A thesis submitted in fulfilment of the
requirements for the award of the degree of
Doctor of Philosophy Civil Engineering

SPLIT-POND DESIGN AND THE USE OF NANO TIO_2 FOR STORMWATER QUALITY IMPROVEMENT

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To my beloved father and mother

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ABSTRAK

Penyelidikan ini telah dicadangkan berikutan peningkatan bilangan kolam takungan air hujan/ribut yang terjadi akibat dari aktiviti pembandaran, pencemaran alam dan masalah yang berpunca daripada pengunaan air yang tercemar. Penyelidikan ini mengandungi dua konsep baru dalam penetapan kolam bagi tujuan meningkatkan kualiti air hujan yang disalur keluar. Memancarkan pertama pemisah mengunakan sebuah pemisah-saluran yang diisi dengan penapis pasir untuk pemaksimuman penyingkiran pepejal terampai, kedua menggunakan campuran konkrit Nano-TiO_2 sebagai penutup pada memancarkan pemisah dan tubuh kolam untuk menyingkirkan bahan yang tercemar dan membuntu kebolehan proses pengoksidaan air. Kadar penurunan kimia 'chemical oxygen demand' (COD) dan nutrient (phosphate dan nitrate) dalam air hujan/ribut mengunakan Nano titanium dioxide (TiO_2) di fotopemangkinan kolam takungan air hujan telah dikaji dangan kehadiran sinar ultraviolet (UV) cahaya matahari semula jadi. Kajian ini dibandingkan dengan yang dijalankan mengunakan kolam pada skal biasa di maknal UTM. Dua jenis serbuk Nano TiO_2 (Anatase dengan purata diameter 25 nm dan Rutile 100 NM Nano particles) telah digunakan dalam dua jenis konkrit mengunakan portland biasa dan simen putih bercampur pada tiga kadar berbeza iaitu 3%, 10% dan 30% berfungsi sebagai sebuah penutup nipis mengelilingi kolam dan partition. Eksperimen dengan mengunakan dan tidak mengunakan pemangkin telah dijalankan untuk tujuan perbandingan dan control. Hasil kajian membuktikan dengan menambahkan 3% hingga ke 30% berat Nano-TiO_2 boleh menurunkan kadar COD sehingga 43% dan nutrient sehingga 25% dalam masa dua hari dan 68% dan 57% masing-masing dalam masa tiga minggu.

ABSTRACT

This research was proposed to enhance stormwater quality due to limited freshwater resources considering water crisis and global warming and public health. Applied treatment methods to improve quality of stormwater; as a source of freshwater; especially in detention ponds are not good enough and problems related to using contaminated water is increasing. The research contains two new concepts in detention pond designation for outflow quality improvement. First flush separation using a channel-partition filled with stratified sand filter inside the pond for suspended solids removal maximization, and second applying immobilized Nano-TiO_2 concrete mixture as a cover on the partitions and pond body for its contamination removal and oxidation abilities fruition. The photo-degradation of COD, phosphate and nitrate in stormwater in the photocatalytic reactor wet detention pond using Nano titanium dioxide (TiO_2) was investigated in the presence of natural ultraviolet (UV) from tropical sunlight in Malaysia. The observations were compared to regular pond at scale model in UTM laboratory. Two forms of TiO_2 Nano powders (Anatase with average diameter of 25 nm and Rutile 100 nm Nano particles) were used in the two different types of concrete that is used ordinary portland and white cement. For weightage optimization purpose they were mixed at three different mixtures of 3%, 10% and 30% of Nano-TiO_2 weightage and cement as a thin cover to surround the body of the pond and partitions. Experiments with and without the catalyst were carried out for comparison and control. "Results revealed that applying the channel partition can physically increase the TSS removal rate up to 92%. More over utilization of various weight of Nano-TiO_2 in average can chemically reduce phosphate, nitrate and COD up to 40%, 11%, and 43% within two days and 83%, 30% and 68% within three weeks, respectively".

