

POLYACRYLIC ACID -  
ACRYLAMIDE BASED WATER  
PURIFICATION SYSTEMS FOR THE  
REMOVAL OF SELECTED ANIONS  
AND CATIONS FROM AQUEOUS  
MEDIA

By

SARNIS KANKANAMGE THILINI THATHSARA

M.Phil

2018

POLYACRYLIC ACID - ACRYLAMIDE BASED WATER  
PURIFICATION SYSTEMS FOR THE REMOVAL OF  
SELECTED ANIONS AND CATIONS FROM AQUEOUS  
MEDIA

By

SARNIS KANKANAMGE THILINI THATHSARA



Thesis submitted to the University of Sri Jayewardenepura  
for the award of the Degree of Master of Philosophy

## Declaration

The work described in this thesis was carried out by me under the supervision of Dr. Thilini D. Gunasekara, Dr. Asitha Cooray, and Dr. Dilru R. Ratnaweera and this has not been submitted in whole or in part to any university or any other institution for another Degree/Diploma



S. K Thilini Thathsara  
2018

### Certification of the supervisor

We certify that the above statement made by the candidate is true and that this thesis is suitable for submission to the University for the purpose of evaluation.



.....  
Dr. Thilini D. Gunasekara

Senior Lecturer

Department of Chemistry,  
Faculty of Applied Sciences,  
University of Sri Jayewardenepura.

Date: 29/03/2018



.....  
Dr. Dilru R. Ratnaweera

Senior Lecturer

Department of Chemistry,  
Faculty of Applied Sciences,  
University of Sri Jayewardenepura.

Date: 29/03/2018



.....  
Dr. Asitha Cooray

Senior Lecturer

Department of Chemistry,  
Faculty of Applied Sciences,  
University of Sri Jayewardenepura.

Date: 29/03/2018

## Table of content

Declaration.....	ii
Certification of the supervisor.....	iii
Table of content.....	iv
List of Tables.....	x
List of Figures.....	xii
Abbreviation.....	xvii
Acknowledgment.....	xx
ABSTRACT.....	1
Chapter 01.....	3
Introduction.....	3
1.1 Water.....	3
1.2 Problem statement and motivation.....	4
1.3 Water purification methods.....	4
1.4 Adsorption Process.....	7
Chapter 2.....	9
Literature review.....	9
2.1 Toxicological aspect of some heavy metals and fluoride.....	9
2.2 Hydrogels as water purification materials.....	11
2.3 Objectives of this research work:.....	14
2.3.1 General objectives.....	14
2.3.2 Specific Objectives.....	14
2.3.2.1 Approach 1.....	14
2.3.2.2 Approach 2.....	14
Chapter 3.....	16
Methodology.....	16
3.1 Materials.....	16
3.2 Preparation of adsorbents.....	16

3.2.1 Preparation of trimetal composite .....	16
3.2.2 Preparation of Fe-La-Ce tri-metallic composite.....	17
3.2.3 Preparation of tri-metal incorporated Alginate and CMC beads.....	17
3.2.4 Preparation of tri-metal coated Alginate and CMC beads.....	17
3.2.5 Preparation of tri-metal incorporated Chitosan beads.....	17
3.2.6 Synthesis of trimetallic composite incorporated polyacrylamide gel.....	17
3.2.7 Preparation of PAA-co-PAM-DETA-Urea.....	18
3.3 Characterization of Fe-La-Ce tri-metallic composite.....	19
3.3.1 Fourier Transform Infrared spectroscopy (FTIR).....	19
3.3.2 X-ray diffraction Analysis (XRD).....	20
3.3.3 X-Ray Fluorescence (XRF).....	20
3.3.4 Scanning Electron Microscope (SEM).....	20
3.3.5 The Point of Zero Charge.....	20
3.4 Characterization of Fe-La-Ce trimetallic composite incorporated PAM (TCIP).....	21
3.4.1 FTIR analysis in attenuated total reflection (ATR) mode.....	21
3.4.2 X-ray diffraction analysis (XRD).....	21
3.4.3 Scanning Electron Microscope (SEM).....	21
3.4.4 SEM coupled with EDS (Energy Dispersive Spectrum).....	22
3.4.5 Thermal Gravimetric Analysis (TGA).....	22
3.4.6 Differential Scanning Colorimetry (DSC).....	22
3.5 Characterization of PAA-co-PAM-DETA-Urea.....	22
3.5.1 FTIR analysis in attenuated total reflection (ATR) mode.....	22
3.5.2 Powder X-Ray diffraction (PXRD).....	23
3.5.3 Scanning Electron Microscopic imaging (SEM).....	23
3.5.4 SEM couple Energy Dispersive Spectrum (SEM-EDS).....	23

