PHTHALIC ACID ESTERS IN URBAN WATERCOURSES OF COLOMBO AND THEIR TREATMENT

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DECLARATION

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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 µg/L, respectively. DMP and DnOP values were below the limits of quantification (DMP-0.5 µg/L, DnOP-1.0 µg/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 µg/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.

TiO_2 nanoparticles were used to remove DEHP through photocatalysis. The photocatalysis with TiO_2 for the destruction of DEHP was found to be a promising technique in removing DEHP from industrial wastewaters. The most economical dosage of TiO_2 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 TiO_2 was around Rs.120 and the cost could be further reduced when the material (TiO_2) is reused for subsequent usage. Even TiO_2 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, TiO_2, MCFA, Photocatalysis

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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_2Cl_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

1. INTRODUCTION

1.1 Introduction

Rapid industrialization and urbanization release several types of chemicals such as Phthalic Acid Esters (PAEs), contaminating air, water, and soil causing health hazards for humans and animals. DEHP is the most abundant man-made industrial chemicals produced in large quantities for nearly 40 years (Fromme et al., 2002), and are mainly used as plasticizers in manufacturing of various plastics and polymers. The existence of PAEs in the environment and their propensity to bio concentrate in animal fat is a prime concern (Jobling et al., 1995). With population growth and rising number of industries that use PAEs, aquatic and atmospheric environments are enriched with PAEs of which bis (2-ethylhexyl) phthalate (DEHP) and di(n-butyl) phthalate (DBP) are profoundly ubiquitous at varying levels in many countries (Peijnenburg & Struijs, 2005). Humans are constantly exposed through numerous pathways, including food, air, water, soil, cosmetics, automobile interior, pharmaceutical products, and medical devices (Pant et al., 2011).

PAEs are chemical compounds that added frequently to plastic and polyvinyl chloride manufacturing industries as a plasticizer to enhance beneficiary attributes of the final products such as softness (Huang et al., 2013), flexibility (Kaneco et al., 2006; Jouni et al., 2008), durability and longevity (Wu et al., 2012), and workability (Kaneco et al., 2006). Also, PAEs are utilized in the production process of pharmaceuticals, cosmetics, personal-care products (Wallner et al., 2016), insect repellants, household-hardware including wire coverings (Ito et al., 2007), cables, tubes, hoses, lubricants, stationery products (such as inks, paints), toys (Wen et al., 2018), and pesticides (Roslev et al., 2007). Among all PAEs, six compounds, namely dimethyl phthalate (DMP), diethyl phthalate (DEP), DBP, benzyl butyl phthalate (BBP), DEHP, and di(n-octyl) phthalate (DnOP) have been included in the priority pollutant list published by Title 40 of the Code of Federal Regulations and are a set of PAEs that are regulated, for which the analytical test methods have been developed. The United States Environmental Protection Agency (US EPA) National Primary Drinking Water Regulations stipulate the Maximum Contaminant Level (MCL) for DEHP to be 6 μg/L (USEPA 2009) and the national standards for drinking water quality in China stipulates the maximum level of DEHP to be 8 μg/L (Ministry of Health of China 2006). Canadian water quality guidelines specify the levels of DEHP and DBP to be 16 and 19 μg/L, respectively, for the protection of aquatic life/aquatic ecosystem (CCME 1999).

Annual global production of PAEs, for multitude uses in 2013, has been reported to be over five million metric tons (Huang et al., 2013). PAEs, often bound to a polymer by dipole interaction through hydrogen bonding and van der Waals forces which are weakly bonded, resulting in easy detachment, may subsequently transport through leaching, migration or evaporation processes (Wittassek et al., 2011; Zia et al., 2013; Wu et al., 2015; Yin et al., 2014; Johns et al., 2015; Mittermeier et al., 2016; Wei et al., 2016). These transport phenomena lead to the ubiquitous presence of PAEs in the environment resulting in an increased human exposure via pathways such as inhalation, ingestion, and through the dermal absorption (Wittassek, et al., 2011; Wu et al., 2015). Some of the PAEs such as DEHP and DnOP weak in biodegradability and hence, subject to bioaccumulation with a likelihood of biomagnification in the aquatic environment, which could pose a high risk of human exposure (Chatterjee and Karlovsky, 2010; Sun and Liu, 2017).

PAEs are reported to be a group of emerging organic contaminants, which are ubiquitously present in the aquatic environment worldwide (Paluselli et al., 2018). It has been shown that several PAEs are endocrine disruptors because of the ability of such PAEs to mimic or block endogenous hormones (Cespedes et al., 2004; Shen et al., 2009), and even they cause carcinogenic and teratogenic effects (Ventrice et al., 2013). Toxicological evaluations have indicated that PAEs with lower molecular weight such as DEP is irritable to eyes, nose, and throat (Sekizawa et al., 2003). Other PAEs with higher molecular weights, such as DEHP and BBP, are suspected carcinogens, as well as toxic to the liver, kidneys, and reproductive organs (Keresztes et al., 2013). Ito and co-workers (2007) have manifested, that direct ingestion of food containing 0.05% DEHP would increase the risk of liver tumors in rats. DEP at an oral dose of 0.57 mg/kg/day has shown a significant weight gain of the liver in rats (Pereira et al., 2006). Moreover, Sun and co-workers (2017) have observed the induced developmental toxicology and dysfunction of developing hearts in Zebrafish embryos by BBP at oral concentrations of 0.6 and 1.2 mg/L. Low testicular testosterone levels of male Sprague Dawley rats have been observed with the exposure to DBP having doses of 50 and 250 mg/kg/day for periods of 30 and 90 days (Zheng et al., 2010).

In this study, the presence of PAEs in watercourses in Colombo was monitored, selecting six PAEs (DMP, DEP, DBP, BBP, DEHP, DnOP) that are reported to be ubiquitously present in aquatic environments (Wittassek et al., 2011; Sun & Liu 2017). Manufacturing industries of polyethylene, paint, plastic, polyvinyl chloride (PVC), polyethylene terephthalate (PET) bottles, children's toys, packaging industries of pesticides, pharmaceuticals, cosmetics and personal care products, apparel industry, and distributors of household-hardware and stationery products mainly house in Colombo and suburbs of Sri Lanka. PAEs in the aquatic environment are attributed to haphazard and ad hoc discharges of untreated or partially treated wastewater from industries mentioned above and indiscriminate dumping of products containing PAEs by households. Furthermore, the introduction of legislation in Sri Lanka in 2017 banned the open burning of plastics, and the use of certain types of polythene without establishing environmentally safe disposal techniques, prompted people to engage in the haphazard disposal of used polythene products in their neighbourhood, thus aggravating the ubiquitous presence of PAEs, especially in the aquatic environment. Moreover, the addition of weight percentages of PAEs to plastic products has not yet been regulated in Sri Lanka, and an estimate of PAEs in the aquatic environment has not been figured out. Although numerous news reports appeared recently in the mass-media on PAEs, no comprehensive study has been undertaken to get an insight into the distribution of PAEs in shallow urban watercourses in Colombo and its suburbs.

However, studies on the presence of PAEs in surface water and effective methods of removal of PAEs have not been addressed in Sri Lanka yet and available water treatment technologies do not provide an appropriate solution to remove these toxic compounds. According to the literature, Nano materials express higher pollutant removal efficiency with a low economic and environmental cost. Nano materials have inherent characteristics such as high reactivity, high surface energy due to large specific surface area, more reactive surface sites, high reaction rate (Chung and chen, 2008). Hence, nanomaterials seem to be the promising technique in removal PAEs.

Therefore, the main objective of the present research study is to investigate the impact on aquatic life in urban watercourses and ensure safety on the water requirement in the long run.

To achieve the main objective below specific objectives were set;

1. Assess the presence of PAEs in selected urban watercourses.
2. Analyze the ecological risk of PAEs on aquatic life being present in the urban watercourses.
3. Evaluate the effectiveness and efficiency of different types of nanoparticles for removal of PAEs from industrial effluents.

1.2 Approach

Chapter 1 presents the introduction to the research study with narrative on PAEs, possible pathways responsible for the presence of PAEs in watercourses, the effect of PAEs on aquatic life as a toxic substance in urban watercourses and their removal. Further, Chapter 1 contains the main objective and specific objectives of the research study.

Chapter 2 delivers a summary of literature available on PAEs, their presence and possible reasons for availability in shallow watercourses, possible degradation mechanisms and microbial degradation of PAEs. Additionally, the effect of PAEs on human health in urban areas has explained. Finally, the techniques for the removal of available PAEs from the water and suitability of using Nano materials for the removal of PAEs from water has been deliberated.

Chapter 3 describes the materials and methods used in this research project. Experimental procedures followed to achieve each objective were described in detail. Specially, experimental setups for each objective, methods followed to obtain chemical characteristics of water are illustrated. Further, analytical methods used for PAEs extraction and analysis in water, removal using nanomaterials and their effectiveness and efficiency were discussed.

Chapter 4 presents the results and discussion of each objective considered in the research project. PAEs presence in surface water and urban watercourses were discussed. The results of the first objective showed that different types of PAEs are present in the urban watercourses in different concentrations as the presents of different PAE using industries around each and every watercourse. In the 2nd objective, risk associated with aquatic ecosystems due to PAEs was calculated and it indicates a significant potential for adverse effects. Removal of PAEs was done with Titanium dioxide (TiO_2) and Modified Coal-derived Fly Ash (MCFA) nanoparticals. DHEP rapidly subjected to photocalatysis with TiO_2 and Adsorbed on to MCFA nanomaterials.

Chapter 5 concludes the major findings of each objective and recommendations for future studies.

2. LITERATURE REVIEW

2.1 Phthalate Acid Esters (PAEs)

Rapid industrialization increases use of PAEs, generally recognized as phthalates, are a class of synthetic organic chemical compounds used as a plasticizer with a wide range of consumer uses and industrial applications (Swan, 2008). Length of ester chains resolves the industrial uses of different PAEs available in the market (Schettler, 2006). Since 1930, phthalates have been widely used in the manufacturing process of polymers and numerous generally used commercial products (Latini, 2005). Higher-molecular-weight PAEs were widely used as plasticizers in the industry as they were added to the polymeric materials with the purposes of improving softness, elasticity, durability, and ease of processing of the product (Meeker et al., 2009; Schettler, 2006).

PAEs increase the polymer flexibility through separating the polymer chains and decreasing the intermolecular frictional forces, which are the main aim of adding plasticizers with polymers. They embed within the polymer chains and tend to increase the free volume of the polymer and reduce glass transition temperatures of producing polymers (Wypych, 2004). PVC final products containing up to 40% of PAEs as PAEs are mainly used in PVCs (Koch & Calafat, 2009, ATSDR, 2002). Plasticized PVC was used in the manufacture of different products such as packaging materials, toys, home furnishings, construction materials, car undercoating, insulators, wires, and cables. In addition to those products, it also found in some medical devices such as blood transfusion bags and intravenous tubes, and in many industrial apparatuses such as conveyor belts and plastic hoses. PAEs also be used as plasticizers in polymers such as rubbers, styrenes, epoxy resins, and cellulose acetate plastics (Swan, 2008; ATSDR, 2002 and 2001). Currently, PAEs are the most commonly used plasticizers that responsible for 80% of the global plasticizers used (Guo & Kannan, 2012).

PAEs with low molecular weight are used as denaturants and solvents to dissolve cosmetic ingredients and keep color and scents in different personal care products such as fragrances and nail polishes. Further, in lacquers, printing inks, paints, and insect repellent to increase their surface adhesion. They are also found in the coating of pharmaceutical products (Meeker et al., 2009; Hauser & Calafat, 2004; ATSDR, 1995). Annually, nearly than 12 billion pounds of PAEs were synthesized worldwide and that DEHP constitutes approximately 50% of all PAEs (ATSDR, 2002).

2.1.1 Chemical and physical properties of PAEs

The different types of PAEs share a similar basic chemical structure, but diverge in the length and ester side chains. So, the physical, chemical and biological properties will not fluctuate highly. Most PAEs are colorless or slightly yellowish odorless oily liquids. PAEs are lipophilic in nature and have high solubility in organic solvents (EPA, 2012).

The common PAEs used in industry can be listed as DMP, DEP, DBP, BBP, DEHP, DnOP. These compounds have been also categorized as main priority pollutants by USEPA.

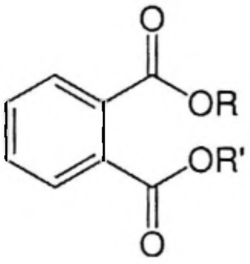
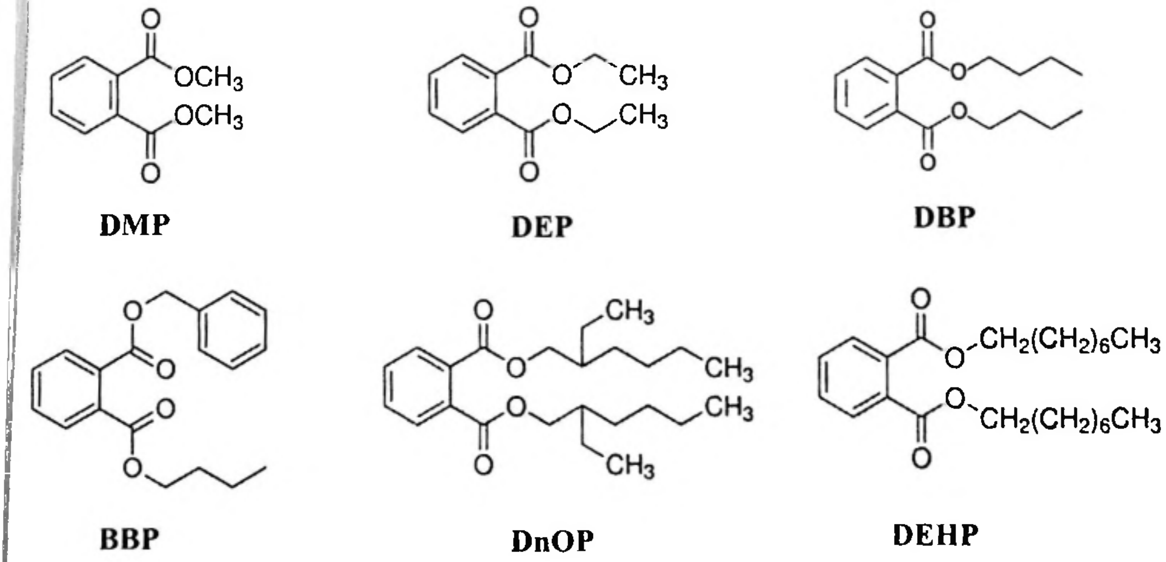


Figure 2.1: General PAE structure



DMP **DEP** **DBP**

BBP **DnOP** **DEHP**

Figure 2.2: Structures of main PAEs

Table 2.1: General properties of main PAEs

Common Name	**Acronym**	**CAS number**	**M.M. (g mol^{-1})**	**B.P. (°C)**	**Water Solubility (mg/L, 25 °C)**
Di Methyl Phthalate	DMP	131-11-3	194.2	282	5220
Di Ethyl Phthalate	DEP	84-66-2	222.2	295	591
Di Butyl Phthalate	DBP	84-74-2	278.3	340	9.9
Butyl Benzyl Phthalate	BBP	85-68-7	312.4	370	3.8
Di (2-ethylhexyl) Phthalate	DEHP	117-81-7	390.6	384	0.0025
Di-n-Octyl Phthalate	DnOP	117-84-0	390.6	390	0.0025

CAS- Chemical Abstracts Agency; M.M. - Molar Mass; B. P. -Boiling point

2.1.2 PAEs Synthesis

PAEs produced as a result of esterification of phthalic anhydride with alcohols which contains desired carbon chain lengths in a closed system through two successive steps. First reaction step is rapid and irreversible. It gives monoesters by alcoholysis of the phthalic acid. Then the second step involves the formation of di-ester in the presence of an acid catalyst at temperatures in the range of 140-165°C. This can happen in the presence of atmospheric catalysts at temperatures range of 200-250°C. Excess alcohol of the solution is recovered and recycled throughout the process. Final resulting PAE was purified by vacuum distillation or activated charcoal (Skrzypek et al., 2008).

2.1.3 Sources responsible for human exposure with PAEs

Phthalates containing consumer products result in human exposure to PAEs through their direct contact, use or indirect contact through leaching and migration. Humans are subject to PAEs at the times of food consumption, exposure to the environment such as air, dust, and soil, and during the manufacturing process of PAE or PAE containing products in large scale (Wormuth et al., 2006). Ingestion, inhalation and dermal absorption (lesser extent) are the main pathways which PAE enter into the human body.

As reported in hospitalized patients, Parenteral PAEs exposure from medical equipment's during treatment facilities (Swan, 2008; Wormuth et al., 2006). According to the past studies, different sources of total phthalate exposure to the general population have been examined and the findings showed that food is dominant in phthalates. In the case of DEHP exposure food is predominant and critical (Schecter et al., 2013; Rudel et al., 2011).

Another significant source is personal care products and indoor air as exposure to low molecular weight PAEs, particularly DMP and DEP. Mouthing of toys and other PAE objects are other important sources for kids' exposure with phthalates (Wittassek et al., 2011, Schettler, 2006). Study of Wormuth et al. (2006) estimated that the average contribution of dietary and non-dietary sources in PAEs exposure using European consumers. As non-dietary sources, air, dust, personal care products, soil, paint sprays, gloves, and mouthing of plastic toys for infants were selected. DEHP, Diisobutul phthalate (DiBP), and DBP indicate that it is the major source of food which is accounted for 55- 95 % of the total exposure. In addition, the contribution of food for the exposure of DMP and DEP was estimated as it to be less than 20 % and indoor air and personal care products seem to be the main exposure sources. The study suggested that the mouthing behavior of plastic objects by infants and small children experienced higher PAE daily exposures than adults.

2.1.4 Toxicity of PAEs on animals

The ubiquitous presence and extensive human exposure of PAEs in the environment have become the subject of various studies to analyze potential health effects. Laboratory animals, in-vitro and human epidemiological researches (Meeker et al., 2009; Hauser and Calaft, 2005; Latini, 2005) were used to analyze the impacts and risk engaged with PAEs. Various expert panels in Europe, Canada, Australia and US such as the US EPA, Australian and Canadian Health Authorities, International

Agency for Research on cancer, the European Food Safety Authority, the U.S Food and Drug Administration (EPA, 2012; Heudorf et al., 2007; Mikula et al., 2005).

Chronic phthalates exposure causes adverse health effects on kidney, liver, respiratory and endocrine systems in a serious manner (Bornehag et al., 2004, Hoppin et al., 2004). Also, Phthalates cause hepatotoxic effects such as liver enlargement, disturbance in liver function and enzyme activity, and formation of liver tumors. These health effect identifications have been conducted using rodents as experimental samples. DEHP has classified as class 2B probable carcinogen and declared that there is satisfactory evidence in experimental rodents by The International Agency for Research on Cancer (IARC). But the evidence in humans for DEHP carcinogenicity is inadequate (Erkekoglu et al., 2014).

The main toxicological concerns of PAEs are endocrine disrupting potency as it affects the endocrine system in various manners. PAEs subsequently cause reproductive and developmental health problems in the human body by interfering with the normal functioning of the hormonal system. Further, phthalates show weak estrogenic activities in the body. Studies were done using Animal and *in-vitro* verified that phthalates have anti-androgenic effects and alteration of testosterone synthesis. The potential risk of PAE interferes with thyroid functions and effect on anti-thyroid effects, according to the studies conducted by Hauser et al., (2007) and Lee and Koo, (2007).

During the pregnancy period, exposure to high doses of PAEs can result in a high incidence of abortion and fetus malformations, and skeletal deformations (Swan, 2008). Other than that, PAEs to be cross the placenta and were found in breast milk resulting in serious fetal reproductive malformations, such as undescended testes, birth defects and defects in the penis and impaired sperms production which called as testicular dysgenesis syndrome (Main et al., 2006, Latini et al., 2003). While human studies conducted are limited with different constraints, epidemiological studies exhibits to show correlations between exposure to phthalate and adverse reproductive outcomes, listed as sexual hormones disorder, decrease anogenital distance in male children, infertility, decrease sperms quality and count, and premature breast development (Hauser et al., 2007, Zhang et al., 2006, Latini et al., 2003). According to the studies, altering thyroid hormone levels, asthma and respiratory allergic symptoms, increased abdominal obesity, and insulin resistance are associated with exposure to phthalates (Meeker et al., 2007, Stahlhut et al., 2007, Hoppin et al., 2004).

2.1.5 PAEs leaching to the environment

PAEs are not chemically bound to the polymer matrix and they are just bonded with weak forces with the polymer matrix. Because of the presence of weak bindings between the polymer matrix and PAEs, they simply leach out from matrixes during their use or after their disposed (Cao, 2010, Wormuth et al., 2006). Other than PAEs migration from direct products, PAEs are able to move into the environment through leachate from landfills, incineration practices of waste plastics or their release during the production process (Huang et al., 2013). Consequently, the general population is increasing and the wide scale of production and processing in increasing. In these circumstances, use of products containing PAEs has resulted in the PAE dissemination in products and their continuous migration and presence in the external environment (Huang et al., 2013; Wormuth et al., 2006).

2.2 PAEs Removal techniques

According to the literature, with the contaminant sources large amounts of PAEs were leached out from municipal landfill sites and contaminated with nearby watercourses (Bauer et al., 1998) while PAE concentrations fluctuate in the range from 10 to 300 mg/L in nearby rivers where a number of chemical plants, industries using PAEs in their production chains. There are numerous removal techniques for PAEs in water addressed by past studies. They can be classified into three groups called, physical or chemical treatments, biological treatments, and advanced oxidation processes.

2.2.1 Physical/Chemical treatments

Phthalic acid esters and dissolved organic matter in landfill leachate can remove the complex flocculation process using ferric chloride, aluminum sulfate, and poly aluminum chloride as coagulants (Zhang & Wang, 2009). There is a feasibility to remove PAEs from fresh and partially stabilized landfill leachate through coagulation and flocculation process (Zheng et al., 2009). Results of the study evaluate that less than 30% PAEs in fresh leachate has been removed. Another efficient PAE removing method is adsorption such as activated carbon, which is one of the ancient water treatment techniques used. Adsorption of landfill leachate, Industrial wastewater in to granular or powder activated carbon shows a great reduction in PAEs as a most effective and reliable physicochemical non-destructive technique (Fettig et al., 1996; Kargi & Pamukoglu, 2004; Zamora et al., 2000). Activated carbon has effective adsorption with the large surface area and chemical structure (Bautista-Toledo et al., 2008; Méndez-Díaz et al., 2010).

Solution pH has a significant role in the adsorption as it determines the charge density of the adsorbent (Radovic et al., 2001) and the chemical form of adsorbate. (Rivera-Utrilla et al., 2009). Chitosan, manganese oxides, clays, multi-walled carbon nanotubes, polymeric resins are also employed to remove PAEs from aqueous solutions. Méndez-Díaz, et al., (2012) reported that the activated carbon comprises phenolic groups, which contribute the affinity to adsorb PAEs. Table 2.2 summarizes a limited number of studies in the removal of PAEs through physical/chemical treatments.

Table 2.2: Previous studies on physical/chemical treatments for the removal of PAEs

Type of treatment	**PAEs**	**Removing ratio**	**References**
Activated carbon (Adsorption)	DEP	82.6–53.2%	Wang et al., 1997
Complexation-flocculation (CF)	DEHP	Fresh Leachate <30% Partial Leachate =50%	Zheng et al., 2009
Adsorption on chitosan beads	**PAEs** DBP, DEHP, DMP **MPEs**: MBP, MMP, MEHP **PA**	PA >PAEs >MPEs	Salim et al., 2010

MPEs: Phthalate monoesters; PA: Ortho Phthalic acid

2.2.2 Biological treatments

Studies on the environmental fate of PAEs investigated that main degradation mechanism is the microbial activities at degradation in aquatic systems such as surface water (Junesonet al., 2001; Sello et al., 2004). PAEs with short ester hydrocarbon chains are rapidly biodegraded and mineralized while with long ester chains are considerably slow (Ejlertsson et al., 1997; Jianlong et al., 2000). Bioremediation gives favorable by-products such as CO_2 and H_2O that are inoffensive to the environment (Wu et al., 2008). But, PAEs degraded by microorganisms is a long time-consuming process that is not readily biodegrading long-chain PAEs (Xu et al., 2005). Table 2.3 summarizes limited studies on the removal of PAEs through biological treatments.

Table 2.3: Previous studies on Biological treatment for the removal of PAEs

Type of treatment	PAEs	Removing ratio	References
Microbial degradation under anaerobic digestion of sludge.	DMP DBP DOP	DMP>90% (4 days) DBP>90% (7 days) DOP< 20% (10 days)	Jianlong et al., 2000
Biodegradation by Pseudomonas Fluorescence	DMP, DEP DIBP, DnBP DnOP DEHP	99% DMP, DEP, DnBP, DIBP 30% DnOP 20% DEHP (3 days)	Zeng et al., 2004
Biodegradation by anaerobic digester sludge	DMP	100 % (12 days)	Wu et al., 2008
Biotic degradation under natural sunlight irradiation	DEHP	20 %	Lertsirisopon et al., 2009

2.2.3 Advanced oxidation processes

Organic compounds that difficult to degrade biologically in to simpler by-products can be detached through advanced oxidation processes easily. Removing mechanism comprises the generation of hydroxyl and other free radicals (Metcalf and Eddy, 2003) that enhance the degradation process, achieving the complete conversion of the target pollutant species to CO_2, H_2O and mineral acids (Joseph et al., 2009).