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LIST OF SYMBOLS

NTU	-	Turbidity
NH_3	-	Ammonia
NO_3^-	-	Nitrates
NO_2^-	-	Nitrites
K	-	Potassium
PO_4^{-3}	-	Phosphate
TiO_2	-	Titanium Dioxide
TN	-	Total Nitrogen
TP	-	Total Phosphor
EC	-	Electrical Conductivity
Ph	-	Potential of hydrogen
A_s	-	Watershed Surface Area
A	-	Reservoir Surface Area
UV	-	Ultraviolet
VB	-	Valence Band
CB	-	Conduction Band
h_v	-	Photons
·OH	-	Hydroxyl Radicals
O_2^-	-	Super-Oxide Anion
W	-	Wolfram
NHE	-	Hydrogen Electrode
e.v.	-	Electron Volt
Ga	-	Gallium
T_c	-	Concentration Time
C	-	Roughness coefficient in FAA
L	-	Sheet Flow Distance in FAA

H	-	slope of land in FAA
P	-	6 hours Rainfall depth
r	-	Kerby's roughness factor
I	-	Rainfall intensity

LIST OF ABREVIATIONS

TSS	-	Total Suspended Solid
TDS	-	Total Dissolved Solids
TKN	-	Total Kjeldahl Nitrogen
TOC	-	Total Organic Carbon
PAHs	-	Polycyclic aromatic hydrocarbons
WHO	-	World Health Organization
BOD	-	Biological Oxygen Demand
COD	-	Chemical Oxygen Demand
E. coli	-	Escherichia col
DO	-	Dissolved Oxygen
CDS	-	Continuous Deflective Separator System
VTS	-	Vortechs Treatment System
USEPA	-	United State Environment Protection Agency
BMP	-	Best Management Practice
LID	-	Low Impact Development
HRT	-	Hydraulic Residence Time
UV	-	Ultraviolet
IUPAC	-	International Union of Pure and Applied Chemistry
VOCs	-	Volatile Organic Compounds
NASA	-	National Aeronautics and Space Administration of the United States
CPC	-	Compound Parabolic Concentrator Reactor
PVD	-	Physical Vapor Deposition
CVD	-	Chemical Vapor Deposition
PEC	-	Photo-electrochemical Cell Reactor

UNESCO	-	United Nations Educational Scientific and Cultural Organization
FAA	-	U.S Federal Aviation Administration formula for Concentration Time
SCS	-	Soil Conservation Service

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CHAPTER 1

INTRODUCTION

1.1 Background

Quality of life is tied to quality of water. According to WHO in the year of 2000 more than 1 billion person in the world did not have access to enough freshwater, and every year more than two million dead occur due to water related disease (WHO 2006). On the other hand limited usable freshwater resources like rivers, lakes and groundwater are less than one percent of total earth planet water (Postel, Daily et al. 1996). Significant amount of this contaminated freshwater directly discharges to the environment without any treatment. High amount of various pollutions such as pesticides, nutrient, oil and greases, organic and inorganic pollution, and heavy metals (from point and non-point resources of pollution) are released to these water bodies due to urbanization, agricultural and industrial human activities.

Hydrologic cycle is reinterring these contaminations from the environment (rivers or lakes) to the using water chain again. As a part of this chain, accumulated pollutions via surface water enter the ponds; and then without any treatment release to the rivers. This problem has dangerous consequences for public health (Papa, Adams et al. 1999) especially in countries like Malaysia, where 97% of water supplies comes from rivers (Yassin, Eves et al. 2009). It seems that nowadays we need more appropriate rules in term of drain water quality control more than any other time (Echols 2002).

Control and degradation of contamination before entering to the river or groundwater is a necessary step that can help to solve this problem. Pollution control will increase the amount of available clean water and also will decreases the water treatment costs. Research on removing the contamination from stormwater runoff is an important approach to save our freshwater resources. Based on WHO guidelines interventions to improve the quality of water provide significant benefits (WHO 2006). Studies on stormwater contamination removal in detention ponds can lead to water supply safety and public health (Gaffield et al. 2003).

Nowadays uncontrolled developing planes for the cities have increased. And it has accelerated the construction process which is a necessity for development and having a better life. It has also increased pavement and impervious surface area and decreased green areas in the cities. These changes affect the topography and natural condition of the environment which consequently causes hydrological cycle changes. Hydrological process in a natural environment has more infiltration, surface storage and plant uptake volumes from the rainfall water compared to a developed environment. More infiltration and lesser drain water will cause safe and stable usable underground water resource and also will decrease downstream overflow risk.

