

LB/DGN/55/2020

DCE 03/157

PHTHALIC ACID ESTERS IN URBAN WATERCOURSES OF COLOMBO AND THEIR TREATMENT

Ushetti Arachchi Appuhamilage Gimhani Danushika

(178059 P)

LIBRARY
UNIVERSITY OF MORATUWA, SRI LANKA
- MORATUWA

Degree Master of Science

Department of Civil Engineering

University of Moratuwa
Sri Lanka

G24 "19"
G24 (043)

DECEMBER 2019

University of Moratuwa



TH4245

TH 4245 + CD-ROM
is not working

TH 4245

DECLARATION

"I declare that this is my own work and this thesis does not incorporate without acknowledgement any material previously submitted for a Degree or Diploma in any other University or institute of higher learning and to the best of my knowledge and belief it does not contain any material previously published or written by another person except where the acknowledgement is made in the text.

Also, I hereby grant to University of Moratuwa the non-exclusive right to reproduce and distribute my thesis, in whole or in part in print, electronic or other medium. I retain the right to use this content in whole or part in future works (such as articles or books)."

Signature:

Date: 21/12/19

The above candidate has carried out research for the Masters thesis under my supervision.

Name of the supervisor: Prof. M.W. Jayaweera

Signature of the supervisor:

UOM Verified Signature

Date: 27

The above candidate has carried out research for the Masters thesis under my supervision.

Name of the co-supervisor: Prof. N.J.G.J Bandara

Signature of the supervisor:

UOM Verified Signature

Date: 27/12/19

The above candidate has carried out research for the Masters thesis under my supervision.

Name of the co-supervisor: Prof. J. M. A. Manatunge

Signature of the supervisor:

UOM Verified Signature

Date: 27/12/2019

Abstract

Urbanization of many cities with industrial, commercial, and residential areas in the world takes place at an unprecedented scale. Di-2 Ethylhexyl Phthalate (DEHP) is commonly used as a plasticizer in a number of industries which has become a precursor to cause DEHP contamination of watercourses through untreated or partially treated industrial wastewater effluents. Such contamination may result in bioaccumulation and bio-concentration in biota, so that it will adversely affect humans through the food chains. The presence of six PAEs (dimethyl phthalate (DMP), diethyl phthalate (DEP), di (n-butyl) phthalate (DBP), benzyl butyl phthalate (BBP), bis(2-ethylhexyl) phthalate (DEHP), and di(n-octyl) phthalate (DnOP)) in 22 shallow urban watercourses in Colombo and suburbs of Sri Lanka was investigated and the effect on fish community was analyzed. EPA 8061A method was used in analyzing PAE concentrations in samples and Gas Chromatography / Mass Spectrometer was used.

Titanium dioxide (TiO_2) and Modified Coal-derived Fly Ash (MCFA) were successfully synthesized and characterized using Fourier-Transform Infrared Spectroscopy, Environmental Scanning Electron Microscopy, and X-ray diffraction. Effectiveness and efficiency of TiO_2 and MCFA in the removal of DEHP from wastewaters was identified.

According to the results obtained, the average concentrations of DEP, DBP, BBP, and DEHP in all watercourses varied between 2.5–265.0, 1.0–32.0, 61–108, and 12–165 $\mu\text{g/L}$, respectively. DMP and DnOP values were below the limits of quantification (DMP-0.5 $\mu\text{g/L}$, DnOP-1.0 $\mu\text{g/L}$) for all watercourses. DEHP was the most abundant PAE in many watercourses. The significant factors affecting the ubiquitous presence of PAEs in watercourses are the inherent properties of each PAEs, the presence of industrial and household products with great potential for the migration of PAEs in the sub-catchments, and the quality of receiving water. The contamination levels of PAEs in most of the watercourses are alarmingly high, as evidenced by higher concentrations of DEHP and DBP than those of Canadian permissible levels for the protection of aquatic life (16 and 19 $\mu\text{g/L}$).

Isolated lakes which are not adjoining to urban industries, showed depleted adverse effects, most of the urban lakes were observed a significant potential for adverse effects on fish. Thus, the ecological risk of PAEs in urban watercourses in Sri Lankan environments should be considered.