Removal of PAEs ranged from 0.0 – 99.99 %, which is depending on the type of PAE and chemical/physical characteristics of them. Some treatments, as for example, direct UV radiation and single H_2O_2, didn't show PAE degradation in single solutions. But in combined UV/ H_2O_2 treatment proven to reduce the initial concentration by 98.6 % after 60 minutes under UV radiation of 133.9 mW/cm^2 and H_2O_2 dose of 20 mg/L for DEP (Xu, et al., 2007). For DMP similar results were found (Xu, et al., 2009).

According to results yielded by a mathematical model, Wolfe et al. (1980) considered photolysis to be the primary PAE degradation pathway in oligotrophic lakes. Table 2.4 summarizes some PAEs oxidation by advanced oxidation process technologies.

Table 2.4: Previous studies on advanced oxidation processes for the removal of PAEs

Type of treatment	**PAEs**	**Removing ratio**	**References**
O_3/H_2O_2	DMP, DEP DBP	40–80%	Wen et al., 2011
$O_3/UV/TiO_2$ supported in γ-Al_2O_3	DMP	90–100%	Chen et al., 2011
O_3/UV	DEP	>95%	Oh et al., 2006

2.3 Nanotechnology for water purification

There is a mounting demand for clean water globally as freshwater sources are depleting with several industry effluents and municipal wastes. Different technologies have been developed in removal mechanisms but nanotechnology has proved to be one of the advanced ways for wastewater treatment nowadays. Development of research has made it possible to invent economically feasible and environmentally stable technologies using nanomaterials for effectively treating wastewater to meet water quality standards. Nanotechnology uses materials of sizes smaller than 100nm in at least one dimension and they are categorized in an initial position in the dimensional chart in Figure 2.2 (Masciangioli& Shang, 2003; Eijkel& Berg, 2005).

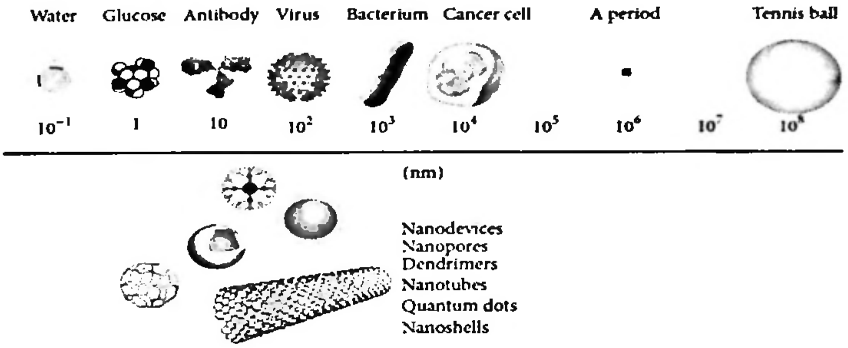


Figure 2.3: Size comparison of nanoparticle with other large-sized material
Source: (Abdel daiem et al., 2012)

At this dimensional scale, material possesses novel and significantly changed the physical, chemical, and biological properties mainly due to their structure, higher surface area-to-volume ratio offering treatment and remediation, sensing and detection, and pollution prevention. These unique properties of nanomaterials, for example, high reactivity and strong sorption, are explored for application in wastewater treatment based on their functions in unit operations.

The higher surface area to volume ratio of nanomaterials enhances the reactivity with environmental contaminants. In the context of treatment and remediation, nanotechnology has the potential to provide both water quality and quantity in the long run through the use of, for example, membranes enabling water reuse, desalination etc.

Table 2.5: Nanomaterial applications in water treatment

Applications	**Some of the novel properties**
Adsorption	High specific surface area and assessable adsorption sites, selective and more adsorption sites, short intraparticle diffusion distance, tunable surface chemistry, easy reuse.

Disinfection	Strong antimicrobial activity, low toxicity, and cost, high chemical stability ease of use.
Photocatalysis	Photocatalytic activity in the solar spectrum, low human toxicity, high stability and selectivity, low cost.
Membranes	Strong antimicrobial activity, hydrophilicity low toxicity to humans, high mechanical and chemical stability, high permeability and selectivity, photocatalytic activity.

2.3.1 Titanium dioxide

With properties such as electronic and optical properties, TiO_2 can be utilized in several fields. They are used in industries such as solar cell production, photocatalyst reactions, sensor manufacturing, and self-cleaning.

In electrochemistry, at acidic and basic media, TiO_2 plays a key role as the conductivity and stability in basic and acidic solutions are high.

TiO_2 found in three types, called anatase, rutile, and Brookite. Most common two types are rutile and anatase while bookite is rarely utilized in most applications. Rutile TiO_2 is larger than anatase TiO_2 in size (Xu et al., 2014; D'Agata et al., 2014; Guo et al., 2007). Among all three types of TiO_2, rutile is the most thermal stable type where temperature above 600°C, brookite and anatase crystals converts into rutile type (Gao et al., 2007; Xu et al., 2014). Rutile type TiO_2 consists linear chains of opposite edge shared octahedral structure in shape and anatase type contains zigzag chains of octahedral models linked to each other (Xu et al., 2014; Chen et al., 2014; Fujimoto et al., 2007) Nontoxicity, long-term photostability, high effectiveness utilizing applications identified as the most beneficial characteristics in mineralizing toxic and non-biodegradable environmental contaminants in wastewaters. In addition to those, mechanical resistance and stability in acidic and oxidative environments help to act as a prime candidate in heterogeneous catalysis.

There are few drawbacks in using TiO_2 catalysis, which they consume a small specific surface area in particles, low adsorption abilities (Bagher et al., 2013; Palcheva et al., 2013), cost difficulties, and difficulty in separation of catalyst from the reaction media etc.

2.3.1.1 TiO_2 as a photo catalyst agent

Photocatalysis process commonly known as an effective treatment approach in the removal of organic pollutants in wastewater as it is not influenced by their toxicity and the process will not produce new pollutants as byproducts (Lai et al., 2012). TiO_2 has been widely applied in several industries in recent years, because of its physical and chemical properties in various states, such as non-toxic, high stability, Strong oxidation power, low environmental cost and simple preparation at the laboratory scale (Chung and Chen.,2008; Lai et al., 2012). TiO_2 has been subject to numerous investigations, as it is an attractive technique for the complete destruction of various contaminants in aqueous phase using solar or artificial light illumination such as DEP (Huang and Chen, 2010), Bisphenol A (Yang et al., 2011), Methylene Blue (Yang et al., 2017) etc. Photocatalytic degradation by TiO_2 under UV light is drive through generated electron (e^-) and hole (h^+) on TiO_2 particles. H_2O trapped on the surface of TiO_2 particle and yield H^+ and · OH free radicals while H^+ and e^- course to yield · H, · H and · OH free radicals. They attack the aliphatic chain of organic pollutants to produce intermediate products and ultimately CO_2, H_2O as the final products.

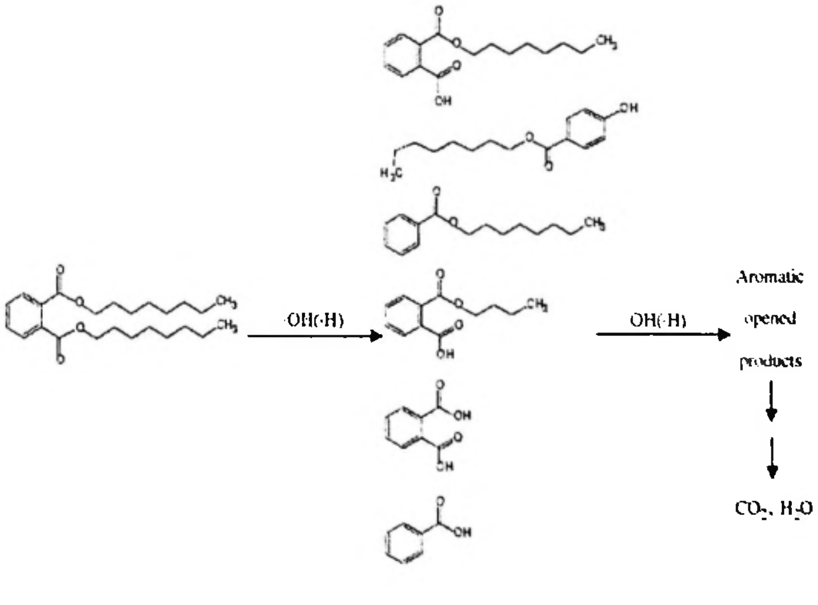


Figure 2.4 Proposed mechanism for DEHP removal through TiO_2

Source: (Chung and Chen, 2008)

2.3.2 Zeolite

Zeolites built with three-dimensional framework of $[SiO_4]^{4-}$ and $[AlO_4]^{5-}$ tetrahedral, linked by sharing oxygen atoms.Zeolite is also called as alumino-silicates (Apak et al., 1998). Weakly bonded cations and water molecules in the pores and voids of the structure are readily cations exchangeable and organized to adsorb organic pollutants. Synthesis conditions determine the composition of the zeolite and further modifications can be arranged to improve the performance.

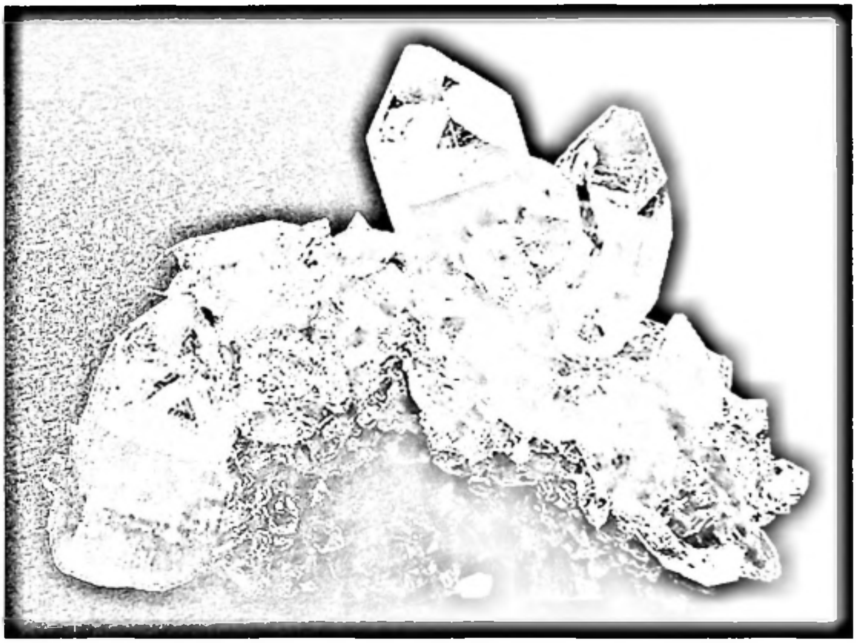


Figure 2.5: Naturally occurring zeolite

Alkali treatment of silica and alumina-bearing materials are the raw materials of synthetic zeolite and they were generally produced by natural or waste origin. Hence, zeolite exists in the natural environment with variable characteristics in their occurrence. Such characteristics like porosity, crystal size, pore diameter, purity (15-20 % to 90-95%) fluctuate with the origin of raw materials. As the raw materials of zeolite are inexpensive, their prices are lower compared to other natural components (Durdzinski, 2015).

With the advantage of the low cost of raw materials used in the synthesis of zeolite, it has been used in different industries and environmental protection treatments for their solutions. Main waste materials used in zeolite synthesis are Coal Fly Ash (CFA), municipal solid waste incineration ash, oil shale ash, rice husk ash etc. (Durdzinski, 2015).

2.3.2.1 Zeolites from Coal Fly Ash (CFA)

Thermal power plants distributed all over the world, produce CFA as their by-product which is considered as a waste. Most of this powdered waste (65% of total production) disposed in landfills or open dumping ash ponds. Those methods, craft serious problems in air pollution and ultimately causes health problems in communities. In every year, more than 500 million tonnes of CFA are generated as a by-product of coal combustion by thermal power plants which formulate serious air and water pollution problems.

CFA disposing problem can be solved by reusing them for the production of materials such as zeolite, which can be used in several treatment processes and this has been emphasized in a large number of scientific articles. They revealed that development and optimization methods for CFA zeolitization are based on alkaline activation of CFA (Durdzinski, 2015).

3. MATERIAL AND METHODS

3.1. Assess the presence of PAEs in selected urban watercourses

3.1.1 Study area and sampling locations

The study area is based on the western and central Colombo and suburbs, Sri Lanka (Figure 3.1). Selected regions have been developed as a mixed-use development area where both residential and industrial zones co-exist. The area was preferred as the industrial outputs containing PAEs mainly are clustered around the region (Figure 3.1). This densely populated regions has increased the use of personal care and household products which containing PAEs, and they are abundant in the nearby watercourses. The study area, includes urban watercourses that are constantly subjected to indiscriminate dumping of waste and discharge of untreated or partially treated industrial or domestic wastewater containing PAEs.

Twenty-two sampling locations were selected in different watercourses (Figure 3.1 and Table 3.1). Most of these sampling locations were in the lower stretches of the watercourses connected to open sea where accumulation potential is expected to be high. Diurnal and semi-diurnal tidal impacts and spring and neap tides usually slow down the flow of water due to salt wedge development resulting in higher hydraulic retention of PAEs in the selected stretches of watercourses. One sample (SP 01) was selected within a sub-catchment as the control, where no industry within the close vicinity has a potential for migration of PAEs. All the other twenty-one samples (SP 02 – SP 22) were selected in different sub-catchments having a multitude of industries with a potential for migration of PAEs (Table 3.2). Most of the watercourses that were considered for this study spread in almost flat terrain where water flow is slow or nearly stagnant and are not major rivers where flow rates are high enough to dilute the PAEs.

Table 3.1 Detailed description of sampling locations

Sampling ID	Sampling site	GPS co-ordinates of the sampling location
SP 01	Sri Wickrama canal	6.9792[1] 79.8760[2]
SP 02	Peliyagoda canal	6.9664[1] 79.8909[2]
SP 03	Main Drain	6.9546[1] 79.8653[2]
SP 04	Beira lake-North lock gate	6.9550[1] 79.8771[2]
SP 05	St. Sebastian canal	6.9499[1] 79.8748[2]

	(North)	
SP 06	Kittampahuwa canal	6.9445^1 79.8864^2
SP 07	St. Sebastian canal (South)	6.9382^1 79.8690^2
SP 08	Raggahawatta canal	6.9411^1 79.9614^2
SP 09	Dematagoda canal	6.9326^1 79.8820^2
SP 10	Beira lake-East	6.9266^1 79.8576^2
SP 11	Kinda canal	6.9221^1 79.8860^2
SP 12	Diyawanna lake	6.8972^1 79.9139^2
SP 13	Kirulapona canal	6.8861^1 79.8728^2
SP 14	Wellawatta canal	6.8791^1 79.8575^2
SP 15	Poorwarama canal	6.8794^1 79.8847^2
SP 16	Dehiwela canal	6.8625^1 79.8616^2
SP 17	MaharagamaEla	6.8434^1 79.9156^2
SP 18	Nadimala canal	6.8358^1 79.8931^2
SP 19	Weras Ganga	6.8147^1 79.9035^2
SP 20	Ratmalana canal	6.7988^1 79.8749^2
SP 21	Kesbawa lake	6.7947^1 79.9387^2
SP 22	Bolgoda lake	6.7761^1 79.8859^2

^{1}-Latitude; ^{2}-Longitude

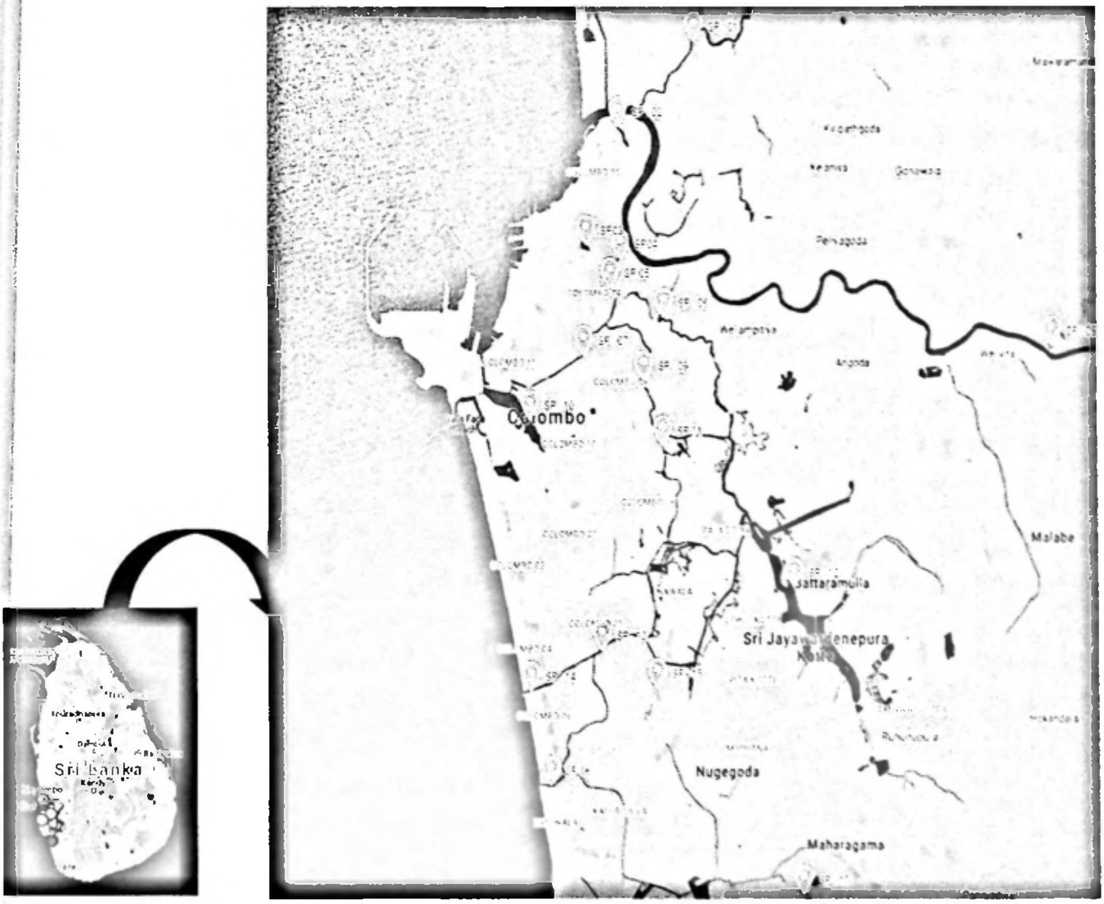


Figure 3.1: Sampling locations

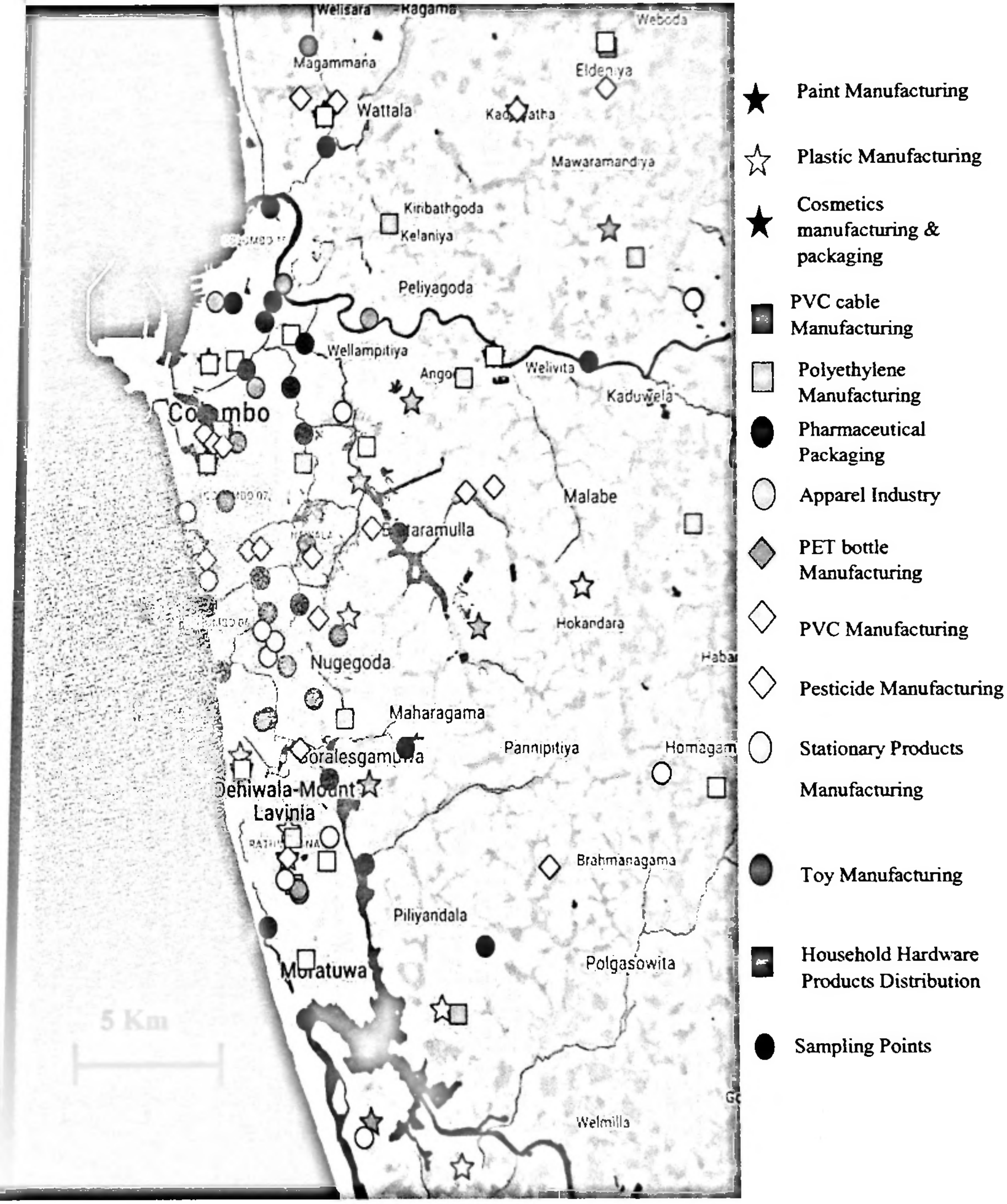


Figure 3.2: Sampling locations and the possible industries that has a possible potential for migration of PAEs from such catchment areas

Table 3.2: Distribution of industries that have a potential for PAEs migration in sub-catchments of sampling locations

	Type 1	Type 2	Type 3	Type 4	Type 5	Type 6	Type 7	Type 8	Type 9	Type 10	Type 11	Type 12	Type 13	Total
SP 01	-	-	-	-	-	-	-	-	-	-	-	-	-	-
SP 02	1	-	-	-	3	1	-	-	1	3	1	1	-	10
SP 03	-	1	1	1	-	1	1	1	2	2	5	3	-	18
SP 04	2	2	1	1	1	3	3	2	3	3	5	4	1	31
SP 05	2	2	1	1	1	3	3	2	3	3	5	4	1	31
SP 06	1	1	-	-	-	1	-	2	2	-	5	3	-	15
SP 07	-	-	-	-	-	-	-	1	-	1	-	-	-	02
SP 08	-	1	-	1	2	2	-	2	-	1	1	2	-	12
SP 09	1	1	-	-	-	1	2	1	1	1	1	2	-	11
SP 10	-	-	3	-	1	-	2	-	1	1	2	-	-	10
SP 11	2	4	-	-	-	1	2	2	2	1	5	4	-	23
SP 12	-	-	-	2	-	2	2	2	1	2	3	4	1	19
SP 13	2	2	-	-	-	1	2	1	2	-	3	2	-	15
SP 14	1	1	-	-	-	-	2	1	1	-	4	1	-	11
SP 15	2	-	-	-	-	-	1	1	2	-	1	-	-	7
SP 16	4	3	-	1	2	2	1	-	-	1	-	1	-	15
SP 17	1	-	-	-	-	-	-	-	-	-	-	1	-	02
SP 18	3	-	-	-	2	2	-	-	-	-	-	1	1	09
SP 19	1	1	-	1	2	2	-	-	-	1	2	1	1	12
SP 20	1	1	-	1	1	1	2	-	-	1	-	-	1	09
SP 21	-		-	1	-	1	-	1	-	-	-	1	-	04
SP 22	-	2	-	1	-	1	-	2	-	-	-	2	-	03

Type 1: Stationery products distributors; Type 2: Children toy manufacturing industry; Type 3: Household-hardware manufacturing industry; Type4: Plastic manufacturing industry; Type5: PET bottle manufacturing industry; Type 6: PVC Cable manufacturing industry; Type 7: Pharmaceuticals packaging industry; Type 8: Cosmetic and personal care product packaging industry; Type 9: PVC manufacturing industry; Type 10: Polyethylene manufacturing industry; Type 11: Pesticides packaging industry; Type 12: Paint manufacturing industry; Type 13: Apparel industry

3.2 Sample collection

Water samples were collected from slow-flowing, or almost stagnant water at each location between 9 am to noon at a depth less than 1.0 m in the dry period (November-December 2017) during which the ambient temperature was between 25–32 °C and no precipitation was observed. At each location, three grab samples were collected by a depth sampler (Model No: 436131, Ruttner, Germany) (Figure 3.3) within three hours to arrest any plausible changes due to tidal impact and any other temporal variation. Amber glass bottles of 1 L capacity (pre-heated at 105 °C for 4 hours for the removal of any residual PAEs) were used to store the grab samples, and all samples were transported to the laboratory within two hours and stored below 4 °C until analysis was performed. pH of the water was adjusted to be in the range of 5–7 using 1 M H_2SO_4 or 1 M NaOH (EPA method 8061A) to avoid hydrolysis of PAEs.