3.5.5 Thermal Gravimetric Analysis (TGA).	23
3.6 Adsorption Studies	23
3.6.1 Select the best adsorbent.	23
3.6.2 Batch sorption studies for removal of fluoride ions from aqueous media using Fe-La-Ce trimetallic composite.	24
3.6.2.1 Effect of Contact time.	24
3.6.2.2 Effect of pH.	25
3.6.2.3 Effect of initial concentration.	25
3.6.2.4 Effect of Competitive Factors.	25
3.6.3 Adsorption Studies for removal of arsenate, chromate and fluorides using TCIP.	25
3.6.3.1 Select the best adsorbent among the prepared tri-metallic composite incorporated or coated synthetic hydrogels and natural polymers for removal fluoride ions from aqueous media.	25
3.6.4 Batch sorption studies for removal of arsenate, chromate and fluoride from aqueous media using TCIP.	27
3.6.4.1 Effect of pH.	27
3.6.4.2 Effect of contact time.	27
3.6.4.3 Effect of competitive factors.	27
3.6.5 Batch sorption studies for removal of Mn(II), Ni(II), Zn(II) and Co(II) from aqueous media using PAA-co-PAM-DETA-Urea.	28
3.6.5.1 The effect of contact time.	28
3.6.5.2 The effect of pH.	28
3.6.5.3 The effect of initial concentration.	29
3.7 The study of adsorption isotherms	29
3.8 Adsorption Kinetics.	29

3.9 Regeneration and applicability for treat natural water samples using prepared adsorbents.....	30
3.9.1 Regeneration study of Fe-La-Ce tri-metallic composite.....	30
3.9.2 Regeneration study of TCIP adsorbent.....	30
3.9.3 Regeneration study of PAA-co-PAM-DETA-Urea adsorbent.....	30
3.9.4. Applicability of prepared adsorbents for treat natural water samples..	31
Chapter 4 .....	32
Results and Discussion.....	32
4.1 Select the best adsorbent among the prepared tri-metallic composite for removal of fluoride ions from aqueous media.....	32
4.2 Characterization results of Fe-La-Ce trimetallic composite for removal of fluorides from aqueous media.....	33
4.2.1 Fourier Transform Infrared spectroscopy (FTIR) for fluoride removal from aqueous media using Fe-La-Ce tri metallic composite.....	33
4.2.2 X-Ray Diffraction (XRD).....	34
4.2.3 X-Ray Fluorescence .....	36
4.2.4 Scanning Electron Microscopic Images .....	37
4.3 Batch sorption studies for removal of fluorides from aqueous media using Fe-La-Ce tri-metallic composite.....	39
4.3.1 Effect of contact time .....	39
4.3.2 Effect of pH.....	40
4.3.3 Effect of initial concentration.....	42
4.3.4 Adsorption Isotherms for removal of fluoride ions from aqueous media using Fe-La-Ce trimetallic composite.....	42
4.3.4.1 Langmuir isotherm .....	43
4.3.4.2 Freundlich Isotherm.....	44
4.3.5 Adsorption Kinetics for removal of fluorides from aqueous media using Fe-La-Ce tri-metallic composite.....	48



