UNIVERSITI PUTRA MALAYSIA

NANOCLAY ENHANCED PHYTOREMEDIATION PROCESS

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ABSTRACT

Adsorption of heavy metals onto nanoclay was studied using techniques of batch adsorption. The aim of this study was to investigate the adsorption potential of low cost adsorbent paddy field clay for removing heavy metals from effluents. To better understand the property relationship of the adsorption process, the paddy field clay was thoroughly defined by XRD, particle size and zeta potential. The effect of contact time, pH, and adsorbent dose has been studied on the adsorption mechanism. Results showed that the adsorption rate initially increased rapidly and the optimal efficiency of removal was achieved in about 45 minutes. Further increase in contact time showed no noticeable change in the equilibrium concentration; that is, the process of adsorption had reached equilibrium. The adsorption was favoured with maximum adsorption at pH 10.0. The adsorption isotherms could be fitted well by the Langmuir model. Thus, the results consider that Nanoclay has considerable potential as physical, safe and efficient aqueous solution adsorbent materials for NH^{4+} adsorption.

ABSTRAK

Penyerapan logam berat ke nano-tanah liat dikaji menggunakan teknik penyerapan kumpulan. Matlamat kajian ini adalah untuk menyiasat potensi penyerapan tanah liat sawah adsorben untuk mengeluarkan logam berat dari pencemaran. Untuk memahami dengan lebih baik hubungan antara proses penyerapan, medan padi tanah liat telah ditakrifkan dengan teliti oleh XRD, saiz zarah dan Zeta potensi. Kesan masa kenalan, pH, dan dos adsorben telah dikaji pada mekanisme penyerapan. Keputusan menunjukkan bahawa kadar penyerapan pada mulanya meningkat dengan pesat dan kecekapan optimum penyingkiran dicapai dalam kira-kira 45 minit. Peningkatan selanjutnya dalam masa hubungan menunjukkan tiada perubahan ketara dalam kepekatan keseimbangan; iaitu, proses penyerapan telah mencapai keseimbangan. Penyerapan telah disukai dengan penyerapan maksimum di pH 10.0. Penyerapan isotherms boleh dipasang dengan baik oleh model Langmuir. Oleh itu, keputusan menunjukkan bahawa nano-tanah liat mempunyai potensi yang besar sebagai fizikal, selamat, dan bahan adsorben cekap dari penyelesaian akueus untuk NH^{4+} penyerapan.

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Abbreviations	**Acronyms**
BOD	Biological Oxygen Demand
COD	Chemical Oxygen Demand
NH^{4+}	Ammonium
HCI	Hydrochloride
NaOH	Sodium Hydroxide
H_2SO_4	Sulfuric acid
CO_2	Carbon Dioxide
DO	Dissolved Oxygen
TSS	Total Suspended Solid
NaCI	Sodium Chloride
XRD	X-Ray Diffraction
SS	Suspended Solid
WQI	Water Quality Index
NO^{2-}	Nitrogen Dioxide
NO^{3-}	Nitrate

CHAPTER 1

INTRODUCTION

1.1 Background Study

Water pollution is one of serious issues in the global environment. Water is important aspect of the ecosystem that is critical for human and economic growth. The major factor of surface water pollution are caused by the rainwater runoff that carries pollutants into the water body and it reduces the amount of oxygen dissolved in the water body. Based on G. McIsaac said that the water drainage and irrigation network leading to surface water tends to be the hydrological mechanism that triggered nitrogen, N pollution that exists in both organic and inorganic forms.

Plants readily have the inorganic N, mainly ammonium (NH^{4+}) and nitrate (NO^{3-}). Nevertheless, it must first be transformed to inorganic forms before the organic N can be taken on. As a by-product of the decomposition of organic matter known as mineralisation, soil microbes have completed this cycle (C. Valenzuela-Solano, D. M. Crohn, and J. A. Downer, 2005). The long retention time of organic N before converted to inorganic N and the accumulation of inorganic N in the bulk affect the environment of the surface water. The ability of macrophytes to carry out their phytoremediation function to assimilate, concentrate and store the converted pollutants can be enhanced by improving the mechanism of the N cycle in surface water as an alternative to the commercial system used in physical and chemical processes (P. Champagne,2007).

Nevertheless, macrophyte application in phytoremediation was less successful due to low levels of nitrogen, N and phosphorus, P uptake. For example, N take-up of several macrophyte species i.e. Typa, Juncus was within the range of 2630-125 kg ha-1 yr-1, whereas macrophyte crops such as Nelumbo Nucifera could only perform about 27.8 kg ha-1 yr-1, while it plays a vital role in providing enough oxygen and altering dissolved oxygen in the water column (Y. S. Ng and D. J. C. Chan,2017; K. Chunkao, C. Nimpee, and K. Duangmal,2012).

In this work we focus on the species Nelumbo Nucifera as it was sufficiently feasible to supply an adequate quantity of 0.2-2.1 mL / min O^2 gas to help increase microbial activities for the treatment or phytoremediation process. However, the gas supplied can not solve the accumulation of N in the method and shows just 18.1 % of the overall efficiency of removal of NO^3 (N. S. Abd Rasid et al., 2019). The concentration of NO^3- from the runoff water and the oxic or anoxic conditions from the aquatic soil often result in the system's overall N efflux (W. M. Kemp and W. R. Boynton ,1990).

The condition was caused by advective fluid flow, which was shown to affect the levels and pathways of N processing in the sediments and caused changes in the concentrations of NH4+ and NO2-/NO3- under water soil topography. (M. Huettel, W. Ziebis, S. Forster, and G. W. Luther ,1998). As a consequence, phytoremediation alone was considered a less effective and time-consuming process (L. Kinidi and S. Salleh,2017). In order to minimize the return of the N cycle to the bulk, treated clay particles are introduced into the system in the order of nano- to sub-micron meter with surface charge adjustment to improve total N accumulations. The clay properties provide the pollutants with sorptive sites to be added to and deposited on its surface.

Soil porosity and wide surface area not only provide strong physical and chemical interactions, but also allow big microbial species to grow plants and absorb nutrients. This is because clay soil porosity has a high negative load to contribute to strong, attractive forces and bonding capability (A. M. Lambooy, 1984). The combination of the plant for phytoremediation and the treatment of nano-clay soil with acid and a specific solution is carried out to provide a broad surface area with different ion exchange power, in order to demonstrate the function of the surface charge. During the study, the characteristic clay soil, the water quality and the surface charge of the treated clay were observed and analyzed. In this work, important parameters which influence the N adsorptive capacity of clays such as type of clay, soil size, zeta potential, and nitrate concentration are the subject matter of concern.

1.2 Problem Statement

Malaysia is undergoing rapid population growth and urbanisation. This rapid growth has led to higher water demand and increased levels of water pollution. Water is one of our most valuable sources. All living organisms need water to sustain life and need 57 per cent water for the human body. The quality of rivers in Malaysia has deteriorated over the last few years. In recent years, more water has been drawn to meet growing demand, but more is the result of the destruction of community generated water, increasing sewage, and other waste. The worst rivers in the country are the amount of waste contained in the Klang River, the Penchala River, the Segget River and the Red Ayer River in Johor, and the Jelutong River, the Juru River and the Pray River in Penang (Aruna, 2014). These rivers have been listed as 'dead' because any form of aquatic life, including fish and aquatic plants, cannot be sustained. Leading to manufacturing operations such as mining, refining, smelting and modification of farm fields with agrochemicals, contaminated soils have increased significantly. Pollutants often have a detrimental impact on soil habitats and should be treated because they have a detrimental effect on the climate.

Biological nitrification-denitrification, chlorination depletion, airflow, chemical deposition, ion exchange and adsorption processes are actually the primary processes for the processing of ammonia-nitrogen. Because of its quick and efficient process, lower operating costs and economical and functional properties, the adsorption method is considered a very promising technique for the removal of ammonia-nitrogen waste. In organically and inorganically contaminated soils, phytoremediation techniques are showing rising potential for use. These techniques have been widely used in our industry to mitigate emissions in the contaminated surface water.

1.3 Objectives

The aim of present work were to characterize the clay type particles available in the soil, and identify the adsorption rate clay particles to enhance the phytoremediation process in order to mitigate the contamination of surface water from the food industry.

1.4 Scope of study

This study will be focusing on the ability of the clay nanoparticles to improve the water quality of contaminated surface waters. The adsorption process is conducted in a batch system. A thorough analysis of the adsorbent dosage, the contact time between the adsorbent and the adsorbate, and the initial pH of the medium were examined during the adsorption process. Clay characteristics such as zeta potential, and particle size are also observed. Analytical methods such as X-Ray Diffraction (XRD) patterns have assisted the proposed process well. For comparison purposes, the results obtained will be compared with a control sample without the addition of clay.

CHAPTER 2

LITERATURE REVIEW

2.1 Water pollution

Contaminated water happens when dangerous contaminants touch water sources such as streams, and waterways. Anthropogenic activities such as mining, improper municipal waste disposal, pesticide production and fossil fuel burning give big impacts on environment. This will degrade the consistency of the water and harm the ecosystem. Water is important natural resource for the worldwide use of drinking water for human health. The World Health Organisation (WHO) has said, 80 per cent of infections are waterborne. In various countries, drinking water does not meet the criteria of the WHO. 3.1 per cent of deaths are due to unhygienic and inadequate water quality.

Waste water is detrimental to wildlife and the marine environment. Toxic chemicals can change the colour of water and increase the amount of minerals. It also has effects on eutrophication that have a negative impact on aquatic life. Other than that, heat emissions also leads to global warming and causes significant threats to aquatic life.

Besides that, water pollution has a negative impact on public health. Many diseases, including diarrhea, cholera, chills, or skin infections, are caused by drinking or contact with polluted water. In areas where drinking water is not available, the key danger is obvious dehydration.

2.2 Fertilizer runoff

In fertilizer, there is nitrogen and phosphorus content that are supplied as nutrients essential to plant growth. But most of the time, these chemical escape into oceans, lakes, waterways and groundwater that called as fertilizer runoff. As the result, it will damage ecosystems and give effect on human health. These nutrients often fuel algae blooms that create dead zones or low areas of oxygen where fish and other aquatic life can no longer survive. Algae are small, naturally occurring plants that will grow and result in algal blooms if they receive excess quantities of chemicals. These algal blooms reduce the oxygen levels in water and affects to other aquatic organism. In addition, algal blooms often foster bacterial growth and raise the amount of toxins in the water.

2.3 Ammonia Nitrogen

Ammonia is a colorless gas and exhibits a pungent odour at ambient temperatures and pressures. It is the principal constituent of concentrations of domestic wastewater. It is very water soluble and exists in water in equilibrium between the species of ionised ammonia (NH3) and ionised ammonia (NH4 +). A number of studies indicated that the effect of unionised NH3 is causing the total toxicity to ammonia. Total ammonia is commonly referred to as the sum of the ammonia and ammonium quantities. Ammonium ions are an important element needed for growth in plants. In particular, ammonia enters the environment through urban, agricultural, industrial, and even natural activities. Also, ammonia enters the environment from natural sources as a result of degradation of organic matter, gas exchange with the atmosphere, animal waste, and nitrogen fixation. There are two types of sources on how ammonia enters the environment, namely, point and nonpoint sources. The point sources of ammonia comes from the release and effluent of various types of industrial plants. In contrast, the nonpoint sources of ammonia are from agricultural, residential, municipal, and atmospheric broadcast.

The presence of ammonia nitrogen in water leads to environmental problems, such as surface water eutrophication, changes in ecosystems, and acidification. In aquatic eutrophication, ammonia nitrogen acts as a source of nitrogen, which is required for nitrate production. In the body of water, high amounts of nitrate and ammonia can contribute to a poisonous atmosphere and, due to the nitrification process, can create a condition of oxygen deficiency. Hypoxic areas, which are death areas where no marine species can live, can contribute to extreme eutrophication.

2.4 Eutrophication

Eutrophication is when the body's water becomes too rich with minerals and nutrients that induce excessive growth of algae. The productivity or fertility of such ecosystems naturally increases as the amount of organic matter that can be broken down into nutrients increases. This process can result in a reduction in the oxygen content of the water body. In reaction to elevated nutrient levels, one example is the 'algae bloom' or phytoplankton rise in the water body. Eutrophication is also caused by the release into aquatic environment of nitrate or phosphate containing detergents, fertilisers, or sewage. Eutrophication most often results from nutrient advantages, most commonly as nitrogen or phosphorus, which leads to the growth of plants and algae in the aquatic ecosystem. After such organisms die, the degradation of their biomass bacteria results in the use of oxygen, thus creating a state of hypoxia. There are several literature reports that nitrogen is the key nutrient affecting the aggregation of algal biomass (Khan et al. 2005). While human activity typically causes eutrophication, it can also be a natural phenomenon, especially in the lake. Eutrophy, for instance, occurs in temperate grasslands in many streams. Climate change, geology, and other external influences are important in controlling the natural productivity of the lake. Some lakes also show the reverse process which is becoming less nutrient-rich over time. The main difference between natural and anthropogenic eutrophication is that natural processes are very slow, occurring on a geologic time scale.

In aquatic ecosystems, species such as algae are increasing in population. Algal blooms limit the sunlight available to the lower organisms and cause a large change in the amount of dissolved oxygen in the water. Oxygen is required by all aerobic plants and animals and is replenished during the day by photosynthesis and algae plants. When dissolved oxygen levels drop to hypoxic levels, fish and other marine animals drown. As a result, creatures such as fish, shrimp, and subterranean dwellers die off. In severe cases, anaerobic conditions occur, promoting bacterial growth. The zone in which this occurs is known as the dead zone.

Moreover, algae blooms can also create health and economic effects for humans, causing rashes and other ailments while eroding tourism revenue for popular lake destinations thanks to their unpleasant looks and odours. High levels of nitrate in water from nutrient pollution can also harm babies, disrupt their ability to send oxygen to tissues and potentially cause "blue baby syndrome."

