

# PHYTOREMEDIATION OF FERTILIZER FACTORY WASTEWATER BY KENAF (*Hibiscus Cannabinus*) IN COMPARE WITH REED (*Phragmites Australis*)

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### PHYTOREMEDIATION OF FERTILIZER FACTORY WASTEWATER BY KENAF (*Hibiscus Cannabinus*) IN COMPARE WITH REED (*Phragmites Australis*)

by

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### CERTIFICATION OF APPROVAL

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January 2015

### **CERTIFICATION OF ORIGINALITY**

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except as specified in the references and acknowledgments, and that the original work contained herein have not been undertaken or done by unspecified sources or persons.

(THIVANY A/P DAVARATENAM)

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### ABSTRACT

Urea fertilizer factory effluents contain high load of nitrogen (N) pollutants which advanced technologies to be reduced to desirable levels. However, the need advanced added technologies are hugely expensive due to the complex processes and cost of chemicals and maintenance. Phytoremediation technique, the engineered use of plants, has been recently considered for N removal from various wastewaters. However, the common phytoremediation plants (reeds and grasses) are not able to remove N effectively due to the recyclable nature of N through decomposition processes. In addition, they require periodic harvestings which impose high cost on system. Kenaf plants, as a tropical fiber plant, has high transpiration capacity which not only compensate the cost of harvest but also their fiber is industrially important. In this study, the growth and phytoremediation potential of kenaf (Hibiscus cannabinus) to treat the urea fertilizer factory wastewater was evaluated. Eight month old kenaf seedlings received 4 different concentrations of N (T1: wastewater alone; T2: T1+50 mgL<sup>-1</sup> NH<sub>4</sub>NO<sub>3</sub>; T3: T1+100 mgL<sup>-1</sup> NH<sub>4</sub>NO<sub>3</sub>; T4: T1+150 mgL<sup>-1</sup> NH<sub>4</sub>NO<sub>3</sub>) in bench-scale constructed wetlands every 4 days for 8 weeks. The solution volumes supplied to each container and plant biomass, N recovery, and tissue nutrient concentration measured. Kenaf plants size was increased with increasing the amount of supplied N. Kenaf seedling showed a considerable potential N recovery up to 73% when they were totally supplied with 1-3 g N compared to reed which able to recover up to 61.73%.

# CHAPTER 1 INTRODUCTION

#### 1.1 Background

Pollution is the introduction of harmful substances, particularly a contaminant or toxin, which produces some kind of harmful impact on the environment or living organisms (Alloway and Ayres, 1997). It is most often used in an environmental concept like water, air, or soil pollution. However, water is one of the most important sustaining factors of life. There is an increasing trend in areas of land, surface waters and groundwater affected by contamination from industrial, military and agricultural activities either due to ignorance, lack of vision, or carelessness (Alloway and Ayres, 1997). There are different types of pollutants which contaminate waters such as excessive nutrients, chemicals, radioactive materials, harmful microorganisms and suspended matter (Ritter et al., 2002).

Most critical water pollution is excessive nutrients in the water which causes oxygen depletion. This is due to the excessive nutrients in the water can cause the rapid growth of weeds and algae, which compete with the aquatic organisms in the water for oxygen. Urea fertilizer factory is one of the industrial activities which produce a huge amount of effluents containing high load of nitrogen (N). Obire (2007) characterized the water quality of the Okrika creek river which was polluted with the effluents from National Fertilizer Company of Nigeria. The high concentration of N in the form of urea and ammonium was reported in the waters.

Removal of N from the effluent has advanced technologies methods such as sequencing batch reactors, membrane bioreactors, oxidation ditch. But these methods are expensive with complex processes and need to use expensive chemicals and maintenance (El Zayat, 2009). As an alternative process, phytoremediation can be used for N removal from the effluents of urea manufacturing. Phytoremediation is the direct use of green plants and their associated microorganisms to stabilize or reduce contamination in soils, sludge, sediments, surface water, or ground water (Ahmadpour et al., 2012).