TiO₂ nanoparticles were used to remove DEHP through photocatalysis. The photocatalysis with TiO₂ for the destruction of DEHP was found to be a promising technique in removing DEHP from industrial wastewaters. The most economical dosage of TiO₂ would be one gram and it needs to be photocatalysed for a period greater than 44 minutes for complying with the permissible level stipulated for DEHP (16 µg/L) for the protection of aquatic life. The cost of the photocatalysis with TiO₂ was around Rs.120 and the cost could be further reduced when the material (TiO₂) is reused for subsequent usage. Even TiO₂ was reused for five times, inherent properties for photocatalysis were not changed.

An initial level of 171 µg/L of DEHP was successfully removed with 98% efficiency by three grams of MCFA dosage and consequently, regenerated with NaOH twice for the effective use. The maximum monolayer adsorption capacity of MCFA was 63.6 µg/g of DEHP. MCFA is a potential candidate for the effective removal of DEHP from industrial wastewaters as its raw materials are readily available.

Key words: Adsorption, Phthalate Acid Esters, TiO₂, MCFA, Photocatalysis



ACKNOWLEDGEMENTS

First of all, I would like to extend my heartfelt gratitude to my supervisor Prof. M.W. Jayaweera, for giving me the opportunity to complete the research. Your guidance and encouragement given at every step of the way in the research helped me to achieve this a success. Your support was immense and it was an honor to designate you as my supervisor. I extremely appreciate the instructions given in experiments, writings and moral assistance given to complete this research.

I am very grateful to my co-supervisors Prof. N.J.G.J. Bandara, Prof. J.M.A. Manatunge, and Dr. W.B. Gunawardena for providing their guidance and support for the research project. Your advice and assistance given is very much appreciated.

I wish to express my sincere thanks to the laboratory staff of Environmental Engineering Laboratory, Department of Civil of Engineering, University of Moratuwa; Ms. Nilanthi Gunathilake, Mr. Justin and Mr. Dananjaya Bandara for the assistance received to conduct my research experiments successfully in the Environmental engineering laboratory. Additionally, I wish to thank Mr. Kasun Zoysa, analytical chemist, for providing his expertise and knowledge for the research, especially with the development of the GC/MS method for Phthalate Acid Ester analysis.

Furthermore, I wish to acknowledge the financial assistance given by the University Research Grant, University of Sri Jayewardenepura, Sri Lanka (Grant No: ASP/01/RE/SCI/2017/12) for the successful completion of this study.

I would like to thank head and the staff of the Department of Civil of Engineering, University of Moratuwa for assisting me in various ways to complete the research study. Additionally, I am grateful to Mr. M.A. Pubudu, Mr. M.T.M.R. Jayaweera and the staff of the Analytical Laboratory, Department of Materials Science and Engineering, University of Moratuwa for the help given in the characterization of laboratory synthesized nanomaterial.

I would like to thank Ms. Ayomi, Ms. Thilini, Ms. Shankani, Ms. Madhurangi, Ms. Hasini and Mr. Janith for their friendship, guidance, strength and assistance given in

the period of the research study. Thank you, Ms. Madhusa for being my research partner and helping me in various ways to complete the research and giving me the moral support for the completion. My special thanks go to Ms. Nipuni for helping me with the experimental work.

I am grateful to my family for being there for me, giving their unconditional love and support to fulfill my aims. Finally, I would like to thank my husband, Dulan Madurange for supporting, encouraging and understanding me in my quest.

TABLE OF CONTENT

DECLARATION.....	ii
ABSTRACT.....	iii
ACKNOWLEDGEMENT.....	v
TABLE OF CONTENTS.....	vii
LIST OF FIGURES.....	xi
LIST OF TABLES	xiii
LIST OF ABBREVIATIONS.....	xv
1. INTRODUCTION.....	1
1.1 Introduction.....	1
1.2 Approach.....	4
2. LITERATURE REVIEW.....	6
2.1 Phthalate Acid Esters (PAEs)	6
2.1.1. Chemical and physical properties of PAEs.....	7
2.1.2. PAEs Synthesis.....	8
2.1.3. Sources responsible for human exposure with PAEs.....	8
2.1.4. Toxicity of PAEs on animals	9
2.1.5. PAEs Leaching to the environment.....	11
2.2 PAE removal techniques.....	11
2.2.1. Physical/Chemical treatments.....	11
2.2.2. Biological treatments	13
2.2.3. Advanced oxidation processes.....	13
2.3 Nano technology for water purification.....	14