No plastic containers and accessories were used during in situ sampling, sample pretreatment, extraction and analysis to ensure decontamination with PAEs. All glassware was cleaned using K_2CrO_4/H_2SO_4 (20 mg/300 mL) solution, rinsed with NaOH solution and deionized (DI) water before analysis.

Figure 3.3: Depth sampler

3.3 In-situ water quality analysis

Temperature, pH, and salinity of the water samples were measured *in-situ* by a portable multi-parameter water quality meter (WQC 24, DKK-TOA, Japan). The repeatability of the measurements of pH, temperature and salinity are ± 0.05, ± 0.25 °C and, ± 0.1 %, respectively.

3.4 Sample extraction and analysis using Gas Chromatography/Mass Spectrometry (GC/MS)

3.4.1 Chemicals and standards

A standard mixture (2,000 μg/mL) of six PAEs (DMP, DEP, DBP, BBP, DEHP, and DnOP) in n-hexane, a surrogate standard containing Diphenyl phthalate (25 g), and an internal standard of Benzyl Benzoate in n-hexane (5,000 μg/mL) were purchased from Sigma Aldrich, USA.

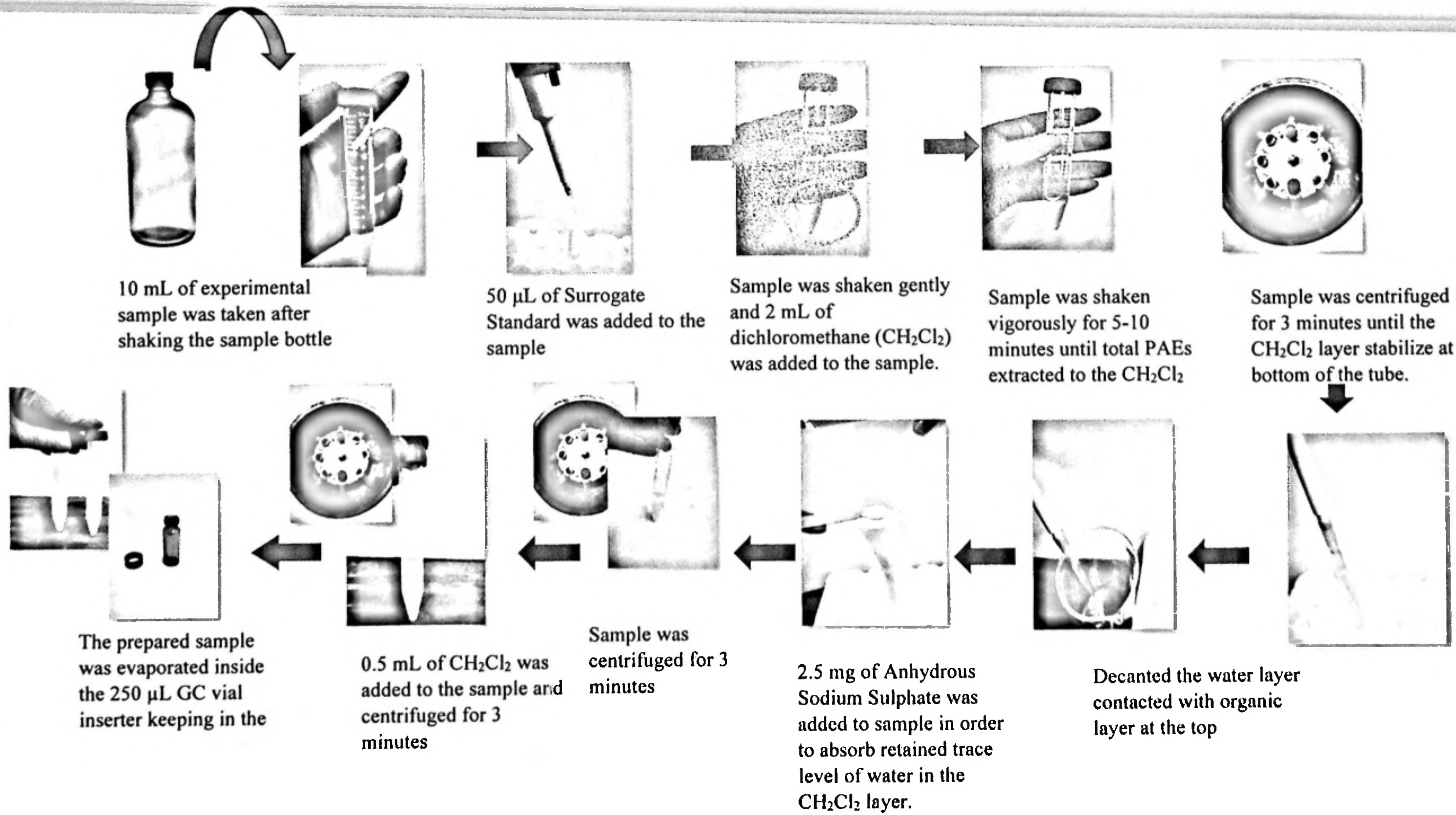
The surrogate standard and the internal standard were diluted to 200 mg/L using methanol and 500 mg/L using n-hexane, before analysis. HPLC-grade solvents (methanol, dichloromethane, n-hexane, and acetone) and anhydrous sodium sulfate (98%) were purchased from Sigma Aldrich, USA. Deionized water (18.2 Ω cm) was prepared using a deionizer (Smart Plus-N, Heal Force, China).

3.4.2 Extraction of PAEs

EPA method 8061A was followed for the extraction and quantification of various PAEs in an aqueous matrix (EPA 8061A). Each sample (10 mL volume) was filtered under vacuum to remove colloids using glass fiber filter papers (GF/F, Whatman, 0.7 μm). Glass fiber filters were cautiously wrapped in pre-cleaned aluminum foil, and baked at 105 °C for 12 hours before use. The filtrate was placed in a 15 mL centrifuge tube which 100 μL of diluted surrogate standard (5 mg/L) was spiked, and the solution was mixed for five minutes. After that, 2 mL of dichloromethane (CH_2Cl_2) was added to the mixture containing sample and surrogate standard, mixed vigorously for another 5 – 10 minutes and allowed for separation. Then samples were centrifuged at 2000 rpm for 3 minutes.

After 30 minutes, CH_2Cl_2 was separated and passed through a column containing 2 – 3 mg of anhydrous sodium sulfate to remove water molecules trapped in CH_2Cl_2. Again 0.5 mL of CH_2Cl_2 was added to the sample and centrifuge for another 3 minutes. CH_2Cl_2 layer was separated and passed through 1 – 2 mg of anhydrous sodium sulfate. Final CH_2Cl_2 layer mixed with a collected CH2Cl2 layer at the previous step. The anhydrous sodium sulfate was baked at 105 °C for 12 hours before use. The decanted sample was concentrated in a rotary evaporator (HS-2005 V-N(CE), Hahn Shin, Korea) until the sample reached a volume less than 1 mL and the final volume was added to GC vial inserter (250 µL). Then all samples was evaporated using N_2 gas and 100 µL of Internal Standard (5 mg/L) was added and fed into the GC/MS.

Modified method was validated with standard EPA 8061A method.



10 mL of experimental sample was taken after shaking the sample bottle

50 µL of Surrogate Standard was added to the sample

Sample was shaken gently and 2 mL of dichloromethane (CH_2Cl_2) was added to the sample.

Sample was shaken vigorously for 5-10 minutes until total PAEs extracted to the CH_2Cl_2

Sample was centrifuged for 3 minutes until the CH_2Cl_2 layer stabilize at bottom of the tube.

Decanted the water layer contacted with organic layer at the top

2.5 mg of Anhydrous Sodium Sulphate was added to sample in order to absorb retained trace level of water in the CH_2Cl_2 layer.

Sample was centrifuged for 3 minutes

0.5 mL of CH_2Cl_2 was added to the sample and centrifuged for 3 minutes

The prepared sample was evaporated inside the 250 µL GC vial inserter keeping in the

Figure 3.4: Schematic diagram of extraction procedure

3.4.3 GC/MS analysis

Gas Chromatograph (7890, Agilent Technologies, USA) coupled with a Mass Selective Detector (5977, Agilent Technologies, USA) with splitless injector was used for the qualitative analysis of PAEs, operating at the full scan and quantitative analysis of PAEs with selective ion monitoring (SIM) mode. Calibration curves were prepared for individual PAEs using the standard mixture for quantification of PAEs. A DB-5MS column (30 m × 250 μm id., 0.25 μm film thickness) from Agilent Technologies was used for PAEs separation. The program for the GC oven was initiated at 80 °C, increased to 265 °C at a rate of 30 °C/min, then ramped to 270 °C at a rate of 5 °C/min, and finally kept for 12 minutes until all the samples were eluted. The sample injector was set at 300 °C using splitless mode. The electron impact ionization energy was 70 eV. The temperatures of the transfer line, ion source and quadruple were maintained at 280 °C, 230 °C and 150 °C, respectively. Ultra-pure helium (99.99 %) was used as the carrier gas at a constant flow rate of 1 mL/min, and the sample injection volume was 1.0 μL.

3.4.4 Validation of the analytical method using GC/MS

Quantification of DMP, DEP, DBP, BBP, DEHP, DnOP concentrations in shallow watercourses using GC/MS was validated, and the key parameters from validation studies, including limit of detection (LOD), limit of quantification (LOQ), and relative standard deviation (RSD) are shown in the following table 3.3. For every batch, a water sample was field-fortified (field blank) with a known concentration of surrogate standard for their recovery. Besides, for each batch, a water sample from a source that PAE concentrations were presumed to be absent was spiked with a known concentration of surrogate standard (procedural blank) and validated for recovery (Table 3.3). Two known concentrations of the standard mixture were spiked with deionized water to be analyzed together with other batch samples for the verification of extraction efficiencies (Table 3.3). Calibration curves were prepared for DMP, DEP, DBP in the range 0.5–10 μg/L and for BBP, DEHP, DnOP in the range 1–10 μg/L with the linearity of R^2between

0.995–0.999 and RSD < 10 %. Precursor ion for DMP was selected as the 163 (m/z), and the same for DEP, DBP, BBP, DEHP, and DnOP was selected as the 149 (m/z).

Table 3.3 Validation parameters of the Optimized GC/MS methodology for PAE quantification

Phthalate Type	**LOD (µg/L)**	**LOQ (µg/L)**	**Recovery efficiency for external standards (RSD %) n=6**		**Recovery efficiency for SS (Field blank) (RSD %) n=6**	**Recovery efficiency for SS (Procedural blank) (RSD %) n=6**
			1µg/L	**5µg/L**		
DMP	0.3	0.5	98 – 102 (8%)	95 – 120 (5%)	–	–
DEP	0.3	0.5	98 – 103 (5%)	95 –120 (3%)	–	–
DBP	0.3	0.5	98 – 104 (6%)	95 –120 (3%)	–	–
BBP	0.5	1	95 – 110 (8%)	95 –120 (5%)	–	–
DEHP	0.5	1	95 – 110 (8%)	95 –120 (4%)	–	–
DnOP	0.5	1	95 – 110 (8%)	95 –120 (5%)	–	–
DPP (SS)	0.3	0.5	–	–	95–105 (4%)	95–110 (6%)

n- Sample size

3.4.5 Statistical analysis

An analysis of the correlation between DMP, DEP, DBP, DEHP, BBP, and DnOP concentrations and key factors influencing the presence of PAEs in water (pH, temperature, and salinity) was performed by calculating the coefficients of correlation for all samples using XLSTAT version 2018.2 (statistical software for Excel). The correlation between two variables was considered significant when $p < 0.05$ and reckoned to be strong, moderate or weak when correlation coefficient > 0.7, 0.7–0.5 or 0.5–0.3, respectively. Student t-test was conducted to determine the significant differences between respective means of PAEs and reckoned significant when $p < 0.05$.

3.5 Analyze the ecological risk of PAEs on aquatic life being present in the watercourses

Ecological risk assessment of PAEs on urban watercourses was done according to the European Commission's Technical Guidance Document (EC 2003) and literature (Staples et al., 2000; Adams et al., 1995). Measured PAE concentrations of watercourses were used to predict potential ecological risk using the risk quotient (RQ) approach. The RQ values were calculated using Measured Environmental Concentration (MEC) and the Predicted No Effect Concentration (PNEC) values. Quotient of toxicologically relevant concentration and a security factor (f) was used to calculate PNEC values. Then RQ calculations were done with L (E) C50 values for ecological communities associated with the DMP, DEP, BBP, DBP, DEHP, and DnOP as the following equation.

$$PNEC = \frac{LC50}{Safety\ factor} \qquad (1)$$

$$\mathrm{RQ} = \frac{MCE}{PNEC} \qquad (2)$$

The maximum probable risk of ecological effects of contaminated water can be interpreted as follows, according to the Wentsel et al., (1996).

RQ <1.00 indicates no significant risk.
1.00 ≤ RQ > 10.0 indicates a small potential for adverse effects.
10.0 ≤ RQ > 100 indicates a significant potential for adverse effects.
RQ ≥ 100 indicates that potential adverse effects should be expected.

Table 3.4: Acute toxicity (L(E)C50) used for the risk assessment for eco communities

	DMP	DEP	DBP	BBP	DEHP
Fish Community (Adams et al., 1995)	50.0	16.7	0.480	1.7	> 0.200
Crustacean Community (Call et al., 2001)	28.1	4.21	0.63	0.46	–

Insects Community (Call et al., 2001)	68.2	31.0	2.64	–	–
Algae Community (Adams et al., 1995)	142	16	0.4	0.21	>.0100
Microorganism Community (Staples et al., 1996)	537	132	7.0	–	–
Oligocheata Community (Staples et al., 1996)	246	102	2.48	1.23	–
Invertebrates Community (Adams et al., 1995)	33	86	3.0	3.7	2.0

3.6 Evaluate the efficiency of different arrays of nanoparticle matrixes for removal of PAEs

3.6.1 Titanium Dioxide (TiO_2)

3.6.1.1 Synthesis of TiO_2

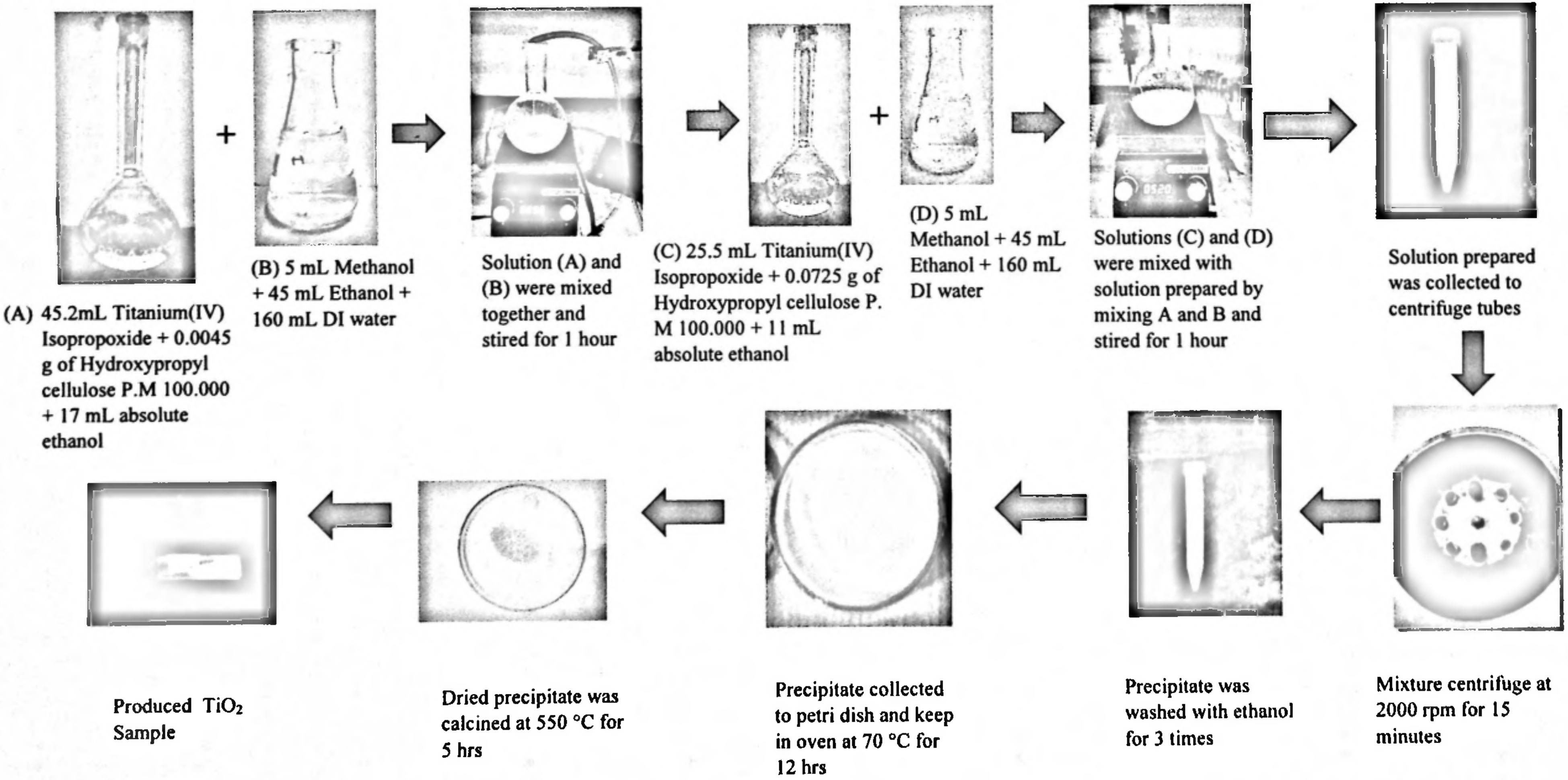
45.2 mL of Titanium (IV) Isopropoxide, 0.0045 g of Hydroxypropyl cellulose P.M. 100.000, and 17 mL absolute Ethanol were mixed together and stirred for 5 minutes. A mixture of methanol (5 mL) and ethanol (45 mL) with a volume ratio of 1:10 was added with 160 mL DI water and then pour into stirring solution.

Then the mixture was kept for 1 hour at 550 rpm. After 1hr, 25.5 mL of Titanium (IV) Isopropoxide, 0.0725 g of Hydroxypropyl cellulose P.M. 100.000 and 11 mL absolute Ethanol were mixed together. DI water, ethanol, and methanol mixture were prepared as the previous step. Then those two added together to the initial solution and kept for another 1 hour at 550 rpm. Then the final mixture kept for another 30 minutes until a white precipitate is appearing. Then the precipitate was separated by centrifugation at 2000 rpm for 3 minutes. The white precipitate was washed with ethanol for three times. The final precipitate was heated at 70 °C for 12 hours and calcined at 550 °C for 5 hrs.

3.6.1.2 Characterization of synthesised TiO_2

Morphology and elemental composition of the TiO_2 were analysed, before and after the experiments using Environmental Scanning Electron Microscopy (ESEM- Carl Zeiss, EVO 18, Secondary Electron Microscope, Germany) coupled with Energy-Dispersive

X-ray Spectroscopy (EDX Z1 analyser, USA). The phase identification of the TiO_2 was performed by the X-ray Powder Diffraction (XRD-D8, ECO, Advance Bruker Diffractometer with filtered Cu Kα radiation, Germany) at 2θ range of 10 – 80° and scanning speed of 2° (2θ) per minute. Fourier Transform-Infrared Spectroscopy (FT–IR, ALPHA Bruker, Germany) was performed in the transmittance mode at ambient temperature in the spectral range of 500 – 4,000 cm^{-1} to identify the functional groups of TiO_2.



(A) 45.2mL Titanium(IV) Isopropoxide + 0.0045 g of Hydroxypropyl cellulose P.M 100.000 + 17 mL absolute ethanol

(B) 5 mL Methanol + 45 mL Ethanol + 160 mL DI water

Solution (A) and (B) were mixed together and stired for 1 hour

(C) 25.5 mL Titanium(IV) Isopropoxide + 0.0725 g of Hydroxypropyl cellulose P. M 100.000 + 11 mL absolute ethanol

(D) 5 mL Methanol + 45 mL Ethanol + 160 mL DI water

Solutions (C) and (D) were mixed with solution prepared by mixing A and B and stired for 1 hour

Solution prepared was collected to centrifuge tubes

Mixture centrifuge at 2000 rpm for 15 minutes

Precipitate was washed with ethanol for 3 times

Precipitate collected to petri dish and keep in oven at 70 °C for 12 hrs

Dried precipitate was calcined at 550 °C for 5 hrs

Produced TiO_2 Sample

Figure 3.5: TiO_2 synthesis procedure

3.6.1.3 Single-solute studies for removal of DEHP

3.6.1.3.1 DEHP removal by TiO_2

Single-solute batch experiments were carried out using TiO_2 to study the DEHP removal efficiency. Experiments were done under two Ultraviolet (UV) lamps (360 nm) and the contact time was varied with TiO_2 dosages of 0.5, 1.0, 1.5, 2.0, and 3.0 g/L to determine the optimum dosage for removal of DEHP. Contact time considered varies from 5 min to 2 hrs. Initial concentration of DEHP solution was 171 μg/L, initial solution pH was 6, the temperature was 28 °C, and the stirring speed was 150 rpm.

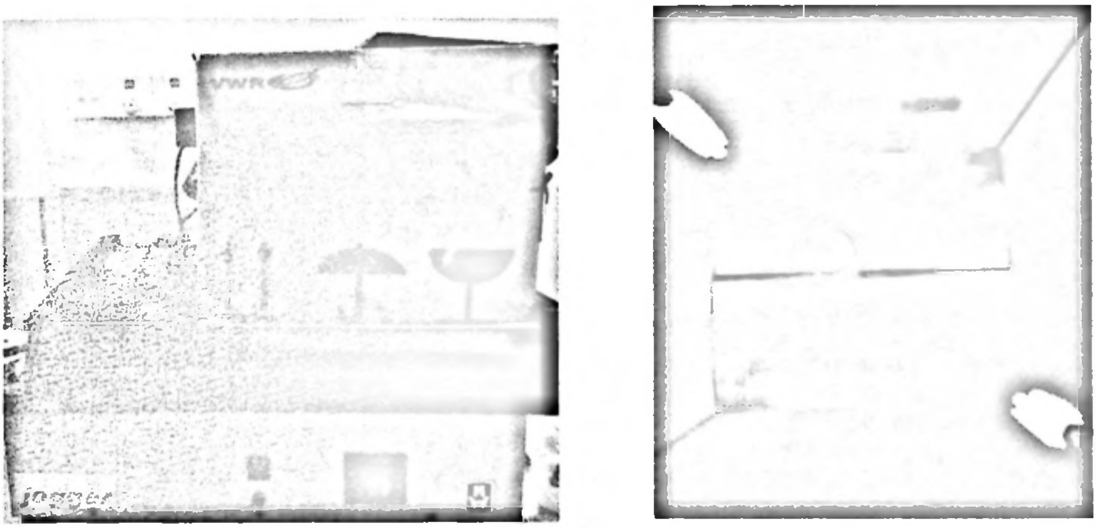


Figure 3.6: The experimental setup for the batch studies on the mechanical stirrer

3.6.1.4 Reusability of TiO_2

The recycling was studied using fresh DEHP solution (1710μg/L) and 1 g of TiO_2. The contact time was 45 minutes and the pH of 6 was maintained throughout the experiment. 100 mL of fresh DEHP solution was mixed with 1 g of TiO_2 and containing flask was kept in a mechanical shaker for 45 minutes at 150 rpm. Then TiO_2 was let to settle at the bottom of the flask before decanting the supernatant. TiO_2 containing conical flask was kept in the oven until a steady weight is reached. The weight of the flask was recorded and then another reuse cycle was carried out. At each step, the supernatant was collected and measured DEHP concentrations. After that, solid was washed with DI water two times and decanted. The recycling process was repeated for five reuse cycles. The weight loss of TiO_2 at each step was kept to a minimum (less than 0.05 g).

