THE EFFECTIVENESS OF *Ceiba pentandra* MODIFIED FIBER IN REMOVING ANION FROM EUTROPHIC WATER

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UNIVERSITI SAINS MALAYSIA

2020

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by

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Thesis submitted in fulfilment of the requirements
for the degree of
Doctor of Philosophy

November 2020

ACKNOWLEDGEMENT

Alhamdulillah, all praise to Allah who is the most Gracious and most Merciful. Without the support from many generous people, this PhD thesis may never see the light.

My sincerest appreciation goes to my supervisor, Professor Dr. Wan Ruslan Ismail, for the patient guidance, motivation and unwearyingly efforts he has made even knowing that I was from different background. My second deepest appreciation goes to my co-supervisor, Professor Dr. Baharin Azahari, who is my second mentor, for his tremendous helps, immense knowledge, advice, and support through my whole PhD journey. His sincerity in guiding me is very much appreciated. Not forgotten Dr. Mohd Firdaus Yhaya and Dr. Asyirah Abd Rahim for their constant care, help and support.

Special thanks to my beloved parents, Mr Abd Rahman Khalid and Mrs Jamaliah Saad for their love, encouragement, prayers and constant support for me. Their sacrifices in term of all aspect really mean a lot to me. Thanks goes to my siblings, Nur Syazwana, Muhammad Syazwan and Muhamad Syazwi as well, for their love, support and prayers. It is an honour for me to thanks my dearest husband, Mohd Farhan Mohd Pilus for his love, sacrifices, patience and understanding through our long-distance relationship marriage. His support and motivational thoughts every single morning keeps me moving until the finishing line. Not forgotten my father and mother in law, Mr Mohd Pilus Jaafar and Mrs Hashimah Md Abu and the extended family members for their understanding, love and support through the journey.

I would like to extend my thanks also to all my friends especially “geng makan je kejenya”, “geng anak bapak”, “geng baru nak up” and “geng BPC” for their help and encouragement. They are part of the person, whom we share our struggle together and witness my journey till reaching my final stage.

My appreciation is also extended to all the lab assistant, technician and staff especially from the School of Humanities and School of Industrial Technology, Universiti Sains Malaysia, who did their great job in helping me through this journey.

Last but not least, I am very thankful for the My Brain15 scholarship given by the Ministry of Higher Education and the Fundamental Research Grant Scheme (FRGS) with grant number 203.PHUMANITI.6711512, which allowed me to complete this research. To those who made their contributions direct or indirectly and cannot all be named, thank you so much from the bottom of my heart.

Sincerely,

NUR SYAZWANI ABD RAHMAN

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LIST OF ABBREVIATIONS

BM	Ball milling time
DMF	Dimethyl formamide
FTIR	Fourier Transform Infrared
N	Nitrogen
NO_2	Nitrite
NO_3	Nitrate
OH	Hydroxyl
pHzpc	pH at zero point charge
PO_4	Phosphate
SEM	Scanning Electron Microscopy
SO_4	Sulphate
TSI	Tropic State Index
TT	Pre-treatment time with sodium hypochlorite
TT1 BM6	Pretreated using sodium hypochlorite for 1 days and ball milled for 6 hours
USM	Universiti Sains Malaysia
WRI	World Resources Institute
XRD	X-ray Diffraction
XBM	Without ball milling
XTT	Without pre-treatment with sodium hypochlorite
XTT BM6	Without pre-treatment with sodium hypochlorite and undergoes ball milling for 6 hours

KEBERKESANAN SERAT KEKABU UNTUK PENYINGKIRAN ANION DARI AIR KUMBAHAN

ABSTRAK

Beberapa kaedah telah diperkenalkan di seluruh dunia untuk menyingkirkan nutrien anionik berlebihan dalam air eutrofik. Disebabkan anion ini sangat halus, penyingkirannya menggunakan karbon teraktif adalah sukar. Tujuan utama kajian ini adalah untuk menyelidik potensi serat kekabu (*Ceiba pentandra*) sebagai bahan penjerap boleh diperbaharui untuk menyingkirkan nutrien anionik. Penjerap berasaskan kertas makmal serat kekabu mikrofibril telah disediakan dengan mendedahkan serat kekabu kepada pra-rawatan menggunakan natrium hipoklorit (TT), diikuti dengan teknik pengisaran bebola basah (BM) pada keadaan tertentu. Untuk meningkatkan sifat mekanikal penjerap berasaskan kertas makmal khususnya dalam keadaan basah, pengubahsuaian klik azida-alkuna telah diperkenalkan. Selepas penilaian sifat-sifat fizikal dan mekanikal, TT1 BM6 yang terklik (serat dirawat selama 1 hari dengan natrium hipoklorit dengan 6 jam masa pengisaran bebola) telah dipilih dan kemudian diubahsuai dengan kumpulan amina kuaterner. Cas-cas positif daripada kumpulan amina kuaterner telah membantu penjerapan cas-cas negatif (anion tak organik) seperti nitrat, nitrit, fosfat and sulfat. Pengubahsuaian telah dilakukan mengikut nisbah berat serat kering ketuhar dan campuran berasaskan epiklorohidrin yang berbeza. Prestasi penjerap kertas makmal terklik kuaterner ditentukan berdasarkan peratusan penyingkiran nutrien anion. Telah dibuktikan bahawa penjerap TT1 BM6 terklik difungsikan dengan nisbah 1:30 serat terhadap campuran berasaskan epiklorohidrin menunjukkan kesan penyingkiran

anion yang terbaik di antara semua. Tambahan pula, untuk memahami mekanisma penjerapan, kajian kinetik dan isoterma penjerapan telah dilakukan. Penjerapan mematuhi turutan pseudo kedua dan menepati model isoterma Freundlich, menandakan bahawa penjerapan adalah jerapan fizikal dan kimiawi, dan berbilang lapis. Keputusan secara keseluruhan membuktikan bahawa serat kekabu terubahsuai amina kuaterner adalah sangat sesuai digunakan sebagai penjerap untuk rawatan air kumbahan. Untuk kegunaan akhir, penjerap kertas makmal tersebut juga diuji menggunakan air eutrofik dari Tasik Harapan USM yang berdekatan.