2.3.1.	Titanium dioxide (TiO ₂).....	16
2.3.1.1	TiO ₂ as a photocatalyst agent.....	17
2.3.2.	Zeolite.....	18
2.3.2.1.	Zeolite from Coal Fly Ash.....	19
3.	MATERIAL AND METHODS.....	20
3.1	Assess the presence of PAEs in selected urban watercourses.....	20
3.1.1.	Study area and Sampling locations.....	20
3.2	Sample collection.....	24
3.3	In-situ water quality analysis.....	25
3.4	Extraction and analysis of PAEs using Gas Chromatography / Mass Spectrometer (GC / MS).....	25
3.4.1.	Chemical and standards.....	25
3.4.2.	Extraction of PAEs.....	25
3.4.3.	GC / MS analysis.....	28
3.4.4.	Validation of the analytical method using GC / MS	29
3.4.5.	Statistical analysis.....	30
3.5	Analyze the ecological risk of PAEs on aquatic life being present in the watercourses.....	30
3.6	Evaluate the efficiency of different arrays of nanoparticles matrixes for removal of PAEs.....	31
3.6.1.	Titanium Dioxide (TiO ₂).....	31
3.6.1.1	Synthesis of TiO ₂	31
3.6.1.1	Characterization of Synthesized TiO ₂	31
3.6.1.3	Single- solute studies for removal of DEHP	35
3.6.1.3.1	DEHP removal by TiO ₂	35
3.6.1.4	Reusability of TiO ₂	35

3.6.2.	Modified Coal – derived Fly Ash (MCFA).....	35
3.6.2.1	Synthesis of MCFA.....	35
3.6.2.2	Charecerization of MCFA.....	35
3.6.2.3	Single- solute studies for removal of DEHP.....	37
3.6.1.3.1	DEHP removal by MCFA.....	37
3.6.2.4	Adsorption isotherms and Kinetic studies for MCFA.....	37
3.6.2.4.1	Adsorption isotherms.....	37
3.6.2.4.2	Kinetic Studies.....	39
3.6.2.5	Regeneration studies for MCFA.....	40
4.	RESULTS AND DISCUSSION.....	41
4.1	Occurrence of PAEs in watercourses.....	41
4.1.1	Comparison of PAE levels of our study with watercourses in different countries.....	42
4.1.2	The quality of the receiving water and inherent properties influencing the ubiquitous presence of PAEs.....	43
4.1.3	Multivariate analysis.....	44
4.1.4	Factors affecting the presence of PAEs in watercourses.....	45
4.1.5	Possible sources and their correlation to the distribution of PAEs.....	46
4.2	Ecological risk of PAEs on fish community being present in the urban watercourses.....	51
4.3	Evaluate the effectiveness and efficiency of different types of nanoparticles for removal of PAEs from industrial effluents.....	60
4.3.1	Characterization of Synthesized TiO ₂	60
4.3.1.1	XRD Analysis.....	60
4.3.1.2	ESEM – EDX Analysis.....	61
4.3.1.3	FT – IR Analysis.....	62

4.3.2 Removal of DEHP by TiO ₂	64
4.3.2.1 Effects of TiO ₂ dosage and contact time of the solution for removal of DEHP	64
4.3.3 Recycling ability of TiO ₂	67
4.3.4 Characterization of MCFA	68
4.3.1.1 XRD Analysis	68
4.3.1.2 ESEM – EDX Analysis	70
4.3.1.3 FT – IR Analysis	71
4.3.5 Removal of DEHP by MCFA	73
4.3.5.1 Effects of MCFA dosage and contact time of the solution for removal of DEHP	73
4.3.5.2 Adsorption isotherms for DEHP removal by MCFA	74
4.3.5.3 Kinetic studies for DEHP removal by MCFA	77
4.3.6 Regeneration studies of MCFA	79
4.3.6.1 ESEM – EDX Analysis	81
4.3.6.2 XRD Analysis	82
4.3.6.3 FT – IR Analysis	83
5. CONCLUSION AND RECOMMENDATION OF THE STUDY	84
5.1. Conclusion	84
5.2. Recommendations	85
REFERENCES	86