Regardless of the harms of flood including loss of live, industrial, economical and agricultural damages, traffic, properties and buildings failure; stormwater quality decreasing is another consequence of urbanization. Various kind of contamination due to different industrial, agricultural and residential human activities are carried out by stormwater and release to the lakes, rivers and environment through the drainage systems without any control or treatment.

Inadequate urban drainage systems and conversion of natural environments to developed and urban environment are the reasons that deteriorate the stormwater related problems. That is the reason why majority of developed areas need to build retention and detention ponds to control the peak flow and prevent overflow, flood or any other hydrological problems. To design a proper drainage system for any developing environment; water quality issues and environment protection policies must be taking into consideration. As per literatures a large number of researches have

indicated that the current flood control facilities and the traditional drainage systems have increased contamination to the rivers, lakes and ground water resources since there is no effective treatment system.

In tropical zone (where the main water sources are rivers) stormwater releases to the rivers through the drainage system. This contaminated runoff effects on the downstream water quality when the stormwater caries various industrial residential and agricultural pollutions. Detaining the stormwater helps to reduce the pollution loading rate but it can worsen the scenario due to re-suspension of settled contaminations followed by the next precipitation.

In order to control stormwater quality, enlarge detaining system must be done to allow small size sediment bound pollution settlement but it is a costly option. As an alternative cost effective option the outflow orifice size can be choose smaller to have longer detaining time. However it causes increasing of the overflow risk due to the next raining during inter-event.

Traditionally, flood control structures and stormwater management methods have mainly focused on stormwater quantity control to minimize the damages as quick as possible. But these methods mostly are not able to apply an effective runoff quality enhancement on the polluted stormwater. However recent stormwater management attending on designing in which quality and quantity aspects both; considering sustainable development and public health (Lim et al. 2015). This study focuses on stormwater quality enhancement methods and strategies, specifically applying new methods in wet detention ponds for more outflow quality improvement. Different kinds of pollution and various treatment methods and structures have ben illustrated and finally the proposed method has been explained. A new idea in pond designation as an online filter is applied in order to improve contamination removal ability for first flush treatment inside the pond during the draining time.

1.2 Sources of Pollution

Stormwater pollutions sources can be categorized into two main groups, point and non-point sources. The first group is point source pollution which is the part of contaminations that release from specific locations such as chemical and industrial factories, or waste treatment plants. But the more important and second part is non-point source pollution, that comes from almost everywhere including, agricultural, or residential areas, vehicles, erosion, atmosphere, etcetera. This part is known to be related to surface water runoff. The importance of non-point source is due to this fact that since there is no particular source, it is difficult to control and monitor this kind of pollution.

While before point sources pollutant were considered as the major source of pollution, but recent researches (Stefanakis et al. 2015) shows that non-point source contamination have more significant role in water quality problems, especially in developing and developed countries (Olem and Flock 1990).

Different treatment methods can be applied easily in site for point source of contamination compared to non-point source. Recently, a large number of studies have analyzed the behavior of pollutions to better understanding of effects and mechanism of contamination on water quality degradation. Related researches on designing devices, filters and infiltration (Kandra et al. 2015), applying ponds and wetland (Vincent et al. 2014), coagulation and chemical methods (El-Mufleh, et al. 2014), Low Impact Development (LED) and Best Management Practice (BMP) (Rivera, G 2015), contamination loading and runoff modeling studies (Daniels et al. 2014), hydrological impacts and watershed-related issues on non-point source pollution (Stefanakis et al. 2015) have illustrated contamination loading rate, behavior, degradation methods, etcetera.

Non-point source of pollution is the main stormwater quality problem in terms of contamination loading. The load of pollution in stormwater depends on several criteria. various parameters such as watershed bed, green area proportion in catchment, rainfall events intense and duration, season (Lee, Lau et al. 2004), land use,

nutrient concentration, topography of basin, latitude, sunny hours, wind, and temperature can effect on the amount of pollution carried by the runoff. Overall to estimate the amount of contamination for each region periodical measurement must be done with samples taken during and after storms to obtain trustable data.