THE EFFECTIVENESS OF *Ceiba pentandra* MODIFIED FIBER IN REMOVING ANION FROM EUTROPHIC WATER

ABSTRACT

Several methods have been introduced worldwide in order to remove the excess anionic nutrient in eutrophic water. Since these anions were diminutive, their removal by using activated carbon was difficult. The main purpose of this study was to investigate the potential of kapok fiber (*Ceiba pentandra*) as a renewable adsorbent material in removing anionic nutrient. Micro fibrillated kapok fiber handsheet based adsorbents were prepared by exposing the kapok fiber to pre-treatment using sodium hypochlorite (TT), proceeded with the wet ball milling (BM) technique for certain time conditions. In order to enhance the mechanical properties of the handsheet based adsorbent especially in wet condition, click azide-alkyne modification was introduced. After evaluation of mechanical and physical properties, the clicked TT1 BM6 (fiber treated for 1 day with sodium hypochlorite with 6 hours ball milling time) was chosen and then modified with quaternary amine group. The positive charges from the latter did help in the adsorption of the negative charges (inorganic anions) such as nitrate, nitrite, phosphate and sulphate. The modification took place with the different ratios of the oven dried weight fiber to the mixture of epichlorohydrine based mixtures. The performance of the clicked quaternary amine handsheet adsorbent was determined with respect to their percentage of nutrient anion removal. It was shown that the clicked TT1 BM6 adsorbent functionalized with 1:30 ratio of fiber to epichlorohydrin based mixtures showed the best effect of ion removal among all. Moreover, in order to understand the mechanism of adsorption, kinetic and isotherm adsorption studies were performed. The adsorption followed the second pseudo order and best fit the Freundlich isotherm model, indicating that the adsorption was physically and chemisorption, and multilayer. Overall results proved that the modified clicked quaternary amine kapok fiber was suitable to be used as an adsorbent for the wastewater treatment. For the final application, the handsheet adsorbent was also tested using the eutrophic water from the nearby USM's Tasik Harapan.

CHAPTER 1

INTRODUCTION

1.1 General introduction

Improper of wastewater disposal management has become the most rising challenges for both developing and develop countries. It is one of the main factors that lead to the water pollution issues. Focusing on the nutrient pollution, or also known as eutrophication, about 50% of lake worldwide, including 60% in Malaysia are considered as contaminated by eutrophication (Koh et al., 2019; Othman et al., 2019). It is also was reported to be one of the most challenging environmental problem that the surface water bodies are facing since last decades (Bhagowati & Ahamad, 2019; Vinçon-Leite & Casenave, 2019). Eutrophication is commonly referring to an ecological process where the enrichment of nutrient occurs into the water bodies, especially from industrialization, agricultural, modernization, and urbanization, that causes some structural changes to the ecosystem (Glibert & Burford, 2017).

The excessive nutrient input, mainly anionic nutrient such as from the nitrogen (N) and phosphate (P) based, are the main factor that lead to accelerating the eutrophication process (Bhagowati & Ahamad, 2019). The increasing of those nutrients may lead to the increasing of algal blooms resulting in the high turbidity and loss of biodiversity. It also may cause unbalance growth of biological component due to the oxygen depletion and decaying of some organism (Reddy et al., 2014). Due to this concern, many researchers are trying to figure out the process to overcome these phenomena before it become more serious.

Various methods of removing nitrate and phosphate have been introduced by many researchers such as chemical precipitation, reverse osmosis, electrocoagulation, and electrodialysis (Ayoob et al., 2008; Jagtap et al., 2012; Mohapatra et al., 2009; Suriyaraj & Selvakumar, 2016). Despite all of the unique advantages in these technologies, the poor regeneration, electric power consumption, membrane fouling and cost factor always remain as an issue and shows limited social interest of these technologies (Ayoob et al., 2008; Bhatnagar & Sillanpää, 2011; Mohapatra et al., 2009; Suriyaraj & Selvakumar, 2016). Most of the researchers have recommended the adsorption process as the most efficient method to remove nitrate and phosphorus. In order to reduce the cost of treatment, most of the researchers preferred to find an alternative to use inexpensive adsorbent (Crini, 2006). Therefore, it would be a great concern to have a renewable adsorbent material and at the same time can easily processed into an adsorbent material.

In order to meet the demand required, paper-based adsorbent technology has been recently introduced. Basically, in this technology, the fiber used was chemically modified in order to improve its properties as an adsorbent or membrane in wastewater treatment (Nongbe et al., 2018). It is an alternative to synthetic polymer for the use as membranes in ultrafiltration and nanofiltration process (Mautner et al., 2016).

Addressing the issues of the cost for raw material, biomass and biomaterial are the great potential and preferred material since they are abundant, cheap and have a high satisfactory adsorption property (Kyzas & Kostoglou, 2014). They can be used either in powder form, fine particle form or fiber form (Liu et al., 2002). The presence of hydroxyl functional group in cellulose helps in providing natural adsorption abilities (Jamshaid et al., 2017). However, the effectiveness of the adsorbent depends on the properties of the fiber. Some of the adsorbents need to be chemically or physically modified of their surface characteristics in order to improve the adsorption capacities (Loganathan et al., 2013).

1.2 Research background

Kapok fiber is reported as a natural fiber with a large hollow structure and endowed it with a porosity more than 90% (Duan et al., 2013; Lou, 2011; Zheng et al., 2015). However, according to Lou (2011), the large lumen and waxy surfaces are not favorable for the access of hydrophilic adsorbates such as coloring agent, dyes, and wastewater with heavy metal and nutrient content. Thus, to alter these intrinsic properties, the kapok fiber can be subjected to surface modification by pre-treated it by using sodium hydroxide, surfactant, and chelators at elevated temperatures to improves its water hydrophilicity (Bozaci, 2019).

Previously, work done by Abdullah et al. (2010) had modified the properties of kapok fiber to hydrophobic-oleophilic characteristic to be used as oil-absorbing material. The modified kapok fiber possesses good buoyancy and does not sink in the mixture of oil and water (Rengasamy et al., 2011). Meanwhile, Higa et al. (2011) had chemically oxidized the kapok fiber by an impregnation process with 2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester to obtain kapok fiber with high metal ion adsorption such as cadmium, copper, nickel and lead (Huynh & Tanaka, 2003). Chung et al. (2013), in the other hand, had converted kapok fiber into activated carbon to remove dyes.

To date, fewer studies have been reported on the modification of kapok fiber as an adsorbent for nutrient removals such as nitrate and phosphate. Thus, this study was conducted considering the potential of kapok fiber to be a promising nutrient adsorbent material, especially for anions such as nitrate and phosphate.

Relate to the development of paper-based technology, recently, nanopapers have been introduced. Nanopaper is produced from cellulose nanofibril via the mechanical pulping process (Hu et al., 2013). The diameter size of fiber was in nanometer (nm) range, while the length will be around micrometers (μm) size. However, according to Mautner et al. (2016), due to the smaller particle size, the permeability of the adsorbent was relatively low, as well as the percentage of ion removal. Furthermore, the mechanical properties were also a big concern since it was easily disintegrated if exposed for too long in an aqueous medium. Smook (2003) also stated that the smaller the fiber size, the lower the mechanical strength.