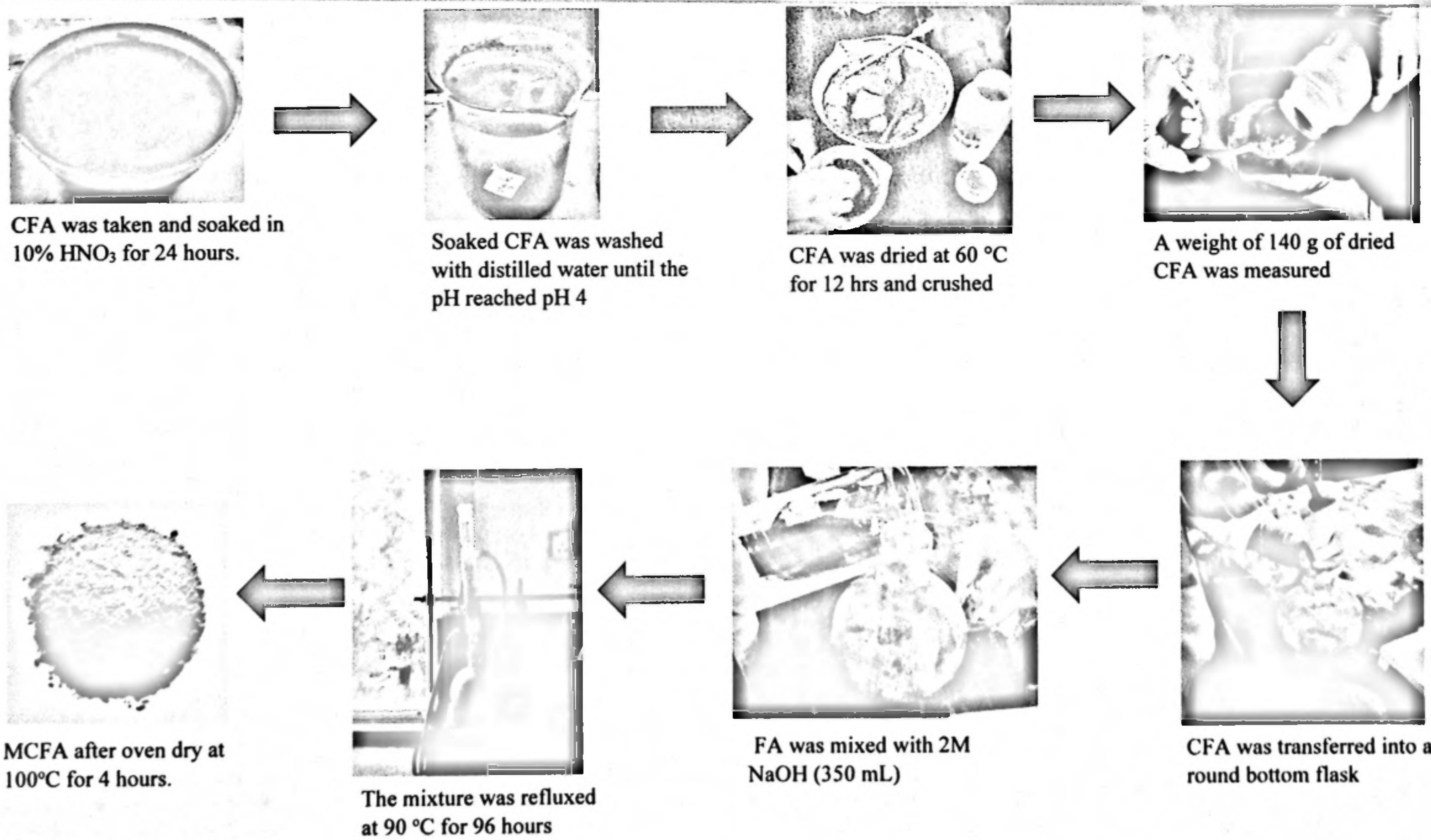
3.6.2 Modified Coal-derived Fly Ash (MCFA)

3.6.2.1 Synthesis of MCFA

500 g of CFA was taken and soaked in 10% HNO_3 for 24 hours. Soaked fly ash washed with distilled water until the pH reaches 4 and then dried at 60 °C for 12 hrs. 140 g of dried fly ash mixed with 350 mL of 2M NaOH and refluxed at 90 °C for 96 hours. Then the mixture filtered and washed with DI water three times and dried in 70 °C for 24 hours.

3.6.2.2 Characterization of MCFA

Morphology and elemental composition of the MCFA were analysed, before and after the experiments using Environmental Scanning Electron Microscopy (ESEM- Carl Zeiss, EVO 18, Secondary Electron Microscope, Germany) coupled with Energy-Dispersive X-ray Spectroscopy (EDX Z1 analyser, USA). The phase identification of the MCFAwas performed by the X-ray Powder Diffraction (XRD-D8, ECO, Advance Bruker Diffractometer with filtered Cu Kα radiation. Germany) at 2θ range of 10 – 80° and scanning speed of 2° (2θ) per minute. Fourier Transform–Infrared Spectroscopy (FT–IR, ALPHA Bruker, Germany) was performed in the transmittance mode at ambient temperature in the spectral range of 500 – 4,000 cm^{-1} to identify the functional groups of the MCFA.



CFA was taken and soaked in 10% HNO_3 for 24 hours.

Soaked CFA was washed with distilled water until the pH reached pH 4

CFA was dried at 60 °C for 12 hrs and crushed

A weight of 140 g of dried CFA was measured

CFA was transferred into a round bottom flask

FA was mixed with 2M NaOH (350 mL)

The mixture was refluxed at 90 °C for 96 hours

MCFA after oven dry at 100°C for 4 hours.

Figure 3.7: Modified Coal-derived Fly Ash (MCFA) Synthesis procedure

3.6.2.3 Single-solute studies for removal of DEHP

3.6.2.3.1 DEHP removal by MCFA

Single-solute batch experiments were carried out using MCFA to study the DEHP adsorption isotherms and kinetics. The contact time was changed with MCFA dosages of 1.0, 2.0, 2.5, 3.0 g/L to determine the optimum contact time in removing DEHP. Contact time considered varies from 5 min to 2 hrs. The initial concentration of DEHP was 171 µg/L, pH of the initial solution was 6, the temperature was 28°C, and the stirring speed was 150 rpm. After that, a series of batch experiments were conducted to determine the isotherm and kinetic behavior varying dosage varying contact time of 5 minutes to 2 hrs. In the experiments, the initial concentration of DEHP was constant at 171 µg/L. Amounts of DEHP adsorbed at equilibrium, (Q_e) ad were calculated.

Figure 3.8: Experimental setup for the MCFA batch experiments and kinetic studies

3.6.2.4 Adsorption Isotherms and kinetic studies for MCFA

3.6.2.4.1 Adsorption Isotherms

This study attempts to describe DEHP removal with the use of adsorption isotherm models. The amount of DEHP removed per unit mass of the MCFA (Q_e in µg/g) was calculated using Eq. 3:

$$Q_e = (C_o - C_e) \times \frac{V}{W} \tag{3}$$

Where C_o and C_e are the initial and the equilibrium concentrations of DEHP in the solution (μg/g) respectively, V is the volume of solution in L, and W is the mass of the adsorbent (g) added.

The Langmuir adsorption isotherm model was used to study DEHP removal and to describe the amount of adsorbate adsorbed per unit weight of adsorbent at equilibrium. The Langmuir adsorption isotherm model assumes that the adsorbent surface is homogeneous with equal sorption sites, only monolayer adsorption occurs with no interaction between adjacent adsorbed ions, and adsorbate ions tend to either adsorb or desorb. Langmuir adsorption isotherm (Langmuir, 1918) is given by Eq. 4:

$$\frac{1}{Q_e} = \frac{1}{Q_m} + \frac{1}{Q_m K_L C_e} \qquad (4)$$

Where C_e is the equilibrium concentration of adsorbate (mg/L), Q_e is the amount of adsorbate adsorbed per unit mass of the adsorbent at equilibrium (mg/g), Q_m is maximum monolayer coverage capacity (mg/g), and K_L is the Langmuir isotherm constant (mg/L).

Essential characteristics of Langmuir adsorption isotherm can express regarding a dimensionless constant separation factor or equilibrium parameter, R_L gives in Eq. 5; where C_o is initial concentration (mg L^{-1}), and K_L is Langmuir isotherm constant. R_L value describes the adsorption mechanisms, which is unfavorable ($R_L > 1$), linear ($R_L = 1$), favorable ($0 < R_L < 1$), or irreversible ($R_L = 0$) (Weber and Chakravorti, 1974).

$$R_L = \frac{1}{[1+(1+K_L C_o)]} \qquad (5)$$

Freundlich model was applied for DEHP removal to ascertain the adsorption characteristics, assuming the heterogeneous surfaces where fluoride or calcium could bind by multi-layer formation, and there exists an interaction among adsorbed ions. Freundlich adsorption isotherm (Freundlich, 1906) is given by Eq. 6:

$$\log(Q_e) = \log(K_f) + \frac{1}{n}\log(C_e) \tag{6}$$

Where K_f isFreundlich isotherm constant (mg/g), n is adsorption intensity, C_e is the equilibrium concentration of adsorbate (mg/L), and Q_e is the amount of adsorbate adsorbed per gram of the adsorbent at equilibrium (mg/g). The Freundlich constant (n) indicates the adsorption mechanism and when $2 < n < 10$, adsorption is favorable, between $1 < n < 2$ moderately difficult and $n < 1$ poor adsorption (Kakavandi et al., 2013).

3.6.2.4.2 Kinetic Studies

Kinetics of DEHP adsorption were analysed usingLagergren's pseudo-first-order kinetic model (Lagergren, 1898) which describes the adsorption of one ion of adsorbate to one adsorption site and the pseudo-second-order kinetic model, which describes the adsorption of one ion of adsorbate to two adsorption sites (Ho and McKay, 1999). These two models identify kinetics of DEHP adsorption processes to be fitted either to chemisorption or physisorption. The pseudo-first order kinetic model and the pseudo-second-order kinetic models expressed in Eqs. (7) and (8):

$$\log(Q_e - Q_t) = \log Q_e - \left(\frac{K_1}{2.303}\right)t \tag{7}$$

$$\frac{t}{Q_t} = \frac{1}{\left[K_2 (Q_e)^2\right]} + \left(\frac{1}{Q_e}\right)t \tag{8}$$

Where Q_e is the amount of adsorbate adsorbed on adsorbent (mg/g) at equilibrium, Q_t is the amount of adsorbate adsorbed on adsorbent (mg/g) at time t (minutes), K_1 is the rate constant (min^{-1}) for pseudo-first order kinetics, and K_2 is the rate constant (mg/g/min) for pseudo-second-order kinetics.

3.6.2.5 Regeneration studies for MCFA

The regeneration was done to identify the best regenerating reagent for MCFA. The regeneration was studied using HCl, EDTA, and NaOH solution with pH 4, 7, and 10 respectively. The batch experiments were conducted using 3 g of MCFA in 100 mL of DEHP solution with a concentration of 1710 µg/L. The contact time was 30 minutes and the pH of 6 was maintained throughout the experiment. After the adsorption cycle, MCFA was let to settle at the bottom of the flask before decanting the supernatant. A volume of 100 ml of regenerating reagent was then added to MCFA containing flask and kept in the mechanical shaker at 150 rpm for 30 minutes. The regeneration reagent was decanted. Then the MCFA solid was washed with DI water for two times and decanted. The MCFA containing flask was kept in the oven until a steady weight is reached. The weight of the flask was recorded and then another adsorption and desorption cycle was carried out. The weight loss of MCFA at each step was kept to a minimum (less than 0.05 g). The DEHP adsorption was measured after every adsorption cycle. This was repeated for three regeneration cycles.

4. RESULTS AND DISCISSION

4.1 Occurrence of PAEs in watercourses

DEP, DBP, BBP, and DEHP were detected in mostof the samples, while DMP and DnOP were below the respective LOQs (0.5 µg/L for DMP and 1.0 µg/L for DnOP) for all samples (Table 4.1).

Table 4.1: PAE concentrations in sampling locations

Sampling Point	DMP (µg/L) n=3	DEP (µg/L) n=3	DBP (µg/L) n=3	BBP (µg/L) n=3	DEHP (µg/L) n=3	DnOP (µg/L) n=3
SP 01	<0.5	22.0 ± 3	17.0 ± 1	< 1	58 ± 2	< 1
SP 02	<0.5	37.0 ± 15	16.0 ± 5	<1	165± 136	< 1
SP 03	<0.5	20.5 ± 8	26.0 ± 11	< 1	105 ± 54	< 1
SP 04	<0.5	61.0 ± 39	27.5 ± 2	61 ± 4	82 ± 16	< 1
SP 05	<0.5	26.0 ± 7	15.5 ± 3	< 1	71 ± 6	< 1
SP 06	<0.5	<0.5	<0.5	< 1	72 ± 1	< 1
SP 07	<0.5	31.0 ± 17	20.0 ± 15	< 1	110 ± 56	< 1
SP 08	<0.5	<0.5	32.0 ± 11	< 1	44 ± 2	< 1
SP 09	<0.5	110.5 ± 51	20.5 ± 3	72 ± 3	114 ± 23	< 1
SP 10	<0.5	265.0 ± 25	27.5 ± 4	75 ± 11	137 ± 6	< 1
SP 11	<0.5	< 0.5	<0.5	< 1	102 ± 2	< 1
SP 12	<0.5	< 0.5	<0.5	< 1	21 ± 3	< 1
SP 13	<0.5	27.5 ± 1	27.0 ± 17	< 1	53 ± 3	< 1
SP 14	<0.5	42.0 ± 7	24.5 ± 5	< 1	12 ± 1	< 1
SP 15	<0.5	25.0 ± 1	19.0 ± 3	< 1	93 ± 12	< 1
SP 16	<0.5	48.0 ± 17	24.0 ± 3	< 1	90 ± 22	< 1
SP 17	<0.5	25.0 ± 8	21.0 ± 3	< 1	108 ± 50	< 1
SP 18	<0.5	<0.5	<0.5	< 1	62 ± 2	< 1
SP 19	<0.5	246.0 ± 26	21.5 ± 6	69 ± 6	101 ± 45	< 1
SP 20	<0.5	26.0 ± 13	27 ± 7	108 ± 7	134± 1	< 1
SP 21	<0.5	2.5 ± 1	2.5 ± 1	< 1	<0.5	< 1
SP 22	<0.5	61.0 ± 15	20.5 ± 4	< 1	98 ± 20	< 1

LOQ for DMP: 0.5 µg/L; DEP: 0.5µg/L; DBP: 0.5µg/L; BBP: 1µg/L; DEHP: 1µg/L; DnOP: 1µg/L

The average concentrations detected for DEP, DBP, BBP, and DEHP were in the range of 2.5–265.0, 1.0–32.0, 61–108, and 12–165µg/L, respectively. These average values were compared with the same detected in the watercourses of different countries (Table 4.2). DEHP and DBP in most of the watercourses of this study exceeded those of Canadian permissible levels (16 and 19 µg/L) for the protection of aquatic life.

4.1.1. Comparison of PAE levels of the study with other watercourses in different countries

Table 4.2: Comparison of PAE levels of the study with other watercourses in different countries

	DMP (µg/L)	**DEP (µg/L)**	**DBP (µg/L)**	**BBP (µg/L)**	**DEHP (µg/L)**	**DnOP (µg/L)**	**References**
Sri Lanka*1	<0.5	2.5–265.0	1.0–32.0	61–108	12–165	<1	This Study. 2017
China*2	0.065–0.208	0.140–0.334	0.190–4.762	<0.001	0.364–2.682	0.001–0.621	Wei et al., 2017
China*3	<0.001	<0.001	6.825	0.21	5.196	NM	Zhang et al., 2011
China*4	<0.010	0.098–0.197	0.146–0.225	<0.010	0.582–2.05	0.010–0.059	He et al., 2010
China*5	<0.001	<0.001	35.65	NM	54.73	0.84	Wang et al., 2007
France*6	<0.01	<0.015	0.086	<0.005	0.090	<.01	Dargnat et al., 2009
Germany*7	NM	NM	0.12–8.80	<0.02	0.33–97.80	NM	Fromme et al., 2002
Japan*8	<0.03	<0.03	3.34	NM	0.97	NM	Hastizume et al., 2002
Sweden*9	0.40	0.63	6.8	0.17	NM	NM	Bastos and hanglund, 2012
South Africa*10	ND	53–813	1343–5600	1–140	107–361	1–5	Olujimi et al., 2012
Spain*11	0.003–0.008	0.300–1.742	NM	0.005–0.122	0.014–0.180	NM	Sanchez-avila et al., 2011
Spain*12	0.158	0.261	<0.125	0.029	0.133	NM	Regueiro et al., 2008
Taiwan*13	NM	0.6–2.5	1–13.5	<0.6	1–18.5	NM	Yuan et al., 2002

*1Canals and lakes; *2Songhua River; *3Wujin river; *4QX section of Yangtze section; *5Wuhan section of Yangtze River; *6Seine River; *7Rivers, Lakes and Canals; *8Tempaku River; *9River water; *10Veldwachters River (Downstream); *11Shallow water bodies; *12River water; *13River water; NM-Not measured

DMP, DBP and DnOP concentrations observed were similar to the order of magnitude reported in other countries, while DEP, BBP and DEHP concentrations observed were more than one order of magnitude to those observed in many of the other countries except in South Africa (Table 4.2).

The possible factors for a vast variation of PAEs of watercourses among different countries include: a varying degree of migration potential of PAEs from industries and households; inherent properties of PAEs such as volatility, solubility, biodegradability, and photodegradability; quality of the receiving water such as pH, salinity, and temperature and the extent to which such PAEs are regulated.

4.1.2 Quality of the receiving water and inherent properties influencing the ubiquitous presence of PAEs

The key influencing factors of the retention of PAEs in the water column included pH (US EPA 8061A), temperature (Xu, et al., 2009), and salinity (Turner and Rawling, 2001; Xu et al. 2008). The minimum values observed were: pH 5.45 (SP 20), temperature 27.5°C (SP 21) and salinity 0% (SP 8, SP 17 to SP 21), and the maximum values were: pH 8.90 (SP 10), temperature 31.5°C (SP 15) and salinity 2.4% (SP 16) (Table 4.3).

Table 4.3: Sampling location and *in situ* parameters measured

Sampling ID	pH	Temperature (°C)	Salinity (%)
SP 01	7.45	29.3	0.7
SP 02	7.50	30.7	0.3
SP 03	7.65	30.0	0.9
SP 04	7.55	28.2	0.9
SP 05	7.30	29.7	0.4
SP 06	6.90	28.6	0.4
SP 07	7.40	30.6	0.1
SP 08	6.45	30.5	0.0
SP 09	8.60	31.1	0.2
SP 10	8.90	30.7	0.7
SP 11	8.10	29.8	0.1
SP 12	7.45	30.7	0.0
SP 13	7.70	28.5	0.1
SP 14	7.65	30.5	0.9
SP 15	7.30	31.5	0.1

SP 16	8.25	28.4	2.4
SP 17	5.80	27.9	0.0
SP 18	6.60	28.7	0.0
SP 19	7.45	29.5	0.0
SP 20	5.45	30.8	0.0
SP 21	7.20	27.5	0.0
SP 22	7.20	30.6	0.1

4.1.3 Multivariate analysis

Multivariate analysis corroborated that PAEs (DEP, DEHP, DBP and BBP) have weak positive correlations with pH and temperature and a weak negative correlation with salinity. Furthermore, all correlation coefficients given below are less than 0.3 and the interactions were not significant ($p > 0.05$) (Table 4.4).

Table 4.4: Multivariate analysis for PAEs with influencing factors

	pH	Temperature	Salinity
DEP	0.23^1	0.39^1	-0.09^1
	0.30^2	0.07^2	0.67^2
DBP	0.26^1	0.03^1	-0.06^1
	0.24^2	0.88^2	0.76^2
BBP	0.13^1	0.14^1	-0.15^1
	0.58^2	0.54^2	0.50^2
DEHP	0.29^1	0.25^1	-012^1
	0.19^2	0.26^2	0.60^2

^{1}: Correlation coefficient ^{2}: P value

PAEs are implicated to be hydrolyzed below pH 5 and above pH 7 where the amount of hydrolysis increases with increasing pH above 7 or decreasing pH below 5 (USEPA 1996; Staples et al., 1997). In contrary to these findings regarding the weak positive relationship of PAEs with temperature; Thomsen and co-workers (2001) have reported that the unimeric solubility of PAE manifests a negative relationship with the temperature of the water column. However, Xu and co-workers (2009) have found that with increasing temperature the partition coefficient of BBP on marine sediments decreases considerably, giving rise to a shift in BBP equilibrium from the solid phase to the aqueous phase (Xu et al., 2009). PAEs have high hydrophobicity with increasing salinity resulting in a negative impact on solubility. In support of the findings on the salinity of water column, it was reported that with increasing concentrations of Cl^- in the water column due to salinity intrusion, the solubility of PAEs in water reduces with increased adsorption of PAEs to colloids in water and sediment layer (Xu et al., 2008). Further, the sorption affinity of colloid-laden PAEs declines with increasing concentrations of Na^+, K^+, Cl^-, and SO_4^{2-} of colloids (Xu et al., 2009). The amount of DBP adsorbed on the sediments increases as the salinity of the marine water increases (Xu et al., 2008).

4.1.4 Factors affecting the presents of PAEs in watercourses

Other factors of concern, including inherent properties of PAEs, constitute solubility in water, Octanol/water partitioning, air/water partitioning, water/solid partitioning, photodegradation, and biodegradation. Water solubility of PAEs is a measure of a propensity on biodegradation and bioaccumulation, and it decreases with an increasing carbon number of the alcohol moiety of PAEs (Staples et al., 1997). Water solubility at 25°C for DMP, DEP, DBP, and BBP is reported to be 4,000,000 μg/L, 1,080,000 μg/L, 11,200 μg/L, 2,690 μg/L, respectively (Howard et al., 1985) and for DEHP, DnOP it is 270 μg/L, 22 μg/L, respectively (Defoe et al., 1990). These results corroborated that concentrations of PAEs at all sampling locations were less than the maximum water solubilities of the respective PAE. Octanol/water partitioning coefficient (K_{ow}) predicts the partitioning behavior of PAEs. PAEs with high hydrophobicity, low solubility, and high molecular weights are persistent in one phase without partitioning to another phase. Log K_{ow} of DMP, DEP, DBP, BBP, DEHP, and DnOP are reported to be 1.61, 2.38, 4.45, 4.59, 7.50, and 8.06, respectively (Staples et al., 1997). In general, results obtained in the study have followed this general trend indicating greater hydrophobicity with increasing Log K_{ow} values. Air/water partitioning, which is usually characterized by Henry's Law constant *(H)*, helps estimate the tendency of PAEs to escape from water to air. The *H* values of DMP, DEP, DBP, BBP, DEHP, and DnOP are estimated to be 1.22 E-7, 2.66 E-7, 8.83 E-7, 7.61 E-7, 1.71 E-5, and 1.03 E-4 (atm-m^3/mol), respectively (Staples et al. 1997). The higher *H* values are reported for PAEs with higher solubilities relative to the vapor pressure indicating that they are migrated to air. The results of DMP manifested extremely low concentrations, perhaps attributed to the relatively high H value, indicating that the retention of DMP in water is extremely remote but may be substantial in the air. The sorption of PAEs to soil/sediments of the watercourses is elaborated with their water-solid partition coefficient (K_{oc}). The K_{oc} value for DMP is 55 L/kg (Osipoff et al. 1981), for DEP, DBP, BBP, DEHP is 69 L/kg, 1975 L/kg, 17,000 L/kg, 87,420 L/kg, respectively (Russell and McDuffie, 1986), and for DnOP 140,800 L/kg (EPA 2012). Observed results could not confirm sorption affinities, as PAEs in sediments were not quantified. Photodegradation of PAEs occurs through absorption of UV irradiance in the range of 290–400 nm with the maximum photolysis half-life of PAEs at near surface of the water column being 144 days; thus, the loss of PAEs due to photolysis would be marginal (Wolfe et al., 1980). Biodegradation within the water column by bacterial mediation seems to be another important pathway of the fate of PAEs in the aquatic phase (Staples et al., 1997). DMP, DEP, DBP, BBP, DEHP, and DnOP show different time laps for complete biodegradation in water at 20–25°Cfor DMP, DEP three days (Ritsema et al., 1989), for DBP four days (Staples et al., 1997), for BBP seven days (Ritsema et al., 1989), for DEHP twenty days (Staples et al., 1997), and for DnOP seven days (Furtmann 1993). However, the effect of biodegradation was not exclusively investigated, but it could greatly influence on the persistence of PAEs in that study area.

4.1.5 Possible sources and their correlation to the distribution of PAEs

The Figure 3.2 shows the spatial variation of possible industries that have a potential for migration of PAEs in the sub-catchments of sampling locations, and Table 3.2 summarizes the types of industries with their densities located in each sub-catchment of the study area. Maximum of thirteen different types of industries that have a potential for migration of PAEs from their productions were identified within each sub-catchment of the study area. Table 4.5 lists individual PAEs present in industrial products or outputs of the respective industries with their typical weight percentages as follows.