1.3 Pollution Control Strategies

In order to control the quality of stormwater runoff in addition to its quantity various strategies have been applied. It seems that no single practice (except major land use change) can control or effectively reduce the load of contaminant in ponds and multiple strategies or devices would be required (Iowa Department of Agriculture and Land Stewardship, 2014). Devices such as flow and first flush separator which can split the water flow in different rates as per their design. Sand filters that can filter different contaminations especially effective on sediment bond pollution removal. Infiltration and wetlands absorb microorganisms and chemical pollutions thorough the soil or consume by plants and stormwater enter to the groundwater aquifers after natural filtration.

Low Impact Development (LID) and Best Management Practice (BMP) can effectively decrease a sizeable proportion of contaminations from their sources (Rivera, G 2015). Recently multi objective flood control structures such as detention and retention ponds have been applied widely to improve the quality of runoff before entering the rivers. It can enhance the quality of runoff via holding it during a designed time and decrease the risk of downstream flood. Some of the ponds have a forebay front of them which can provide cleaner stormwater in the main pool since it can trap the sediments and debris. Other methods such as chemical method for example, applying Aluminum sulfate or Moringa Olifiera seeds enhance the efficiency of wastewater and runoff quality control process due to coagulation.

Nowadays researches tends to new manners which are more cost effective and environment friendly including applying membranes, micro filters and Nano materials

(semiconductors) especially in waste and drinking water industry (WHO 2006). One of this methods that is going to be commercialized in water treatment industry is applying Nano titanium dioxide (TiO_2) under ultra violet illumination for make use of its ability in decompose various harmful type of contaminations to harmless nitrogen, CO_2 and H_2O (Zhang, T. C. 2009).

The continuous water circulation from the ground (and even underground) to the atmosphere and vice versa through different ways is called hydrologic cycle (Linton et al. 2014). During this dynamic cycle the total quantity of water in different forms of water, snow, and steam (liquid, solid, gas) etcetera is constant. However the quality of water can be different due to erosion and other effective parameters like human activities during the time for a specific region. Figure 1.1 shows schematic hydrologic cycle in a natural and a developed environment.