4.3.5.1 Pseudo first order Kinetics .....	48
4.3.5.2 Pseudo second order kinetics.....	49
4.3.5.3 Intraparticle diffusion model.....	49
4.3.6 The effect of competition of interfering anions.....	55
4.3.7 Regeneration ability of Fe-La-Ce tri-metallic composite.....	56
4.3.8 Applicability of Fe-La-Ce tri-metal composite for treat natural water samples .....	57
4.4. Optimization studies.....	60
4.5. Characterization results of TCIP for removal of arsenate, chromate and fluorides from aqueous media. ....	62
4.5.1 Fourier Transform Infrared Spectroscopy (FTIR).....	62
4.5.2 Powder X-Ray Diffraction (PXRD).....	66
4.2.3 Scanning Electron Microscopic Imaging (SEM). ....	69
4.5.4 The composition analysis using SEM-EDS .....	71
4.5.5 TGA and DTA analysis.....	72
4.5.6 DSC analysis of TCIP .....	73
4.6.1 Effect of contact time .....	74
4.6.2 Effect of pH.....	75
4.7 Adsorption Isotherms for removal of arsenate, chromate and fluoride ions from aqueous media using TCIP. ....	77
4.8. Adsorption kinetics for removal of arsenate, chromate and fluorides from aqueous media. ....	83
4.9.3 Regeneration ability and reusability of TCIP.....	90
5.0 Characterization of PAA-co-PAM-DETA-Urea for removal of Mn(II), Ni(II), Zn(II) and Co(II) from aqueous media.....	91
5.1 FTIR analysis - Attenuated total reflection (ATR) mode.....	91
5.2 Powder X-Ray diffraction (PXRD) analysis.....	95

5.3 Scanning Electron Microscopic imaging (SEM).....	96
5.4 SEM-EDS analysis .....	99
5.5 Thermal Gravimetric Analysis (TGA) .....	100
5.6 Batch sorption studies for removal of Mn(II), Ni(II), Zn(II) and Co(II) from aqueous media using PAA-co-PAM-DETA-Urea.....	105
5.6.1 Effect of contact time .....	105
5.6.2 Effect of pH.....	106
5.7 Adsorption Isotherms for removal of Mn(II), Ni(II), Zn(II) and Co(II) ions from aqueous media using PAA-co-PAM-DETA-Urea.....	107
5.8 Adsorption Kinetics for removal of Mn(II), Ni(II), Zn(II) and Co(II) using Paa-co-PAM-DETA-Urea. ....	113
5.9 Effect of interfering ions for adsorption process.....	116
5.9.1 Feasibility of Natural water samples .....	117
5.9.2 Regeneration and reusability of prepared adsorbent.....	119
Chapter 05 .....	120
Conclusion.....	120
Chapter 06 .....	122
Recommendations .....	122
6.1 International level.....	122
6.2 National level.....	122
References .....	124
Appendixes.....	a
List of publications.....	b
Appendix 2.....	c

## List of Tables

Table 1: Advantages and disadvantages of heavy metal removal methods.....	6
Table 2: Absorption capacities of tri-metal composites.....	32
Table 3: The XRF analysis of metal compositions of tri-metal adsorbent before and after fluoride adsorbed onto Fe-La-Ce tri-metallic composite.....	37
Table 4: The summery of adsorbent isotherms.....	47
Table 5 The summery of dimensionless index at different temperatures and pH 7.00.....	47
Table 6: The summery of kinetic data at 300 K and pH 7.00.....	54
Table 7: Percent interference for fluoride ions adsorbed onto adsorbate with presence in different concentration of chloride, sulfate and bicarbonate. ....	56
Table 8: Summery of regeneration ability for removal of fluoride ions at pH 10. ....	57
Table 9: Fluoride removal efficiency of Fe-Ce-La tri-metal composite in natural water samples.....	58
Table 10: Amount of fluoride adsorbed per unit of CMC, Alginate and Chitosan .....	59
Table 11: Elemental composition of the PAM, TCIP and after adsorbed arsenate (TCIP-As), chromate (TCIP-Cr) and fluoride (TCIP-F) onto TCIP.....	72
Table 12: Adsorption isotherms results for arsenate, chromate and fluoride adsorbed onto TCIP.....	80
Table 13: Kinetic model parameters for adsorption of arsenate, chromate and fluoride at 50 °C.....	85
Table 14: Percent interference for arsenate, chromate and fluoride ions adsorbed onto adsorbate with presence in 0.1 mol dm <sup>-3</sup> of chloride, sulfate, nitrate and bicarbonate.....	86
Table 15: Fluoride, arsenate and chromate removal efficiency of TCIP in natural water samples.....	88
Table 16: Summary of regeneration ability for removal of fluoride, arsenate and chromate ions at pH 10. ....	89