2.5 Water pollution in Malaysia

Water pollution is arguably the most important environmental issue in Malaysia, as the pollution problem begins with water pollution caused by three traditional industries of tin, natural rubber, and palm oil. The government's environmental programs therefore give high priority to control of water pollution.

Malaysia does not post accurate estimates of river water quality for individual monitoring sites. Instead, the water quality status was published under three levels (clean, slightly contaminated, and contaminated), using the Water Quality Index (WQI) based on six parameters: pH, Dissolved Oxygen (DO), Biochemical Oxygen Demand (BOD), Chemical Oxygen Demand (COD), ammonia nitrogen, and Suspended Solids (SS).

The sources of pollution identified as contributors to BOD loading include agriculture-based industries (natural rubber and palm oil production) the manufacturing industry, and the livestock industry. Likewise, the domestic livestock and sewage industry has been cited as a source of deteriorating ammonia nitrogen, and civil engineering and landscaping work has been blamed for the deterioration of Suspended Solids (SS) status.

2.5 Phytoremediation

2.5.1 Definition

Phytoremediation is a meaning come from Ancient Greek and Latin words which is *'Phyto'* means plant and *'remedium'* meaning restoring balance that refers to the technologies in using plants to clean up contaminants in soil, air and water. Phytoremediation is a green technology that uses plants and their associated microorganisms to clean up contaminated soil and water and it is considered a promising economic strategy for removing organic pollutants from soil (Vangronsveld et al., 2009; Weyens et al. 2009). It is defined as the use of green plants and microorganisms related to proper soil amendment and agronomic techniques to remove toxic environmental pollutants. Phytoremediation is the use of in-situ or ex-situ use of plants to remove or control contaminants and to induce fluid damage by microorganisms in the plant. It is a passive technology that involves the separation, removal, absorption or destruction of organic and inorganic substances in soil and water through plant-based biological, chemical and physical processes. As a technology, it is considered sustainable, especially compared to conventional approaches to the recovery and management of contaminated sites, as it is considered to be primarily solar powered. The phytoremediation could be effective to decrease of heavy metals from municipal wastewater (Mojiri et al., 2012).

Phytoremediation is the process that introduces plants into an environment and allows their roots and leaves to assimilate contaminants. Such a process was used to clean heavy metals, pesticides and xenobiotics (Suresh and Ravishankar, 2004), organic compounds (Newman and Reynolds, 2004), toxic aromatic pollutants (Singh and Jain, 2003), and drainage of acid mines (Archer and Caldwell, 2004). It is interesting to note that phytoremediation was recognised and documented by humans over 300 years ago, but the scientific study and development of suitable plants was not carried out until the early 1980s (Lasat, 2000).

Phytoremediation is considered to be an environmentally friendly technology that is both a safe and cheap way to remove contaminants. However, such technology cannot necessarily be effective all the time or be used in contaminated sites of any type. If the pollution runs too deep or the concentration of toxic compounds is too high, then the soil cannot be remediated effectively by plants alone (Cunningham et al,. 1995).

2.5.2 Techniques in Phytoremediation

Phytoremediation techniques include different modalities, depending on the chemical nature and properties of the contaminant and the plant characteristics (Figure 2.1). Therefore, phytoremediation is basically made up of six different technique, though more than one can be used by plants simultaneously.

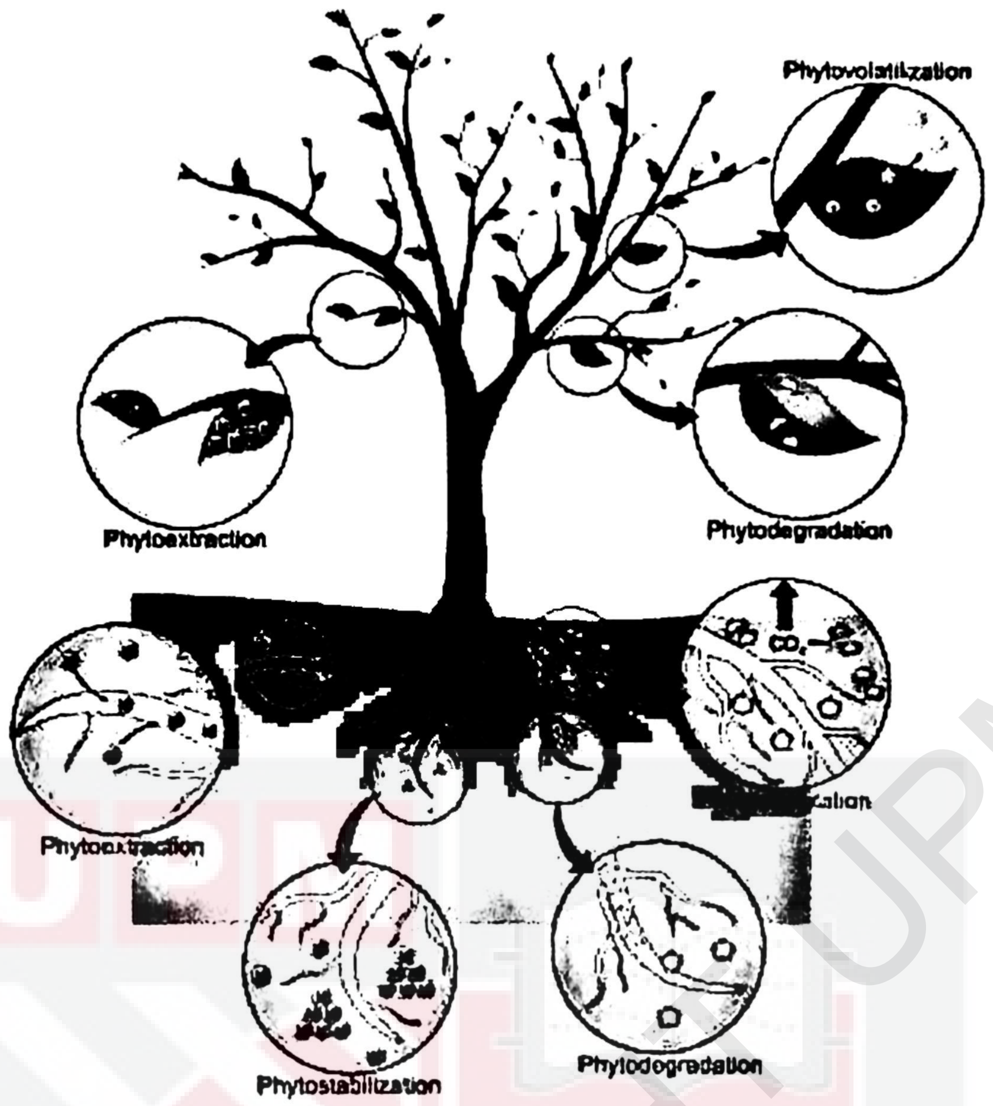


Figure 2.1 Phytoremediation processes in multiple part of a plant

(Favas et al., 2014).

Table 2.1 Different techniques of phytoremediation

(Ali, H., Khan, E., & Sajad, M. A., 2013).

Technique	Description
Phytoextraction	**Accumulation of pollutants in harvestable biomass i.e., shoots**
Phytofiltration	**Sequestration of pollutants from contaminated waters by plants**
Phytostabilization	**Limiting the mobility and bioavailability of pollutants in soil by plant roots**
Phytovolatilization	**Conversion of pollutants to volatile form and their subsequent release to the atmosphere**
Phytodegradation	**Degradation of organic xenobiotics by plant enzymes within plant tissues**
Rhizodegradation	**Degradation of organic xenobiotics in the rhizosphere by rhizospheric microorganisms**
Phytodesalination	**Removal of excess salts from saline soils by halophytes**

2.5.3 Advantages and limitations of Phytoremediation

Phytoremediation provides some benefits, but also several drawbacks that should be taken into account when implementing this technology (Table 2.2). It is not easy to pick plants with the efficiency for simultaneous remediation of varied pollutants. The limitations and possibilities of this plant entering the food chain, must be taken into account when using this technology.

Table 2.2 Advantages and limitations of phytoremediation (Favas et al., 2014).

Advantages	**Limitations**
In situ and passive technique	Limited to shallow soils or where contamination is localized to the surface (< 5 m)
Uses solar energy and is low cost	Still under development and therefore not accepted by many regulatory agencies
Has reduced environmental impact and contributes to the landscape improvement	There is little knowledge of farming, genetics, reproduction and diseases of phytoremediating plants
High acceptance by the public	Metal concentrations in the soil can be toxic and lethal to plants
Provides habitat for animal life	Generally, plants are selective in metal remediation
Reduction in dispersal of dust and contaminants by wind	Treatment slower than the traditional physico-chemical techniques
Reduction of surface runoff	Contamination may spread through the food chain if accumulator plants are ingested by animals
Reduction of leaching and mobilization of contaminants in soil	Efficient phytoremediating plants may not adapt to climatic and environmental conditions at contaminated sites
Harvesting of the plants or organs that have accumulated metals is easy to accomplish with existing technology	If the plants release compounds to increase the mobility of the metals, these can be leached into groundwater
The harvested biomass can be economically valuable	The area to be decontaminated must be large enough to allow application of cultivation techniques
Plant process more easily controlled than those of microorganisms	Toxicity and bioavailability of degradation products remain largely unknown

2.5.4 Lotus plant

Nelumbo Nucifera can assimilate higher phosphorus content than aquatic plants currently used for water recovery. Floating leaves and Lotus flowers have long stems, which contain air space to maintain buoyancy. Lotus plants are commonly found in Australia, China, India, Iran and Japan (Anon., 1966). Lotus was introduced from China to Japan and cultivated for over 1000 years (Komatsu et al., 1975).

Nelumbo nucifera belongs to the family Nelumbonaceae such as Indian lilies, Chinese water candles and holy lilies and synonyms (Nelumbium nelumbo, N. speciosa, N. speciosum and Nymphaea nelumbo). Lotus is an aquatic herb, large and rhizomatous with slender, long, branched, creeping stems consisting of nodes, membranous leaves, peltates (60-90 cm and above). It has a long, rugged stem with small pimples and white, pink flowers (Fig. 2.2a). In addition, it fruits are ovoids that have nuts like achenes which are black, hard and ovoid seeds (Figure 2.2b, c).

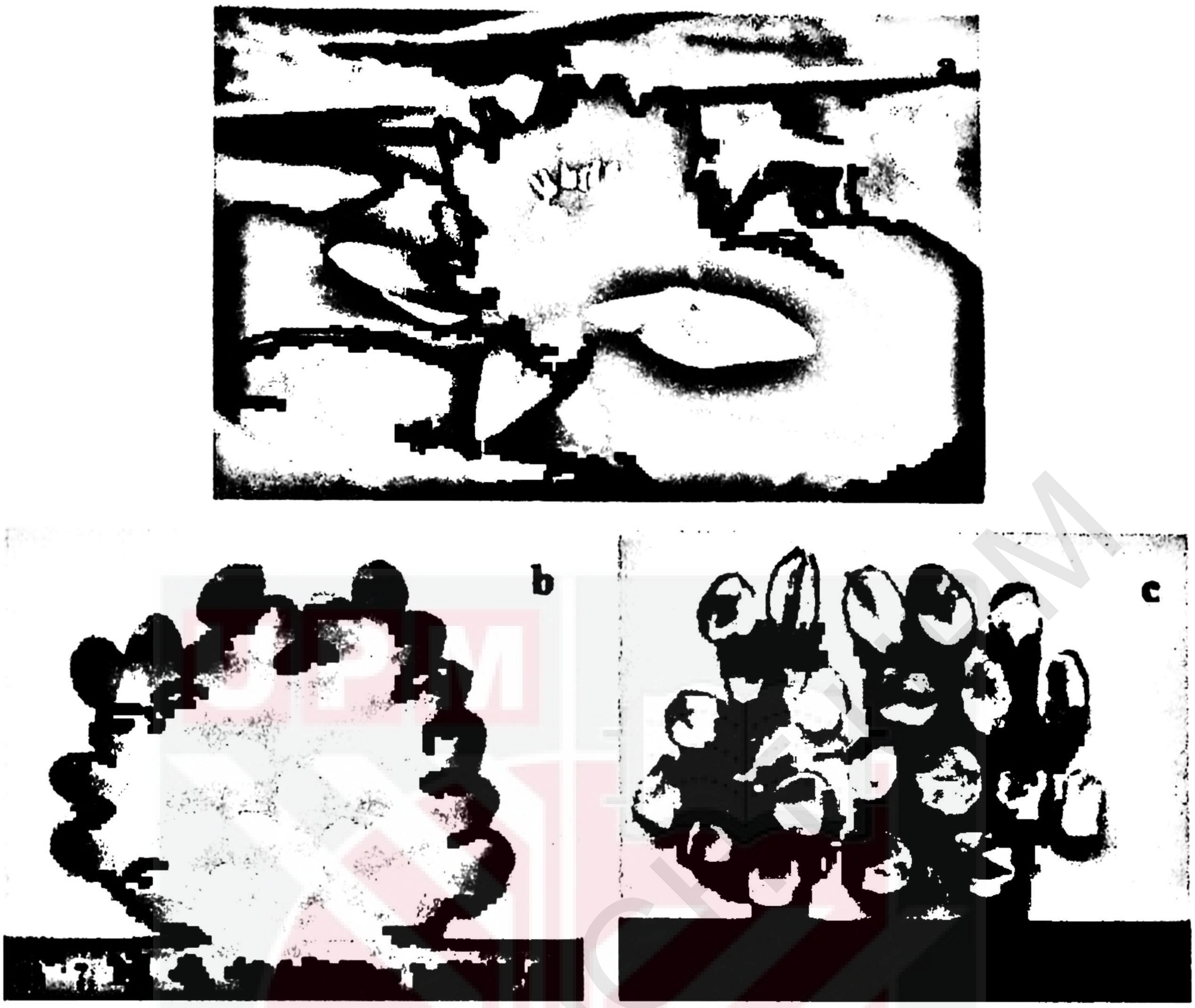


Figure 2.2 (a) Lotus (Nelumbo nucifera) flower, (b) dry seeds and (c) cut open seeds with embryo within seed

Lotus rhizomes are eaten as vegetables in Asian countries, widely in China and Japan. They are sold in whole or in pieces, fresh, frozen, or canned. They are fried or cooked mostly in soups, soaked in syrup or pickles in vinegar with sugar, chilli and garlic (YU et al., 2002; Tian et al., 2007). Rhizomes contained a significant number of starch (31.2%) without any taste or odour. Texture resembles raw potatoes (Mukherjee, n.d). The overall structure of Nulembo Nucifera can be seen at figure 2.3.