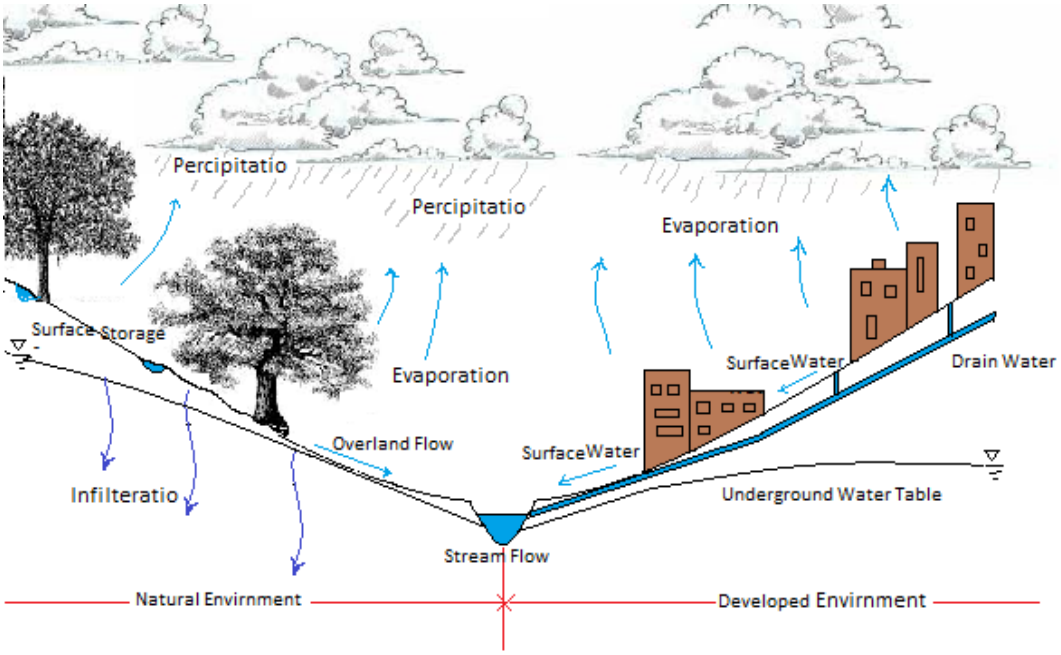

Figure 1.1 Schematic hydrologic cycle in natural and developed environments

The underground water table for the developed area is usually lower than natural area due to impermeable pavements. In the above figure (Figure 1.1**)** the most important ways to transform the water during the hydrologic cycle have been illustrated. These ways are including precipitation, evapotranspiration and infiltration.

1.4 Problem Statements

Due to the increasing of the impermeable surfaces and pavements in cities; stormwater volume has increased and infiltration has decreased. Building the channels and drainage systems results rapid peak runoff with less lag time and more volume; compared to natural streams. Due to the necessity of peak flow or flood control in the catchments; to build flood control facilities such as retention and detention ponds and avoid downstream flooding is essential (Figure 1.2). But beside peak flow and quantity control, quality control as another important parameter must be considered. This is the reason why the detention pond outflow quality enhancement is carried out to increase stormwater quality.

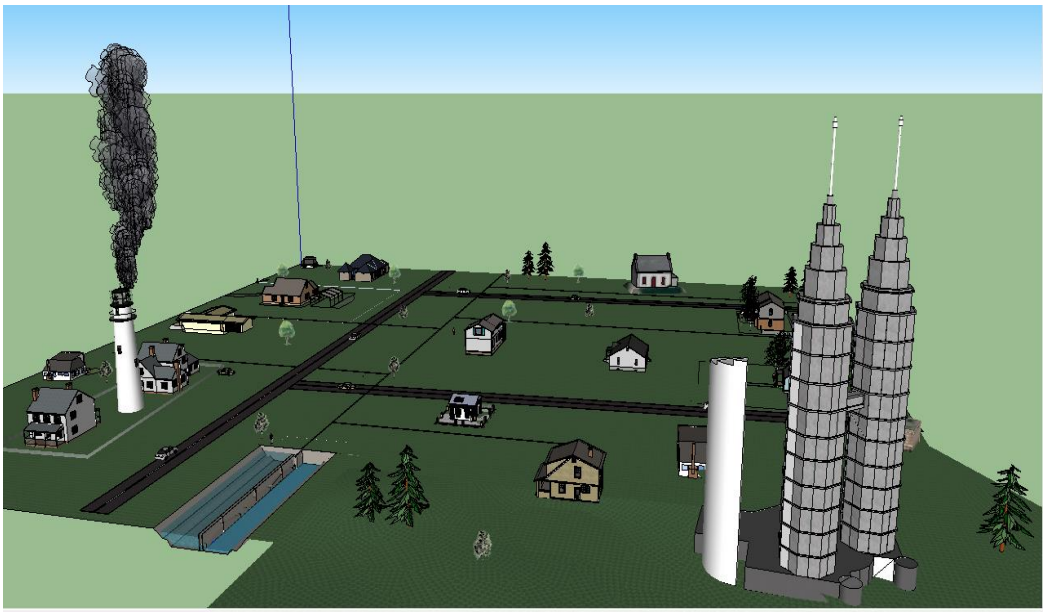

Figure 1.2 Urbanization which increases the pollutants in developed areas

Traditionally, detention ponds detain storm water and release that during special designed time (24-48 hours). It can enhance stormwater quality due to settling, chemical, and biological reactions; in addition to flood and rainfall peak flow control. Detaining time prolongation in the ponds can provide higher outflow quality but it will increase downstream overflow risk follow the next precipitation. Therefore inter-event time plays an important role in obtaining and optimizing detaining time. The first drawback in traditional pond's designing is that they are not able to provide desirable detaining time and appropriate outflow quality.