Considering the size of the fiber, in this research, microsized fiber was used. The kapok fiber underwent chemo-mechanical pulping at the same time since the beginning. To make it fibrillated, the kapok fiber underwent wet ball milling process. The fibrillation provided more exposure to hydroxyl sites. Thus, it helped to enhance the mechanical properties of the paper-based adsorbent. The effect of ball milling was studied in order to observe the effect on mechanical properties.

In order to make it function as an absorbent, especially for anion removal such as nitrate and phosphate, the introduction of quaternary amine groups was proposed. The quaternary amine groups acted as ion exchanger since the amine group possessed positive charges, which helped in enhancing the adsorption of negative charge on anion such as nitrate and phosphate ion (Kalaruban et al., 2016). According to Jamshaid et al. (2017), the chemical modified forms of fiber offered much better adsorption capacities as compared to its original forms. The exposure of more hydroxyl sites on the microfibrillated kapok fiber also helped in providing the active sites for crosslinking of quaternary amine groups.

1.3 Research gap and problem statement

In paper-based technology adsorbent, nanopaper is commonly used as a membrane in various applications. It has become among the efficient bioadsorbent which combines few properties such as good flexibility, high surface area and versatile surface chemistry. However, there are some challenges which related to the usage of nanofiber especially fiber with diameter less than 100 nm in size. The smaller nanofiber size caused a lower permeability of the membrane produced. The lower permeability was due to the disordered and close entanglement between the fibers during paper formations (Xiao et al., 2017). Furthermore, the shorter fiber length also would affect the exposure of the hydroxyl group on the surface of the fiber. When the fiber was already introduced to certain functional group, less modification could be done afterwards. Therefore, the adsorption rates for ion, especially nitrate and phosphate ions, were limited (Mautner et al., 2016). To tackle this problem, microfiber was introduced in order to provide more active hydroxyl groups on the surface of the fiber since the fiber was much longer compared to the nanofiber size. The ball milling technique also helped to turn the longer fiber into micro sized fiber easily and at the same time formed fiber fibrillation. The fibrillation could increase the active hydroxyl group exposure on the surface of the fiber.

With regards to the mechanical properties of the paper-based adsorbent, the strength of the adsorbent was also a major concern. Hydrogen bonds between the fibers are the principal forces in determining the strength of interactions between fiber in paper structure (Przybysz et al., 2016). In dry condition, the hydrogen bonds are mainly formed between the hydroxyl groups of the cellulose in the fiber. However, in wet condition, the hydrogen bond between the fibers would be interfered by the water molecules. Thus, it might lead to weakening the fiber-to-fiber bonds. During the application of the paper-based adsorbent in water, the mechanical strength was affected. To encounter this problem, azide-alkyne click chemistry was introduced. Azide-alkyne click chemistry is a very selective reaction. The reaction only takes place between the azide and alkyne components. The crosslinking effect between both azidated and alkylated functional group helped to hold the fiber together, especially in wet condition. Therefore, when the adsorbent was exposed to water, the bonding between those fibers is not easily disrupted.

Moreover, based on the previous studies, most of the researchers only focused on the single functionality of the fiber which related to the adsorption properties of adsorbent. Normally the hydroxyl group on the fiber functionalized with quaternary amine group which acted as an ion exchanger to remove the nitrate and other anion nutrients. However, in this study, the focus was divided into two functionalities, where some parts of the hydroxyl groups were functionalized by 'click' modification, which related to the concern of mechanical properties, while the other parts of hydrogen groups left were functionalized with quaternary amine group to observe the effect of the adsorption properties. The optimum condition of both functionalizations was considered as a step forward in tackling the problem of nutrient adsorption with better mechanical properties.

1.4 Objectives of the study

The objectives of the study are:

1) To study the characteristic of kapok fiber treated with sodium hypochlorite and ball milled using wet ball milling technique on the chemical composition and particle size of the fiber.

2) To investigate the effect of azide-alkyne click chemistry on the different size of kapok fiber by observing the mechanical properties of the handsheet produced.

3) To study the effect of the grafting the ball milled kapok fiber with quaternary amino exchanger on the removal of anions in water.

4) To determine the kinetic and mechanism involved in the adsorption process.

5) To determine the effectiveness of functionalized ball milled kapok fiber on the adsorption of the mix anions in eutrophic water.

1.5 Scope of study

This study focuses on the utilization of micro fibrillated kapok fiber as the raw material for the production of paper-based adsorbent. The average size used was in range of 60-70 μm. Those fibrillated fiber undergoes two types of modification. The first modification was the click azide-alkyne modification which focused on the wet mechanical properties of the adsorbent. The analysis was carried out using a statistical tools- two ways ANOVA. The optimal condition was determined and proceed to the next synthesis.

The other focus was on the synthesis of the selected clicked micro kapok fiber with the quaternary amine group. The effectiveness of the modification was tested in the efficiency removal of the anion nutrient such as nitrate, nitrite, and phosphate. The comparison also was made with the blank micro kapok fiber and the blank click kapok fiber adsorbent. To examine the practicality of the prepared adsorbent, the adsorbent was later applied in the treatment of eutrophic wastewater.

1.6 Thesis organization

This thesis explored the possibilities of the kapok fiber to undergo dual modification in order to act a paper-based adsorbent for the removal of anion in eutrophic water. The organization of the thesis is as follows.

Chapter 2 provides a general information on the relation of how kapok fiber can be utilized as a paper-based adsorbent in order to remove the nutrient anion, especially nitrate and phosphate in the eutrophic water. The information on how the modification of the kapok fiber may help to improve in the removal of inorganic anion and at the same time providing a good mechanical strength also was discussed. This chapter also contains information on the relation of how eutrophic water lead to the deterioration of the water quality.

In Chapter 3, the discussion was more on the method development to modify the kapok fiber, characterize and examines the effect of modification on the application as adsorbent. Two types of modification's method were developed which is the click azide-alkyne modification which focus on the mechanical properties of the paper-based adsorbent and followed with the modification via grafting amine groups for the removal of anion.