List of figures

Figure 2.1: General PAE Structure.....	7
Figure 2.2: Structures of main PAEs.....	7
Figure 2.3: Size comparison of nanoparticles with other large-sized materials.....	15
Figure 2.4: Proposed mechanism for DEHP removal through TiO ₂	17
Figure 2.5: Naturally occurring zeolite.....	18
Figure 3.1: Sampling locations.....	21
Figure 3.2: Sampling locations and the possible industries that has a possible potential for migration of PAEs from such catchment areas.....	22
Figure 3.3: Depth sampler.....	24
Figure 3.4: Schematic diagram of extraction procedure of PAEs.....	27
Figure 3.5: Titanium dioxide (TiO ₂) synthesis procedure.....	33
Figure 3.6: The experimental setup for the TiO ₂ batch studies on the mechanical shaker.....	34
Figure 3.7: Modified Coal-Derived Fly Ash (MCFA) synthesis procedure.....	36
Figure 3.8: Experimental setup for the MCFA batch experiments and kinetic studies.....	37
Figure 4.1: XRD Pattern of TiO ₂ (a) before (b) after photodegradation of DEHP.....	61
Figure 4.2: ESEM – EDX Pictures of TiO ₂ (a) before and (b) after photodegradation.....	62
Figure 4.3: FT – IR spectra of TiO ₂ (a) before and (b) after photodegradation of DEHP.....	63
Figure 4.4: FT – IR spectra of TiO ₂ (a) before and (b) after photodegradation of DEHP.....	63
Figure 4.5: DEHP Removal percentage with TiO ₂ dosage.....	64
Figure 4.6: (a) DEHP Concentration changes with TiO ₂ dosage (b) Cost analysis.....	65
Figure 4.7: FT – IR spectra of TiO ₂ after (1)1st Recycle (2)2nd Recycle (3)3rd Recycle (4)4th Recycle (5)5th Recycle times.....	67
Figure 4.8: XRD profile of TiO ₂ after (1)1 st Recycle (2)2 nd Recycle (3)3 rd Recycle (4)4 th Recycle (5)5 th Recycle times.....	68
Figure 4.9: XRD profile of MCFA (a) before and (b) after DEHP adsorption.....	69

Figure 4.10: (a) ESEM – EDX pictures of CFA (b) ESEM – EDX pictures of synthesized MCFA (c) ESEM – EDX pictures of MCFA after DEHP adsorption...	71
Figure 4.11: FT-IR spectra of MCFA (a) before and (b) after photodegradation.....	73
Figure 4.12: DEHP concentration changes with MCFA dosage.....	74
Figure 4.13: Adsorption batch experiments results in DEHP removal by MCFA.	74
Figure 4.14: Graphs for (a) Langmuir Isotherm Model (b) Dubinin-Radushkevich Isotherm Model (c) Tempkin Isotherm Model (d) Freundlich Isotherm Model.....	75
Figure 4.15: Langmuir isotherm model for DEHP removal by MCFA.....	76
Figure 4.16: Pseudo 1 st order kinetic model for DEHP removal by MCFA.....	77
Figure 4.17: Pseudo 2 nd order kinetic model for DEHP removal by MCFA.....	78
Figure 4.18: (a) The SEM Image of MCFA (b) The SEM Image of MCFA after three cycles of regeneration with NaOH (c) The SEM Image of MCFA after three cycles of regeneration with EDTA (d) The SEM Image of MCFA after three cycles of regeneration with HCl.....	81
Figure 4.19: The XRD Spectrum of MCFA (b) The XRD Spectrum of MCFA after three cycles of regeneration with NaOH (c) The XRD Spectrum of MCFA after three cycles of regeneration with EDTA (d) The XRD Spectrum of MCFA after three cycles of regeneration with HCl.....	82
Figure 4.20: The FT – IR Spectrum of MCFA (b) The XRD Spectrum of MCFA after three cycles of regeneration with NaOH (c) The XRD Spectrum of MCFA after three cycles of regeneration with EDTA (d) The XRD Spectrum of MCFA after three cycles of regeneration with HCl.....	83