In other hand in quality standpoint, stormwater can be divided in two main parts. First and most contaminated part (First Flush) that contains a significant percentage of pollutions compared to its small quantity which is first half-one inch of precipitation (Guo 2001), (Kuo and Zhu 1989), and second and cleaner part which contains higher storm water quality and quantity. Obviously traditional pond due to mixing and holding these two parts in the pond can decrease easier treatment chance for first flush (Rad, Shamsudin et al. 2014). In other word to enhance contaminates removal efficiency; first flush need to be detain separately and be release during longer time compared to second part of runoff which is cleaner. This is the second drawback of current detention ponds which are not able to do so.

This research is associated with the amount of stormwater pollution and indexes include nitrate and phosphate loadings, total suspended solids (TSS), chemical oxygen demand (COD) and dissolved oxygen (DO) in a scale model detention pond during various detaining times. Stormwater quality improvement for real samples have been investigated via above parameters measurement when stormwater was detained for various holding periods in a scale model detention pond. The pond was retrofitted with a first flush separator (channel-partition) and the body of pond and also the first flush partition was covered with a thin layer of concrete mixed with Nano titanium dioxide (TiO_2) as pollution remover and oxidizer. Also first flush separator (the channel-partition) was filled with stratified filter media including zeolite, and sand which first flush have to pass through this channel-partition before entering the second part of the detention pond.

Stormwater quality improvement was expected during detaining time due to pollution oxidation-reduction ability of neon TiO_2 under natural ultra violet (UV) illumination and also first flush separation. The main study questions that is answered after this research can be listed as below:

i) How the new concept of first flush separator in the pond can effect on total suspended solids (TSS) compared to normal detention ponds?

ii) Dose applying Nano TiO_2 on the body of the pond and partition effect on stormwater quality indicators improvement?

iii) Dose the type of applied cement (Portland and white cement) effect on the results?

iv) How the first flush separators manage the detaining time in order to achieve higher outflow quality?

These statements and questions are explained, illustrated and answered during this research.

1.5 Significance of Research Contributions

A rather significant portion of the earth's overall precipitation is by annual rain in tropical areas. Meanwhile, in developed and developing countries urbanization has changed and is changing the natural environment which directly affect the quantity and quality of stormwater runoff. A quick look at the world health organization statistics on deaths and diseases caused by using contaminated water (Sobsey 2002) global warming, water crisis around the world, as well as taking advantage of stormwater as a water source are some of clear signs of the necessity of investigation within this field.

Contamination in stormwater has hazardous consequences in public health stand point. Polluted runoff carries large amounts of dissolved pollution and sediment bond contaminations to the rivers which are main source of water supply in some regions especially in Malaysia. Moreover as an indirect effect, impacts of pollution on rivers and lakes wild life such as fishes are important as some people depend to fishing in lakes and rivers. In recent years, the number of multi-objective flood-control facilities such as detention ponds for storm water quantity and quality control has been increased (Vincent et al. 2014).

These structures can remove a variety of stormwater pollutants before discharge to the environment as can avoid downstream flood due to detaining time and settling, however, they do not have attractive outflow quality as yet. This work has applied 3 new strategies include first flush separation, inline filtration and applying nano material in the current ponds in order to enhance the stormwater quality in detention ponds. Several contributions which this research is going to consider can be stated as bellows:

i) The evaluation of the channel partition application in the new split pond design concept to reduce the amount of TSS in the pond

ii) Estimation of the pollution elimination efficiency of Nano TiO_2 in detention pond applying different dosage of Nano TiO_2

ii) Contamination removal efficiency assessment of Nano TiO_2 in the pond using different type of cement (Portland and white cement)

iii) Detention time management improvement in the pond as per stormwater quality level for first flush and the rest of the runoff respectively

1.6 Objectives of Study

The aim of this research is to propose an inexpensive and sustainable solution to remove a wide range of contaminants, and improve outflow water quality in detention ponds before discharge to environment. This research in addition to applying Nano materials such as TiO_2 in stormwater treatment in the ponds; will generate a new detention pond design called "split pond" which has four remarkable characteristics and cover traditional pond drawbacks.