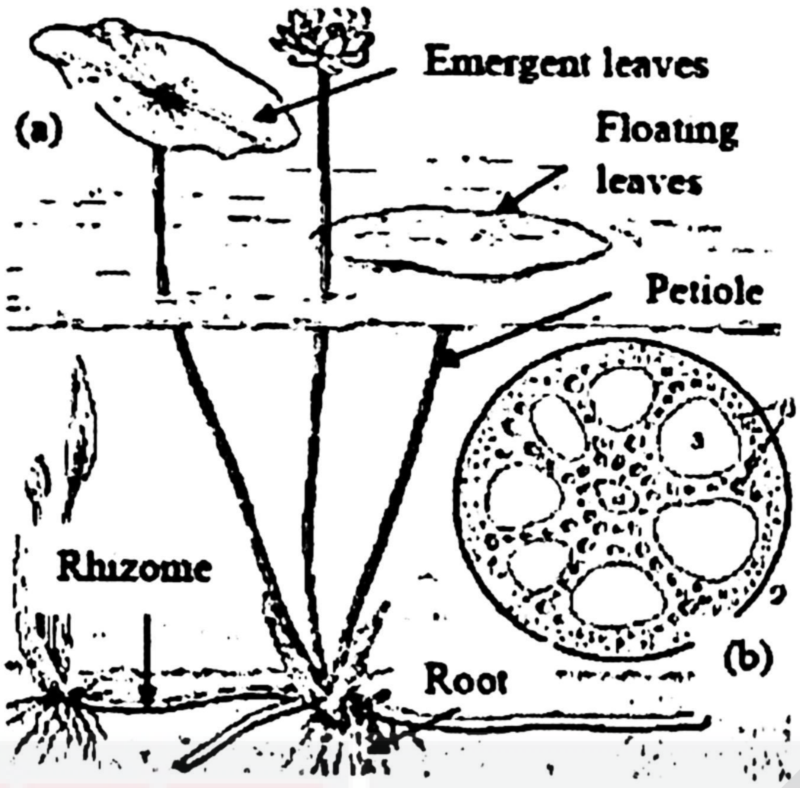


Figure 2.3 Illustration of Nelumbo nucifera plant inside water body (b) The cross sectional of the petiole ("Nelumbo nucifera Gaertn., n.d.)

2.5.5 Role of lotus in Phytoremediation

Nelumbo nucifera demonstrates high potential for use in wastewater treatment to remove contaminated compounds and heavy metals (H.M. Anawar, 2008; Virendra Mishra, 2009; Fallego et, al., 1996). Many studies have shown the use of N. nucifera to successfully overcome eutrophication of water (Othman, Rashidi, 2014; Liu, C.-Q., 2013). Lotus is evaluated for the recovery of trace elements that focus on manganese (Mn, organic compounds and filtration of aquatic wastewater). Lotus plant acts as a phytoremediator of nutrient runoff and solids suspended from wastewater from intense aquaculture systems (Warner S., 2012). Ushimaru et al. (2001) found that anoxia-tolerant lotus (N. nucifera) seedlings grown in Japanese ponds showed underwater germination indicating that seedlings were tolerant of oxygen deprivation during hypoxia conditions.

2.6 Water Quality Parameters

2.6.1 pH

Soil pH is a measure of acidity or alkaline of the soil. The pH of clay soil are important because it influences several soil factors affecting plant growth such as soil bacteria, nutrient availability, toxic elements, nutrient leaching and soil structure. For most plants, the optimum pH range is from 5.5 to 7.0 (J. Nesmith and E.W. McElwee, 2003). Soil pH plays a vital role in the mobility and bioavailability of soil heavy metals and can influence the solution and surface complexation reactions of cations, ion exchange and other metal bonding processes. A rise in the pH of acid paddy soils would result in the production of more negatively charged sorption sites on the surfaces of soil colloid and organic matter and, therefore, a reduction in metal supply. With increasing soil pH, soil OH− concentrations increase, forming a precipitate of carbonate or hydroxide (Wu et al., 2016). The Ammonium Nitrogen sorption was significantly affected by initial pH of the solution (Eturki et al., 2012). Maximum uptake of $N\text{-}NH^{+}{}_{4}$ ions at pH 8 and decreased below this pH value. This is because, decrease in the electrostatic attraction between positively charged sorbent surface and $N\text{-}NH^{+}{}_{4}$ ions. Increasing the temperature resulted in increasing the amount adsorbed on clay (Aljlil et al., 2014).

Moreover, the lower the pH, the more cationic the surface layer of the clay, making it susceptible to adsorb anionic pollutants. The presence of negative charge increases the electron density on the clay surface thereby facilitating the interaction between the clay surface and the phenolic hydrogen (Tetteh et al., 2018). At lower pH values, the adsorption efficiency was decreased. The effect of pH changes due to the adsorbent type, its behavior in the solution and the type of ions adsorbed (Veli et al., 2007).

2.6.2 Biochemical Oxygen Demand (BOD)

The BOD test is used to measure waste loads to treatment plants, determine plant efficiency and control plant processes. A BOD test is required 5 days to obtain the results. When a measurement is made of all oxygen consuming materials in a sample, the result is termed "Total Biochemical Oxygen Demand" (TBOD), or often just simply "Biochemical Oxygen Demand" (BOD). Because the test is performed over a five day period, it is often referred to as a "Five Day BOD", or a BOD_5. Lotus plants have been found able to reduce BOD concentrations of lake water to 42% at 15 days and 71% at 20 days because the unique mechanism of thermodynamic gas transporting O_2 from the leaves on the surface of the water to the buried rhizome lies in the anoxic sediment.

2.6.3 Chemical Oxygen Demand (COD)

Chemical oxygen demand (COD) is a measure of the ability of water to consume oxygen during decomposition of organic matter and oxidation of inorganic chemicals such as ammonia and nitrite. COD is used as a general indicator of water quality and is part of all water quality management programs. In addition, COD is often used to estimate BOD (Biochemical Oxygen Demand) as a strong correlation between COD and BOD, but COD is a faster and more accurate test. Table 2.3 below show waste water characteristic.

Table 2.3 WasteWater Characteristic (Aris et al., 2008; Belo et al., 2013).

Parameters	DOE discharged limit(1986 onwards)^a	Environmental Quality Act^b
BOD_3 (mg/L)	50	100
COD (mg/L)	1000	1000^c
Total solids(mg/L)	1500	1500^c
Suspended solids (mg/L)	400	400
Oil and grease (mg/L)	50	50
Ammoniacal nitrogen (mg/L)	100	150^c
Total nitrogen (mg/L)	200	200^c
pH	5.0	5.0-9.0
Temperature (°C)	45	45

a. Malaysia Department of Environment (DOE)

b. Parameters Limit of Environmental Quality (Prescribed Premises) (Crude Palm Oil) (Amendment) Regulation 1997

c. No new value stipulated since 1982

2.6.4 Nitrate

Nitrate (NO3-) and nitrite (NO2-) are naturally occurring ions everywhere. As part of the cycle required by all living systems to produce complex organic molecules, such as enzymes and other proteins, both are products of nitrogen oxidation (Environment Canada, 2003; IARC, 2010). The more stable type of oxidised nitrogen is nitrate. However, under anaerobic conditions and in the presence of a source of carbon, nitrate can be reduced by the relatively unstable and moderately reactive microbial activity of nitrite. The denitrification process further reduces nitrite to nitrogen gas under low oxygen conditions (Appelo & Postma, 1996). Nitrification is a two-step mechanism in which ammonia by ammonia-oxidizing bacteria is oxidised to nitrite and nitrite is further oxidised by nitrite-oxidizing bacteria to nitrate (USEPA, 2002a; IARC, 2011). In addition to bacterial nitrification, mineralization and hydrolysis will turn organic sources of nitrogen, such as organic matter in soil, manure and urea fertilisers, into nitrate. (Ward et al., 2005; Cartes et al., 2009)

Domestic sewage is also an important source of nutrients for plants, primarily nitrates and phosphates. In water, excess nitrates and phosphates encourage algae growth, often causing extremely dense and rapid growths known as algae blooms. When the algae die, oxygen dissolved in the water decreases because microorganisms use oxygen during the decomposition process to digest the algae. Then anaerobic organisms metabolise the organic waste, releasing gases such as methane and hydrogen sulphide that harm the aerobic life forms.

Contaminated water nitrates can cause tumors and ulcers. Water pollution also causes an increase in cases of constipation, diarrhea and intestinal infections. It also has a harmful effect on the developing fetus in pregnant women. One of the biggest threats to developing countries is the disease caused by contaminated water cholera caused by drinking water to Malaria where mosquitoes breed in polluted water. Regular intake of contaminated water can cause sclerosis, skin leggings, and circulatory problems, mineral deposits in bone, certain cancers and nervous system diseases. Waterborne diseases such as jaundice, hepatitis, gasteroenteritis are more common due to water pollution. Water-borne diseases are the leading cause of death worldwide. The toxic substance moves through the food chain and affects humans through the fish and meat we eat. In addition, contaminated water causes the food and plant life to be destroyed, affecting the climate and the environment necessary for human survival.

2.7 X-Ray Diffraction Technique

X-ray diffraction (XRD) is one of the most commonly used methods for nanoparticular characterisation. XRD typically provides information about crystalline structure, phase character, lattice parameters and crystalline grain size. The latter parameter is estimated using the Scherrer equation using the extension for a specific sample of the most intense peak of an XRD measure. A benefit of the XRD techniques, typically performed in powder type samples, generally after drying their corresponding colloidal solutions, is that this results in statistically representative, volume-averaged values. Comparing the location and intensity of the peaks with the reference patterns available from the International Center for Diffraction Data (ICDD, formerly known as the Joint Committee on Powder Diffraction Standards, JCPDS) database will determine the composition of the particles. It is however not ideal for amorphous materials and the XRD peaks are too large for particles of below size 3 nm.

2.8 Removal of Ammonium by adsorption

Adsorption is accumulation of molecules on a surface layer of molecules in contact with water phase. A solid material can selectively remove dissolved components from an aqueous solution by attracting the dissolved solute to its surface. The clay minerals have similar layer arrangements which adsorb cations at the sorption sites through the ion exchange process, resulting from cation interactions with negative permanent loading of planer sites (Malandrino et al., 2006).

Paddy field clay (PFC) is cheap and, because of its special qualities, can be used as low-cost absorbers and have no toxic effects on the environment. Several factors influence the nature of the nano-adsorbents produced which are the shape and size of particles, surface chemistry, and their solubility and chemical composition. Clay with high ammonium adsorption rates can be used to remove ammonium in contaminated water.

2.8.1 Material Selection: Adsorbent Clay Particles

Clay has strong sorption and complexation ability. A few years ago, clay get attention for phytoremediation due to their low cost, ready availability, high surface area, lack of toxicity and potential for ion exchange. There are many types of clay such as kaolinite, montmorillonite, smectite, illite and chlorite. When the initial concentration of –N, pH values and temperatures increased, the ammonium adsorption capacity of clay increased. Moreover, the adsorption potential of the clay increased as contact time and initial concentration grew. The adsorbed quantity was increased by using clay of soil nanoparticle size, as the diffusion molecules in the aqueous process progressively became faster with an increased adsorption temperature, thus facilitating the interaction between the molecules and cations on the surface of soil clay. Soil nano-clays have greater percentage of adsorbed because of the increased surface area and greater pore volume. Clay minerals are typical constituents of underlying sandstones in sedimentary basins in Malaysia. Kaolinite, illite, mixed-layer illite / smectite, chlorite, smectite and chlorite / smectite mixed-layer were all found (Hill et al,. 1992).

2.8.2 Adsorbate: B'Green Fertilizer

Fertilizer is a natural or artificial substance that contains the chemical elements which improve plant growth and productivity. Fertilizers improve the existing soil fertility or substitute previous crops with the chemical elements extracted from the soil. B'green Seaweed is an organic liquid fertilizer extracted from seaweed. It has balance nutrient for growth, flowers and develop healthy fruits. It is also rich with organic mineral, natural growth hormone, vitamin, acid amino and additional nutrient which is required by all plant. It is suitable for all type of plants. B'Green seaweed act as adsorbate in batch adsorption system as shown in Figure 2.4.

Figure 2.4: B'Green Seaweed Fertilizer

2.8.3 Factors that affect clay ammonium adsorption

According to Liang et al., (2016), there are many factors that affect clay ammonium adsorption such as the absorbent dosage, pH value, particles size, ammonium nitrogen in inlet, time and temperature. The adsorption rate increase significantly when the dosage of clay is added. This impact can be due to an increased number of active surface sites for NH4 + adsorption, enhancing the adsorption capability significantly (Alshemeri et al., 2018). Moreover, pH value also affect clay ammonium adsorption. The main reason why the pH value affects adsorption process of ammonia nitrogen is that pH has changed the form of ammonia nitrogen in water. In the range of pH 2 to 4, the adsorption rate increased with the increase of pH value. In the range of pH 5 to 8, the adsorption rate gradually stabilized with the increase of pH. When pH>10, the adsorption rate decreased rapidly. Maximum uptake of ammonium ions at pH 8 and decreased below this pH value. This is because the electrostatic attraction between positively charged sorbent surface and ammonium ions is decrease (Eturki et al., 2012). Besides, the particle size of clay has a great influence on the adsorption capacity. The smaller the particle size is, the more ammonia nitrogen will be adsorbed. In addition, the optimum contact time for heavy metals removal is at 75 min, after that the adsorption percentage of metal ions gradually decreased with increase in contact time (ElSayed, E. E. 2018).