Table 17: SEM-EDS analysis results for PAA-co-PAM-DETA-Urea and after adsorption of metals ions onto the adsorbate.....	99
Table 18: Langmuir adsorption isotherm and Freundlich adsorption isotherms for process of adsorption of Mn(II), Ni(II), Co(II) and Zn(II) onto PAA-co-PAM-DETA-Urea adsorbent. ....	111
Table 19: The summery of kinetics data at 28 °C and pH 7.0.....	114
Table 20: Percent interference for Mn(II), Ni(II), Co(II) and Zn(II) adsorbed onto adsorbate with presence in 0.1 mol dm <sup>-3</sup> of calcium, magnesium, sodium and potassium. ....	117
Table 21: PAA-coPAM-DETA-Urea in natural water samples collected from different areas in Sri Lanka.....	118
Table 22: Summery of regeneration ability for removal of Mn(II), Ni(II), Co(II) and Zn(II) ions at pH 2.....	119

## List of Figures

Figure 1: Schematic diagram for preparation of PAA-co-Pam-DETA-Urea. ....	19
Figure 2: FTIR Spectra of (a) virgin and (b) fluoride treated adsorbed onto the Fe-La-Ce tri-metallic composite. ....	34
Figure 3: XRD spectrum of (a) Fe-La-Ce tri-metal composite, (b) La(OH) <sub>3</sub> , (c) FeO(OH) and (d) Ce(OH) <sub>3</sub> . ....	35
Figure 4: XRD spectra of (a) virgin tri-metal composite and (b) fluoride treated tri-metal composite. ....	36
Figure 5: SEM images of Fe-La-Ce tri-metallic composite. ....	38
Figure 6: SEM images for after fluoride adsorption of fluoride ions onto Fe-La-Ce tri-metal adsorbent. ....	38
Figure 7: The effect of contact time for fluoride ions adsorption onto Fe-La-Ce tri-metallic composite at 28 °C, pH 7.0, 0.1 g/L of adsorbent dose and 10 mg/L of initial fluoride concentration. ....	39
Figure 8: The effect of pH on fluoride adsorbed onto adsorbate at 28 °C, 0.1 g/L of adsorbent dose and 10 mg/L of initial fluoride concentration. ....	41
Figure 9: The point of zero charge ( $\Delta$ pH vs pH) on fluoride adsorbed onto adsorbate at 28 °C, 0.1 g/L of adsorbent dose and 10 mg/L of initial fluoride concentration. ....	41
Figure 10: The effect of initial fluoride concentration for fluoride ions adsorption process at 28 °C, pH 7.0 and 0.1 g/L of adsorbent dose. ....	42
Figure 11: Langmuir adsorption isotherm for the fluoride adsorption onto adsorbate at a) 301 K, b). 310 K, c). 320 K and d). 330 K. ....	45
Figure 12: Freundlich adsorption isotherm for the fluoride adsorption onto adsorbate at a) 300 K b) 310 K c) 320 K and d) 330 K. ....	46
Figure 13: Fluoride adsorption data fitted to pseudo-first order kinetics. ....	52
Figure 14: Fluoride adsorption data fitted to pseudo-second order kinetics. ....	52
Figure 15: Fluoride adsorption data fitted to intra-particle diffusion model. ....	53