Table 4.5: Typical percentages of different PAEs in industrial final products

Type		Percentages by weight in final products						
		DMP	DEP	DBP	BBP	DEHP	DnOP	References
1	Stationery products distributors			10[1]	37.5[1]	3.75[1]	20[1]	[1] Earls et al., 2003
2	Toy manufacturing industry				0.1[2]	0.001–0.02[2]	<0.00–1[2]	[2] Stringer et al., 2000
3	Household-hardware manufacturing industry				14[3]	14–40[4]		[3]Rodgers et al., 2014; [4] Schettler, 2006
4	Plastic manufacturing industry					67[4]		[4] Bauer and Herrmann, 1997
5	PET bottle manufacturing industry					8[5]		[5] Biscardi et al., 2003
6	PVC Cable manufacturing industry					40[6]		[6]Calafat et al., 2004
7	Pharmaceutical packaging industry		2.7[7]	2.7[7]				[7] Edgren et al., 1990
8	Cosmetic and personal care product packaging industry	1.0[8]	72[8]	8[8]	6[8]	4[8]		[8] Houlihan et al., 2002
9	PVC manufacturing industry					40–50[9], 67[10]		[9]Latini et al., 2010;[10]Koniecji et al., 2011
10	Polyethylene manufacturing industry					20[11]		[11] Yang et al., 2017
11	Pesticide packaging industry	2[12]	2[12]	1[12]				[12] Jones et al., 1947
12	Paint manufacturing industry	4–10[14]		1[13]	10[13]	4–10[14]		[13]Schripp et al., 2014;[14] Reynolds, 1995
13	Apparel industry	1–4[15]	10–60[16]	10–60[16]				[15]Kitchloo et al., 2000; [16] Lippmann, 1942

Trace levels of DMP (<0.5 µg/L) were detected in all samples. Among 13 different types of industries in the sub-catchments, DMP is added in industries of manufacturing and packaging of cosmetic and personal care products, pesticides, paints and apparel in which the maximum percentage weights are 1% (Houlihan et al., 2002), 2% (Jones et al., 1947), 10% (Reynolds, 1995), and 4% (Kitchloo et al., 2000), respectively. DMP is a low-cost, low odorous, safe, and non-irritable solvent with low molecular weight, which is ubiquitously detected in personal care products such as cosmetics, creams, fragrances, perfumes, candles and shampoo (European Commission 2007). The possible reasons for trace levels of DMP detected in all sampling locations could be attributed to its high volatility, the presence of a lesser number of industries contributing to the migration of DMP in sub-catchments, and shorter lapse time for complete biodegradation.

Concentrations of DEP in our samples varied two orders of magnitude (Table 4.1). Among all types of industries in the sub-catchments, DEP is frequently added to the manufacturing and packaging industries of pharmaceutical products (2.7%, Edgren et al., 1990), cosmetics and personal care products (72%, Houlihan et al., 2002), pesticides (2%, Jones et al., 1947), and apparel industry (60%, Lippmann, 1942). Even though DEP is highly evaporative, the mean concentration of DEP of all sampling locations were significantly higher than the corresponding mean concentration of DMP ($p < 0.05$) possibly due to the contribution from multitude industries containing DEP with considerably higher weight percentages. Contribution of thirteen industries (Table 4.5) in this sub-catchment, was found to be the major source of DEP additions to the contribution from households. SP 10, which is in Beira Lake constituted the highest average DEP concentration (265.0 μg/L) among all sampling locations. Beira Lake is almost a non-flowing watercourse, where average BOD and COD levels were 20 mg/L and 52 mg/L, respectively, and is connected to another highly polluted shallow watercourse (St. Sebastian canal with average BOD and COD with 60 mg/L and 187.2 mg/L, respectively). However, only five industries are attributable to the DEP budget, and the contribution from households seems to be extremely high as this sub-catchment has a very high population density (20,300 per km^2). The second highest average DEP concentration (246.0 μg/L) was observed at SP 19 even with the presence of four industries within its sub-catchment. SP 19 is in Weras Ganga, which is comparatively a large shallow watercourse, which receives numerous industrial wastewater inflows. In addition to the contribution from industries, high DEP concentration at SP 19 was attributed to the migration of DEP with raw leachate from the municipal solid waste open dump located just upstream with daily dumping of more than 400 metric tons/day.

In this study, DBP concentrations ranged one order of magnitude. Among all types of industries in the sub-catchments, DBP is often added in PET bottles (56%, Bosnir et al., 2006), stationery product distributors (10%, Earls et al., 2003), manufacturing and packaging of pharmaceutical products (2.7%, Edgren et al., 1990), cosmetic and personal care products (8%, Houlihan et al., 2002), pesticides (1%, Jonsen et al., 2001), paint industry (1%, Schripp et al., 2014), and apparel industry (60%, Castillo and Barcelo, 2000). Nevertheless, these industries showed no direct relationship with concentrations of DBP of sampling locations. Although DBP is evaporative, the significantly lower mean concentration of DBP than the corresponding mean concentration of DEP ($p < 0.05$) could be due to the higher microbial degradation potential and the lesser weight percentages added in industrial products. Similar observations have been reported by Hashizume et al., (2002) in a study where biodegradability of PAEs by microbes isolated from river water showed the lowest biodegradation by bacterial isolates for DMP (0%) and DEP (61%) while some isolates completely degraded DBP.

BBP was found in 5 industries out of 13 (Table 4.5) with different percentages of weight and varied one order of magnitude in all our samples. BBP is a compound having inherent properties such as low molecular weight, long shelf life, low water solubility, and low volatility. SP 04, SP 09, SP 10, and SP 19 showed comparatively higher concentrations of BBP (61, 72, 75, and 69 µg/L), which agrees with the general trend observed for probable sources and respective elevated concentrations of DEP.

Among all 22 sampling locations, SP 20(Rathmalana canal) manifested the highest BBP concentration (108 µg/L) and attributed to industrial inputs with comparatively high weight percentages and a substantial contribution from households from the sub-catchment (population density = 12,000 per km^2).

DEHP was also found in ten industries out of 13 (Table 4.5) with higher percentages added in the manufacturing industries of plastic (67%, Bauer and Herrmann 1997), PVC products (67%, Konieckiet al., 2011), PET bottles (40 %, Bosniret al., 2006), toys (40%, Bouma and Schakel, 2002), household-hardware product manufacturing

(40%, Schettler, 2006) and PVC cables (40%, Calafatet al., 2004). The results corroborated that among all samples, DEHP concentrations varied two orders of magnitude with the occurrence of the highest levels. The mean concentration of DEHP for all locations was higher than that of DEP, but no significant difference was found ($p > 0.05$). The occurrence of comparatively high concentrations of DEHP could be due to its higher molecular weight with less biodegradability compared to other PAEs. Given the inherent properties such as high molecular weight, low volatility, low conductivity, long shelf life and ease of handling, DEHP is the most desired PAE of all PAEs by industrialists. SP 04, SP 09, SP 10, SP 19 and SP 20 showed comparatively higher concentrations of DEHP (82, 114, 137, 101, and 134 µg/L, respectively), which are ascribed to the similar observations reported for those of DEP and BBP. SP 02 in Peliyagoda canal and SP 03 in the Main drain also showed comparatively higher concentrations of DEHP (165 and 105 µg/L) possibly attributable to manufacturing industries, especially PVC cables and other products, and PET bottles. SP 7 in St. Sebastian canal and SP 17 in Maharagama Ela reported higher concentrations (110, 108 µg/L) attributable to the contribution mainly from households, as there is no major contribution from industries.

DnOP was detected in toys (1%, Stringer et al., 2000) and stationary products distributors (20%, Earls et al., 2003). DnOP has similar properties to those of DEHP with high molecular weight, stain resistant, long service life, low odor, and ease of processing. Among 13 industries, only two add DnOP to their products. Trace levels of DnOP (< 1 µg/L) were detected in all samples possibly due to the minute contribution from industries, low volatility and low solubility in water due to high molecular weight.

SP 06 in Kittampahuwa canal, SP 08 in Raggahawatta canal, SP 12 in Diyawanna lake, SP 18 in Nedimala canal, and SP 21 in Kesbewa canal showed very low concentrations of all PAEs for which reasons are not clearly identifies due to the complex nature of the interactions and time-bound variations of ingress of PAEs in the watercourses.

4.2 Ecological risk of PAEs on fish community being present in the urban watercourses

Continuous inputs of intrinsic toxic components are the main parameters that influence the effects on the stability of ecosystems. Technical Guidance Document on risk assessment (European Commission 2003) has been used to estimate the $L(E)C_{50}$ values for fish community. In this study risk assessment was conducted according to the $L(E)C_{50}$ values recorded in the technical guidance document and other literatures. RQ values were calculated using the lowest $L(E)C_{50}$ and a safety factor of 100 (European commission 2003). Table 3.4 presents the relevant concentrations ($L(E)C_{50}$)used for the RQ calculations. Tables 4.7 to 4.12represent the RQ values for fish community at each sampling location. Among the PAEs measured, DEP, DBP, BBP, and DEHP presented the main contribution to the ecological risk on Fish, Crustacea, Insects, Algae, Microorganism, Oligocheata, and Invertebrates.

Table 4.6: RQ values (*Lepomis macrochirus*- Fish community) for DMP, DEP, DBP, BBP, DEHP and DnOP and the Sum of RQs for each location

	DMP	**DEP**	**DBP**	**BBP**	**DEHP**	**DnOP**	**Sum of RQ values**
SP 01	0.0	0.1	3.5	0.0	29.0	0.0	32.6
SP 02	0.0	0.1	3.3	0.0	82.5	0.0	86.5
SP 03	0.0	0.1	5.4	0.0	52.5	0.0	58.0
SP 04	0.0	0.3	5.7	3.5	41.0	0.0	50.6
SP 05	0.0	0.1	3.2	0.0	35.0	0.0	38.3
SP 06	0.0	0.0	0.0	0.0	36.5	0.0	36.5
SP 07	0.0	0.1	4.1	0.0	55.0	0.0	59.3
SP 08	0.0	0.0	6.6	0.0	22.0	0.0	28.6
SP 09	0.0	0.7	4.2	4.3	57.0	0.0	66.1
SP 10	0.0	1.6	5.7	4.4	68.5	0.0	80.2
SP 11	0.0	0.0	0.0	0.0	51.0	0.0	51.0

SP 12	0.0	0.0	0.0	0.0	10.5	0.0	10.5
SP 13	0.0	0.2	5.6	0.0	26.5	0.0	32.2
SP 14	0.0	0.3	5.1	0.0	6.0	0.0	11.3
SP 15	0.0	0.2	3.9	0.0	46.5	0.0	50.6
SP 16	0.0	0.3	5.0	0.0	45.0	0.0	50.2
SP 17	0.0	0.1	4.3	0.0	54.0	0.0	58.5
SP 18	0.0	0.0	0.0	0.0	31.0	0.0	31.0
SP 19	0.0	0.1	4.4	4.0	50.5	0.0	59.1
SP 20	0.0	0.1	5.6	7.8	67.0	0.0	80.6
SP 21	0.0	0.0	0.5	0.0	0.0	0.0	0.5
SP 22	0.0	0.3	4.1	0.0	49.0	0.0	53.4

The RQs indicates significant potential for adverse effects ($10 \leq RQ > 100$) from DEHP in all Sampling points for fish community.

According to the sum of RQ values that calculated for each sampling location, based on the effect of available PAEs (DEP, DBP, BBP, and DEHP) indicated that there was a significant potential for adverse effects on fish community by all sampling locations except SP 21. Lakes isolated and not adjoining to urban industries, which showed no or low adverse effects, most of the urban lakes were observed to have expected or significant potential for adverse effects on fish.

Table 4.7: RQ values (*Hyalella Azteca*–Crustacea community) for DMP, DEP, DBP, BBP, DEHP and DnOP and the Sum of RQs for each location

	DMP	**DEP**	**DBP**	**BBP**	**DEHP**	**DnOP**	**Sum of RQ values**
SP 01	0.0	0.52	2.70	0.19	0.0	0.0	3.42
SP 02	0.0	0.88	2.54	0.35	0.0	0.0	3.77
SP 03	0.0	0.49	4.13	0.12	0.0	0.0	4.73
SP 04	0.0	1.45	4.37	0.33	0.0	0.0	6.15
SP 05	0.0	0.62	2.46	0.25	0.0	0.0	3.33
SP 06	0.0	0.00	0.0	0.0	0.0	0.0	0.00
SP 07	0.0	0.74	3.17	0.23	0.0	0.0	4.14
SP 08	0.0	0.00	0.0	0.0	0.0	0.0	0.00

SP 09	0.0	2.62	3.25	0.81	0.0	0.0	6.69
SP 10	0.0	6.29	4.37	1.44	0.0	0.0	12.10
SP 11	0.0	0.00	0.0	0.0	0.0	0.0	0.00
SP 12	0.0	0.00	0.0	0.0	0.0	0.0	0.00
SP 13	0.0	0.65	4.29	0.15	0.0	0.0	5.09
SP 14	0.0	1.00	3.89	0.26	0.0	0.0	5.14
SP 15	0.0	0.59	3.02	0.20	0.0	0.0	3.81
SP 16	0.0	1.14	3.81	0.30	0.0	0.0	5.25
SP 17	0.0	0.59	3.33	0.18	0.0	0.0	4.11
SP 18	0.0	0.00	0.0	0.0	0.0	0.0	0.0
SP 19	0.0	5.84	3.41	1.71	0.0	0.0	10.97
SP 20	0.0	0.62	4.29	0.14	0.0	0.0	5.05
SP 21	0.0	0.06	0.40	0.15	0.0	0.0	0.61
SP 22	0.0	1.45	3.25	0.45	0.0	0.0	5.15

The RQ values indicate a small potential for adverse effects on crustacean community ($1 \leq RQ \leq 10$) for SP 04, SP 09,SP 10,SP 14,SP 16,SP 19 and SP 22 while other sampling points indicate no significant risk on crustacean community due to DEP presence in watercourses.

BBP concentrations gives RQ values ($1 \leq RQ \leq 10$) which indicates a small potential for adverse effects on crustacean community for SP 01–05, SP 07, SP 09, SP 10.SP 13–17, SP 19, SP 20, and SP 22 while other sampling locations indicates no significant risk on crustacean community.

Due to BBP concentrations, RQ values for the sampling locations indicated that all sampling points except SP 10, and SP 19 had a small potential for adverse effects on crustacean community.

According to the sum of RQ values that calculated for each sampling location, based on the effect of available PAEs (DEP, DBP, BBP) indicated that there was a significant potential for adverse effects on crustacean community by SP 10 and SP 19 while six sampling locations (SP 06, SP 08, SP 11-12, SP 18, SP 21) were not significant in terms of risk on crustacean community and all other sampling locations had a small potential for adverse effects on crustacean community.

Table 4.8: RQ values (*Chironomus tentans* - Insecta community) for DMP, DEP, DBP, BBP, DEHP and DnOP and the Sum of RQs for each location

	DMP	DEP	DBP	BBP	DEHP	DnOP	Sum of RQ values
SP 01	0.0	0.07	0.03	0.00	0.0	0.0	0.10
SP 02	0.0	0.12	0.01	0.00	0.0	0.0	0.14
SP 03	0.0	0.07	0.03	0.00	0.0	0.0	0.09
SP 04	0.0	0.20	0.01	0.00	0.0	0.0	0.21
SP 05	0.0	0.08	0.02	0.00	0.0	0.0	0.11
SP 06	0.0	0.00	0.00	0.00	0.0	0.0	0.0
SP 07	0.0	0.10	0.02	0.00	0.0	0.0	0.12
SP 08	0.0	0.00	0.00	0.00	0.0	0.0	0.0
SP 09	0.0	0.36	0.00	0.00	0.0	0.0	0.36
SP 10	0.0	0.85	0.00	0.00	0.0	0.0	0.86
SP 11	0.0	0.00	0.00	0.00	0.0	0.0	0.0
SP 12	0.0	0.00	0.00	0.00	0.0	0.0	0.0
SP 13	0.0	0.09	0.02	0.00	0.0	0.0	0.11
SP 14	0.0	0.14	0.01	0.00	0.0	0.0	0.15
SP 15	0.0	0.08	0.02	0.00	0.0	0.0	0.10
SP 16	0.0	0.15	0.01	0.00	0.0	0.0	0.17
SP 17	0.0	0.08	0.02	0.00	0.0	0.0	0.10
SP 18	0.0	0.00	0.00	0.00	0.0	0.0	0.0
SP 19	0.0	0.79	0.00	0.00	0.0	0.0	0.80
SP 20	0.0	0.08	0.02	0.00	0.0	0.0	0.11
SP 21	0.0	0.01	0.22	0.00	0.0	0.0	0.23
SP 22	0.0	0.20	0.01	0.00	0.0	0.0	0.21

The RQs calculated for DEP, and DBP had no significant risk on insect community for all 22 sampling locations.

According to the sum of RQ values calculated for each sampling location, based on the effect of available PAEs (DEP, DBP) indicated that there was no significant risk insect community all sampling locations.

Table 4.9: RQ values (*Lumbriculus Variegatus* - Oligocheate community) for DMP, DEP, DBP, BBP, DEHP and DnOP and the Sum of RQs for each location

	DMP	**DEP**	**DBP**	**BBP**	**DEHP**	**DnOP**	**Sum of RQ values**
SP 01	0.0	0.02	0.08	0.26	0.0	0.0	0.37
SP 02	0.0	0.04	0.05	0.74	0.0	0.0	0.83
SP 03	0.0	0.02	0.09	0.23	0.0	0.0	0.34
SP 04	0.0	0.06	0.03	2.01	0.0	0.0	2.10
SP 05	0.0	0.03	0.07	0.37	0.0	0.0	0.46
SP 06	0.0	0.00	0.00	0.00	0.0	0.0	0.00
SP 07	0.0	0.03	0.06	0.52	0.0	0.0	0.61
SP 08	0.0	0.00	0.00	0.00	0.0	0.0	0.00
SP 09	0.0	0.11	0.02	6.60	0.0	0.0	6.72
SP 10	0.0	0.26	0.01	37.93	0.0	0.0	38.20
SP 11	0.0	0.00	0.00	0.00	0.0	0.00	0.00
SP 12	0.0	0.00	0.00	0.00	0.0	0.00	0.00
SP 13	0.0	0.03	0.07	0.41	0.0	0.0	0.50
SP 14	0.0	0.04	0.04	0.95	0.0	0.0	1.04
SP 15	0.0	0.02	0.07	0.34	0.0	0.0	0.44
SP 16	0.0	0.05	0.04	1.24	0.0	0.0	1.33
SP 17	0.0	0.02	0.07	0.34	0.0	0.0	0.44
SP 18	0.0	0.00	0.00	0.00	0.0	0.0	0.00
SP 19	0.0	0.24	0.01	32.69	0.0	0.0	32.94
SP 20	0.0	0.03	0.07	0.37	0.0	0.0	0.46
SP 21	0.0	0.00	0.73	0.00	0.0	0.0	0.73

SP 22	0.0	0.02	0.07	0.35	0.0	0.0	0.44

RQ Values of DEP, and DBP indicated that there is no significant risk on oligocheate community (1 ≤ RQ).

RQ Values calculated for BBP at SP 19 indicated that there is a significant potential for adverse effect on the oligocheata community while the SP 04, SP 09, SP 10, and the SP 16 indicate a non-significant potential for adverse effect and other sampling locations indicate no significant risk on oligocheata community.

According to the sum of RQ values calculated for each sampling location, based on the effect of available PAEs (DEP, DBP) indicated that SP 10 and SP 19 indicates a small potential adverse effect. All other sampling locations had no significant risk on oligocheata community.

Table 4.10: RQ values (*Tetrahymenapyriformis* - Microorganismcommunity) for DMP, DEP, DBP, BBP, DEHP and DnOP and the Sum of RQs for each location

	DMP	**DEP**	**DBP**	**BBP**	**DEHP**	**DnOP**	**Sum of RQ values**
SP 01	0.0	0.02	0.24	0.0	0.0	0.0	0.26
SP 02	0.0	0.03	0.23	0.0	0.0	0.0	0.26
SP 03	0.0	0.02	0.37	0.0	0.0	0.0	0.39
SP 04	0.0	0.05	0.39	0.0	0.0	0.0	0.44
SP 05	0.0	0.02	0.22	0.0	0.0	0.0	0.24
SP 06	0.0	0.00	0.00	0.0	0.0	0.0	0.00
SP 07	0.0	0.02	0.29	0.0	0.0	0.0	0.31
SP 08	0.0	0.00	0.00	0.0	0.0	0.0	0.00
SP 09	0.0	0.08	0.29	0.0	0.0	0.0	0.38
SP 10	0.0	0.20	0.39	0.0	0.0	0.0	0.59
SP 11	0.0	0.00	0.00	0.0	0.0	0.0	0.00
SP 12	0.0	0.00	0.00	0.0	0.0	0.0	0.00
SP 13	0.0	0.02	0.39	0.0	0.0	0.0	0.41

SP 14	0.0	0.03	0.35	0.0	0.0	0.0	0.38
SP 15	0.0	0.02	0.27	0.0	0.0	0.0	0.29
SP 16	0.0	0.04	0.34	0.0	0.0	0.0	0.38
SP 17	0.0	0.02	0.30	0.0	0.0	0.0	0.32
SP 18	0.0	0.00	0.00	0.0	0.0	0.0	0.00
SP 19	0.0	0.19	0.31	0.0	0.0	0.0	0.49
SP 20	0.0	0.02	0.39	0.0	0.0	0.0	0.41
SP 21	0.0	0.00	0.04	0.0	0.0	0.0	0.04
SP 22	0.0	0.05	0.29	0.0	0.0	0.0	0.34

RQ values for DEP and DBP indicate that there is no significant risk to the microorganism's community according to the present concentration levels.

Table 4.11: RQ values (*Chlorella Pyrenoidosa* – Algae community) for DMP, DEP, DBP, BBP, DEHP and DnOP and the Sum of RQs for each location

	DMP	**DEP**	**DBP**	**BBP**	**DEHP**	**DnOP**	**Sum of RQ values**
SP 01	0.0	0.14	0.01	0.48	58.00	0.0	58.63
SP 02	0.0	0.23	0.01	0.48	165.00	0.0	165.72
SP 03	0.0	0.13	0.01	0.48	105.00	0.0	105.62
SP 04	0.0	0.38	0.00	29.05	82.00	0.0	111.44
SP 05	0.0	0.16	0.01	0.48	71.00	0.0	71.65
SP 06	0.0	0.00	0.00	0.00	0.00	0.0	0.00
SP 07	0.0	0.19	0.01	0.48	110.00	0.0	110.68
SP 08	0.0	0.00	0.00	0.00	0.00	0.0	0.00
SP 09	0.0	0.69	0.00	34.29	114.00	0.0	148.98
SP 10	0.0	1.66	0.00	35.71	137.00	0.0	174.37
SP 11	0.0	0.00	0.00	0.00	0.00	0.0	0.00
SP 12	0.0	0.00	0.00	0.00	0.00	0.0	0.00
SP 13	0.0	0.17	0.01	0.48	53.00	0.0	53.66
SP 14	0.0	0.26	0.01	0.48	12.00	0.0	12.75

SP 15	0.0	0.16	0.01	0.48	93.00	0.0	93.65
SP 16	0.0	0.30	0.01	0.48	90.00	0.0	90.78
SP 17	0.0	0.16	0.01	0.48	108.00	0.0	108.65
SP 18	0.0	0.00	0.00	0.00	0.00	0.0	0.00
SP 19	0.0	1.54	0.00	32.86	101.00	0.0	135.40
SP 20	0.0	0.16	0.01	51.43	134.00	0.0	185.60
SP 21	0.0	0.02	0.11	0.48	0.50	0.0	1.11
SP 22	0.0	0.38	0.00	0.48	98.00	0.0	98.86

RQ values for DBP indicate no significant risk to the algae community at all sampling locations.

Due to DEP concentration, there was a small potential adverse effect on the algae community at the sampling points of SP 10 and SP 19 while other locations had no significant risk to algae community.

RQ Values calculated according to the BBP concentrations indicated that SP 04, SP 09, SP 10, SP19, and SP 20 had a significant adverse effect (RQ ≥ 100)on algae community and all other sampling locations did not indicate any significant risk to algae community.

According to the sum of RQ values calculated for each sampling location, based on the effect of available PAEs (DEP, DBP, BBP, DEHP) indicated that there was a significant adverse effects (10≤ RQ ≤ 100) on algae community at SP 02–04, SP 07, SP 09, SP 10, SP 17, SP 19 and SP 20 while few other sampling locations (SP 01, SP 05, SP 13–16, and SP 22) indicates a small significant (1≤ RQ≤ 10) risk on algae community and all other sampling locations had no significant risk on algae communities.