CHAPTER 3

METHODOLOGY

3.1 Introduction

The overall workflow of this project is shown in figure 3.1. It is divided into three main sections which are project preparation, experiment run, and water quality analysis. In the project preparation part, several steps are taken. First, the obtained clay is reduced into nano-size. Second, the stability of the nanoclay particles is observed under different pH conditions. Third, characterize of nanoclay. Fourth, batch adsorption are set up with nanoclay particles added in each at a different pH. This experiment is carried out in a natural environment exposed to outdoor conditions. In order to compare, a blank is set up with fertilizer water without any nanoclay particle addition.

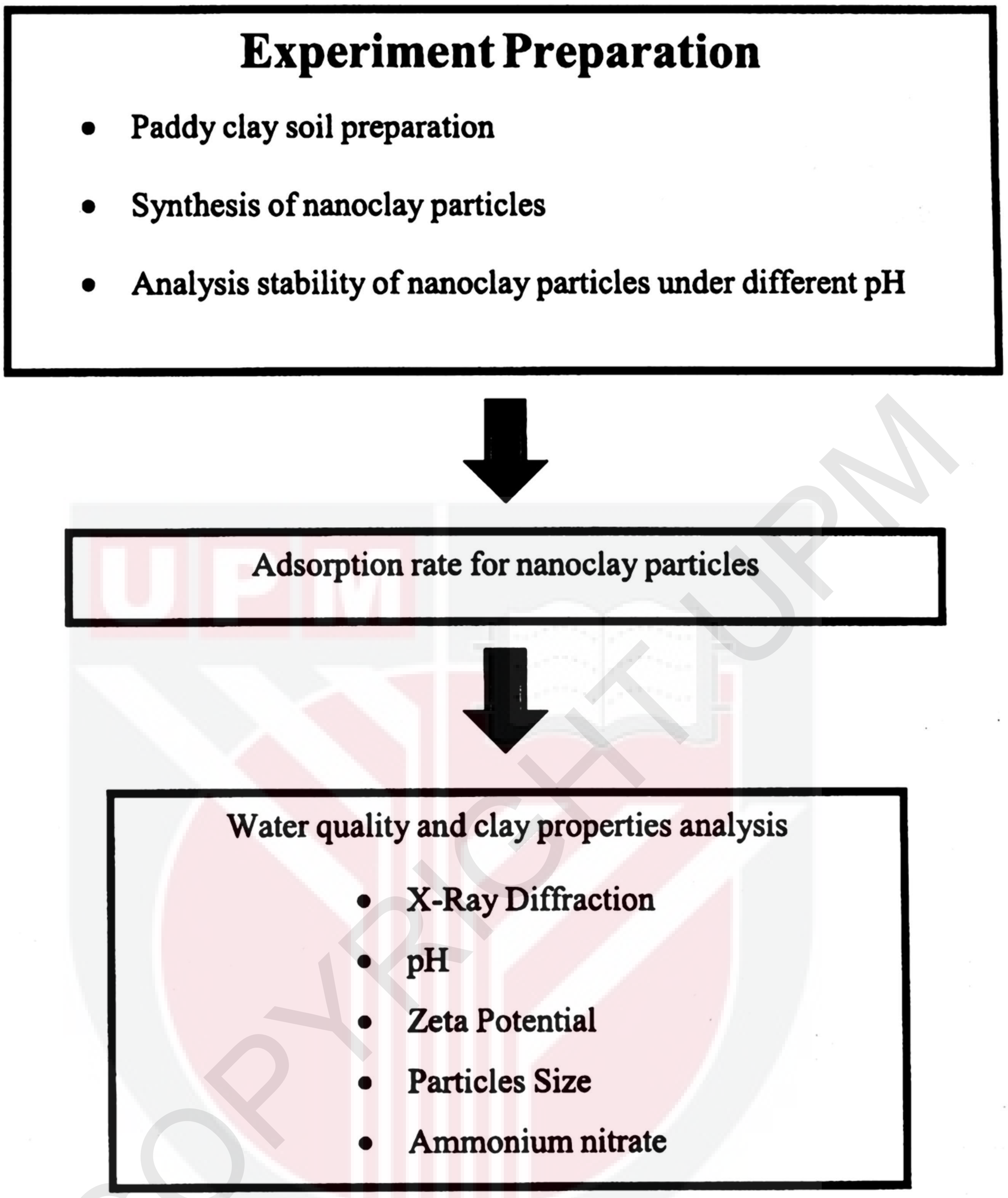


Figure 3.1 Experiment Flow

3.2 Experiment Preparation

3.2.1 Paddy clay soil preparation

Paddy clay soil was collected from a municipality in the Kelantan. The sample was collected from a paddy field. Using hoe and shovel, 5 kg of clay were collected and then packed in airtight sealed plastic bags. Under sunlight bulk samples were dried until they reached a constant weight. They were then mechanically processed, powdered in a ball mill, and passed through 63 μm (230 mesh). 1 kg samples was mixed and homogenized to form a single representative sample that was used for all the tests.

3.2.2 Nanoclay Particles Synthesis

Nanoclay particles are synthesized through processes of drying and purification of obtained paddy clay soil. A grinder, sieving, and an ultrasonic probe are used to reduce the size of the obtained clay into nano-size. First, the obtained paddy clay soil is dried by direct sunlight and put it in the oven for one day to remove the residual moisture content in the paddy soil. Second, the clay is grinded by using soil grinder (SHTG, China) to facilitate the milling process and to break hard clay soil. Third, the clay soil is sieve (AS200 Digit CA, Germany) by using larger mesh to the fine mesh for separate unnecessary thing with clay in different size. Next, the pH of the clay was adjusted through the addition of 0.1 M HCL and 0.1 M NaOH solution. Different pH solutions of clay are made in order to analyze the behavior of the clay. The pH values of 2.0, 4.0, 6.0, 8.0, and 10.0 are used for analysis. Finally, the pH clay solutions are stirred by a Q500 Sonicator (Qsonica, US), at 500 W, 20 kHz, an amplitude of 50% for 10 minutes. This ultra-sonication is a secondary process to make particles smaller with an increased surface area for adsorption.

3.2.3 Nanoclay particles Stability analysis

The behavior of the sonicated nanoclay particles is analyzed under different solutions of pH 2.0, 4.0, 6.0, 8.0 and 10.0 through the measuring the zeta-potential of all the solutions. The zeta-potential is measured using the Particulate Systems zeta/nano particle analyzer Nanoplus (Micrometrics, USA). The flow-cell attachment is used to measure the zeta-potential of the different pH clay solutions. The clay is allowed to sediment and then the supernatant is injected into the flow-cell for zeta-potential measurement of the nanoclay particles. To ensure that all particles greater than nanosize are not in the supernatant, the solution are centrifuged for 180 minutes under a speed of 5000 rpm using a 5804R Centrifuge (Eppendorf, Malaysia).

3.2.4 Adsorbent preparation

Before the nanoclay solutions of pH 2.0, 6.0, and 10.0 are applied to the batch adsorption process, the clay solutions are dried at 60°C with hot air flow in the oven. The clay is then grinded by lab mill 120 (Perten, Sweden). 0.3 g of clay nanoparticles of different pH are added to each of the three beakers while the fourth control beaker is left without the addition of nanoclay.

3.2.5 Characterization of clay

X-Ray Diffraction study obtained the chemical composition of the clay sample as received and after sieving. Powder X-ray diffraction (XRD) experiments have been conducted using a Bruker D8 Advance diffractometer with Cu-K5-007 (5-007 = 0.154 nm) radiation at 30 kV and 30MA and described using JCPDS files between 20 ° and 70 ° (25-007). Based on the peak positions and intensities, the context and peak positions were identified, and a search-match routine was conducted.

3.2.6 Adsorption experiment

Stock solution (1000 mg L^{-1}) was prepared by dissolving 1.9096 g anhydrous ammonium chloride to 500 mL of deionized water. This was further diluted to get desired concentration for the experiment. Adsorption tests were carried out by batch method for pH 2.0, 6.0, and 10.0. Initial concentration fertilizer, adsorption time, and optimum adsorbent dosage were determined by adsorption tests at room temperature. A preliminary kinetic experiment was carried out to establish the equilibration time for ammonium adsorption. Tests were conducted in duplicate samples in 50 mL polypropylene test tubes. Clay samples (0.3 g) were shaken with 10 mL of Fertilizer solutions (40 mg L^{-1}) on a centrifuge at 200 rpm for 2 h to attain the equilibration time at room temperature. After shaking, 10 mL of supernatant were withdrawn and filtered with 0.45 lm syringe driven filter (Millex-LH, PTFE, Millipore Corp., Ireland). The filtrates were analyzed for the Ammonium concentrations using an UV Spectrophotometer (UltroSpec3100 Pro, England). All experiments were run in duplicate. The experiments were conducted with controls-with only Fertilizer in tube (no adsorbents).

The specific amount of Ammonium adsorbed and % Ammonium adsorption was calculated using the following equation:

$$C_S = \frac{(C_0 - C_e) \cdot V}{W}$$

$$\% \text{ absorbent} = \frac{(C_0 - C_e) \cdot 100}{C_0}$$

Where: Cs is the adsorption capacity (mg g^{-1}) in the clay at equilibrium;

Co is initial concentrations of Ammonium (mg L^{-1})

Ce is equilibrium concentrations of Ammonium (mg L^{-1})

V is the volume of the aqueous solution (L)

W is the mass (g) of adsorbent used in the experiments.

3.2.7 Analysis using UV Spectrophotometer

Calibration of stock ammonia solution was done using UV Spectrophotometer. Ammonia was calibrated at 1 ppm, 2 ppm, 3 ppm, 4 ppm and 5 ppm at 640 nm wavelength. Since the UV Spectrophotometer cannot be used to identify the concentration of adsorbent present in it for colourless solutions we add Phenol reagent in order to find out the adsorbent concentration present in the stock solution (10ml/50ml of stock solution). The color was allowed to develop for 1 hour. After 1 hour, a blue color was developed ranging dark blue to pale blue. The solution's colour depends on the amount of ammonia in the solution that helps distinguish the amount of ammonia left over after adsorption by the UV spectrophotometer.

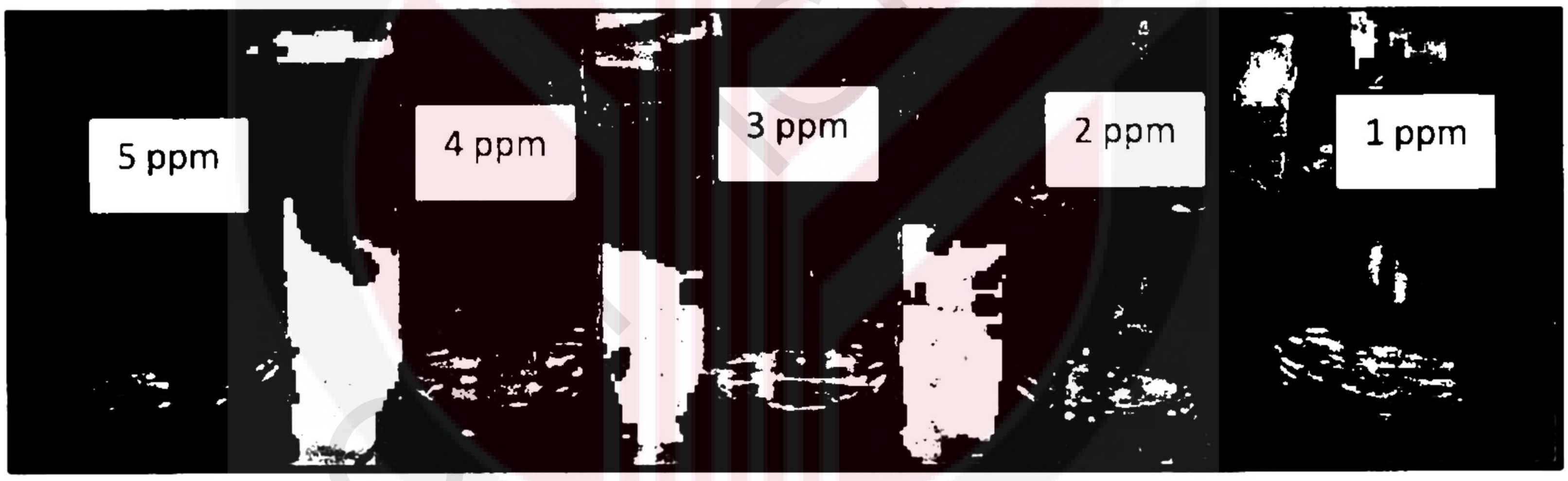


Figure 3.2 Color changes after 1 hour

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Identification of clays using XRD analysis

The X-ray diffraction pattern of paddy clay powder is shown in Figure 4.1. The XRD characterization is employed to evaluate the presence of chemical and minerals in the Clay samples. It shows that all the paddy field clay are composed almost entirely of paddy clay minerals and a few impurities such as quartz, kaolinite, and Feldspar. Consequently, the high purity of PFC (94% – 99%) can potentially contribute to NH4+ adsorption.