Figure 16: Fluoride adsorption capacity of Fe-La-Ce tri-metal adsorbent in the presence of interfering anions at 28 °C, pH 7.0, 0.1 g/L of adsorbent dose and 10.76 mg/L of initial fluoride concentration.....	55
Figure 17: Variation of the adsorption capacity of TCIP on arsenate, chromate and fluorides with respect to different amounts of tri-metal percentages embedded at 28 °C and pH 7.0.....	60
Figure 18: The variation of the adsorption capacity of TCIP on arsenate, chromate and fluorides with respect to different cross-linker percentages at 28 °C and pH 7.0.....	61
Figure 19: FTIR spectra of before adsorption of arsenate, chromate and fluoride adsorbed on to TCIP. ....	63
Figure 20: FTIR spectra for after adsorption of arsenate on to TCIP.....	64
Figure 21: FTIR spectra for after adsorption of chromate on to TCIP.....	65
Figure 22: FTIR spectra for after adsorption of fluoride on to TCIP. ....	65
Figure 23: XRD spectra of pristine tri-metallic composite incorporated PAM (TCIP) .....	67
Figure 24: XRD spectra of after adsorption of arsenate onto pristine tri-metallic composite.....	67
Figure 25: XRD spectra of after adsorption of chromate onto pristine tri-metallic composite incorporated PAM. ....	68
Figure 26: XRD spectra of after adsorption of fluoride onto pristine tri-metallic composite incorporated PAM. ....	68
Figure 27: SEM image for PAM.....	69
Figure 28: SEM image for tri-metallic composite incorporated Polyacrylamide...70	70
Figure 29: SEM image of after adsorption of arsenate onto TCIP.....	70
Figure 30: SEM image of after adsorption of Chromate onto TCIP.....	70
Figure 31: SEM image of after adsorption of fluorides onto TCIP.....	71
Figure 32: The TGA and DTA spectra for TCIP.....	73
Figure 33: The DSC analysis OF TCIP. ....	74
Figure 34: The effect of contact time on arsenate (a), chromate (b) and fluoride (c) ions adsorption onto TCIP.....	75

Figure 35: The effect of pH on arsenate (a), chromate (b) and fluoride (c) ions adsorption onto TCIP.....	77
Figure 36: Langmuir adsorption isotherm for arsenate, chromate and fluoride adsorption onto TCIP at 28 °C.....	78
Figure 37: Freundlich isotherm model for arsenate, chromate and fluoride adsorption onto TCIP at 28°C.....	79
Figure 38: Freundlich isotherm model for arsenate, chromate and fluoride adsorption onto TCIP at 50 °C.....	79
Figure 39: The graphs of Pseudo first order rate model at 28 °C.....	84
Figure 40: The graphs of pseudo second order rate model at 28 °C.....	84
Figure 41: The graphs of and intra-particle diffusion model at 28 °C.....	85
Figure 42: FTIR spectra for PAA-co-PAM (black line), PAA-co-PAM-DETA (red line) and PAA-co-PAM-DETA-Urea (blue line).....	92
Figure 43: The FTIR spectra of after adsorption of Mn(II) on to PAA-co-PAM-DETA-Urea.....	93
Figure 44: The FTIR spectra of after adsorption of Ni(II) on to PAA-co-PAM-DETA-Urea.....	94
Figure 45: The FTIR spectra of after adsorption of Zn(II) on to PAA-co-PAM-DETA-Urea.....	94
Figure 46: The FTIR spectra of after adsorption of Co(II) on to PAA-co-PAM-DETA-Urea.....	95
Figure 47: The XRD spectra for PAA-co-PAM, PAA-co-PAM-DETA and PAA-co-PAM-DETA-Urea.....	96
Figure 48: The SEM images for pristine PAA-co-PAM-DETA-Urea.....	97
Figure 49: The SEM images for after adsorbed Mn(II) onto the PAA-co-PAM-DETA-Urea.....	97
Figure 50: The SEM images for after adsorbed Ni(II) onto the PAA-co-PAM-DETA-Urea.....	98
Figure 51: The SEM images for after adsorbed Zn(II) onto the PAA-co-PAM-DETA-Urea.....	98
Figure 52: The SEM images for after adsorbed Co(II) onto the PAA-co-PAM-DETA-Urea.....	99