Table 4.12: RQ values (*Daphnia Magna* - Invertebratecommunity) for DMP, DEP, DBP, BBP, DEHP and DnOP and the Sum of RQs for each location

	DMP	**DEP**	**DBP**	**BBP**	**DEHP**	**DnOP**	**Sum of RQ values**

SP 01	0.0	0.03	0.57	0.05	12.55	0.0	13.19
SP 02	0.0	0.04	0.53	0.08	6.61	0.0	7.27
SP 03	0.0	0.02	0.87	0.03	31.51	0.0	32.43
SP 04	0.0	0.07	0.92	0.08	11.85	0.0	12.91
SP 05	0.0	0.03	0.52	0.06	8.83	0.0	9.44
SP 06	0.0	0.00	0.00	0.00	0.00	0.0	0.00
SP 07	0.0	0.04	0.67	0.05	12.33	0.0	13.09
SP 08	0.0	0.00	0.00	0.00	0.00	0.0	0.00
SP 09	0.0	0.13	0.68	0.19	3.63	0.0	4.63
SP 10	0.0	0.31	0.92	0.34	2.73	0.0	4.29
SP 11	0.0	0.00	0.00	0.00	0.00	0.0	0.00
SP 12	0.0	0.00	0.00	0.00	0.00	0.0	0.00
SP 13	0.0	0.03	0.90	0.04	25.33	0.0	26.30
SP 14	0.0	0.05	0.82	0.06	13.66	0.0	14.58
SP 15	0.0	0.03	0.63	0.05	13.80	0.0	14.51
SP 16	0.0	0.06	0.80	0.07	11.47	0.0	12.39
SP 17	0.0	0.03	0.70	0.04	16.86	0.0	17.63
SP 18	0.0	0.00	0.00	0.00	0.00	0.00	0.00
SP 19	0.0	0.29	0.72	0.40	1.80	0.0	3.20
SP 20	0.0	0.03	0.90	0.03	26.79	0.0	27.76
SP 21	0.0	0.00	0.08	0.03	2.39	0.0	2.51
SP 22	0.0	0.07	0.68	0.10	6.58	0.0	7.44

RQ values for DEP, DBP, and BBP indicate no significant risk on invertebrate community at all sampling locations.

RQ values of DEHP indicate that there was a significant adverse effect (10≤ RQ ≤ 100) on invertebrate community at the sampling points of SP 01, SP 03, SP 04, SP 07, SP 13–17, and SP 20 while few other locations (SP 18, SP 06, SP 08, SP 11, and SP 12) had no significant risk on invertebrate community. Other sampling locations indicate that RQ values in the range of 1 –10 which indicates there was a small potential for adverse effect on invertebrate community.

According to the sum of RQ values calculated for each sampling location, based on the effect of available PAEs (DEP, DBP, BBP, and DEHP) indicated that there was a significant adverse effect on the algae community at SP 01, SP 03, SP 04, SP 07, and SP 13–17, while few sampling locations (SP 02, SP 05, SP 09, SP 10, SP 19, SP 21, and SP 22) indicate a small significant risk to algae community and other all sampling locations had no significant risk on algae communities.

4.3 Evaluate the effectiveness and efficiency of different types of nanoparticles for removal of PAEs from industrial effluents

4.3.1 Characterization of synthesized TiO_2

4.3.1.1 XRD analysis

The Figure 4.1 shows X-Ray Diffraction (XRD) pattern of synthesised TiO_2 exhibiting major photocatalyst phases of 25.3°, 37.8°, 48.0°, 53.9°, 55.1°, 62.7°, 68.8°, and 72.3° which can be assigned to diffraction of (101), (004), (200), (105), (211), (204), (116), and (215) planes respectively (Yang et al., 2017, Lia et al, 2016). 25.3° is the characteristic peak for Anatase TiO_2 (Ijadpanah-Saravy et al., 2014) which exhibits high photocatalytic activity in photocatalytic degradation of pollutants (Deng et al., 2014, Nakamura et al., 2002). Sharpness attributed to the crystallinity of TiO_2 nanoparticles (Bhattacharyya et al., 2004) and the sharp XRD peaks indicated highly crystalized TiO_2 particles. The average crystalline size of the TiO_2 was calculated using Scherrer Formula as given in Eq. 9

$$D = \frac{0.9\lambda}{\beta \cos \Theta} \tag{9}$$

D is the average crystal size, K is the scherrer constant of diffraction peak. For TiO_2 crystal K is 0.89, λ is the wavelength of the X-ray radiation, $\beta_{1/2}$is the full width at 2θ value of 25.3° of half maximum of a diffraction peak, and θ is the angle of diffraction. Average crystalline size obtained from XRD data was 42.5 nm, which confirms that a major fraction of TiO_2 was within the nano-scale. Small size TiO_2 nanoparticles (4 – 30 nm), aggregates rapidly in a suspension which loses its surface area as well as the catalytic efficiency (Bhattacharyya et al., 2004). Therefore, synthesized TiO_2 particles size is favorable for the catalytic activity.

There is no change in the XRD profile before and after DEHP removal mechanism which indicates that the structure of TiO_2 does not change during the photocatalytic process, and the stability of the photocatalytic activity depends on the stability of the structure (Yang et al., 2017).

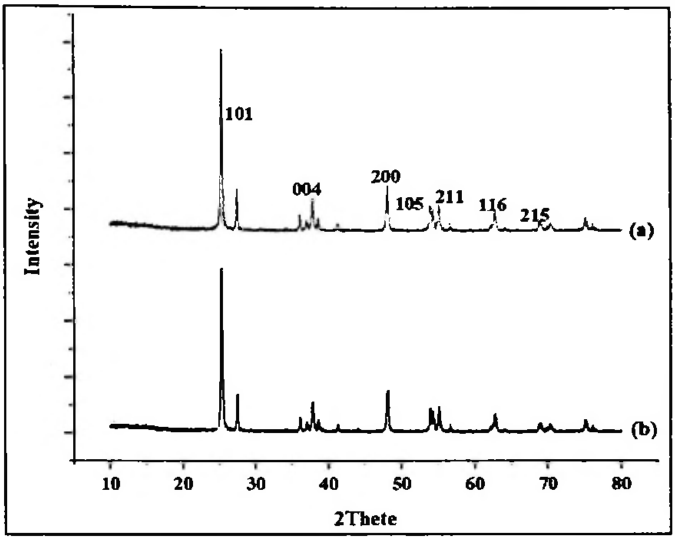


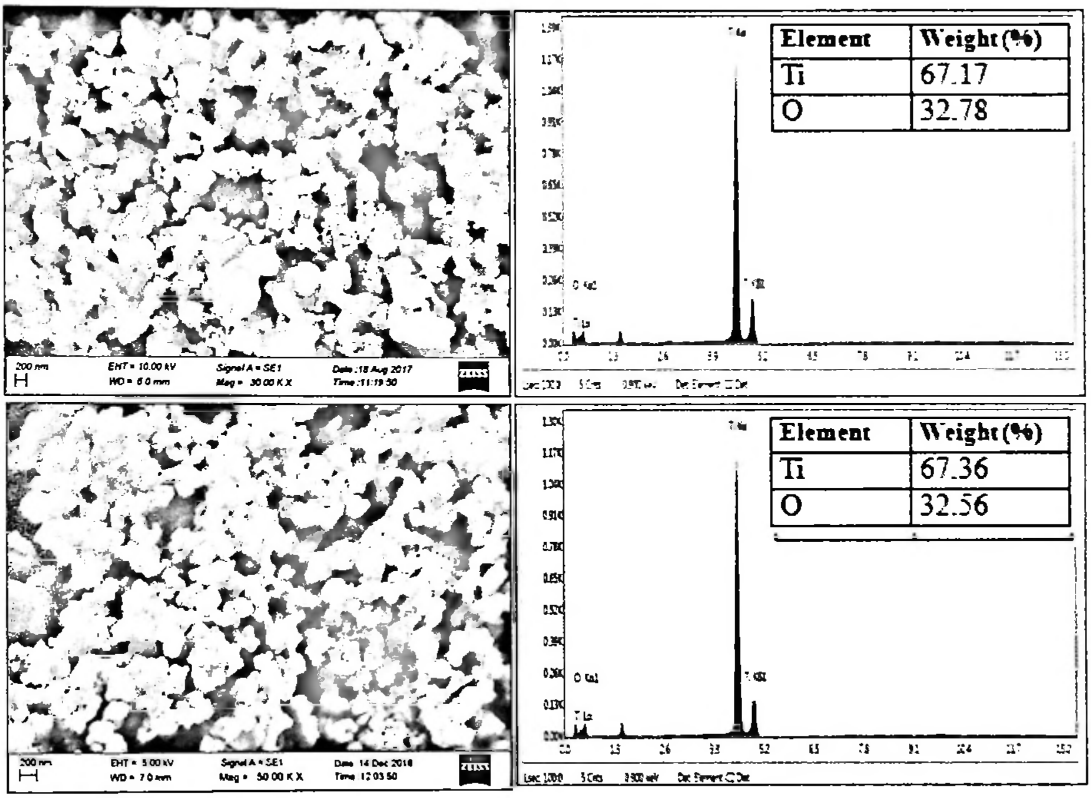
Figure 4.1: X-Ray Diffraction pattern of TiO_2 (a) before and (b) after photo degradation of DEHP

4.3.1.2 ESEM – EDX analysis

Uniformly distributed particles are almost uniform in size and spherical shape. Some of the larger particles in Figure 4.2 can be the aggregations of the smaller particles due to van der waals forces (Rence, 2013). Sharpe edges of the particles attributed to crystalline structure of TiO_2 (Timmusk et al., 2018; Thamaphat et al., 2008). Similar observations of crystalline structure of TiO_2 have reported by Bhattacharya et al., (2004), Timmusk et al., (2018) and Thamaphat et al., (2008) in their studies.

The EDX analysis (Figure 4.2) shows that nanoparticles are composed of Titanium (Ti) and oxygen (O) only. Except for Ti and O, no other peak for any other element has been found in the spectrum which confirmed that the nanoparticles are pure TiO_2 (AL-harbi et al., 2011). Similar observations on the formation of the crystalline structure of TiO_2 have reported by Lin et al., (2009) and Azzam et al., (2016). ESEM analysis of TiO_2 after photodegradation shows spherical-shaped agglomerated particles with sharp edges (Figure 4.2.b) which confirms there is no morphological change after DEHP removal reaction.

EDX after photodegradation reported that there is a small change in weight percentages of Ti and O as they utilized for catalytic activities. XRD profile confirm this change where the XRD pattern after photodegradation indicated a small reduction in intensity of peaks at each crystal phases (Sorathiya et al., 2016).



Element	Weight (%)
Ti	67.17
O	32.78

Element	Weight (%)
Ti	67.36
O	32.56

Figure 4.2: ESEM – EDX pictures of TiO_2 (a) before and (b) after photo degradation of DEHP

4.3.1.3 FT – IR analysis

FT–IR spectrum of TiO_2 shows the specific peaks reflecting the surface functional groups and the complex nature of the surface of TiO_2. The FT–IR spectra of synthesised TiO_2 before and after the adsorption are plotted in Figure 4.3and Figure 4.4. It shows an intense peak at 545cm^{-1}, which can be attributed to stretching vibrations of Ti – O bond. This is similar to the observation reported by Yang et al., (2017), Al-Amin et al., (2016), amd Gardy et al., (2017).

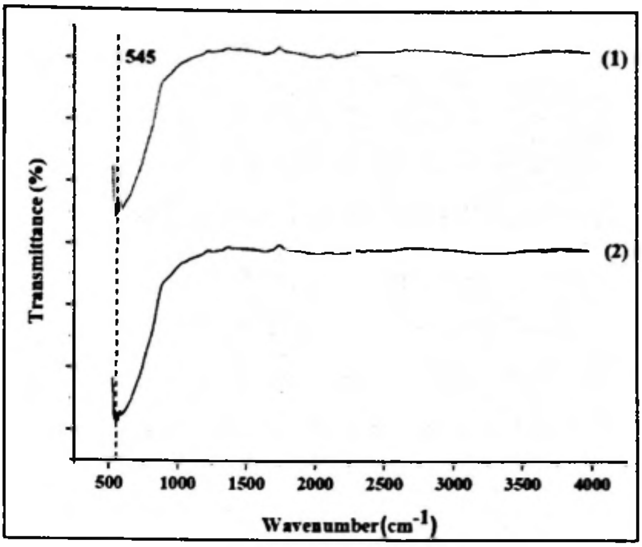


Figure 4.3: FT – IR spectra of TiO_2 (1) before and (2) after photodegradation of DEHP

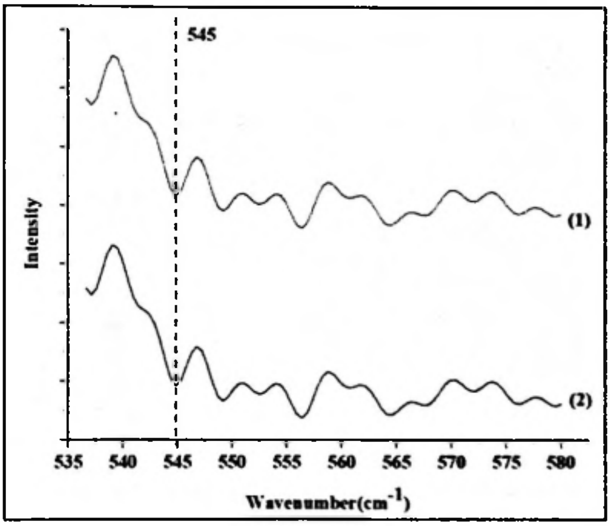


Figure 4.4: FTIR spectra of TiO_2 (1) before and (2) after photodegradationof DEHP

After the photodegradation, the functional groups were not changed on the TiO_2 surface as shown in the line spectrum 2 in figure 4.3 where both FT–IR spectrums are showing the same intense peak and there are no changes. This attributed to the stability of TiO_2 during the removal reaction. Figure 4.4 shows that there are no changes in the characteristic peak and match with XRD results.

4.3.2 Removal of DEHP by TiO_2

4.3.2.1 Effects of TiO_2 dosage and contact time of the solution for removal of DEHP

The effect of TiO_2 dosage in removing DEHP was determined by varying the TiO_2 dosage from 0.5 g/L to 3.0 g/L for the sample containing 171 µg/L initial DEHP concentration (Figure 4.4). The increase of TiO_2 dosage increased the particle density in a unit volume and high particle density increased the interaction between TiO_2 particles and pollutant materials which lead to high removal efficiency. The concentration of DEHP did not show substantial variation beyond 1 g of TiO_2 and those dosages are unfavourable as the synthesis cost is considerably high. The reference level for the aquatic life according to the Canadian Council of Ministers of the Environment is 16 µg/L for Aquatic life (Updated 2018) and it reached at nearly 44 minutes by 1 g TiO_2 dosage. 0.5g dosage does not reach the reference level and other dosages (1.5g, 2g, and 3g) reached in 15 minutes.

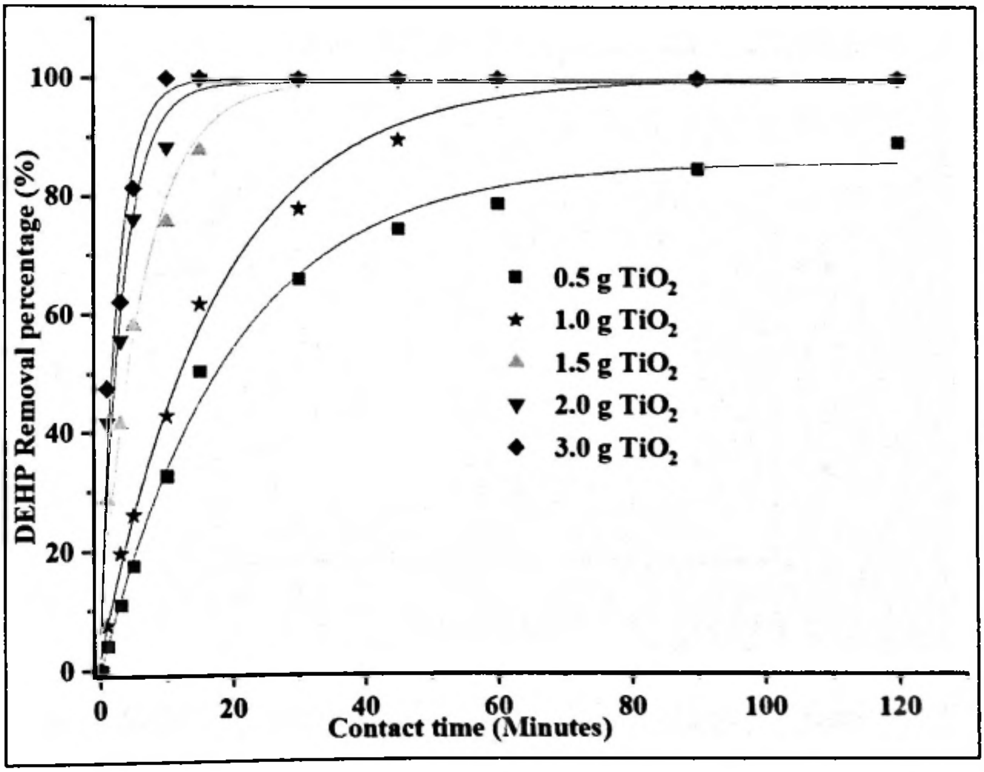


Figure 4.5: DEHP Removal percentage with TiO_2 dosage

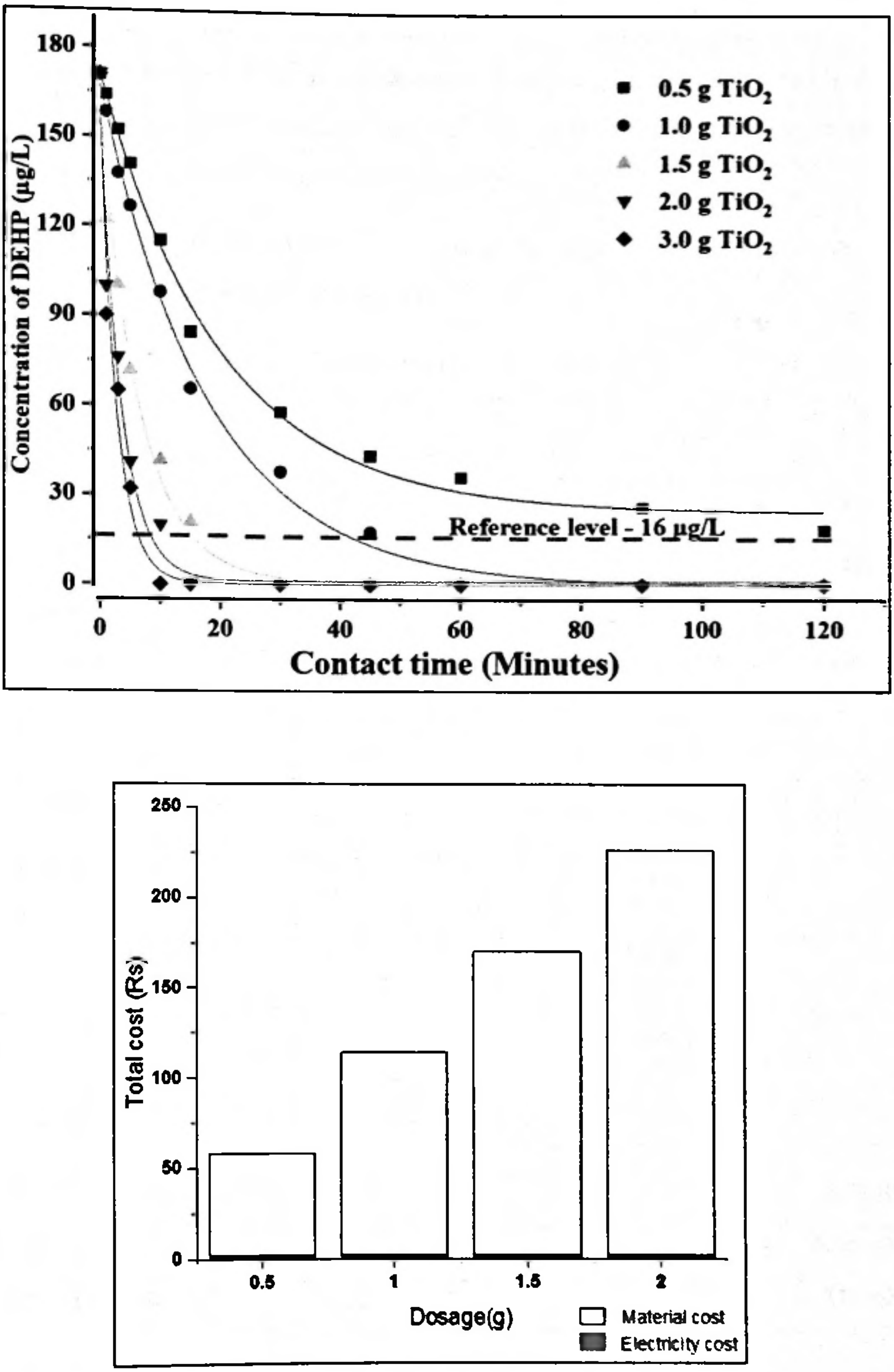


Figure 4.6: (a) DEHP Concentration changes with TiO_2 dosage (b) Cost analysis

DEHP removal percentage increases with the increased dosage of TiO_2. It is suggested that the increase of efficiency was due to the increase of total surface area for the photocatalytic reaction when the amount of TiO_2 increased (Chung and Chen, 2008). When the amount of TiO_2 overdosed, the surface area was saturated and the intensity of Ultraviolet (UV) was thus attenuated because light penetration decreased and light scattering increases (Wong and Chu, 2003).

Synthesis cost for 1 g of TiO_2 is shown as follows in Table 4.7. According to the cost calculations, Material cost per 1 g is Rs. 118.68.

Table 4.13: Cost calculation for the synthesis of one gram of TiO_2

Description		**(Rs)**
PI (0.077 g)		29.00
Ethanol (27 ml)		205.60
TIPT (70 ml)		1860.50
Material Cost		**2095.10**
Electricity cost for furnace		
Watt value of furnace	4000 W	
Calcination hours	4 hrs	
Total Watt value	16000 wh	
Kwh	16 Kwh	
Cost of synthesis procedure		**160.00**
Total cost		**2255.10**
Cost per 1 g of TiO_2		**118.68**

Table 4.14: Cost calculation for the catalyst reaction of TiO_2

Electricity cost for two UV bulbs	
Watt value of furnace	95 W

Calcination hours	1 hrs	
Total Watt value	95 wh	
Kwh	0.095 Kwh	
Kwh for two bulbs	0.19 Kwh	
Cost for two UV bulbs		**1.9**

According to the cost calculations of TiO_2. Synthesis cost is much higher than the operating cost for the catalysis reaction. Data obtained from DEHP removal investigated that below 1 g dosage gives sufficient DEHP removal. But when the dosage is increased it is attributed to increases in material cost. Hence the use of low weight for the reaction is favorable. As 0.5 g dosage doesn't sufficient for the adequate removal mechanism, 1 g of TiO_2 dosage selected as the optimum dosage.

4.3.3 Recycling ability of TiO_2

Regeneration cycles of TiO_2 show that there is no significant difference between the removal capacity of virgin TiO_2 and TiO_2 after each recycling time. According to the GC/MS results in all five cycles able to remove 171 µg/L DEHP concentration up to below the reference level (16 µg/L) which indicated TiO_2 is stable after 5 photocatalysis cycles for sufficient removal.