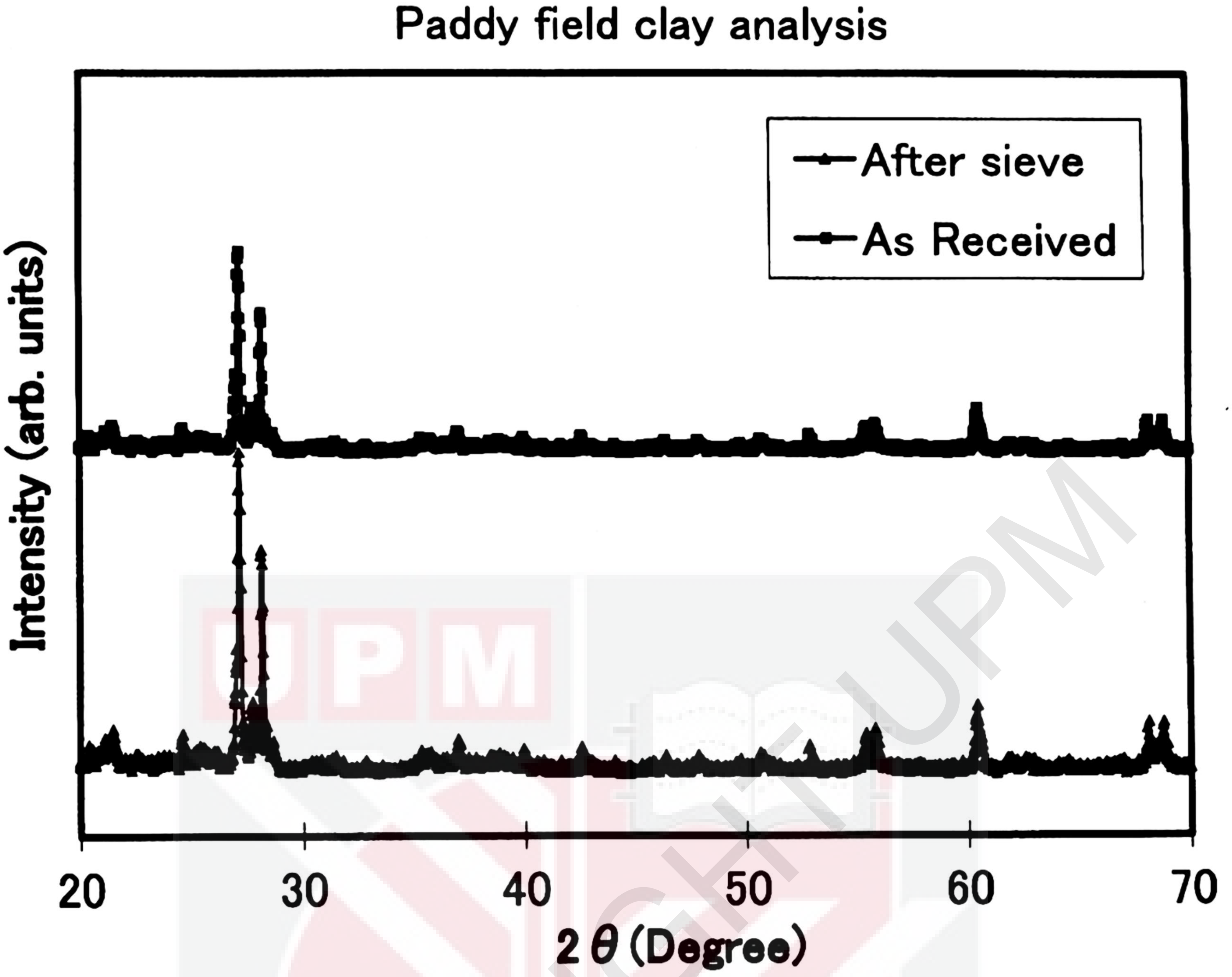


Figure 4.1 X-Ray Diffraction diagram of paddy field clay

The XRD patterns as received and after sieve shows different in intensity, which is as received clay has higher intensity compare to after sieve. The intensity change and peak broadening of the paddy field clay XRD patterns due to a change in the particle size of the nanoparticles that is in good agreement with the particle size: the smaller the particle the lower the intensity and the greater the peaks. As received clay samples has higher intensity compare to after sieve sample because of the size of the clay. It has large structure compare to after sieve sample because there are some foreign material in the sample such as leaves, sandstone and limestone that will disturb paddy clay structures. These foreign material will give high intensity in the X-Ray Diffraction analysis.

The sharp peaks in the pattern infer that the clay is polycrystalline in nature. The diffraction peaks at the angles 21.36°, 24.56°, 27.20°, 27.76°, 28.14°, 60.36°, 68.04°, and 68.76°correspond to the crystal planes. The precision of the peak intensities for values below $2\theta = 5°$ is relatively small. Quartz was the major component of the clay mineral. Paddy field clay has a considerable presence of quartz at peaks around 21.36°, 27.76°, 60.36°, and 68.04° (Worasith et al., 2011; Manoharan et al,. 2012). Feldspar are also had in the sample at peaks 27.20°, 28.14° and 36.96° (Macías-Quiroga et al,. 2018). There is also contain Kaolinite at the peaks $2\theta = 24.56°$ as been reported in previous studies (Gougazeh, M., & Buhl, J.-C., 2014). In general, the presence of great abundance of kaolinite, feldspar, and the residual minerals mainly quartz are clearly related to tropical weathering. The chemical, mineralogical and thermal behavior results of paddy field clays are well agreement with the reported results of previous studies. This is also supported in research (Sultan and Shazili, 2010) that showed sediments from the Kelantan River basin are sandy loam to sand in texture and consisted mostly quartz. Table 4.1 shows the chemical compositional of the paddy field clay soil. The paddy field clay dominated by Si and Al, which were found in kaolinite, illite and montmorillonite.

Table 4.1 Chemical composition of Paddy field clay soil

(Rosales-Landeros et al., 2013)

Mineralogical Composition		Chemical Composition	
Illite	23% - 37%	SiO_2	64.79%
Kaolinite	6% - 12%	Al_2O_3	16.26%
Chlorite	3% -5%	Fe_2O_3	7.22%
Quartz	30% - 45%	MgO	2.38%
Hematite	3% - 6%	K_2O	2.68%
		CaO	0.4%
		TiO_2	0.91%
		MnO	0.09%

4.2 Characterization of Adsorbents

After the synthesis of the nanoclay, the particles size and initial zeta potential value of the nanoclay were measured at different pH value at 2.0, 4.0, 6.0, 8.0 and 10.0 by immersed the particles in pure water as shown in Figure 4.2 below.