Figure 53: TGA analysis of PAA-co-PAM. ....	101
Figure 54: TGA analysis of PAA-co-PAM-DETA.....	102
Figure 55: TGA analysis of PAA-co-PAM-DETA-Urea. ....	102
Figure 56: TGA analysis of after adsorption of Mn(II), onto the PAA-co-PAM-DETA-Urea.....	103
Figure 57: TGA analysis of after adsorption of Ni(II), onto the PAA-co-PAM-DETA-Urea.....	103
Figure 58: TGA analysis of after adsorption of Zn(II), onto the PAA-co-PAM-DETA-Urea.....	104
Figure 59: TGA analysis of after adsorption of Co(II), onto the PAA-co-PAM-DETA-Urea.....	105
Figure 60: The effect of contact time for Mn(II), Ni(II), Zn(II) and Co(II) ions adsorption onto PAA-co-PAM-DETA-Urea at 28 °C, pH 7.0, 0.1 g/L of adsorbent dose and 10 mg/L of initial metal ions concentration.....	106
Figure 61: Effect of pH for adsorption of Mn(II), Ni(II), Co(II) and Zn(II) onto the PAA-co-PAM-DETA-Urea. ....	107
Figure 62: Langmuir adsorption isotherms for Mn(II), Ni(II), Zn(II) and Co(II) removal at 28 °C.....	109
Figure 63: Langmuir adsorption isotherms for Mn(II), Ni(II), Zn(II) and Co(II) removal at 50 °C.....	110
Figure 64: Freundlich adsorption isotherms for Mn(II), Ni(II), Zn(II) and Co(II) removal at 28 °C.....	110
Figure 65: Freundlich adsorption isotherms for Mn(II), Ni(II), Zn(II) and Co(II) removal at 50 °C.....	111
Figure 66: Pseudo first order kinetics (initial ion concentration 10 mg/L, contact time 5 hours, sample dosage 1 g/L, temperature 28 °C, Stirring speed 200 rpm, initial pH 7).....	115
Figure 67: Pseudo second order kinetics (initial ion concentration 10 mg/L, contact time 5 hours, sample dosage 1 g/L, temperature 28 °C, Stirring speed 200 rpm, initial pH 7).....	115



Figure 68: Weber and Morris kinetic model. initial ion concentration 10 mg/L, contact time 5 hours, sample dosage 1 g/L, temperature 28 °C, Stirring speed 200 rpm, initial pH 7.....116

## Abbreviation

1/n	Heterogeneity factor
AAS	Atomic Adsorption Spectroscopy
C	Intercept of the plot of intra-particle diffusion model (mg/g)
C <sub>e</sub>	Equilibrium concentration of the adsorbate (mg/L)
C <sub>liquid</sub>	Liquid phase concentration (mg/L)
CMC	Carboxy Methyl Cellulose
C <sub>0</sub>	Initial concentration (mg/L)
C <sub>solid</sub>	Solid phase concentration at equilibrium (mg/L)
DETA	Diethylenetriamine
DSC	Differential Scanning Colorimetry
FTIR	Fourier transfer infrared spectroscopy
%In	Percentage of interference
k <sub>1</sub>	Rate constant for pseudo first order adsorption (min <sup>-1</sup> )
k <sub>2</sub>	Rate constant for pseudo first order adsorption (g/mg min)
K <sub>F</sub>	Freundlich constant (mg/g)
k <sub>id</sub>	Rate constant for intra-particle diffusion model (mg g <sup>-1</sup> min <sup>-1/2</sup> )
KPS	Potassium persulphate

$K_L$	Langmuir constant
$m$	Weight of the adsorbent (g)
NBIS	N,N'-methylene-bis-acrylamide
PAA	Polyacrylic acid
PAM	Polyacrylamide
$pH_{pzc}$	Zeta-Potential
PXRD	Power X-ray diffraction
$q_e$	Adsorption capacity at equilibrium (mg/g)
$q_{max}$	Maximum adsorption capacity (mg/g)
$q_t$	Adsorption capacity at time $t$ (mg/g)
$q_{wo}$	adsorption capacity of fluoride without interfering ions
$q_w$	adsorption capacity of fluoride with interfering ions
$R$	Universal gas constant ( $J\ mol^{-1}\ K^{-1}$ )
$R_L$	Dimensionless adsorption intensity
$T$	Absolute temperature (K)
$t$	Time (min)
$\Delta G_o$	Standard Gibbs free energy change
$\Delta H_o$	Standard enthalpy change
$\Delta S_o$	Standard entropy change
SEM	Scanning Electron Microscopy
SEM-EDS	SEM-Energy Dispersive Spectroscopy

TCIP	Trimetallic composite incorporated polyacrylamide
TEMED	Tetraethyl methylenediammine
TGA	Thermal Gravimetric Analysis
V	Volume
XRF	X-Ray Fluorescence

## Acknowledgment

I would first like to thank my supervisors Dr. Thilini D. Gunasekara, Dr. Dilru R. Ratnaweera and Dr. Asitha Cooray of the Department of Chemistry, Faculty of Applied Sciences, University of Sri Jayewardenepura with great respect and honor for the guidance and encouragement throughout my research project. The door to Dr. Thilini D. Gunasekara, Dr. Dilru R. Ratnaweera and Dr. Asitha Cooray were always open whenever I ran into a trouble spot or had a question about my research or writing. .