The objectives of this work have been listed as below:

i) To develop new detention pond concepts by considering the first flush phenomena and amalgamating detaining time for the purpose of outflow water quality improvements.
ii) To investigate the effect of applying the first flush channel partition and embedding the stratified sand filter on the Suspended Solid (SS) physical contamination removal.
iii) To estimate the status of various stormwater quality parameters improvement through retrofitting the pond to fixed bed photocatalytic reactor and applying Nano TiO_2.
iv) To optimize the dosage of Nano TiO_2 application in line with various cement types on water quality contamination removal efficiency.

1.7 Scope and Limitation of Research

For this research a desk study followed by an experiment on stormwater quality improvement is carried out. For an assumed catchment are a detention pond is designed and then a 1:20 scale model of this designed pond is sat up for experiment purpose. The limitations during this work and scope of the research have been summarized as bellow:

i) Real stormwater samples are collected and tested but standard solution was not used

ii) The research was performed based on a scale model detention pond not in large in-site detention pond

iii) The investigations can be carried out with more repetitive tests and also other water quality parameters for long term evaluation

iv) Samples were kept in open area under natural UV and the ambient conditions could not be completely controlled

v) Five water quality parameters including phosphate, nitrate, chemical oxygen demand, dissolved oxygen, and total suspended solid during the investigation were tested.

vi) Since the test was done in a fiberglass scale model, the natural effects of aquatic plants, wildlife and soil (in terms of microorganisms) in the normal detention ponds are not considered.

1.8 Outline and Structure

This research is including 5 chapters. The first chapter is introduction that covers the stormwater quality problem, pollution resource and significance of stormwater treatment, research intents and problem statement, objectives, scope and limitation of work. Finally research outlines are briefly described in this chapter. In the second chapter, background of stormwater quality; types of pollutants and parameters is described, traditional and new stormwater management strategies and treatment methods facilities such as filters, devices, BMPs, ponds, chemical process or LIDs in order to control runoff peak flow and contamination rates in ponds are illustrated, and finally proposed method is explained. Various kinds of physical,

chemical, and biological stormwater pollutions and their sources are explained. Different application of Nano-materials as purifier especially in water treatment and different types of photocatalytic reactors are briefly described.

Third chapter as the methodology of this research is a desk study followed by several laboratorial designs, set up and test. It is described that how test requirements for scale model pond, channel partition structure, inlet , outlet and floater, flow switcher, appropriate cement types, Nano TiO_2 (Anatase and Rutile type) are provided and also what are the methods used. In the fourth chapter, testing results are analyzed. Five stormwater quality indicator including nitrate and phosphate, dissolved oxygen and chemical oxygen demand, and total suspended solids are measured and monitored. The ability of first flush channel partition to manage the stormwater holding period as per its quality level, and the flow switcher in switching runoff between two parts of pond are tested and optimized. Scale-up feasibility of scale model detention pond is discussed in order to achieve an appropriate strategy in stormwater quality controlling. Finally useful guidelines and outcomes are obtained; limitations and future research suggestions have concluded this research.

1.9 Summary

Most part of stormwater in developed and developing countries directly discharges in to the environment after being contaminated which can effect on water resources and public health consequently. Therefore applying efficient stormwater treatment methods can avoid dissemination of contaminates. Traditional stormwater treatment and contamination removal procedures have some drawbacks beside their advantages. As an example detention ponds are unable to separate first flush from the stormwater. In this research first flush via applying a channel partition separator has been separated from the rest of runoff and more effective treatment has been applied on that during longer detaining time compared to the rest of runoff which is more clean. This channel-partition will be filled with different level of filter media to provide higher quality after the settlement process. Some more a new strategy which is applying nano materials under the natural ultraviolet (UV) from the tropical daylight in Malaysia to eliminate the pollution has been applied.

In fact in this work three different strategies including, first flush separation, filtration, and decomposition using Nano materials have been added to a normal detention pond to convert it to a more efficient stormwater treatment structure in order to enhance stormwater runoff quality before it releases to the environment. The first flush separation works based on a floating gate. This floating gate can direct the second part of the rain water to the second part of the pond. Then the next step is physical filtration of the held first flush followed by settlement when the stormwater passes through the channel-partition which is filled with stratified sand filter. And last is using Nano titanium dioxide which can chemically decompose and remove various kind of organic and inorganic pollution in the pond.

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