Chapter 4 was divided into five section which focus on the analysis of the result obtained from the experiment. The first section was focus on discussion of the characterization of the kapok fiber before and after the pre-treatment and wet ball milling was conducted. Then followed with the second section which discuss on the effect of click azide-alkyne towards the mechanical properties. The third and fourth section discussed more on the effect of the modification of clicked kapok fiber via grafting amine group, on the anion removal and the mechanism of adsorption study. The final section in this chapter was the application part. This section discussed on the ability of the click quaternary amine kapok fiber handsheet adsorbent to remove the nutrient especially anions such as nitrate, nitrite, sulphate and phosphate in the water sample taken from the Tasik Harapan.

Chapter 5 concludes the thesis and discussed the future opportunity of the clicked quaternary amine kapok fiber towards the opportunity to be used for a novel application such as a fertilizer in future.

CHAPTER 2

LITERATURE REVIEW

2.1 Water and water scarcity

Water has become one of the main vital substances on earth. The water covered two-third of the earth surface, and 97 % of the water is saltwater while 2% of the earth's water is stored as freshwater in glaciers, ice caps, and snowy mountain ranges. Only less than 1% in freshwater streams, and lakes are available for daily water supply needs. The global environmental changes that we are experiencing now is due to the excessive human pressures on the earth, which have an impact on the safe and secure water in the world. Some environmental disaster related to the climate changes also threatens to cause major alterations to the hydrological cycle. The major alterations might affect the availability of freshwater and at the same time, relate to water scarcity.

Water scarcity (Figure 2.1) is a phenomenon where the viability of water resources in certain area is insufficient to meet the demand of water usage in certain region. It involves water shortage, water deficits, water stress, and water crisis. According to Fedoroff et al. (2010), water scarcity has become a part of the critical concern of the world. In 2015, the World Economic Forum reported that the water crisis was listed among the top global risk that might have potential impact for future generation (World Economic Forum, 2015).

This was in line with the prediction of the United Nations in 2006 whereby in the 21st century, water scarcity will be one the defining features to be faced by any society in this world (United Nation, 2006). They also predicted that due to the imbalance between availability and demand, about 1.9 billion people would face absolute water scarcity by 2025. About two-third of the world population will suffer under water stress condition by 2025 due to water shortage.

Figure 2.1 Water scarcity effect, mangrove in a parched land, French Guiana (World Wild Life, 2018)

2.2 World Water demand and quality

The imbalance between demand and availability are one of the factors that contribute to water stress and scarcity. Based on the data reported by United Nation, (2014) (Figure 2.2) the global water demand are predicted to increase by around 55% by 2050 due to the increase in the manufacturing sector, hydropower electricity generation and domestic usage (Boretti & Rosa, 2019; Leflaive, 2012; Mekonnen & Hoekstra, 2016; United Nation, 2014). Thus, the demand for freshwater will increase, and the stress level of water resource available is getting worst day by day. This phenomenon may result in severe water stress in 2050.

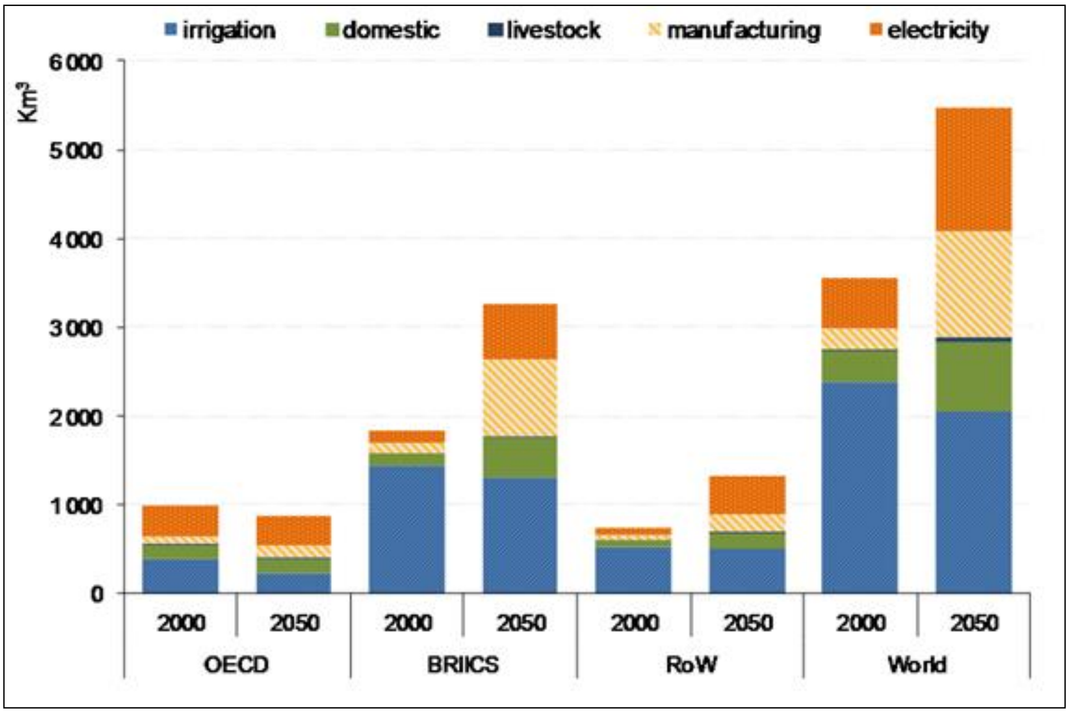

Figure 2.2 Global water demand and prediction for the whole world water demand during 2050 based on the following categories: Organization for Economic Co-operation and Development (OECD), Brazil, Russia, India, Indonesia, China, South Africa (BRIICS), Rest of world (RoW) and the whole world (World) (Leflaive, 2012).

Moreover, as shown in Figure 2.3, the water consumption and withdrawal rates have increased rapidly than the population growth. The freshwater is distributed throughout the world quite unevenly. Furthermore, it is impractical to provide the water-demanding area with much-needed water from surplus areas. Thus, water scarcity in many parts of the world becoming serious problem. As a result, the water withdrawal in fast-growing populated areas, especially for agricultural and industrial regions are depleted and consequently becoming degraded (Hassan, 2016).