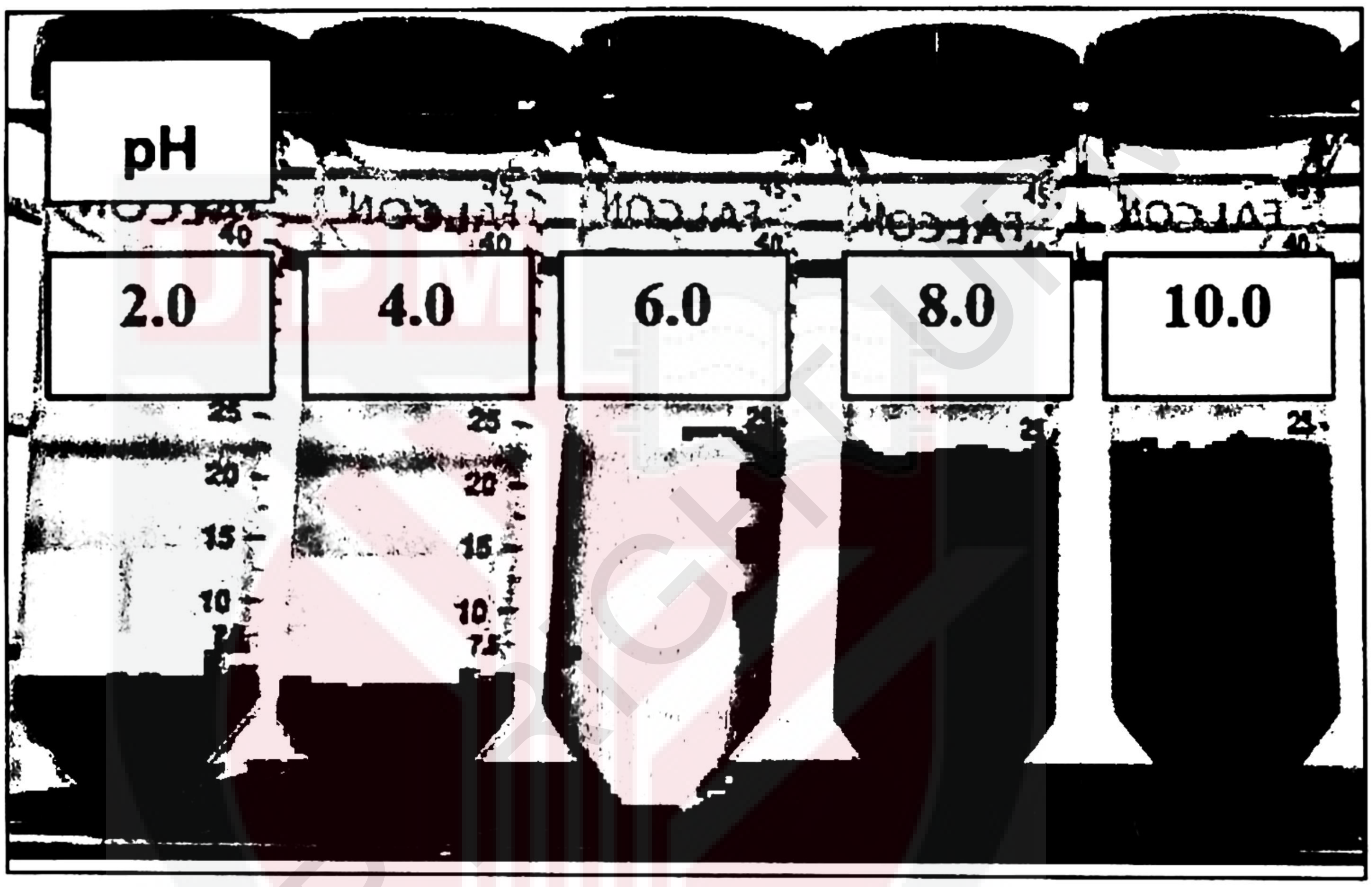


Figure 4.2 Solution at different pH

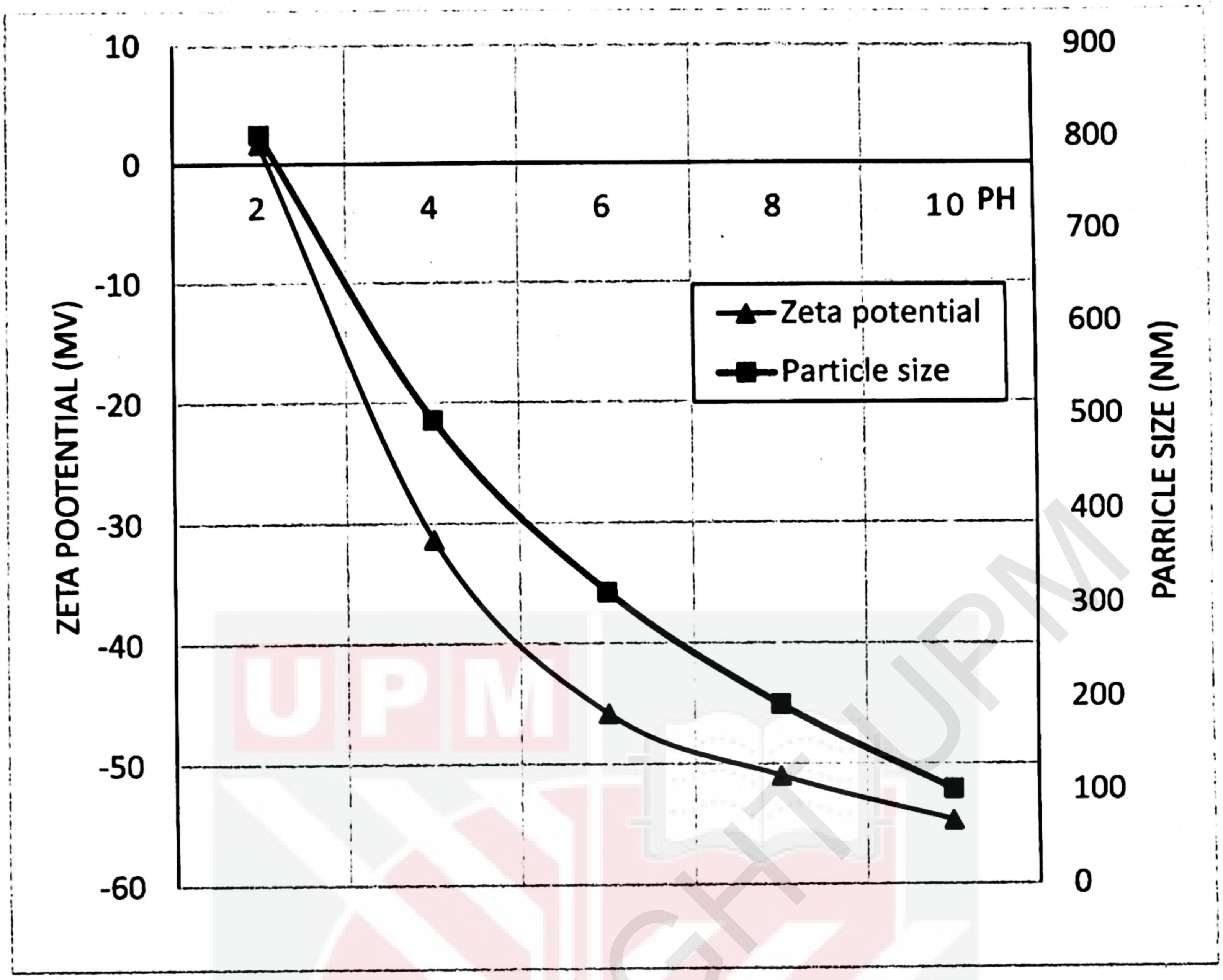


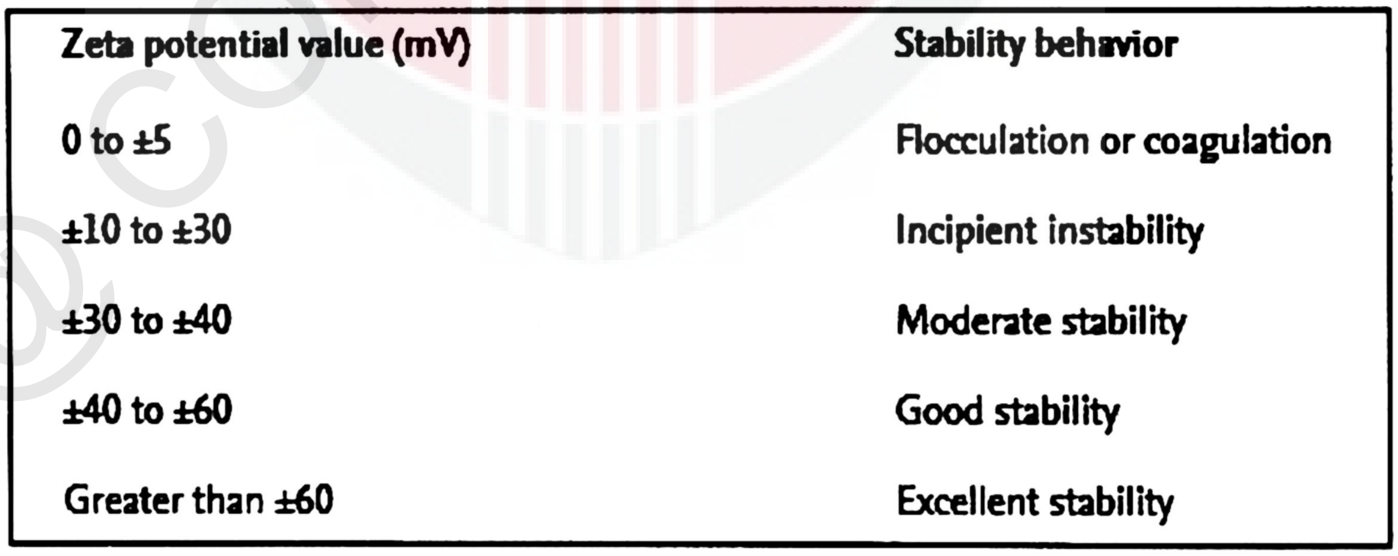
Figure 4.3 Initial Zeta potential and Particle size of nanoclay at different pH conditions

The surface characteristics of nanoclay were analysed by zeta potential. Zeta potential is a good indicator for whether nanoclay were stable or whether they agglomerate/aggregate to each other. Figure 4.3 shows the change in particle size and zeta potential of nanoclay in water as a function of solution pH. As the solution's pH changes the particle's effective charge state, zeta potential value changes as well. With increasing pH the zeta potential became more negative throughout the pH range tested. Previous research (Yeliz & Abidin, 2016) have shown that the zeta potential of montmorillonite, illite, kaolinite and quartz paddy clay has become more negative as the pH of the solution rises, which is in good alignment with the evolving zeta potential patterns in this report. With the increasing of pH, the zeta potential of nanoclay decreases, reflecting a more negative charge on the nanoclay surface. The zeta potential was -45.8 mV at pH 6.0 and increased to 1.7 mV at pH 2.0 in this study. The positive zeta potential can be attributed to the absorption of H+ and/or Al^{3+} on the surface of clay with decreasing pH from 6.0 to 2.0. This indicates that the electric repulsion between soil particles was minimized at pH 2.0, whereas molecular attraction was maximized. Thus, at pH from 6.0 to 2.0, the soil particle size increased as a result of molecular attraction between soil particles in addition to Al^{3+} induced aggregation. In contrast, in the pH 2.0, the positive charges on clay particles 1.7 mV resulted in electric repulsion between the particles, while Al^{3+} caused particle aggregation, resulting in increased clay particle size and decreased turbidity. For pH > 6.0, the soil particles were negatively charged, and the electric repulsion between particles led to a decrease in soil particle size. OH^- and $Al(OH)^{4-}$ were thought to contribute to the negative charges on the soil particles under alkaline conditions, and soil particles did not obviously aggregate in the pH range. The electric repulsion between soil particles at pH > 6 increased the mobility of the soil particles regardless of the surface tension of pore water.

It was reported that the zeta potential of paddy clay showed positive values under acidic conditions as Al^{3+} can compress diffuse double layer (Yeliz & Abidin, 2016). In addition, the zeta potential becomes more positive in the presence of salt cation such as Ca^{2+} and Mg^{2+} since they can compress the diffuse double layer of the minerals. They precipitate as salt hydroxide at alkaline pH values and the zeta potential becomes more positive due to precipitated covered solid (Yeliz & Abidin, 2016). Thus in this analysis the zeta potential at pH condition was completely shifted to positive direction due to Al, Ca, and Mg, resulting in changes in the physical properties of the simulated soils. The changing zeta potential patterns were in good alignment with the one of the previous study.

Other than that, the difference in the zeta potential of nanoclay is due to the acids used to change the pH of the solution. The addition of HCI to purified water decreases the pH values and raises the concentration of H^+ ions in the solution. The adsorption of H^+ ions on nanoclay particles compresses the diffuse electrical double layer resulting in lower zeta potential values. On the other hand, the addition of NaOH to purified water increases the pH of the solution because of the high concentration of OH^- in the systems. OH^- ion adsorption on nanoclay solution results in a large diffuse double layer providing a higher zeta potential value (Chorom and Rengasamy, 1995). The higher the pH particles acquire a more negative net surface charge or zeta potential (Tagalog et al, 2019). The negatively charged surface refers to the tendency of the mineral to adsorb positive charged ions (Elmoubarki et al., 2015; Ngulube et al., 2017).

Table 4.2 Stability behaviour for zeta potential (Arulprakasajothi et al., 2018)



Zeta potential value (mV)	**Stability behavior**
0 to ±5	Flocculation or coagulation
±10 to ±30	Incipient instability
±30 to ±40	Moderate stability
±40 to ±60	Good stability
Greater than ±60	Excellent stability

Additionally, absolute zeta potential values greater than ± 30 mV are known to be representative of stable dispersions. Lower zeta potential than ± 30 mV indicates unstable dispersion. Only the magnitude of the zeta-potential indicates the sample's stability, while the zeta-potential sign indicates whether positive or negative charges predominate on the surface. From the figure above, zeta potentials at pH 10 have good stability which is -54.7 mV compare to other pH value. However, the zeta potential at pH 4, although an acidic pH, is not as positive as that exhibited in pH 2. This may indicate that H+ did not stick to the surface of the nanoclay particles. Particles at pH 2 have zeta values 1.7 mV, will experience flocculation and coagulation. The particular adsorption of ions to a particle surface, even at low concentrations, may have a drastic effect on the particle dispersion zeta potential.

Moreover, pH play important role in the size of nanoclay. At high pH reduction rate is high. At low pH, reduction oxidation will occur. At very high pH (above 8) reduction rate will be too much high resulting an aggregation of nanoclay. So, pH 10 is desirable in order to synthesized smaller size nanoclay. From the Figure 4.3, the size of nanoclay decrease when the pH increase. The particle size decreased with the increasing pH at a given time frame resulting in lower aggregation in the higher pH regime and increased particle stability. (Fernando & Zhou, 2018).

The particle size of the prepared nanoclay can be affected by the amount of ions attached to the particles' surface. Due to the attraction of H+ ions to the surface of the nanoclay at pH 2.0 until pH 6.0, it can be seen that the particle size of the nanoclay is greater than 200nm as seen in Figure 4.3. This may be due to particles or ions being adsorbed to the particles surface due to the high adsorption at this pH value. The nanoclay is shown not to be very absorbing at pH 10.0, as it has a particle size of below 200 nm at a value of about 101.5 nm. Because pH 2.0, 6.0, and 10.0 show the minimum, medium, and maximum values of both zeta potential and particle size, these pH conditions were used in this study to see how the adsorption of the nanoclay particles will be affected and to determine which pH value helps in increasing the overall efficiency of the phytoremediation process. In summary, pH has significant effects on the physical properties of nanoclay, although the mechanism varies.

4.3 Batch Adsorption

4.3.1 Graph of corrected absorbance against concentration of NH_4-N/L

A straight line graph was obtained by plotting absorbance against concentration of nitrite. The graph shown below is the calibration curve of ammonia which is later used to determine the ammonia concentration in stock solution.

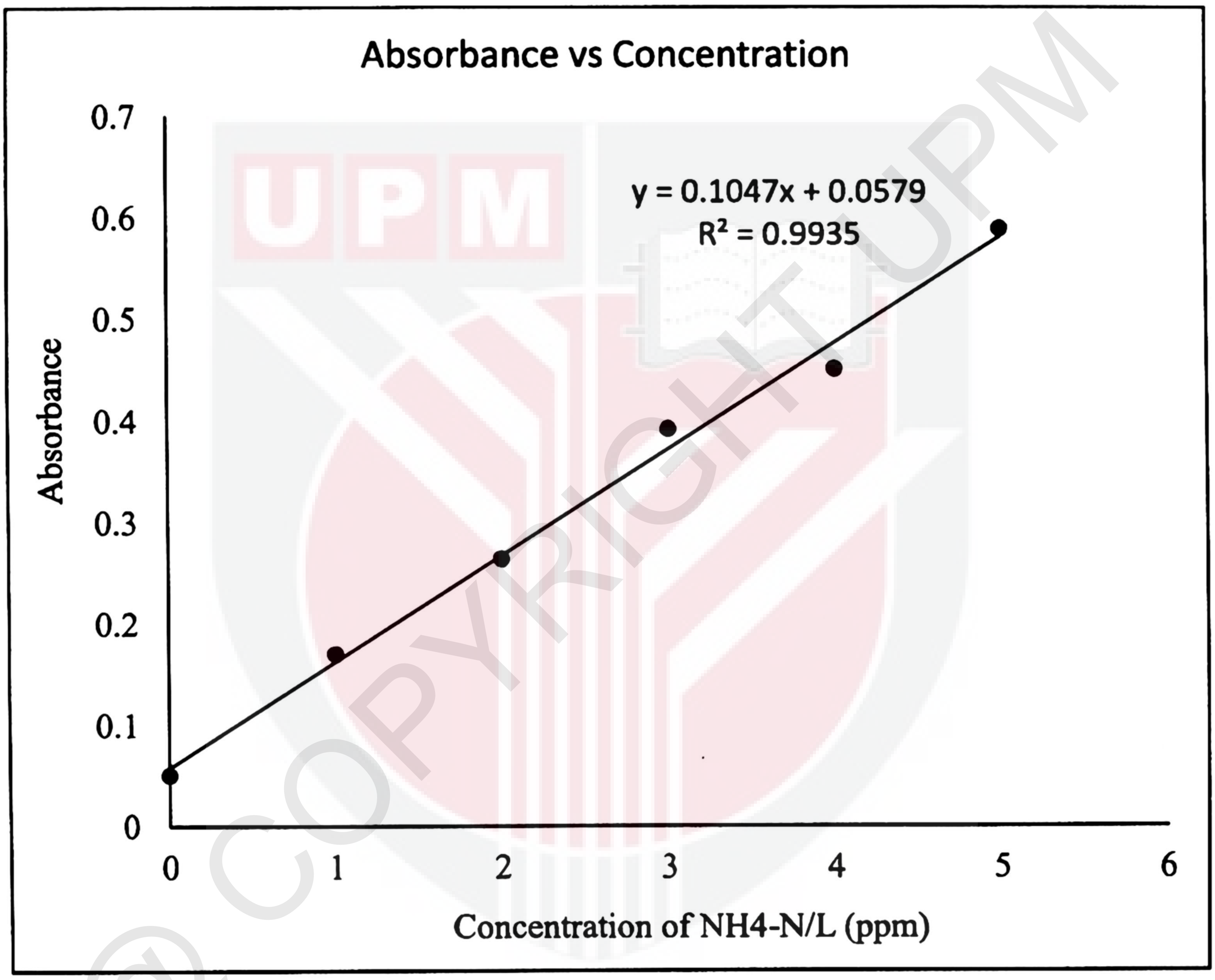


Figure 4.4 Standard curve of ammonia – nitrogen using phenate method

The initial wastewater quality analysis of the Paddy field clay sample was carried out in order to determine the environmental variables under which the clay adsorption-coagulation takes place. Figure 4.5 shows the relationship between ammonia concentration and the absorbance with the colour development duration of an hour.

NaOH was used to maintain the solution under basic conditions and to form phenate. The slope obtained by this study was 0.10 ($R^2 = 0.9935$) it is in a good consistency with the precision date given in Table 4500-NH3 of the ASM, where the slope of linear relationship of NH3-N concentration and optical density ranged 1.10 ~ 1.29. It means that our experiments and the results are reliable.

As stated in the above section, NaOH dosage appeared to be significant variable of ammonia sensitivity analysis. Since the amount of NaOH affects the solution's pH. The highest dosage of NaOH shows the highest pH. Therefore, the rise in pH with decreasing NaOH related closely with the decreasing phenol dosage. The changes of phenol and NaOH dosage may not only affect the absorbance sensitivity but also the color development rate and stability. An intensely blue compound, indophenol, is formed by the reaction of ammonia, hypochlorite, and phenol catalyzed by sodium nitroprusside. Ammonia reacts with phenol to form indophenol in presence of alkali and oxidising agent. Sodium nitroprusside acts as catalyst. The developed blue colour absorbs light of 640 nm wavelength.

4.3.2 Effect of Time

The results show that the equilibrium time required for the adsorption of phenol on all samples is about 90 min as illustrated in Figure 4.6.

