K	Pb (II)			Co (II)		
	$\Delta^\circ G$ KJ mol ⁻¹	$\Delta^\circ H$ KJ mol ⁻¹	$\Delta^\circ S$ KJ mol ⁻¹	$\Delta^\circ G$ KJ mol ⁻¹	$\Delta^\circ H$ KJ mol ⁻¹	$\Delta^\circ S$ KJ mol ⁻¹
293	-13.087	43.565	0.191	-13.616	28.317	0.133
303	-13.924			-14.310		
313	-16.573			-15.860		
323	-18.878			-16.633		
333	-19.463			-18.102		
343	-22.808			-19.177		

4.4.2.8. Validation of the proposed method

For the validation of proposed method, solid phase microextraction experiments were carried out for the determination of Pb(II) and Co(II) in certified reference material like

TMDA-64.2 fortified water and SPS-WW2 wastewater as shown (Table 4.29). Recovery results show that the method is accurate and valid for the determination of Pb(II) and Co(II) at trace level.

Table 4.29: Validation of the proposed solid phase microextraction of Pb and Co at trace level using certified water reference material (pH: 6, Amount of adsorbent: 0.1 g, Volume of sample: 15 mL, Final volume: 2mL).

Metal	Pb(II)			Co(II)		
	Certified value (μgL^{-1})	Found value (μgL^{-1})	% Recovery	Certified value (μgL^{-1})	Found value (μgL^{-1})	% Recovery
SPS-ww2	500	510 $\pm$ 13	102	300	281 $\pm$ 11	94
TMDA 64.4	286	284 $\pm$ 10	99	253	247 $\pm$ 6	97
TMDA 62.2	98.4	96.25 $\pm$ 5	98	95.0	90.25 $\pm$ 8	95

For applicability to real samples the method was applied to three environmental water samples (dam water, sea water, waste water) and the recovery results are given in the Table 4.30. The quantitative percent recovery in the range of (96 %-102%) shows, that the method can be successfully applied to the determination of Pb (II) and Co (II) in the complex environmental samples. The application of the method to the certified reference material and environmental shows that the method is accurate and valid for the determination of Pb (II) and Co (II) in different type of water samples.

Table 4.30: Real samples recovery results for Pb (II) and Co (II) using the proposed solid phase micro extraction method (pH: 6, amount of SiMCNTs-PAN: 0.1 g, volume of sample: 15 mL, Final volume: 2 mL (N=3)).

Sample	Pb (II)			Co (II)		
	µg added	µg found	% Recovery	µg added	µg found	% Recovery
Dam water	0.0	BDL	...	0		
	0.8	0.82 ± 0.02	103	0.4	0.4± 0.008	100
	1.2	1.15 ± 0.04	96	0.6	0.6± 0.04	100
Sea water	0.0	0.36 ± 0.08	...	0	0.45± 0.02	
	1.2	1.52 ± 0.05	96	0.6	1.06± 0.01	102
	1.4	1.8 ± 0.04	104	0.7	1.16± 0.005	101
Waste water	0.0	0.24 ± 0.03	...	0		
	1.0	1.22 ± 0.02	100	0.7	0.66± 0.03	94
	1.6	1.82 ± 0.03	98	0.8	0.76± 0.02	96

Conclusions

A variety of methods have been proposed for the preconcentration and determination of heavy metals. The first method is based on magnetic solid phase extraction for the preconcentration and determination of Cd(II) using MNPs and SiMNPs as adsorbents. Factors effecting extraction efficiency like solution pH, sorbent dose, desorption condition, sample volume and matrix effect were investigated and optimized. The develop method was highly sensitive with low values of limit of detections $0.31 \mu\text{g L}^{-1}$ and $0.30 \mu\text{g L}^{-1}$ for MNPs and SiMNPs, respectively, relatively selective with negligible interfering effect from the matrix ion, highly reproducible with smaller values of percent relative standard deviations of 4.6 and 5.2 for MNPs and SiMNPs respectively. Kinetic data fit to pseudo second order kinetics while thermodynamic data shows that the method is feasible in nature. The method was successfully applied to environmental water samples like Tap water and River waters with satisfactory results.

The second method is based on magnetic solid phase extraction method using on MNPs and MNPs-BP for the preconcentration and determination of Pb(II) in real environmental water sample. Analytical parameter like limit of detection and relative standard deviation shows that the method is highly sensitive and reproducible. Kinetic data shows that this adsorption studies follow pseudo second order kinetics while the equilibrium data can be best explained by Langmuir adsorption isotherm. Thermodynamic data shows that the method is endothermic and spontaneous in nature. The standard addition method was applied to real water samples to check the validity of the solid phase extraction method.

The third method of solid phase extraction is based on utilization of orange peel impregnated with magnetic nanoparticles (MNPs-OP) for Ni(II) from water samples. Result indicates that the

adsorption of Ni(II) on Fe₃O₄-OP depends on pH and maximum adsorption of Ni(II) was achieved at pH 7. Adsorption rate was higher in the beginning and then become constant. The kinetic models shows that the data fit to the pseudo-second order kinetics. The experimental data fit to the Langmuir adsorption isotherm with monolayer adsorption capacity of (1110.12 mg g⁻¹). The thermodynamic parameter shows that the adsorption process is endothermic and spontaneous in nature. The effect of coexisting metal ions were studied which showed that the presence of these metals has insignificant effect on the removal efficiency Ni(II) from the aqueous solution. The new adsorbent (MNPs-OP) not only showed high adsorption capacity and rapid kinetics but was found simple, inexpensive and environment friendly.

In the fourth method magnetic solid phase extraction of Pb(II) and Co(II) were carried out using silica coated magnetic carbon nanotube impregnated with 1-(2-Pyridylazo)-2-naphthol (SiMCNTs-PAN) as an adsorbent. Kinetic model shows that the data fit to pseudo first order kinetics. The method is highly selective as there are no significant interferences from matrix cations and anions even at high concentration except Cu(II), Ni(II) and Mn(II). Thermodynamic studies show that the method is endothermic and spontaneous in nature. The method was successfully applied to TMDA 64.2 environmental water, TMDA 62.2 environmental water and SPS-WW2 waste water certified water reference materials for trace metal determination. The method was also successfully applied to real water samples for heavy metal analysis.