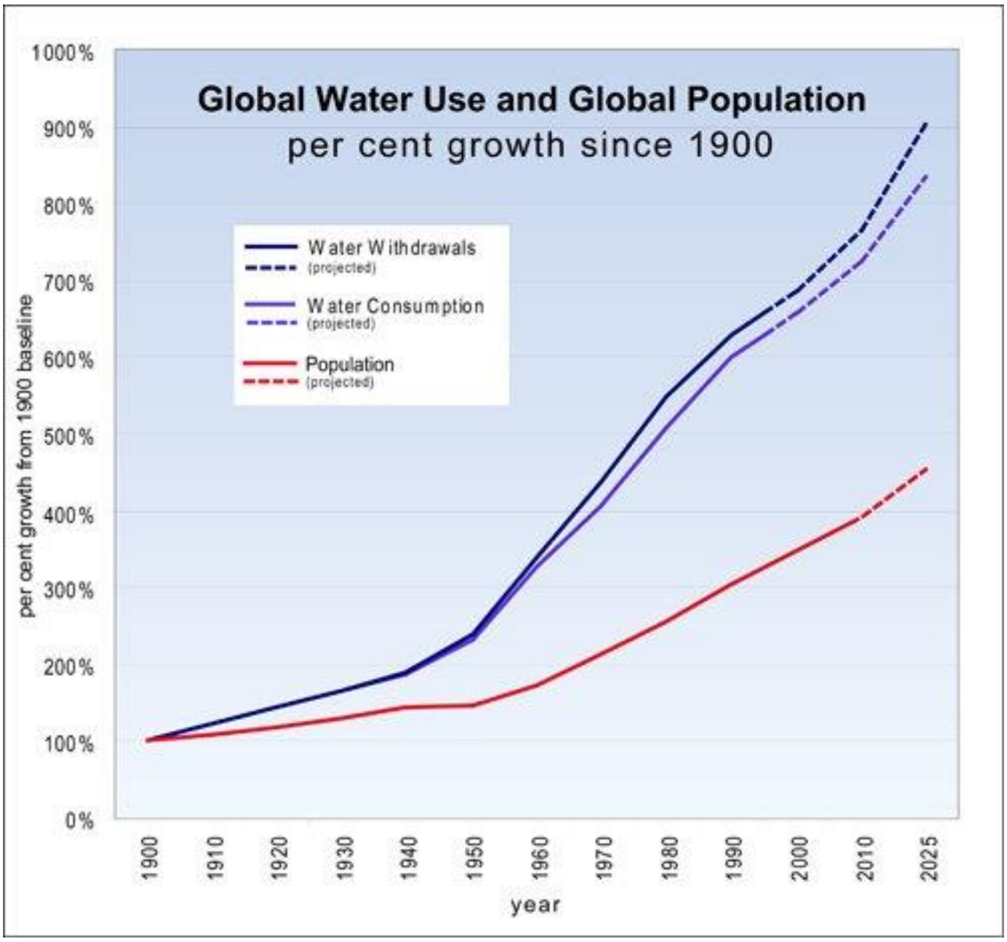

Figure 2.3 Global water consumption and global population (Hassan, 2016).

The result also was supported by the prediction from the World Resource Institute that by 2025, about half of the global population could be facing water scarcity compared to the year 2012 (Figure 2.4). Most of the extremely high-stress area water stress (which indicate in red) was predicted to be at the region with a high population area. McKinsey (2009) also has estimated that by 2030, the global water phenomena will occur from 4500 billion m^3 per year to 6900 billion m^3 per year. Malaysia is one of the countries facing serious water risks.

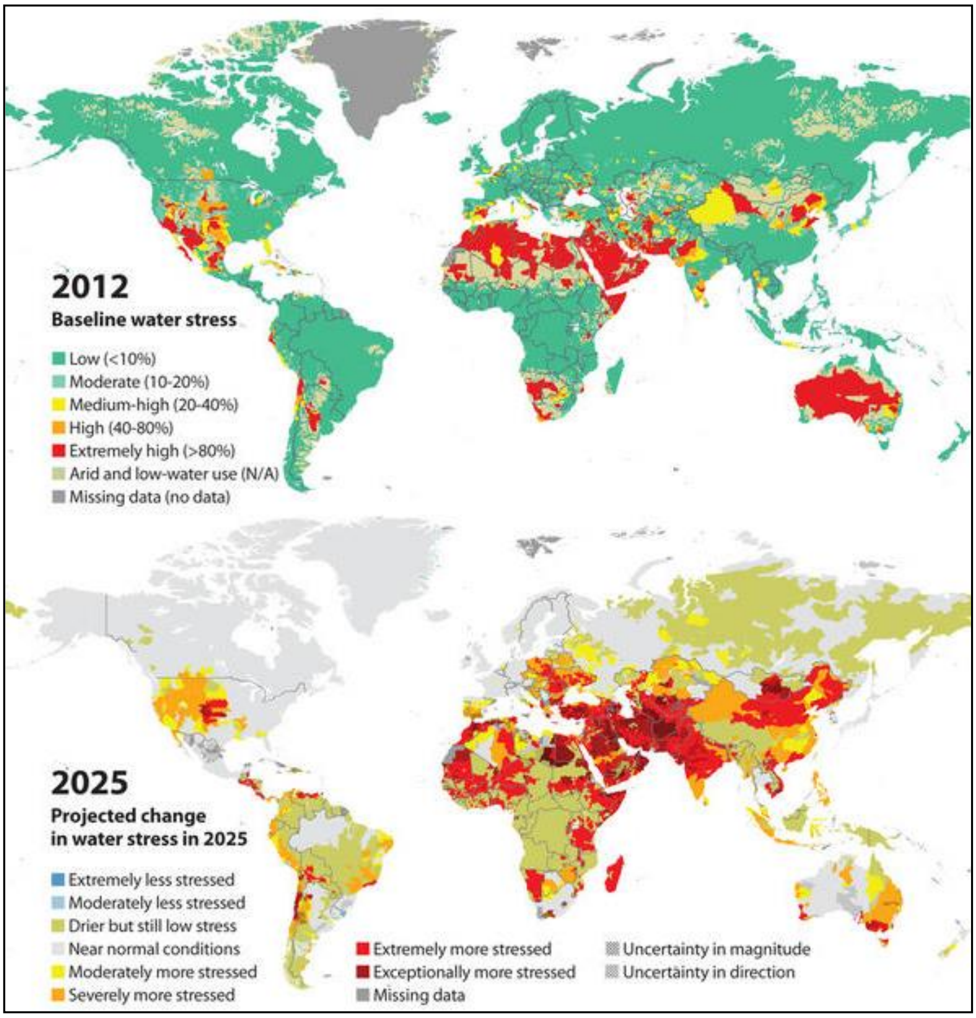

Figure 2.4 Water scarcity prediction (World Resource Institute, 2011).

2.3 Water risks in Malaysia

Over the past decades, Malaysia is known as a country with plenty of water resources since it is located in the tropical zone which received high rainfall every year. However, lately, the water supply situation has changed from one relatively bounty to scarcity.