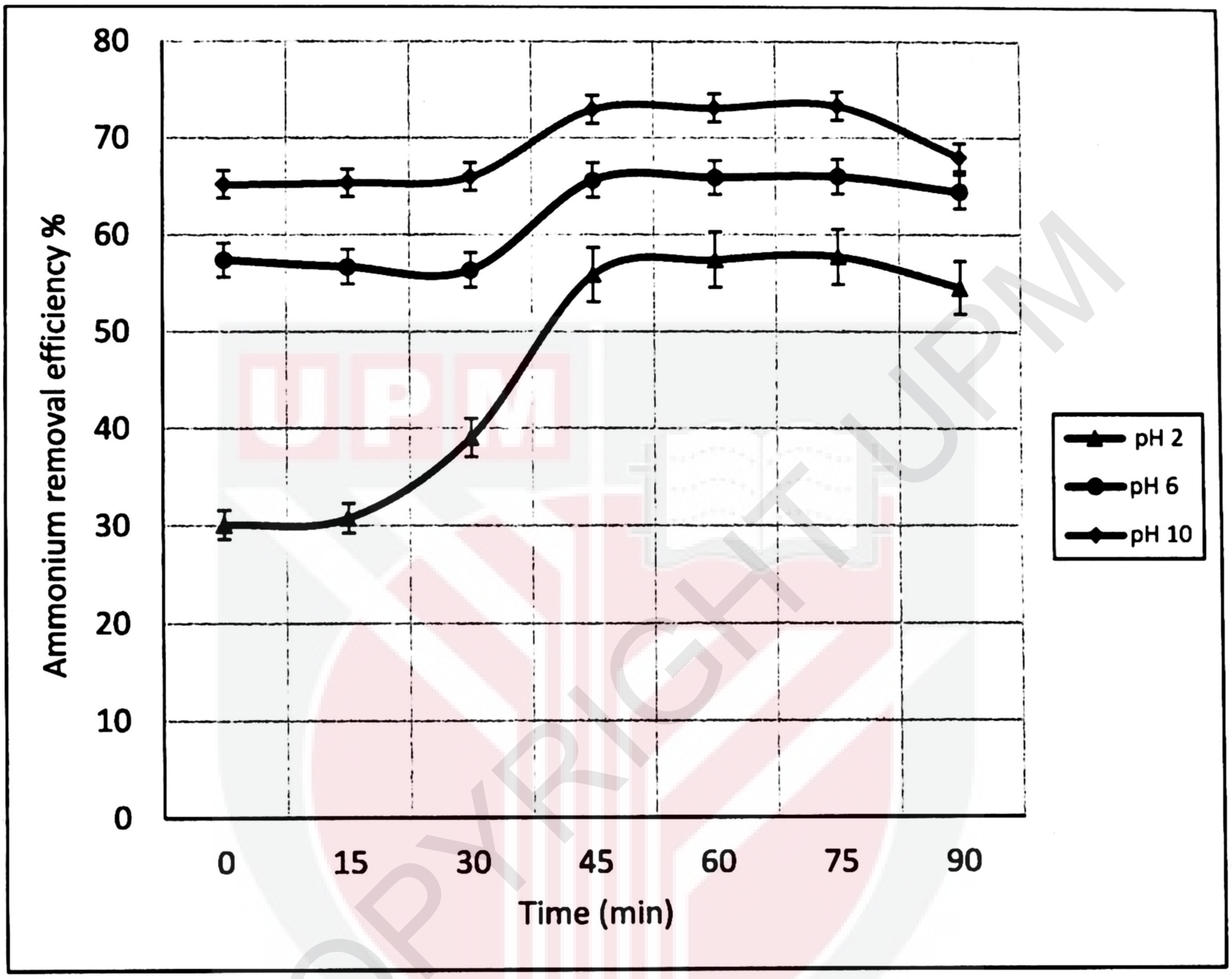


Figure 4.5 Effect of agitation time on the NH^{4+} adsorption three different pH

As shown in Figure 4.6, the removal efficiency of NH4+ on all Paddy field clay increases with the increasing reaction time and reaches equilibrium in 45 min. Previous findings on the adsorption of phenolic compounds by various clay-based adsorbents have shown a wide range of adsorption time (Song and Sandi, 2001). The adsorption of NH^{4+} on paddy field clay is very rapid and reaches equilibrium within 45 min. This may be attributed to the utilization of readily available adsorption sites of the paddy field clay leading to a fast diffusion and rapid equilibrium attainment (Jha and Hayashi, 2009; Alshameri et al., 2014c). When the adsorption of the exterior surface of the adsorbent reaches a saturation point, NH^{4+} ions enter into the pores of adsorbent and are absorbed by the interior surface of particles (Zaghouane-Boudiaf and Boutahala, 2011; Sun et al., 2015; He et al.,2016). It has been widely proposed that fast adsorption kinetics play an important role in the efficiency and field deployment of adsorbents (Mohammadi et al., 2011; Alshameri et al., 2014b; Xia et al., 2016). Therefore, the outcome of this current study is therefore in accordance with the other results published. Up to 70 and 60% of ammonium was successfully adsorp from the aqueous solution by paddy clay. As an effective adsorbent, this proves the effectiveness of activated paddy clay. (Tahaniet al. 1999; 1960 by Giles et al.). Solution pH is one of the essential important parameters for the adsorption of metal ions from aqueous solutions. The solution pH is influenced by the surface charge of the adsorbent, the degree of ionisation, and the speciation of the adsorbate during the adsorption process. In the Figure 4.6, pH 10.0 show higher ammonia removal efficiency compare to pH 2.0 and pH 6.0. The NH^{4+} removal was 73% at pH 10, 65% at pH 6.0 and 57% at pH 2.0. This is because small quantities of metal ions have been adsorbed at low pH, leading to electrostatic repulsion on the adsorbent surface with the occupied H+ ions. As the pH value increases, the adsorbent surface becomes negatively charged, and thus the metal ion adsorption increases and reaches equilibrium.

Other than that, pH 2.0 shows less efficient to adsorb contaminate from the surface water. Contamination of surface water with pathogenic organisms could result in the transmission of waterborne diseases for people who use the water resource for domestic and other purposes downstream.

4.3.3 Effect of adsorbent dosage

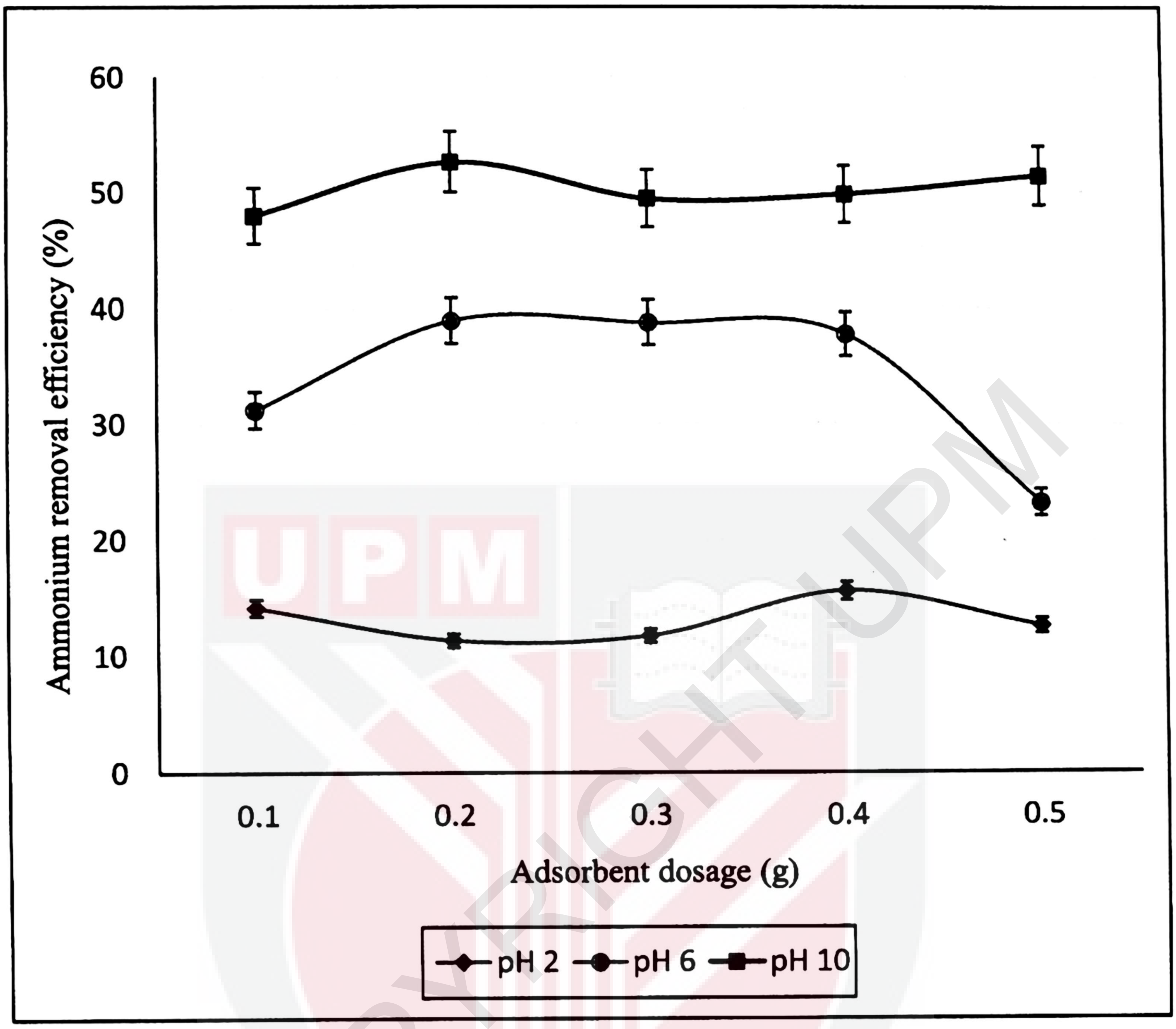


Figure 4.6 Effect of adsorbents dosage on the Ammonium removal efficiency

The effect of adsorbent dosages on the percent removal of ammonium has been shown in Figure 4.7. The removal efficiency of NH4+ ions by three type of pH paddy clay increases with increasing adsorbent dosage from 0.1 g to 0.2 g for pH 10.0 and pH 6.0. This effect can be attributed to an increased number of active surface sites for the NH4+ adsorption thereby significantly enhancing the adsorption capacity (Saltalı et al., 2007; Angar et al., 2017). At higher adsorbent concentration number of active sites is higher. Figure 4.7 also show 0.5 g for pH 2 and pH 6 decrease in ammonium removal efficiency. This is because with the increase in adsorbent dosage aggregation of particles take place, as a result efficiency and ammonium uptake decreases. Considering the low cost and high removal efficiency, 0.4 g was selected as the optimal dosage for all paddy clay and used in the subsequent experiments.

4.3.4 Adsorption capacity

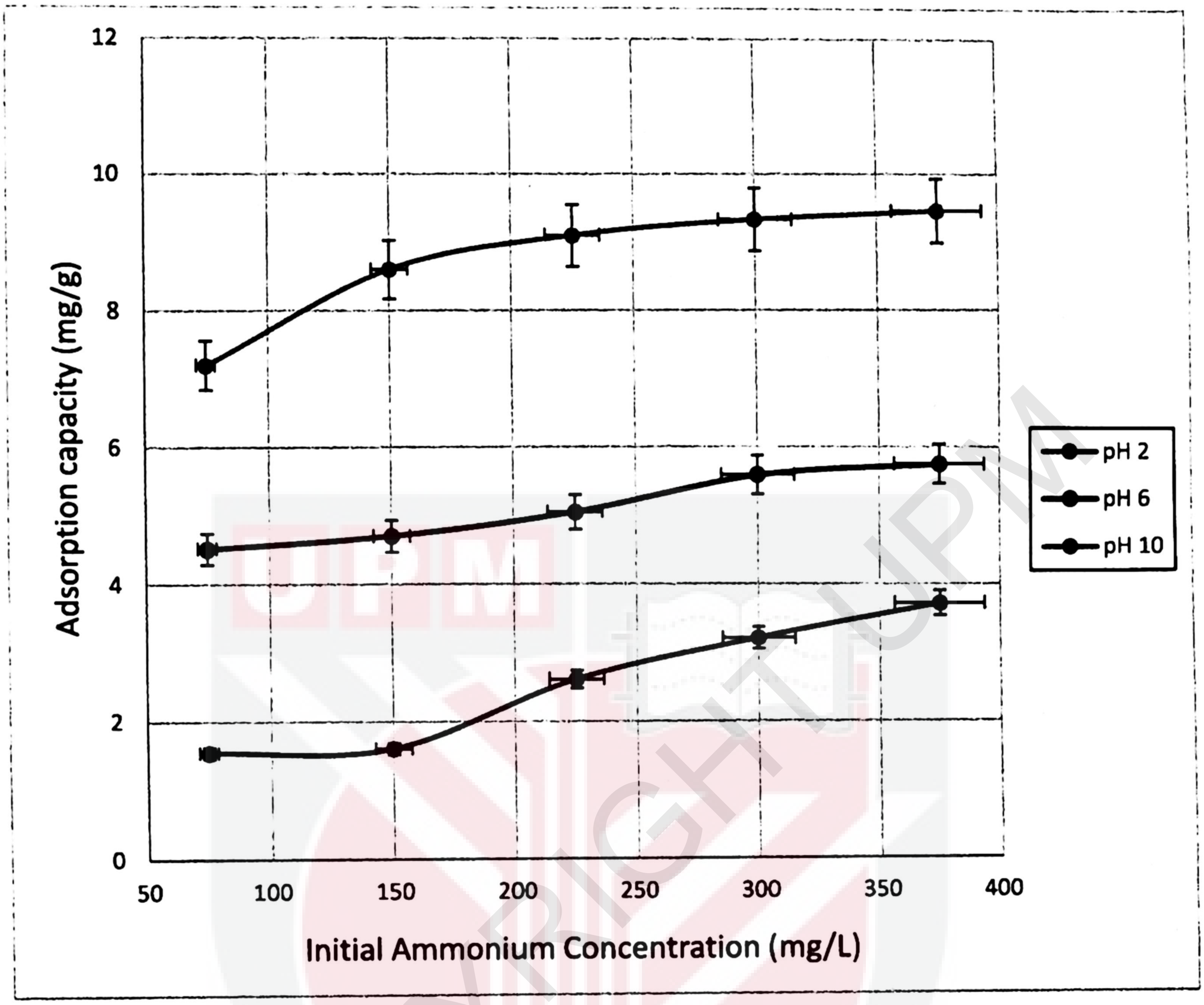


Figure 4.7 Initial ammonium concentration onto Paddy clay.