I would also like to extend my special thanks to the University Research Grants (ASP/01/RE/SCI/2015/31, ASP/06/RE/SCI/2014/06 and ASP/01/RE/SCI/2015/29 for financial support, Advanced Material Research Center, Instrument Centre at the Faculty of Applied Sciences, University of Sri Jayewardenepura have facilitated the instrumental analysis for this study and Department of Chemistry, University of Sri Jayewardenepura for providing required facilities to carry out my research successfully.

Finally, I must express my very profound gratitude to my parents to my loving husband and my friends (specially our research assistant family) for providing me with unfailing support and continuous encouragement throughout my years of study and through the process of researching and writing this thesis. This accomplishment would not have been possible without them.

Thank you.

S. K Thilini Thathsara

## ABSTRACT

### **POLYACRYLIC ACID-ACRYLAMIDE BASED WATER PURIFICATION SYSTEMS FOR REMOVAL OF SELECTED ANIONS AND CATIONS FROM AQUEOUS MEDIA**

Sarnis Kankanamge Thilini Thathsara

Access to safe drinking water has declined over the last decades in almost every part of the world. High consumption rates of metals and chemicals in industrial processes have resulted in generation of large quantities of effluents that contain high level of toxic heavy metals. In addition to heavy metals, high concentration of fluorides could also impart toxicity towards humans and animals.

In this endeavor, water purification systems were developed using modified polymeric hydrogels under two approaches. The first approach was to fabricate polyacrylamide (PAM)/metal composite for selective removal of fluoride ions, from aqueous media and the second approach was to modify acrylic acid (AA)/acrylamide (AM) hydrogel using strong metal complexing ligands with the expectation of removing heavy metals from water. Diethylenetriamine (DETA) are the identified ligand in this regards.

Developed novel tri-metal composite of Fe-La-Ce has shown a significant binding efficiency towards fluoride ions in the presence of the other competing anions. The removal efficiency of fluorides was 161.29 mg/g at 28 °C and pH 7.00. The amount of fluoride adsorbed onto adsorbate is highly pH dependent and the adsorption capacity of 303.03 mg/g was achieved around pH 4.

Further, fabricate Fe-La-Ce tri-metallic composite incorporated polyacrylamide hybrid material was used to remove arsenate and chromate from aqueous media. A novel tri-metal composite incorporated polyacrylamide (TCIP) has shown a significant binding efficiency towards arsenate, chromate and fluoride ions in the presence of the other competing anions. The maximum adsorption capacities ( $q_{max}$ ) of 43.85, 42.25 and 107.52 mg/g were achieved for arsenate, chromate and fluoride

respectively at 300 K and in pH 7. Arsenate, chromate and fluoride adsorbed onto adsorbate is highly pH dependent.

The second approach is to focus more on removing cationic form of the heavy metals from aqueous media. In the second approach, that have been used the crosslinker with urea, that's the novelty of this endeavor. At the second stage, PAA-co-PAM cross-linked DETA modified urea was fabricated. The effect of contact time on Co(II), Ni(II), Mn(II) and Zn(II) onto the PAA-co-PAM-DETA-Urea was established. The adsorption capacity of Ni(II) and Mn(II) were rapidly increased within initial 120 minutes. The adsorption capacity of Mn(II) reached equilibrium state within 60 minutes while Co(II) took 180 min to reach the equilibrium. The adsorption process of Mn(II), Ni(II), Co(II) and Zn(II) onto the PAA-co-PAM-DETA-Urea was highly depend on the pH of the medium. The calculated results clearly indicated that developed PAA-co-PAM-DETA-Urea has ability to regenerate and reuse. Therefore it is great advantage to use PAA-co-PAM-DETA-Urea for removal of Mn(II), Ni(II), Co(II) and Zn(II) from aqueous media.

Keywords: Isotherms, Kinetics, Fluoride, Arsenic, Chromate, Polyacrylamide, Polyacrylic acid, Diethylenetriamine.