In recent years, Malaysia is experiencing an increased demand for water. Based on the study conducted by Ahmed and co-workers (2014), the demand for water, especially in agricultural, industrial and domestic purposes in Malaysia, has shown an increment from 8.9 billion m^3 in 1980 to 15.5 billion m^3 in 2000. The World Resources Institute (WRI) in 2016 has predicted that by 2020 the water stress level in some areas in Malaysia such as Kedah, Penang, Perak, Selangor, Kuala Lumpur, Negeri Sembilan, Melaka, Johor and Kelantan will be having about 1.4-fold increment over the current level. Kuah in Kedah is expected to have a greater increment in water stress level, which is about two-fold increment.

As seen in Figure 2.5, most of the highlighted area is high developing area and densely populated. Normally the densely populated area is correlated with the economic development and industrialization area. The urban activities and municipal wastewater are considered as part of the major causes of contamination in surface water bodies (Liyanage & Yamada, 2017). Pollutant discharge from this area may cause extensive organic pollution, poisonous pollution, eutrophication and severe ecological destruction (Zhang et al., 2020). These crucial issues lead to the degradation and rapid deterioration of water quality in the area (Liyanage & Yamada, 2017; United Nations Water, 2015).

Langkawi, on the other hand, has expected to have double fold increase in water stress level due to the location as an island with no big river on the island. It is also infeasible to transport freshwater from other places using ships or pipes over the seabed due to the high cost. Moreover, the water demand in Langkawi was predicted to increase about 107 million of litre per day (MLD) by 2020 and 128 MLD by 2030 (Yang, 2018).

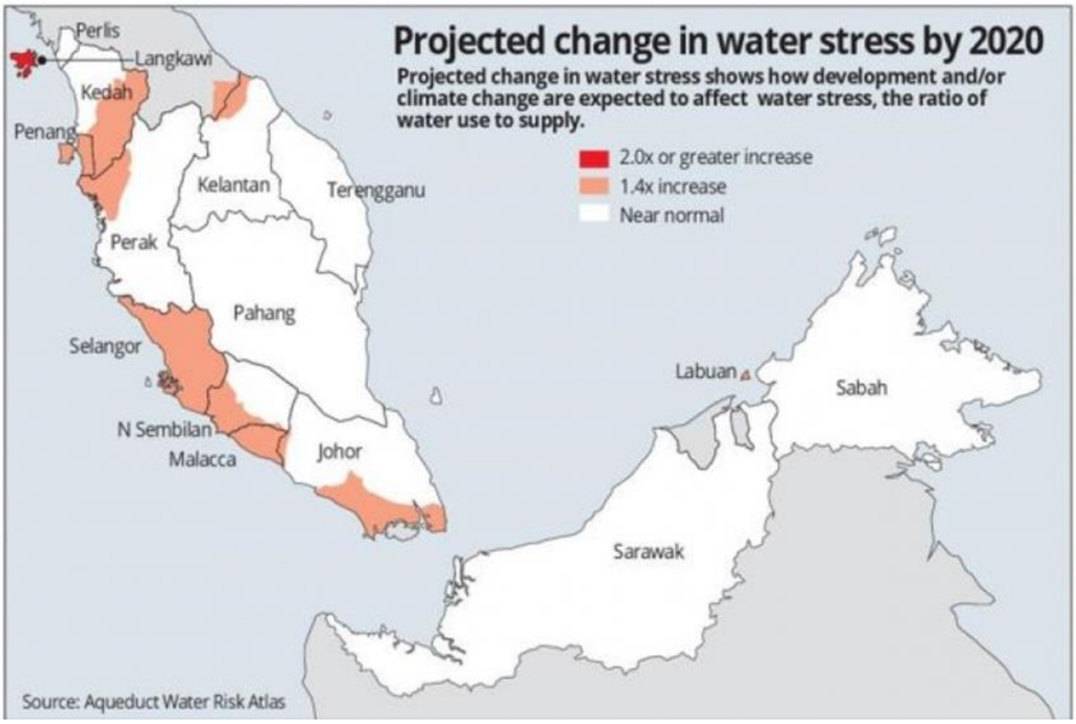

Figure 2.5 Water stress projected by 2020 in Malaysia (Sivanandam, 2016).

In addition, climate change and global warming also are part of the reason that leads to the water crisis in some state in Malaysia. The extreme temperature may cause many unfavorable events such as a rise in sea level, which due to increasing temperature, storms, and floods (Bebbington & Larrinaga-González, 2008; Rosentau et al., 2017). According to Tangang and co-author (2012), by at the end of the 21st century, the average temperature of Malaysia may increase about three to five degree Celsius. The increase of temperature related to the global climate change may affect on the extremes, with more pronounced droughts and more severe flooding.

Moreover, pollution from nutrients and sediments also has become a serious threat to Malaysian lakes, causing the water quality to deteriorate to varying degrees. This type of pollution or also known as eutrophication, is normally due to the enrichment of nutrients which causes the changes of ecosystem such as the abnormal growth of algae and other aquatic plants, the depletion of fish species and the deterioration of water qualities (Hu et al., 2020). Based on the Status of Eutrophication of Lakes in Malaysia by National Hydraulic Research Institute of Malaysia, NAHRIM, about 62% of the 90 major lakes and reservoirs in Malaysia evaluated were eutrophic (NAHRIM, 2009). Tasik Chini and Bera in Pahang, Tasik Timah Tasoh in Perlis, and Tasik Kenyir in Terengganu are some of the lakes that were evaluated as eutrophic based on the Carlson's Tropic State Index (TSI) values. The TSI value is the measurement to characterize the state of the lake with respect to the biological activities. It was calculated based on the interaction of the three water quality variable, which is total phosphorus (TP), the chlorophyll-a (Chl-a), and the Secchi depth (SD) (Opiyo et al., 2019). The classification scales run from 1 to 100 with indication oligotrophic, mesotrophic and eutrophic with TSI value less than 40, 40-50, and 50-100, respectively. Moreover, from the TSI value also, the classification of the lakes can be referred to the terms 'good' with value of TSI below than 37.4, between 37.4 and 47.4 is 'moderate' and over than 47.4 is 'bad' as well (Shahabudin & Musa, 2018). Those lakes mention above were part of the lakes that were graded as "bad" based on the allowable nutrient loading, which was correlated to Carlson's TSI value (Huang et al., 2015; Shahabudin & Musa, 2018).