List of Tables

Table 2.1: General properties of main PAEs.....	8
Table 2.2: Previous studies on physical/chemical treatments for the removal of PAEs.....	12
Table 2.3: Previous studies on Biological treatments for the removal of PAEs.....	13
Table 2.4: Previous studies on Advanced oxidation processes for the removal of PAEs.....	14
Table 2.5: Nanomaterial applications in water treatment.....	15
Table 3.1: Detailed description of sampling locations	20
Table 3.2: Distribution of industries that have a potential for PAEs migration in sub-catchments of sampling locations.....	23
Table 3.3: Validation parameters of the optimized GC/MS methodology for PAE quantification.....	29
Table 3.4: Acute toxicity (L (E) C50) used for the risk assessment for Eco communities.....	30
Table 4.1: PAE concentrations in sampling locations.....	41
Table 4.2: Comparison of PAE levels of our study with other watercourses in different countries.....	42
Table 4.3: Sampling locations and in-situ parameters measured.....	43
Table 4.4: Multivariate analysis for PAEs with influencing factors.....	44
Table 4.5: Typical percentages with different PAEs in industrial final products.....	47
Table 4.6: RQ Values (Fish community) for DMP, DEP, DBP, BBP, DEHP and DnOP and the sum of RQs for each location.....	51
Table 4.7: RQ Values (Crustacea community) for DMP, DEP, DBP, BBP, DEHP and DnOP and the sum of RQs for each location.....	52
Table 4.8: RQ Values (Insect community) for DMP, DEP, DBP, BBP, DEHP and DnOP and the sum of RQs for each location.....	54
Table 4.9: RQ Values (Oligocheata community) for DMP, DEP, DBP, BBP, DEHP and DnOP and the sum of RQs for each location.....	55
Table 4.10: RQ Values (Microorganism community) for DMP, DEP, DBP, BBP, DEHP and DnOP and the sum of RQs for each location.....	52

Table 4.11: RQ Values (Algae community) for DMP, DEP, DBP, BBP, DEHP and DnOP and the sum of RQs for each location.....	57
Table 4.12: RQ Values (invertebrate community) for DMP, DEP, DBP, BBP, DEHP and DnOP and the sum of RQs for each location.....	58
Table 4.13: Cost calculation for the synthesis of 1 gram of TiO ₂	66
Table 4.14: Cost calculation for the catalyst reaction of TiO ₂	66
Table 4.15: characteristic peaks of Zeolite.....	72
Table 4.16: Peaks obtained after DEHP adsorption	72
Table 4.17: Summary of R ² values of the adsorption isotherm models.....	76
Table 4.18: The data fitted to the Langmuir isotherm model.....	76
Table 4.19: Gibbs free energy of the adsorption reaction.....	78
Table 4.20: Cost calculation for the synthesis of one gram of MCFA.....	79
Table 4.21: The regeneration of MCFA using NaOH, EDTA and HCl.....	80
Table 4.22: The regeneration of MCFA using NaOH, EDTA and HCl.....	80

LIST OF ABBREVIATIONS

Abbreviation	Description
PAEs	Phthalic Acid Esters
DEHP	Bis(2-ethylhexyl) phthalate
DBP	Di(n-butyl) phthalate
DMP	Dimethyl phthalate
DEP	Diethyl phthalate
BBP	Benzyl butyl phthalate
DnOP	Di(n-octyl) phthalate
USEPA	United States Environmental Protection Agency
MCL	Maximum Contaminant Level
PVC	Polyvinyl Chloride
PET	Polyethylene terephthalate
TiO ₂	Titanium dioxide
MCFA	Modified Coal-derived Fly Ash
DiBP	Diisobutyl phthalate
CFA	Coal Fly Ash
GC/MS	Gas Chromatography/Mass Spectrometry
CH ₂ Cl ₂	Dichloromethane
FT-IR	Fourier Transform – Infrared Spectroscopy
XRD	X-Ray Diffraction Spectroscopy
ESEM	Environmental Scanning Electron Microscopy
EDX	Energy-Dispersive X-ray Spectroscopy

LOD	Limit of Detection
LOQ	Limit of Quantification
RSD	Relative Standard Deviation
RQ	Risk Quotient
MEC	Measured Environmental Concentration
PNEC	Predicted No Effect Concentration
DI	Deionized
C	Carbon
Ti	Titanium
O	Oxygen
UV	Ultraviolet