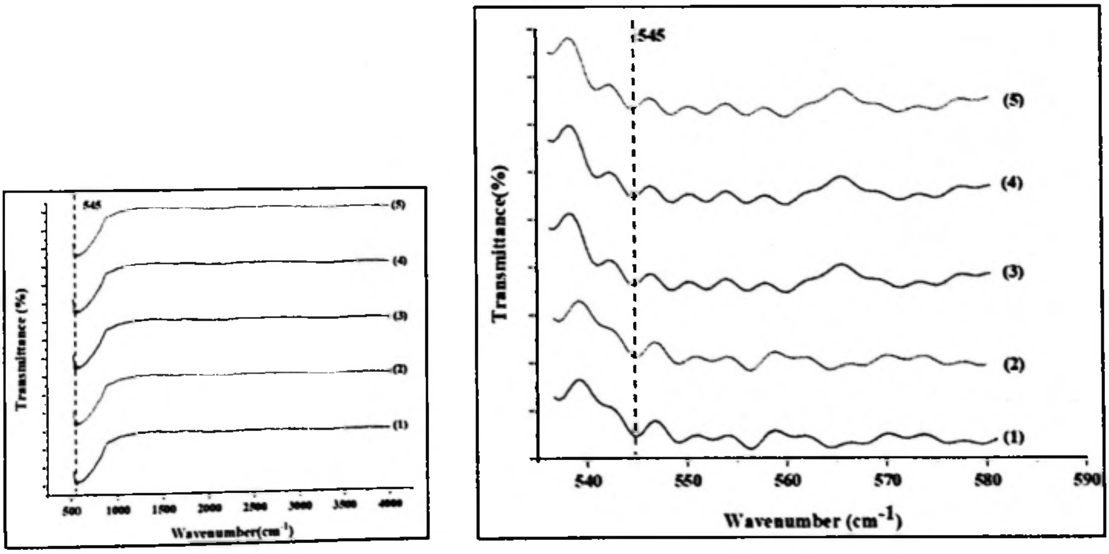


Figure 4.7: FT – IR spectra of TiO_2 after (1) 1st Recycle (2) 2nd Recycle (3) 3rd Recycle (4) 4th Recycle (5) 5th Recycle

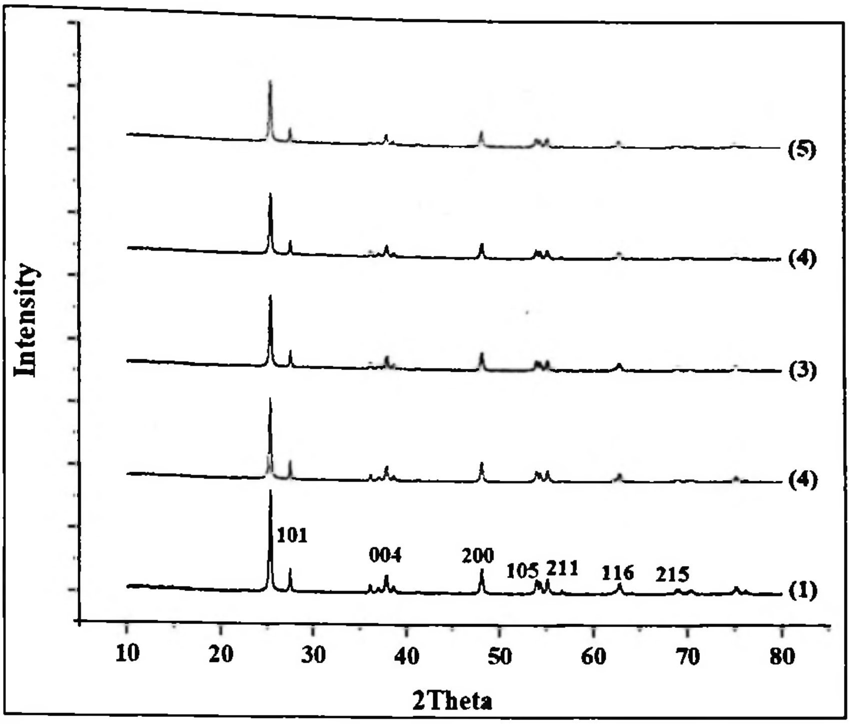


Figure 4.8: XRD profile of TiO_2 after (1) 1st Recycle (2) 2nd Recycle (3) 3rd Recycle (4) 4th Recycle (5) 5th Recycle

After 1st and 2nd cycle, there are no changes in FT-IR spectra. But FT-IR after the 3rd cycle shows a slight shift in a peak at 545 cm^{-1}. In XRD profile, Intensity and peak width has been decreased according to the data obtained after each recycle time. The decrease in peak width indicates a reduction in crystallinity of the material (Sorathiya at el., 2016). So the material crystallinity has changed with each reaction cycle. FT-IR data and XRD data proved that there are no significant changes as they are stable in their structure after five times of photocatalytic reactions.

4.3.4 Characterization of MCFA

4.3.4.1 XRD analysis

The Figure 4.9 shows X-Ray Diffraction (XRD) pattern of synthesized MCFA is exhibiting peaks at 12.4°, 17.6°, 21.6°, 28.0°, 30.9°, 33.3°, 51.4°, and 62.8°, which can assign to diffraction of the (110), (020), (311), (131), (022), (112), (804), and (916) planes, respectively, of the nanoparticles. Kokotailo and Fyfe, (1995), Abidin et al., (2017; and Burton et al., (2009) have reported the same observations.

XRD pattern after the DEHP adsorption has been changed. Few peaks have disappeared and some peaks reduce their intensity at planes. The peak at 804 plane is charecterize peak in XRD pattern and only the difference in before and after the adsorption is intensity of peak height and slight peak shifts. Furthermore, some peaks have been dissapeared after adsorption and with the adsorption of DEHP, crystalinity of MCFA has been changed.

The average crystalline size of the MCFA was calculated from the XRD spectrum using Scherrer Formula as given in Eq. 10 (Chekli et al., 2016):

$$D = \frac{K\lambda}{\beta\cos\Theta} \quad (10)$$

Where D is the average crystalline grain size, K is the scherrer constant of diffraction peak. For MCFA, crystal K is 0.89, λ is the wavelength of the X-ray radiation, $\beta_{1/2}$is the full width at 2θ value of 30.9° of half maximum of a diffraction peak, and Θ is the angle of diffraction. The average crystalline size obtained from XRD data was 44.2 nm, which confirms that a major fraction of MCFA was within the nano-scale.

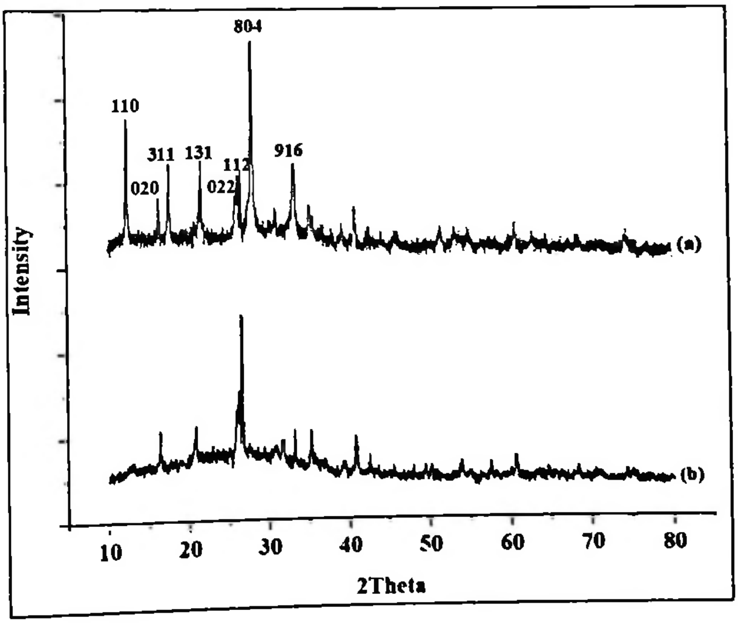


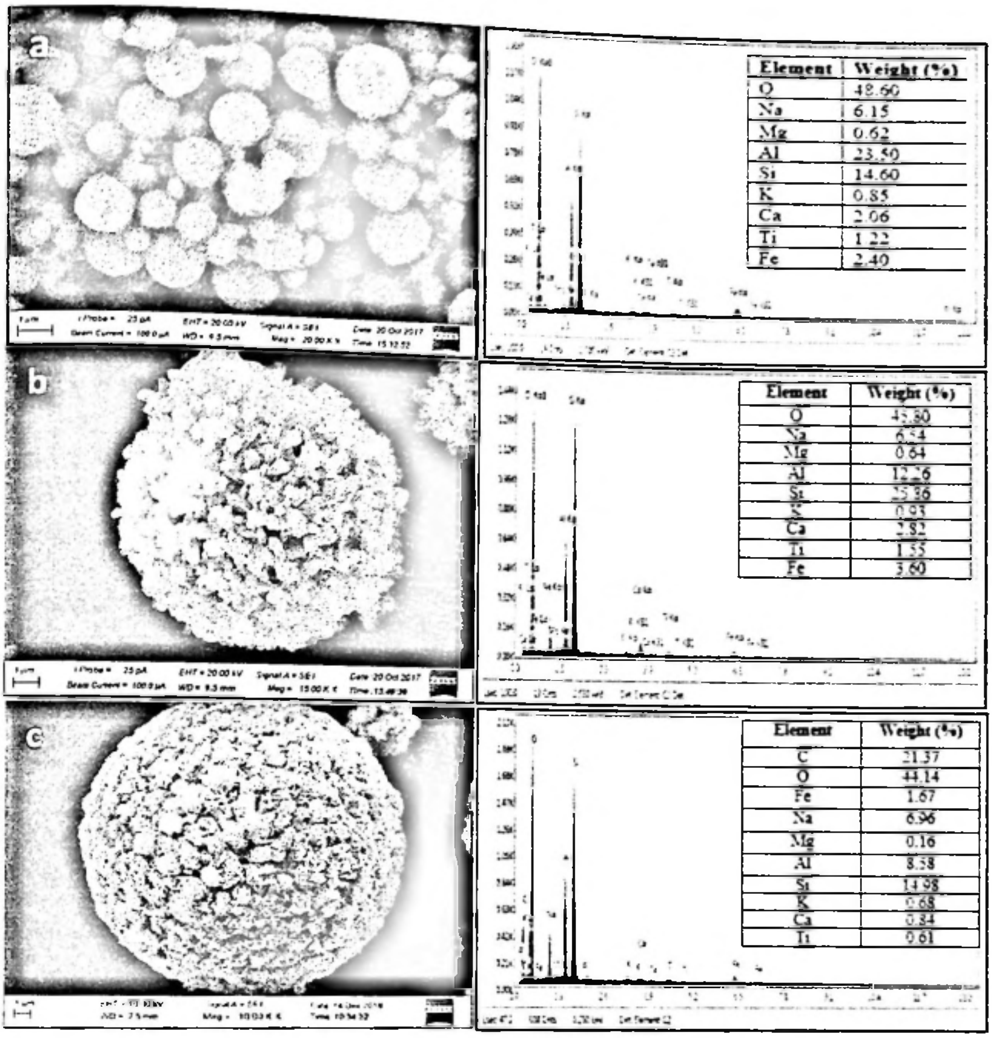
Figure 4.9: XRD profile of MCFA (a) before (b) after DEHP adsorption

4.3.4.2 ESEM – EDX analysis

The ESEM image of synthesized MCFA (Figure 4.10) shows the presence of small particles in the shape of the solid - building block-like with sharp-edged solid prisms and this makes a high surface area for the adsorption activities. The surface is fully covered with these prisms perpendicular to the surface. Similar observations on agglomeration and formation of the crystalline structure of MCFA have reported by Manafia and Joughehdoust, (2008) and Ferrarini et al., (2016). In contrast, the SEM image after DEHP removal clearly shows small aggregates of 'tightly-coiled-frizzy-hair-like' configuration because of the strong adsorption of DEHP. The solid prism crystals that were present in MCFA is covered by the sheets and the aggregates in SEM picture after DEHP adsorption.

The EDX analysis of MCFA shows that the surface was composed of Si, O and Al with no other dominant impurities and the diffraction narrow peaks confirmed the crystalline structure of MCFA without any impurities. Similar observations on agglomeration and the formation of the crystalline structure of MCFA have reported by Manafi and Joughehdoustb, (2008) and Ferrarini et al., (2016).

After the adsorption mechanism, SEM analysis shows absorbed materials on the surface which indicates DEHP particles on a MCFA surface like warms. Morphology has been changed than the initial morphology of MCFA. Also with the EDX analysis, it shows that the Carbon (C) weight percentage increased by 21.37% as there is no C presence in pure MCFA (before DEHP adsorption). It confirms that compound with C has adsorbed onto MCFA surface. DEHP contains a high amount of C and the presence on MCFA surface is due to adsorption of DEHP.



Element	Weight (%)
O	48.60
Na	6.15
Mg	0.62
Al	23.50
Si	14.60
K	0.85
Ca	2.06
Ti	1.22
Fe	2.40

Element	Weight (%)
O	45.30
Na	6.54
Mg	0.64
Al	12.26
Si	25.36
K	0.93
Ca	2.82
Ti	1.55
Fe	3.60

Element	Weight (%)
C	21.37
O	44.14
Fe	1.67
Na	6.96
Mg	0.16
Al	8.58
Si	14.98
K	0.68
Ca	0.34
Ti	0.61

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

4.3.4.3 FT–IR analysis

MCFA shows broad bands near the wavelengths given in Table 4.9. According to band analysis, it could be inferred that the structure that was proposed by XRD analysis is compatible with the FT–IR results. The FT–IR spectrum of MCFAshows the specicific peaks reflecting the surface functional groups and the complex nature of the surface of MCFA. The FT–IR spectra of synthesised MCFA (Figure 4.11) shows broad bands around 3417, 1635, 990 cm^{-1}which were due to O–H stretching vibrations, H–O–H bending, and Si–O stretching vibrations, Si–O–Si stretching vibrations, bending vibrations of O–Si–O, and stretching vibration of Si–O–Al respectively (Mozgawa et al., 2011). Characterized peaks of Zeolite are as follows,

Table 4.15 Characteristic peaks of Zeolite

Functional group	**Wave number (cm^{-1})**
OH stretching	3650 – 3400
H-O-H bending	1620 – 1640
TO$_4$ (T = Al, Si) stretching	900 - 1200

In virgin Zeolite, above three peaks are dominant which confirms the structure of zeolite nanomaterial(Holub et al., 2016). In the FT–IR shape of (b) in Figure 4.11, two peaks revealed at 1448 cm^{-1}, and 1735 cm^{-1}which indicates CH-, C=O bonds, respectively. The band which are obtained after DEHP adsorption are shown as follows in Table 4.10 due to adsorbed PAE compounds (Ayob and Abdullah, 2012, Qiu et al., 2011).

Table 4.16: Peaks obtained after DEHP adsorption

Functional group	**Wave number (cm^{-1})**
OH– stretching	3650 – 3400
H–O–H bending	1620 – 1640
TO$_4$ (T = Al, Si) stretching	900 – 1200
C–H bending (Methyl group)	1448
C=O Steaching (Esters)	1735

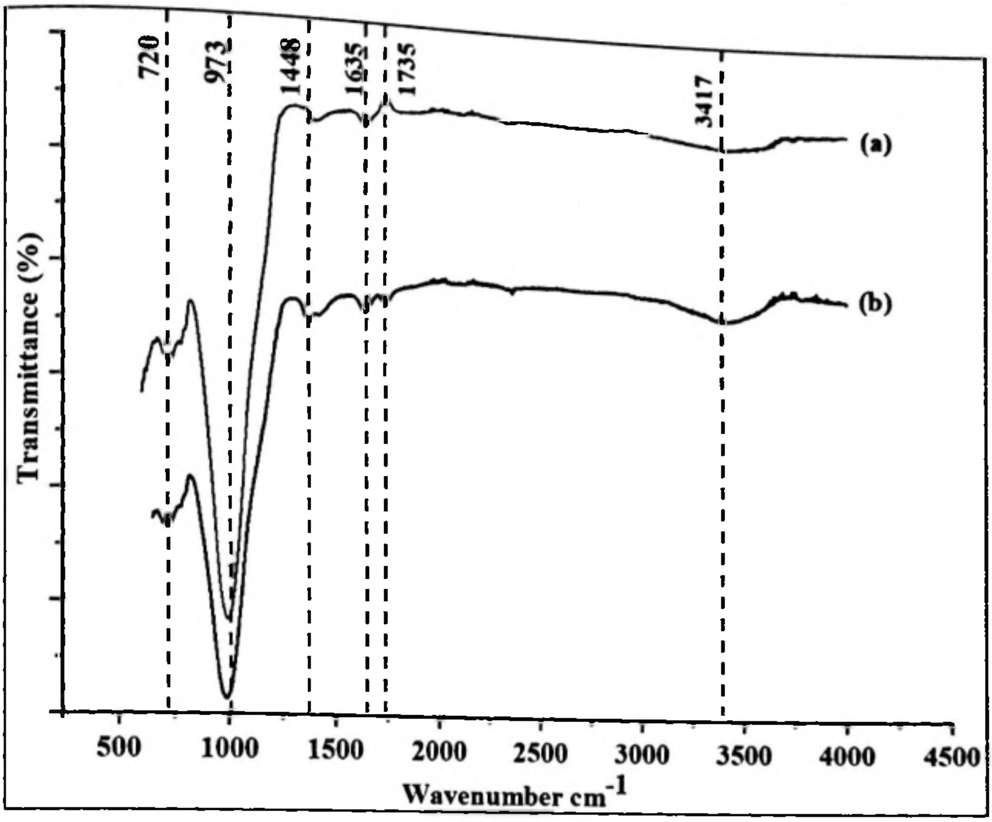


Figure 4.11: FT–IR spectra of MCFA (a)before (b)after adsorption

4.3.5 Removal of DEHP by MCFA

4.3.5.1 Effects of TiO₂ dosage, contact time of the solution on removal of DEHP

The effect of Contact time in removing DEHP was determined by varying the MCFA dosage from 1.0 to 3.0 g/L. Contact time was vary up to 120 minutes for the DEHP removal. A considerable change in the percentage of DEHP removal was not observed beyond 120 minutes contact time, where maximum DEHP removal was 98 %. Dosage of 2.5 g and 3.0 g shows effective DEHP removal with the contact time of 28 minutes and 60 minutes respectively. With concerning MCFA synthesis cost, its is Rs. 6.2 per gram. As the cost is not significant factor in MCFA its favourable to select 28 minutes as the optimum contact time.

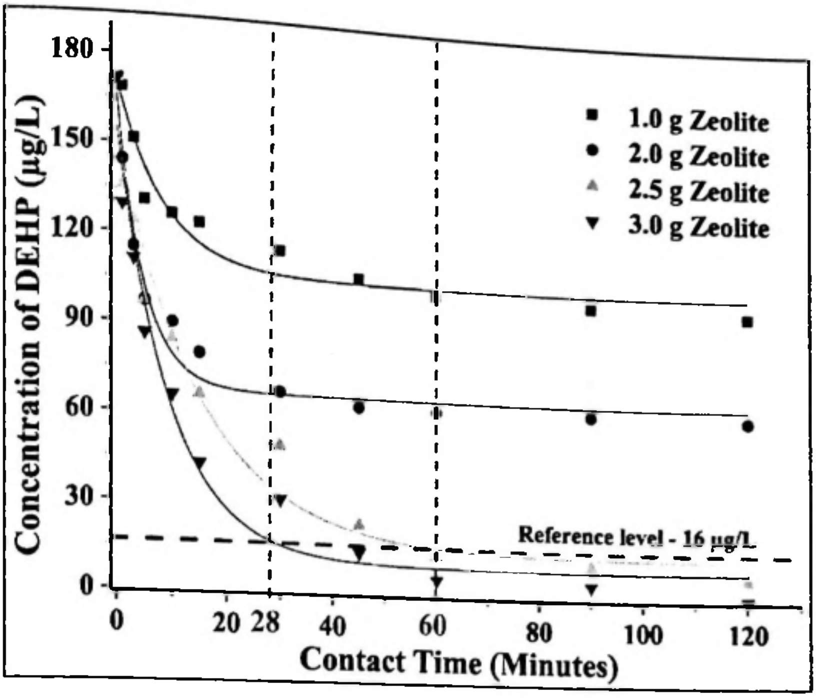


Figure 4.12: Adsorption batch experiments results with DEHP removal by MCFA

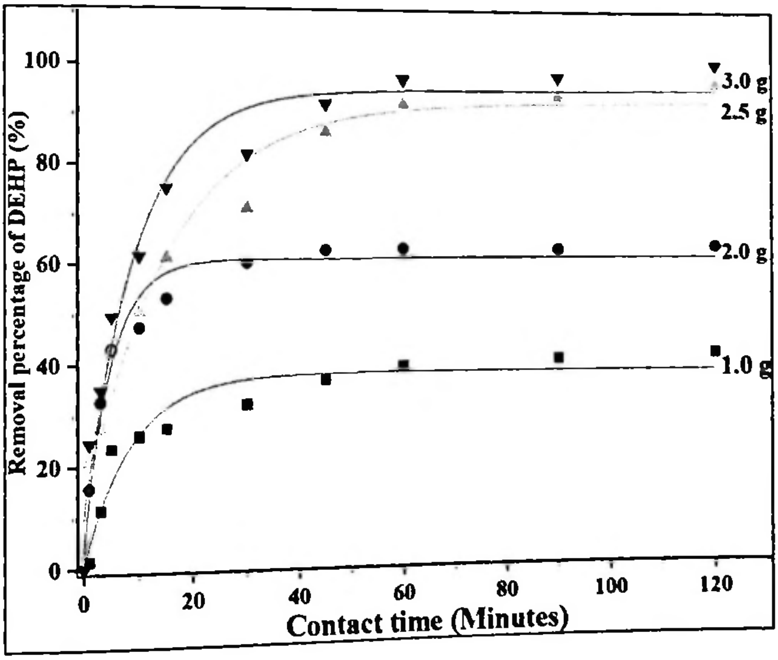


Figure 4.13: Adsorption batch experiments results with DEHP removal by MCFA

4.3.5.2 Adsorption isotherms for DEHP removal by MCFA

Batch experiments were conducted to investigate the adsorption isotherm behaviour of the MCFA in the removal mechanism of DEHP. The results obtained from batch experiments were fitted with Tempkin, Dubinin-Radushkevich, Freundlich, and Langmuir. R^2 values obtained for Tempkin, Dubimin-Radushkevich, Freundlich, and Langmuir are 0.72, 0.86, 0.94 and, 0.98 respectively. Langmuir model fitted with the results obtained giving $R^2 = 0.98$. The R^2 values of the isotherm models fitted with experimental results summarize in Table 4.12 as follows.

The maximum monolayer adsorption capacity (Q_m) of MCFA based on the Langmuir model was 63.6 µg/g for DEHP. The equilibrium parameter (R_L) was between 0.02–0.04 for DEHP, which indicated that the monolayer adsorption mechanism was favorable.

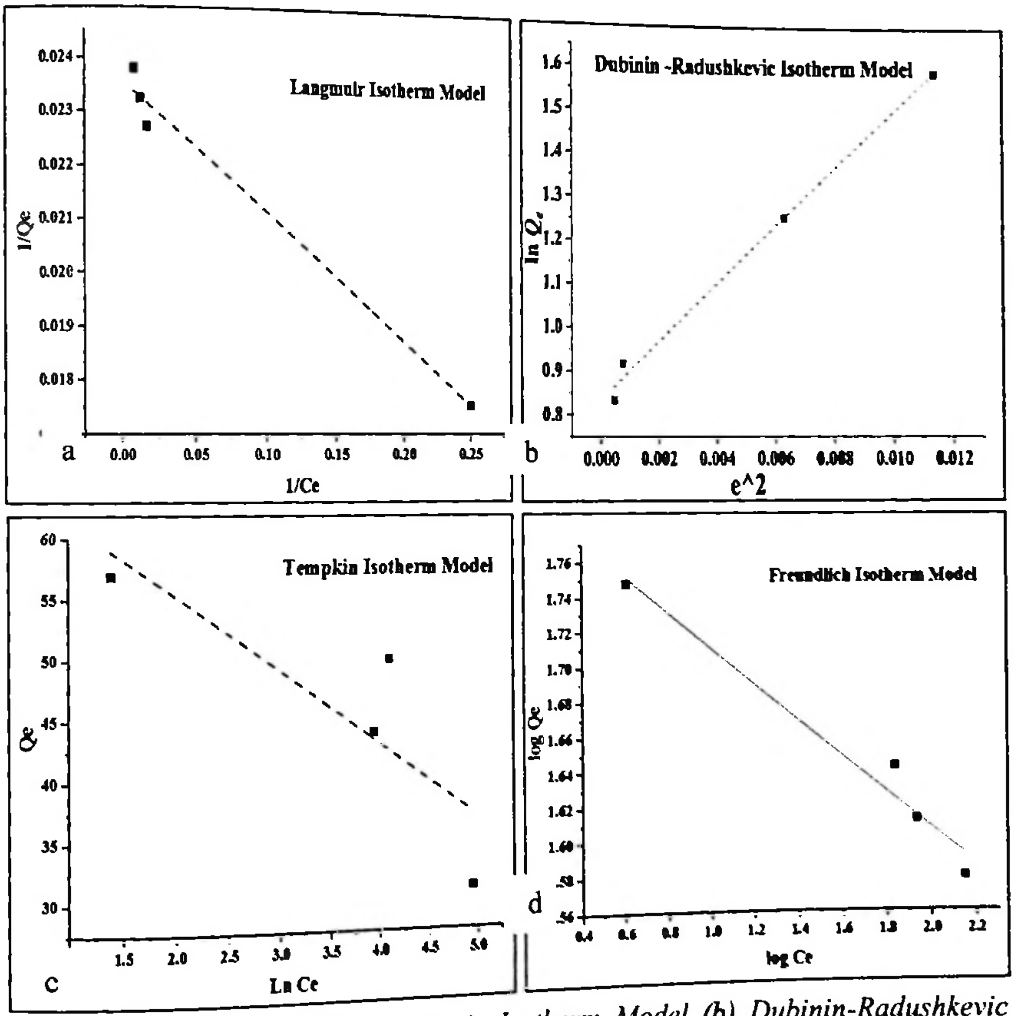


Figure 4.14: Graphs for (a) Langmuir Isotherm Model (b) Dubinin-Radushkevic Isotherm Model (c) Tempkin Isotherm Model (d) Freundlich Isotherm Model

Table 4.17: Summary of R^2 values of the adsorption isotherm models

Temkin	Dubinin-Radushkevich	Freundlich	Langmuir
$R^2 = 0.72$	$R^2 = 0.86$	$R^2 = 0.94$	$R^2 = 0.98$

Table 4.18: The adsorption data fitted to Langmuir model

Dosage (g)	Initial DEHP concentration (µg/L)	Final DEHP concentration (µg/L)	V/M (L/g)	Qe (µg/g)	1/Qe (g/µg)	Ce (µg/L)	1/Ce (L/µg)
1 g	171	128	1	42	0.023	128	0.007
2 g	171	84	0.5	43	0.023	84	0.011
2.5 g	171	60	0.4	44	0.022	60	0.016
3 g	171	4	0.33	57	0.017	4	0.25

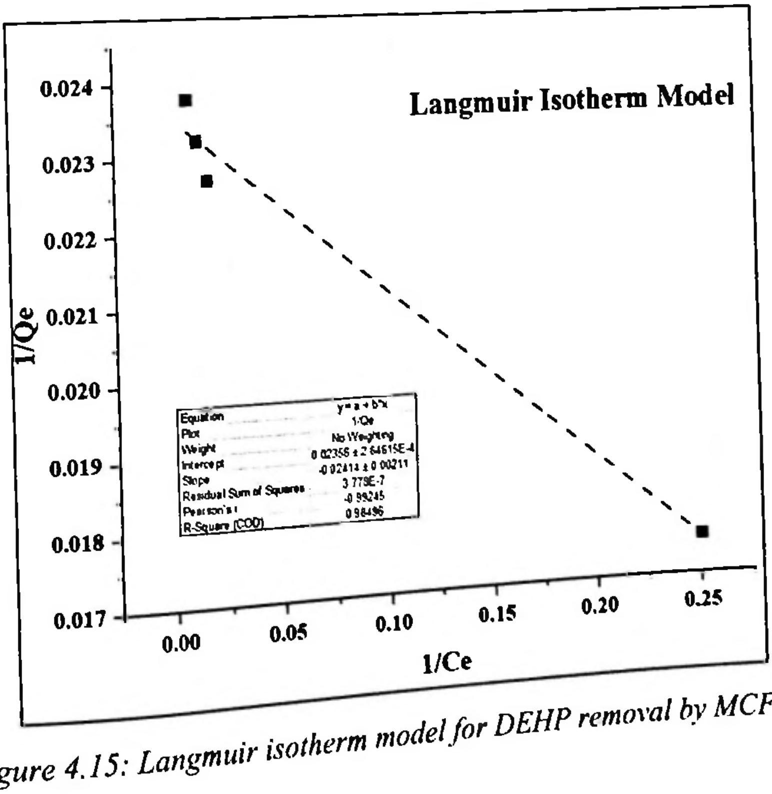


Figure 4.15: Langmuir isotherm model for DEHP removal by MCFA

Q_m	43.48 μg/g
K_L	0.98 L/ μg

Q_m the maximum monolayer coverage capacity is 43.48 μg/g, and K_L the Langmuir isotherm constant was 0.98 L/μg.