2.4 Eutrophication

Eutrophication or also known as nutrient pollution in water is one of the most serious problems for water bodies worldwide (Ambulkar, 2017). The excessive input of the nutrient into the water are considered harmful and toxic to human and animal even at low concentrations (ppb) (Bhatnagar & Sillanpää, 2011; Glibert, 2017). The most important elements of nutrient involved are carbon, nitrogen, phosphorus, fluoride and sulphide (Soetan et al., 2010; Weldeslassie et al., 2018). Normally, most of the nutrient is released by point sources and non-point sources into the water bodies. Point source pollution originates from a single, and specific site such as industrial or municipal waste and it is easily monitored, identified and regulated. Non-point source pollution may result from urban and agricultural run-off and run-off from mining and construction sites. Therefore, they are often difficult to identify since pollutants originate from many different sources.

Wastewater, especially from the urban and agricultural activities, are the source of most nutrient which inhibiting the growths of algae. The excessive nutrient such as nitrate and phosphate may cause algae and other aquatic organisms to grow and leads to the accumulation of organic load in the water. Thus, at the same time may cause complex effects on the productivity and biodiversity of aquatic ecological balance (Yu et al., 2017). The presence of algae blooms also limits the light penetration into the water, lower the dissolved oxygen levels, increased the pH level and may disturb the growth of the plant in the littoral zone (Chislock et al., 2013; Qi et al., 2019). Thus, the oxygen supply to support most of the aquatic habitat in water is limited.

Other than the creation of dense algae bloom, which can reduce the water clarity and quality, eutrophication also may produce the unpleasant smell of phytoplankton as well. The effect of high nutrient concentration, especially nitrate, in drinking water also can lead to the potential risk of public health. One of the potential effects is the "blue - baby syndrome" (methemoglobinemia), particularly in infants, and the carcinogenic nitrosamine formation which responsible for causing various kinds of cancers in humans (Nur, 2014; Sudha et al., 2019).

Due to the link between health issues and excessive nutrient concentration in drinking water, the World Health Organization (WHO) and regulatory agencies in various countries have set the nutrient concentration limits allowable in water as stated in Table 2.1 below.

Table 2.1 The minimum limit of nutrient allowed in water (WHO, 1998)

Nutrient	Minimum % allowed
Fluoride (mg/L)	1.5 (P)
Sulphate (mg/L)	500
Chloride (mg/L)	250 [a]
Nitrate	50
Nitrite	3
Phosphate	5

a Health-based guideline value, (P): provisional

In general, nitrate and phosphate are among the most problematic pollutants that affect the surface and groundwater worldwide (Wang et al., 2019). So, in this research, the study will be more focusing on the nitrogen-based (such as nitrate and nitrite) and phosphorus-based (such as phosphate) pollution.

2.4.1 Nitrogen-based pollution

Nitrogen is a very dynamic element. It can be biochemically or chemically transformed through a series of processes that are conceptually summarized as the nitrogen cycle (Xia et al., 2018). The transformation of nitrogen involved oxidation (loss of electron) and reduction (gain of the electron) of the N atom by biological as well as chemical processes. The nitrogen cycle involved four steps, as shown in

Figure 2.6, namely nitrogen fixation, ammonification/mineralization, nitrification and denitrification. In nitrogen fixation, the nitrogen gas in the atmosphere was fixed by the bacteria in root nodules of legumes of the plant. In this stage, the nitrogen gas (N_2) turned to ammonia (NH_3). The nitrogen fixation can occur by bacteria fixation, lightening fixation or industrial fixation. Then the process followed with ammonification. The dead animal and plant undergo decomposition by bacteria, and they release ammonia into the soil. The ammonia (NH_3) was then converted to ammonium salt (NH_4^+). When the ammonium is release in the soil, most of it will often be altered chemically by a particular type of autotrophic bacteria. The Nitrosomonas bacteria will convert it into nitrite (NO_2^-), while the Nitrobacer bacteria will convert the nitrite to nitrate (NO_3^-). In deep soil, the reverse nitrification can occur where the bacteria convert NO_3^- is converted into N_2 and other gaseous compounds like NO_2. This process is called as denitrification. These gases will diffuse back to the atmosphere, and the cycle is repeated.

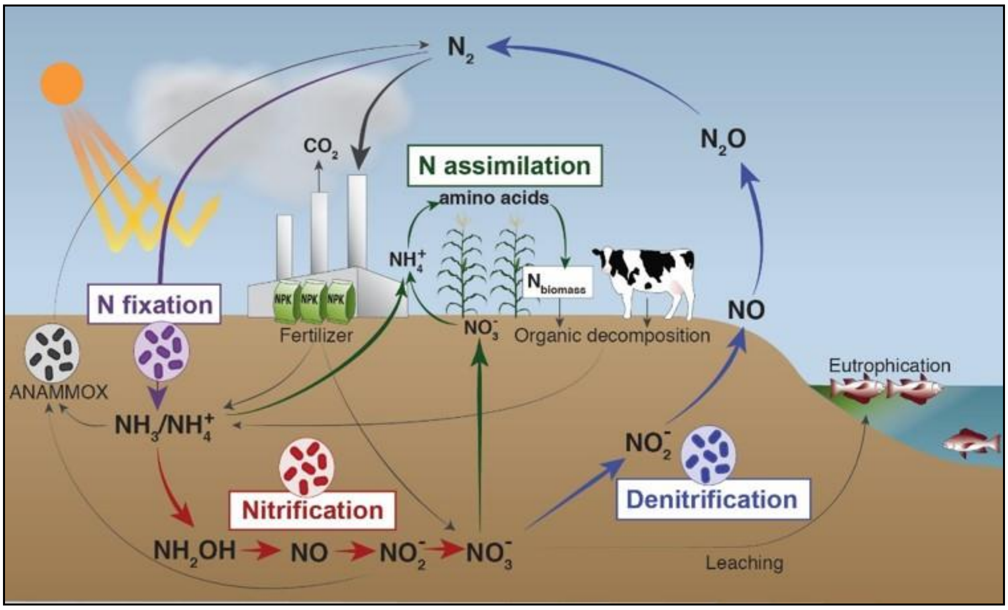

Figure 2.6 The nitrogen cycle (Lehnert et al., 2018)

However, human activities have severely altered the nitrogen cycle. The intensive agricultural and application of chemical such as fertilizer have resulted in contamination of groundwater and other water bodies. Since nitrate is highly water soluble, it would possibly be the most widespread contaminant in groundwater, causing a serious threat to the drinking water supply (Bhatnagar & Sillanpää, 2011). Excessive addition of nitrogen-based fertilizer may also be washed by surface runoff into the lakes, rivers and streams which can lead to eutrophication. It could be from a point source or non-point source pollution. Moreover, livestock farming and sewage waste also part of the factors that contribute to the increase of ammonia content through leaching, runoff and groundwater flow.