The equilibrium adsorption capacities as functions of the different initial Ammonium concentrations on Paddy clay are presented in Figure 4.8. It shows an increase in the adsorption capacities for all Paddy clay with an increase of initial ammonium concentration from 75 to 375 mg NH4+ mg/L. After that, no remarkable change in adsorption capacities can be observed. This result suggests that the increase in the initial NH^{4+} concentration increases the mass transfer driving force of the NH^{4+} between the aqueous solution and adsorbent phase, which leads to an increase in NH^{4+} adsorption capacity (Angar et al., 2017).

Some studies have shown that the adsorption capacity is obviously improved with the increase of initial ammonia concentration, which may result in low ion concentration, and low concentrations. There are too many vacant active sites in the paddy field clay, so the adsorption capacity depends on the initial concentration. However, with the increase of ion concentration, more NH4 + appears on the active site because of the increase of adsorption capacity. Interestingly, it was found that rapid and efficient adsorption of NH^{4+} could be obtained at low ion concentrations; this indicates that Paddy clay can be considered as a suitable adsorbent at low ion concentrations of NH^{4+} in contaminated water and wastewater treatment facilities. According to result by master student, kinetics study has revealed that the adsorption isotherms complies well with the Langmuir isotherm equilibrium model.

CHAPTER 5

CONCLUSION AND RECOMMENDATIONS

5.1 Conclusion

Phytoremediation technology is still in its early development stages and full scale application are still limited. Since it appears to be common sense among scientists, engineers, and regulators about the more widespread use of this technique in the future, it is crucial that public knowledge of this technology is taken into consideration and that clear and accurate information is made accessible to the general public to improve its acceptability as a widely-used global sustainable technology. Three types of pH Paddy clay based adsorbents for NH4+ were investigated and compared to understand their adsorption behaviors.

Batch adsorption experiments have demonstrated significant effects on NH4 + adsorption with the contact time, initial NH4 + concentration, adsorbent dosage, and solution pH. Kinetics study has revealed that the adsorption isotherms complies well with the Langmuir isotherm equilibrium model. Among all the paddy field clay studied, Quartz, Feldspar and Kaolinite have the highest NH^{4+} adsorption capacities and the capacities decrease in an order of Quartz > Feldspar > Kaolinite. For all paddy clay studied, the maximum adsorption capacities were obtained within 45 min with a dosage of 0.4 g/25 mL at pH of 10.

XRD and Zeta potential have revealed that the higher NH4 + adsorption capacity could be attributed primarily to the exchange of cations. Furthermore, negatively charged surface area, water absorption process and surface morphology could also contribute to the high NH4 + adsorption capacity. The structure and surface properties of Paddy clay are the key factors that affect the adsorption capacities for NH^{4+}. Due to time constraints, phytoremediation tank process with Nelumbo Nucifera plant cannot be continued and will be studied for future research soon. As a conclusion, the objective of this study were achieved. Contaminated surface water should be treated well to avoid health risk such as diarrhea and cholera to the users of surface water resources. This study suggests that paddy field clay can be considered as ideal adsorbents for NH^{4+} removal from contaminated surface water owing to their low cost, high safety, and good adsorption efficiency.

5.2 Recommendations

In this project, due to the lack of time, some parameter is just optimized from the literature review. Therefore, there are some recommendation to vary some parameter in order to obtain a better result:-

- The use of clay materials with natural polymer coatings is very promising for water treatment. The mineral adsorption capacity of nanoclay increases with the polymer coating on it.
- The relationship between adsorbates and adsorbents must be studied in more detail. Some of the analysis can be made such as SEM analysis, HRSEM analysis, FTIR analysis, and BET analysis.
- Increase surface area of paddy clay minerals by grinding the clay to the very fine particles. These contribute to a large proportion of atoms and molecules being adsorbed on the surface and interfaces to enhance substantial abundance and affinity, enhance the surface and increase the number of possible sites, and eventually increase the surface energy to eliminate a particular pollutant.
- Conduct TG-DTA tests to assess the adsorption capability, micropore structure, thermostability, and components of soils under chemical solutions.
- Use other adsorbent such as Activated Carbon and Charcoal to treat the water from contamination that will risk our environment, safety and health.

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APPENDICES

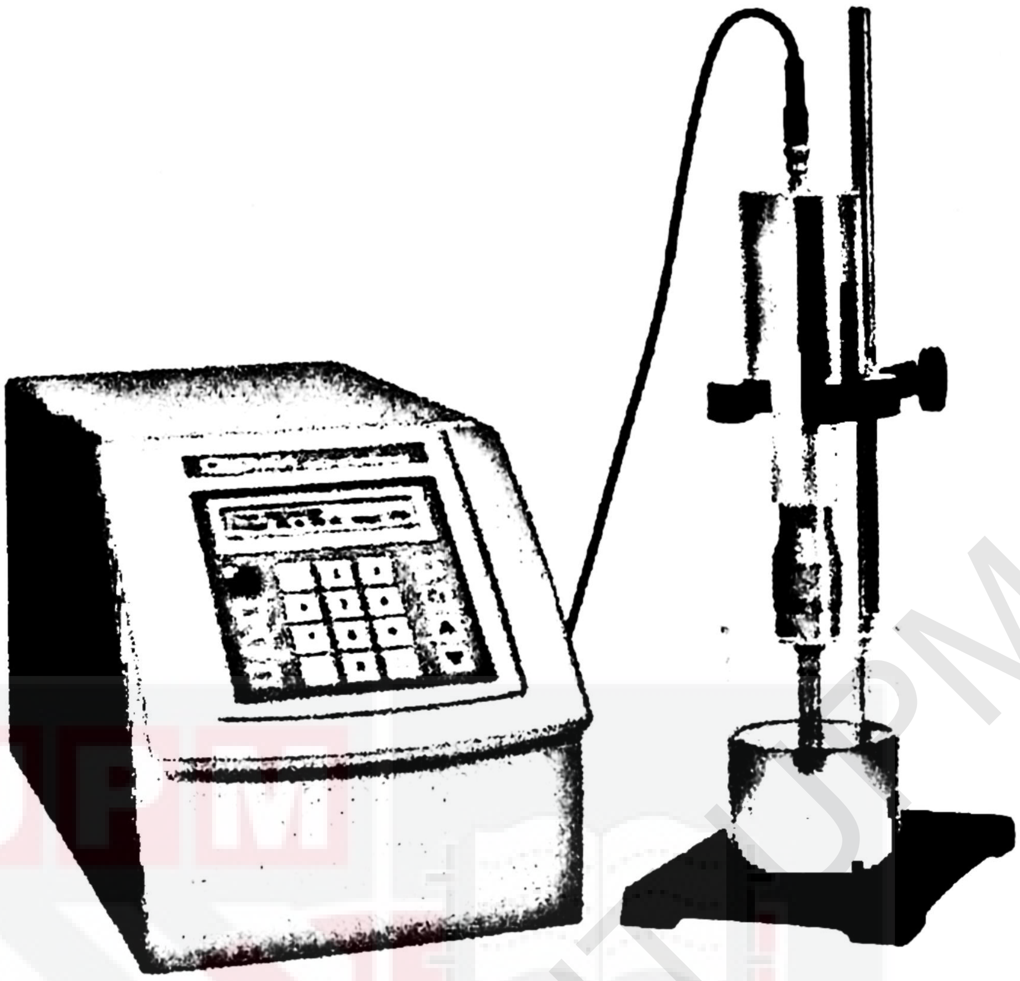

Figure 1: Q500 Sonicator (Qsonica, US).

Figure 2: Particulate Systems zeta/nano particle analyzer Nanoplus (Micrometrics, USA).

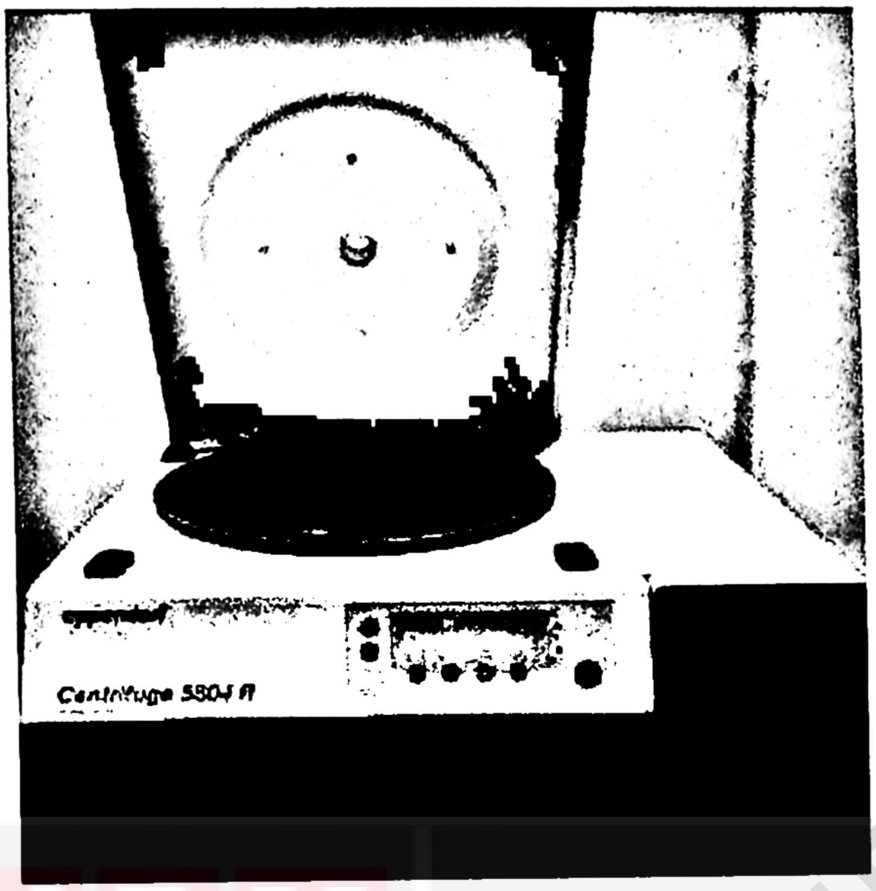

Figure 3: 5804R Centrifuge (Eppendorf, Malaysia).

Figure 4: UV Vist Spectrophotometer (Ultrospec 3100 pro, Sweden).

Table 1: Particle size and Zeta potential

pH	Particle size	Zeta particles
2	803.6 ± 180.74	1.7
4	495.7 ± 21.81	-31.34
6	312.1 ± 10.86	-45.8
8	192.2 ± 5.79	-51
10	101.5 ± 16.51	-54.7

Table 2: Standard Curve Adsorption process

Concentration	Absorbance (640nm)			Average
0	0.055	0.048	0.049	0.0506 ± 0.003
1	0.144	0.192	0.175	0.1703 ± 0.024
2	0.234	0.285	0.274	0.2643 ± 0.268
3	0.35	0.4	0.427	0.3923 ± 0.039
4	0.445	0.45	0.458	0.4511 ± 0.006
5	0.543	0.67	0.556	0.5896 ± 0.069

Table 3: Effect of agitation time

Time	pH 2	pH 6	pH 10
0	30.067	57.401	65.211
15	30.777	56.692	65.389
30	39.070	56.337	65.992
45	55.875	65.637	72.914
60	57.401	65.921	73.056
75	57.721	66.028	73.269
90	54.562	64.466	68.016

Table 4: Effect of adsorbents dosage on pH 2

Time (min)	0.1 g	0.2 g	0.3 g	0.4 g	0.5 g
0	15.22	12.05	14.83	13.89	9.613
30	15.67	8.98	12.95	14.48	11.63
60	17.24	9.61	16.19	14.97	13.96
90	17.72	13.02	17.38	16.61	15.39
120	4.98	13.09	-2.61	18.18	12.50
average	14.16	11.35	11.75	15.63	12.62

Table 5: Effect of adsorbents dosage on pH 6

Time (min)	0.1 g	0.2 g	0.3 g	0.4 g	0.5 g
0	25.07	38.87	39.84	38.69	20.41
30	32.70	39.63	40.22	39.63	20.09
60	34.27	39.95	39.91	40.19	23.61
90	35.24	38.14	40.85	34.13	25.70
120	28.87	37.82	32.60	35.66	26.43
average	31.23	38.88	38.69	37.66	23.25

Table 6: Effect of adsorbents dosage on pH 10

Time (min)	0.1 g	0.2 g	0.3 g	0.4 g	0.5 g
0	44.37	51.75	51.16	51.20	50.01
30	47.09	52.10	51.48	51.48	52.07
60	47.85	52.62	52.35	51.37	50.64
90	49.14	52.94	51.54	48.69	52.10
120	51.58	53.60	40.43	46.01	52.10
average	48.01	52.60	49.39	49.75	51.38

Table 7: Adsorption Isotherms

Initial Ammonium Concentration (mg/L)	75	150	225	300	375
pH 2	2.59	1.54	1.64	3.19	3.84
pH 6	5.86	5.62	4.72	5.01	4.64
pH 10	7.20	9.51	9.35	9.04	8.79