Adsorption studies suggested that DEHP follows the Langmuir isotherm model indicating monolayer adsorption. The maximum monolayer adsorption capacity of MCFA was 43.48 μg/g. According to the fitted isotherm models, DEHP slightly fitted with Freundlich model (R^2=0.94). Hence remaining DEHP adsorb on to the MCFA surface as multilayers. The dominant adsorption mechanism is monolayer adsorption.

4.3.5.3 Kinetic studies for DEHP removal by MCFA

Kinetic studies for the removal were conducted to investigate reaction order of the mechanism. The reaction order assists us to conclude the adsorption mechanism in combine with adsorption isotherm model.

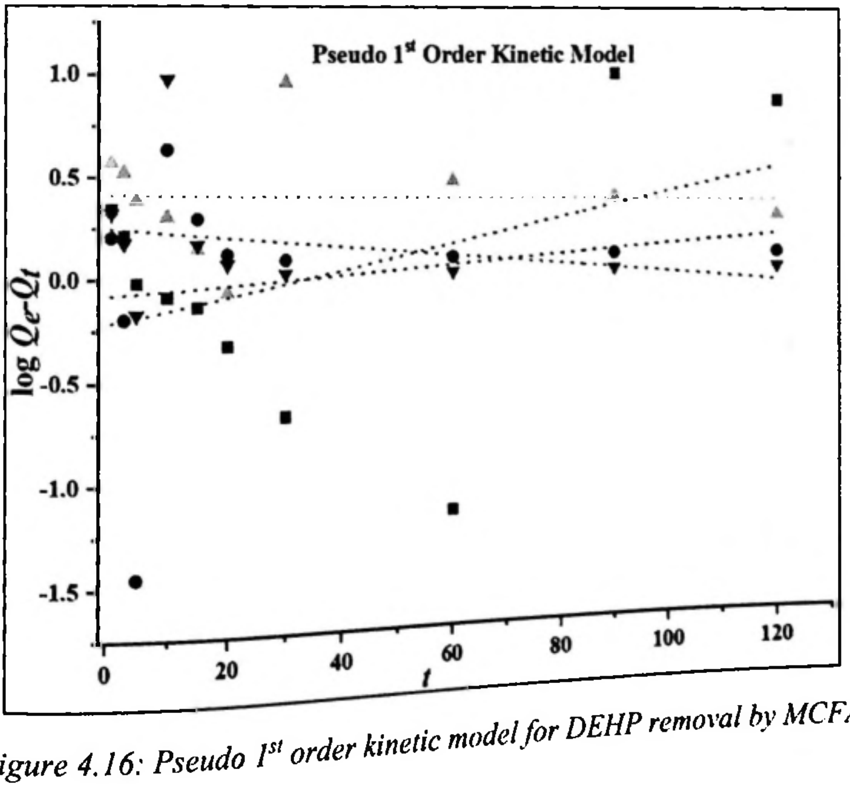


Figure 4.16: Pseudo 1st order kinetic model for DEHP removal by MCFA

Data obtained was not fitted to pseudo-first order, thus the reaction does not follow the first order kinetics. Adsorption kinetics of DEHP with MCFA are described well by a pseudo second-order model. Hence, the rate-limiting factor DEHP adsorption by MCFA is chemisorption, which agrees with covalent bonding by sharing or exchange of electrons among adsorbate and adsorbent.

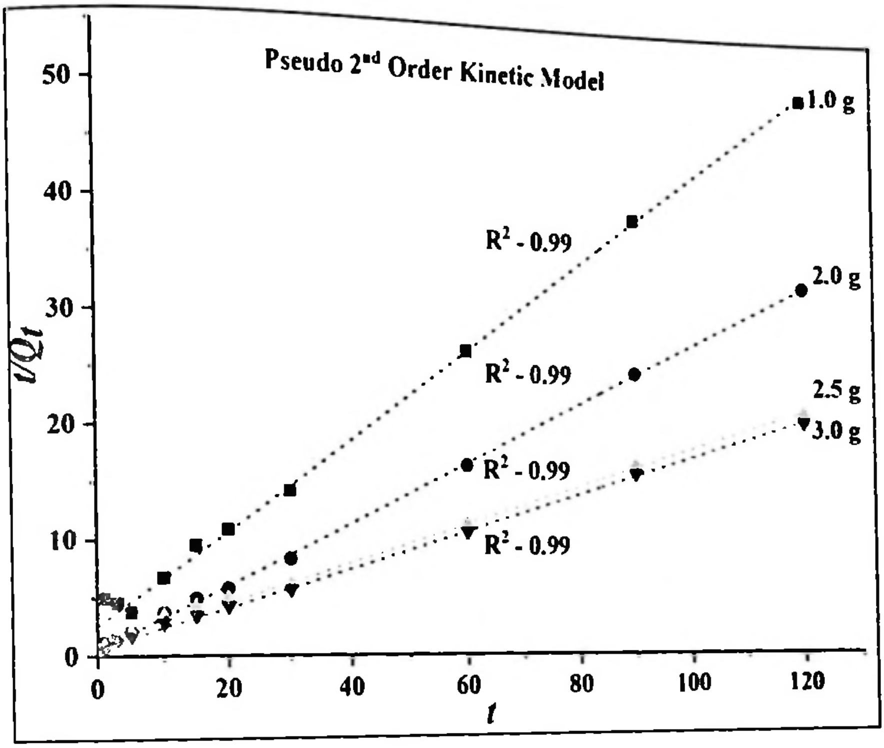


Figure 4.17: Pseudo 2^{nd} order kinetic model for DEHP removal by MCFA

Gibs free energy of each reaction confirmed that the adsorption mechanism is a chemisorption mechanism. Gibs free energies calculated for the reactions at each dosage were summarized in Table 4.13 as follows.

Table 4.19: Gibs free energy of the adsorption reaction

MCFA Dosage (g)	**Qe (Experimental) (µg/L)**	**Qe (Calculated) (µg/L)**	**R^2**	**Gibs free Energy $\Delta G^o = -RT \ln(Kc/Kc^o)$ ($kJ\,K^{-1}\,mol^{-1}$)**
1	2.39	2.48	0.99	-6913.68
2	3.42	3.66	0.99	-5140.22

2.5	5.56	5.72	0.99	-8851.72
3	3.42	5.88	0.99	-8115.37

Data obtained from Gibs energy calculations confirmed that the reaction occurs during the adsorption mechanism is exothermic. Hence the adsorption mechanism with MCFA is chemisorption.

4.3.6 Regeneration studies of MCFA

Wastewater purification by adsorption technology is economical when the material synthesis cost is low and if the adsorbent can regenerate. Reuse of adsorbent helps in reducing environmental impacts related to inappropriate adsorbent disposal (Amin et al., 2014) as well. The cost calculation for the synthesis of 1 g of MCFA are as follows in Table 4.14)

Table 4.20 Cost calculation for the synthesis of one gram of MCFA

Description		**(Rs)**
Coal Fly ash (140 g)		00.00
NaOH (350 mL)		700.00
HNO_3 (10 mL)		15.00
Distilled water (4 L)		40.00
Material Cost		**755.00**
Refluxing for the zeolite synthesis		
Watt value of refluxer	500 W	
Refluxing time	96 hrs	
Total Watt value	24000 wh	
Kwh	24 Kwh	
Cost of synthesis procedure		**240.00**
Total Cost		**995.00**
Cost per gram		**6.21**

As the synthesis cost of one gram of MCFA is cheap, determination of regeneration possibility is worth considering use for wastewater purification. Desorption after a reuse time of adsorption can be done with a different solution (solutions at different pH levels). Here the adsorbent contacted with different solution which comprising no adsorbate. In this study, adsorbent regenerated with HCl (pH=4), EDTA (pH=7), NaOH (pH=10) solutions for three reuse cycles.

The results obtained for the adsorption and desorption percentages were indicated that after the 2nd reuse cycle the adsorbent is not given a sufficient DEHP removal. DEHP concentrations after each reuse cycle and desorption percentages after each desorption time were as follows in Table 4.15 and Table 4.16.

Table 4.21: The regeneration of MFA using NaOH, EDTA and HCl

	Initial Concentration	Final Concentration		
		Regeneration cycle 1	**Regeneration cycle 2**	**Regeneration cycle 3**
NaOH	171 µg/L	6 µg/L	12 µg/L	50 µg/L
EDTA	171 µg/L	8 µg/L	16 µg/L	52 µg/L
HCl	171 µg/L	8 µg/L	15 µg/L	54 µg/L

Table 4.22: The regeneration of MCFA using NaOH, EDTA and HCl

	Percentages of desorption		
	Regeneration cycle 1	**Regeneration cycle 2**	**Regeneration cycle 3**
NaOH	95.2 %	82.2 %	45.6 %
EDTA	88.1 %	78.6 %	35.5 %
HCl	87.2 %	76.8 %	34.8 %

The regeneration studies show that when the number of regeneration cycles increases, the final concentration of the solution will increase. This shows that with cycles of desorption, some previously active sites are no longer enable to adsorbing DEHP. NaOH was identified as the best eluent as it desorbed 95.2 % adsorbent at the first regeneration cycle and 82.2 % in 2nd regeneration cycle which, after 3rd regeneration cycle, the final concentration of the treated solution is not reach the recommended level of concentration.

4.3.6.1 ESEM-EDX Analysis

SEM images obtained after three regeneration cycles for eachsolutions used for the regeneration studies (NaOH, EDTA, HCl) were shown in figure 4.18.

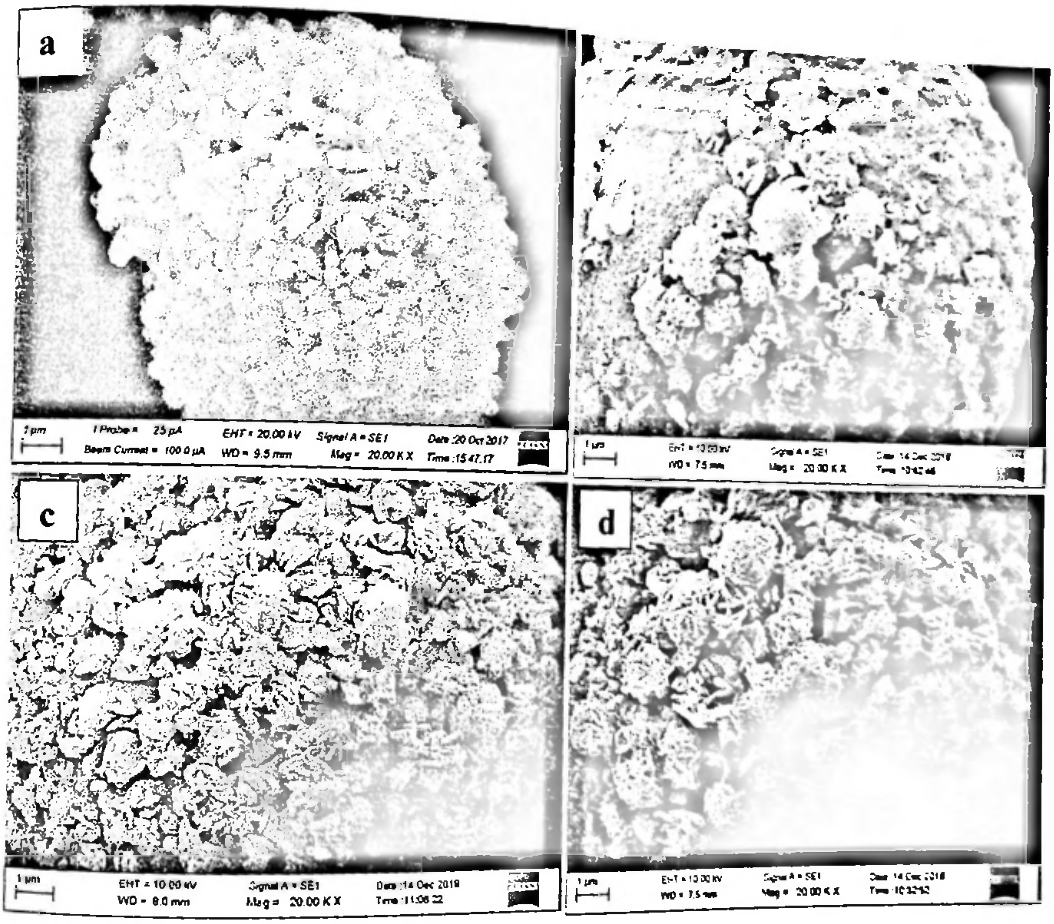


Figure 4.18: (a)The SEM Image of MCFA (b) The SEM Image of MCFA after three cycles of regeneration with NaOH (c)The SEM Image of MCFA after three cycles of regeneration with EDTA (d) The SEM Image of MCFA after three cycles of regeneration with HCl

Images indicate evidence in the reduction of desorption of adsorbate as well as the concentration reduction in final solutions. It's evident that the morphology of the surface area of adsorbent has significantly altered to tightly-coiled-frizzy-hair-like morphology due to DEHP desorption. MCFA treated with HCl is representing the most significant morphological change among three solutions selected for the regeneration studies. 4.17 (b), the figure shows solid-building block-like structure less covered with adsorbed DEHP particles when compared to Figure 4.17 (c), (d). SEM images of after regeneration with EDTA are showing less vacant areas for adsorption then the figure of 4.17(b) attributed to removal percentage is a reduction of DEHP. MCFA surface crystal structures have disappeared after regeneration occurs.

4.3.6.2 XRD Analysis

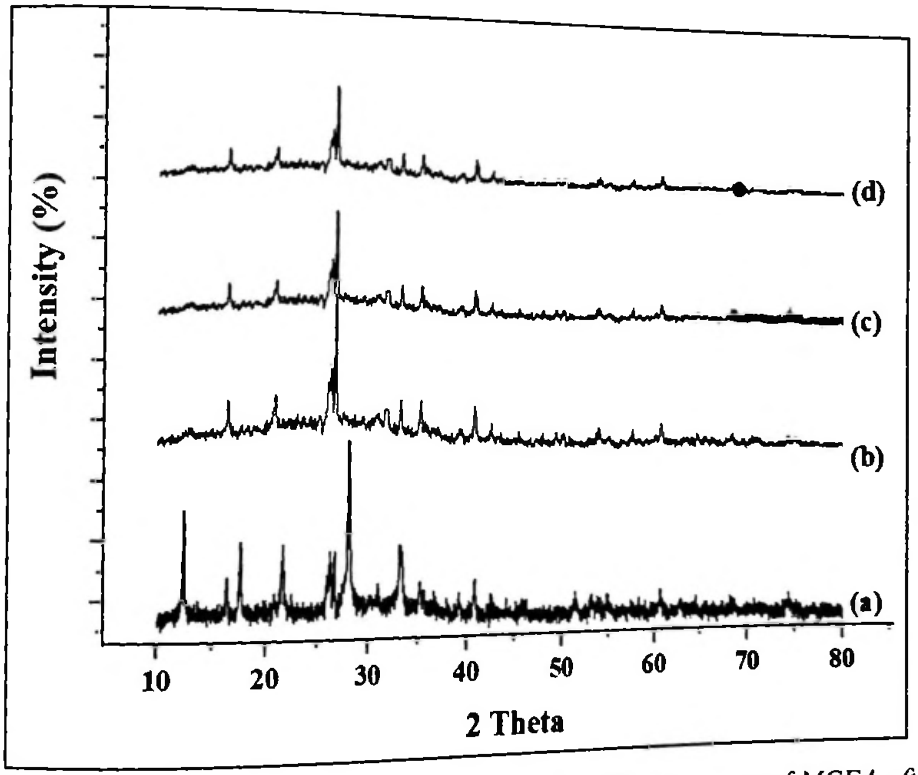


Figure 4.19: (a)The XRD Spectrum of MCFA (b)The XRD Spectrum of MCFA after three cycles of regeneration with NaOH (c)The XRD Spectrum of MCFA after three cycles of regeneration with EDTA (d)The XRD Spectrum of MCFA after three cycles of regeneration with HCl

XDR spectrum shown in figure 4.19 indicated the changes in the XRD pattern after three regeneration times with NaOH, EDTA, HCl respectively. XRD spectrum of the regeneration cycle with NaOH shows less Intensity change than EDTA and HCl, which attributed to the less coverage of adsorption phases on crystal structure.

4.3.6.3 FT – IR Analysis

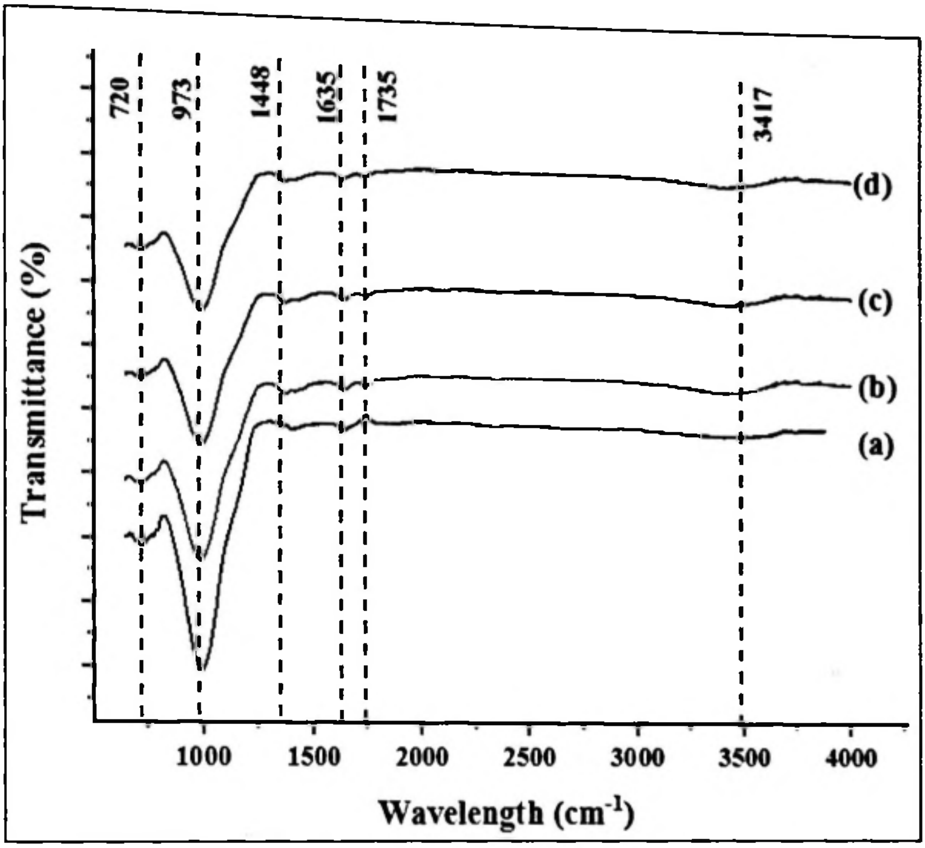


Figure 4.20: (a) The FT – IR spectrum of MCFA (b) The FT – IR spectrum of MCFA after three cycles of regeneration with NaOH (c) The FT – IR spectrum of MCFA after three cycles of regeneration with EDTA (d) The FT – IR spectrum of MCFA after three cycles of regeneration with HCl

FT– IR spectrum indicates similar results of XRD where, Figure 4.20 (a) and 4.20 (b) are giving same pattern with changed insanities while other two Figure 4.20(c) and 4.20 (d) are slightly changed than Figure 4.20 (a). Figure 4.20 indicated that FT–IR spectra after all three solution regeneration activity is giving spectrum identical to the referencing graph Figure 4.20 (a)which, C=O peak and $-CH_3$ peak present in all samples with different abundance.

CONCLUSION

The presence of six PAEs (DMP, DEP, DBP, BBP, DEHP, and DnOP) in 22 shallow open watercourses in Colombo and its suburbs, Sri Lanka, was investigated. In all watercourses, DMP and DnOP were less than their LOQs (0.5 μg/L for DMP and 1.0 μg/L for DnOP) because of the less contribution from the nearby industries and urban sprawl. The average concentrations detected for DEP, DBP, BBP, and DEHP were in the range of 2.5–265.0, 1.0–32.0, 61–108, and 12–165 μg/L, respectively, because of factors such as their high solubility in water, lower volatility, and greater contribution from industries and urban sprawl. It is apparent that the contamination of PAEs in most of the watercourses is detrimental for the protection of aquatic life, as concentrations of DEHP and DBP were higher than those of Canadian permissible concentrations (16 and 19 μg/L). Nevertheless, a comprehensive analysis needs to be undertaken to study the fate and transport phenomena of PAEs to get an insight into the possible adverse impacts on the environmental matrices.

The photocatalysis with TiO_2 for the destruction of DEHP was found to be an effective process in removing DEHP from industrial wastewaters. The most economical dosage of TiO_2 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 TiO_2 was around Rs. 120 and the cost could be further reduced when the material (TiO_2) is regenerated for subsequent usage. TiO_2 was regenerated five times with inherent properties for photocatalysis is not changed. This technique could be successfully applied to lessen the DEHP levels in the urban watercourses of Sri Lanka.

MCFA was found to be an effective, low-cost adsorption technique to remove DEHP from wastewaters and an initial level of 171 μg/L of DEHP was successfully removed with 98% efficiency within 28 minutes. MCFA was regenerated with NaOH twice and used effectively.

RECOMMENDATIONS

According to the results obtained, PAEs have recorded alarmingly high concentrations in the nearby watercourses, since PAE-containing materials being discharged into the watercourses. It is recommended to promulgate and enforce a suitable legal framework to combat the release of PAEs for the industries.

Sri Lanka has been a fabulous country in producing shellfish [crustacea (such as shrimps, crabs, lobsters) and mollusks (such as clams, mussels, oysters, scallops)], which is a delicacy for many. However, with the unprecedented levels of PAEs found in the coastal aquatic environments, the shellfish industry may topple in no time with a likelihood of Sri Lankan seafood being banned for human consumption. Such a bleak era seems to be close at hand unless the general public would be proactive collectively to say 'no' to sources containing and spewing astounding levels of PAEs. In this context, regulations on PAEs that are to be added to different diverse products need to be promulgated and enforced. Further, it is imperative that a rigorous scheme of PAE measurements is paramount, as the behavior of PAEs in the aquatic environment seems to be not fully understood. It is my fervent obligation to leave the coastal environments free of PAEs for better ecological sustenance for which strict principles of resilience need to be implemented so that a bizarre situation detrimental to ecological health could be avoided.

This study recommends that the applicability of $TiO_2$and MCFA as effective and efficient materials for removing DEHP from wastewater. It is recommended to use such materials as the tertiary treatment in wastewater treatment plants of industries.

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