2.4.2 Phosphorus-based pollution

Phosphorus also is part of the crucial nutrient for the plant. Unlike nitrogen, phosphorus does not have a gas phase. The atmosphere does not play a significant role in phosphorus. However, it has a high affinity for soil and sediment particles. As shown in Figure 2.7, in the phosphorus cycle, the organic form of phosphorus is converted into an inorganic form during decomposition. Then, the element will end up in sediments or rock formations, where it will remain for millions of years. Finally, phosphorus is released to the soil by weathering and absorbed by the plants and the cycle repeated. The phosphorus cycle also was known as the slowest cycle of all the biogeochemical cycles (Carpenter & Bennett, 2011).

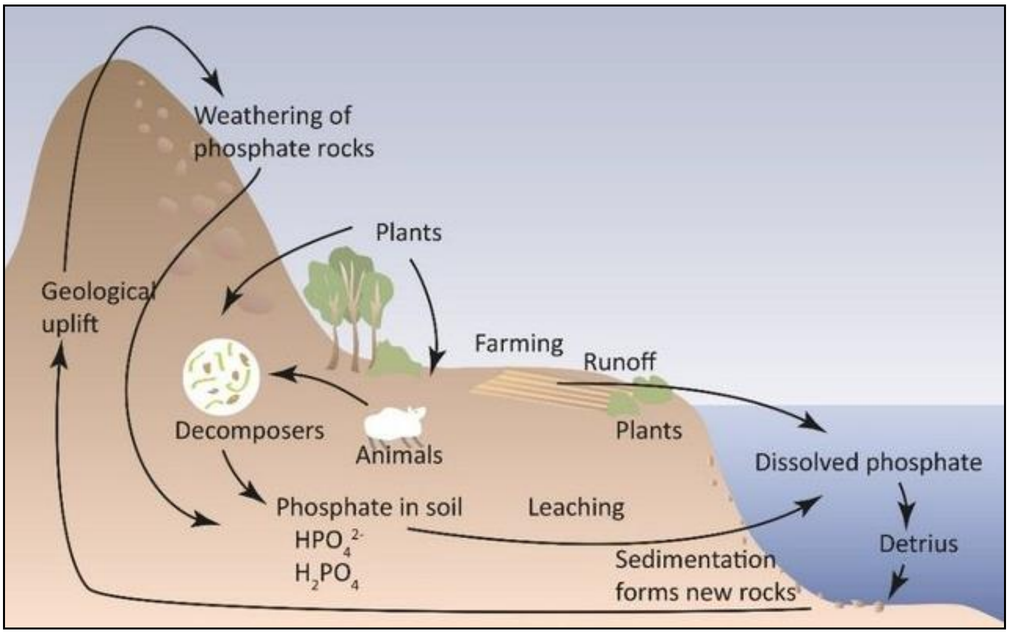

Figure 2.7 The phosphorus cycle (Lappalainen et al., 2016).

In nature, phosphorus in the aquatic environment are normally divided into particulate phosphate or dissolved phosphate. The particulate phosphate are normally attached to the suspended solid particle while the dissolved phosphate are normally referring to the dissolved phosphate ion such as orthophosphate, polyphosphate and organic phosphate in water (Liang et al., 2011). The dependency of phosphate, especially in agricultural is quite important. The excess usage of phosphate-based fertilizer also may contribute to eutrophication. The phosphate-based fertilizer will be carried in the surface runoff to the water bodies and form new sedimentary layers. The increased level of phosphate in the water bodies may cause the excessive growth of algae and lead to eutrophication. Eutrophication makes the water non-portable and toxic to human and other livestock (Schindler, 2006; Smith et al., 2006). In addition, the widespread usage of the phosphate-based product in food and mining industries and municipal discharges also contribute to the increase of phosphate level in water bodies. The use of detergent in laundry also contributed to the rapid increase in phosphate concentrations in aquatic environments.

2.5 Inorganic anion removal anion technologies

Excessive concentration of nutrient in the water bodies and the strict regulation from the authorities make it necessary to search for appropriate treatment technologies. Basically, the nutrient removal involved many techniques and can be divided into three categories which are biological, chemically and physicochemical approaches as simplified in Table 2.2.

Table 2.2 Common technique involved in nutrient removal

	Biological	Chemical	Physiochemical
Nitrogen	Suspended growth - Activated sludge Biofilm - Trickling filter Biological nitrification/ denitrification	- Chemical denitrification by using zero-valent iron (Ahn et al., 2008; Lee et al., 2017)	- Ion exchange - adsorption
Phosphate	- Phoredox - Anaerobic bacteria	- metal salt addition - lime addition - alum (Huang et al., 2017; Liang et al., 2011)	- ion exchanger - adsorption - coagulant - flocculation

In order to make sure the removal was effective, each approach differed to one another nutrient. The biological approach involved the usage of microorganism such as bacteria along the process to decompose organic contaminants into harmless or volatile compounds. For nitrogen-based nutrient removal, it involves the usage of heterotrophic bacteria in the absence of oxygen (anaerobic conditions) convert nitrate-N and nitrite-N into nitrogen gas (Nur, 2014; Park & Yoo, 2009; Pungrasmi et al., 2015).

While for phosphate removal, activated sludge process was used by introducing an anaerobic and/or anoxic zone ahead of an aerobic stage. However, the disadvantages of using a biological approach are the process is very time consuming since it involved pH and temperature adjustment and a post-treatment process to disinfect the micro-organisms.

For the chemical approach, one of the familiar methods to remove nitrogen-based nutrient such as nitrate is by using a zero-valent agent. It normally involves iron which may act as a reducing agent in the system. However, this method has its limitation such as low reactivity due to its intrinsic passive layer, narrow working pH, low selectivity for the target contaminant especially under toxic conditions, and reactivity loss with time due to the precipitation of metal hydroxides and metal carbonates. For phosphorus nutrient removal, the chemical approach involved the addition of metal salt, alum and lime. The reaction between phosphorus in water with a metal salt, alum or lime basically will form a precipitate of sparingly soluble phosphate and subsequently can be removed from the liquid using solids separation process. However, this method was not preferred since it involved high cost and difficult handling process.

Since most of the nutrient is highly soluble in water, it is impossible to separate them using a physical method such as settling and flotation method. Thus, the addition of some chemicals such as coagulants or flocculants will help to change the physical state of the nutrient ion and allow them to remain in a stable form with settling properties. This approach is called as physicochemical. Most common physicochemical method are chemical coagulation, filtration, adsorption and ion exchange. According to Kim & Chung (2014) chemical coagulation are normally use