Phytoremediation is a low cost, solar energy driven cleanup technique and useful for treating a wide variety of environmental contaminants (Susarla et al., 2002). The nutrients absorption in plants occurs primarily through the root system. The root system provides an enormous surface area that absorbs and accumulates the water and nutrients essential for growth (Muller and Touraine, 1992). Even though reeds and grasses are widely used around the world for phytoremediation method but it does not have the ability to remove high quantity of N due to the recyclable nature of N (Kaoru et al., 1997).

In other words, up taken N by plants will come back again to the soil or water through decomposition process. In that case, the use of fiber plants to remove N can be a proper alternative for reeds and grasses since their fiber can be used commercially. Fiber plants can be used as N phytoremediator and then can be harvested and removed from the area for fiber manufacturing. Kenaf (*Hibiscus cannabinus*) is a fiber plant which has high biomass rate (Muir, 2001; Alexopoulou *et al.*, 2007). Kenaf fibre are used as rope, twine, coarse cloth and paper (Taylor and Kugler, 1992). Uses of kenaf fibre include engineered wood, insulation, clothing-grade cloth, soil-less potting mixes, animal bedding, packing material, and material that absorbs oil and liquids (De Andres et al., 2010). Therefore kenaf plant is introduced in this project

#### **1.2 Problem Statement**

Water quality is defined as water which is safe and appealing to all life on earth. It should contain no chemical or radioactive substance that is harmful to any life. It should be free of disease-causing organisms and stable in terms of corrosion or scaling. Polluted water is water that is not safe and not healthy for people and animals to drink or to wash (Van den Brandt and Smit, 1998). Polluted water is particularly dangerous to water plants and animals. At present, even though the water pollution has reached high levels, there are still many people who are ignorant of the enormity of the situation. People are still doubtful to accept the fact that our rivers and oceans are in serious danger (Weinstein, 1988). All life in the water is dependent on the interaction within the river itself and in the surrounding catchment. These processes can either maintain a healthy ecosystem or disrupt ecological processes and degrade the water supply. Excessive nutrients in the water can cause the rapid growth of weeds and algae, which compete with the organisms in the water for oxygen. Oxygen depletion in the water could take place as a result of proliferate algae and weed growth (Provasoli, 1958).

Nutrient pollution is highly toxic for living organisms and makes eutrophication which cause extensive damage to the water quality characteristics. To prevent and protect the ecology, phytoremediation is introduced as an alternative way from other complex and expensive methods (Ghosh and Singh, 2005). Reeds is a common plant used for phytoremediation method (Bonanno and Giudice, 2010). But because of the recyclable nature of N, reeds have to be harvested in short periods of time which impose extra cost on the system. Moreover the harvested product from reed is a waste and need to composed back where there is no function on the harvested reeds (Lin, 2012)

### 1.3 Objective

The aim of this study is to investigate the N removal from fertilizer production factory wastewater by kenaf plant. In order to achieve the aim of this study, the following objectives must be accomplished:

- i. To evaluate the growth, tolerance efficiency and phytoremediation potential of kenaf (*Hibiscus cannabinus*) to remove N from urea fertilizer factory wastewater in a bench-scale constructed wetland.
- ii. To compare the kenaf plant with reed (*Phragmites australis*) as a conventional plants to remove N.

### 1.4 Scope of Study

PETRONAS Fertilizer Kedah Sdn Bhd (PF(K)SB) is a Malaysian urea production company and a wholly owned subsidiary of PETRONAS. The company is located near the town of Gurun in the northern state of Kedah Darul Aman in Malaysia (Figure 1.1). The company is involved in petrochemical manufacturing, mainly producing granular urea for use in local and foreign agricultural industries (Figure 1.2). PF(K)SB's primary product is granular urea, with ammonia. Currently, the plant has a rated urea output of 2100 MT per day.



Figure 1.1: Plan view of PETRONAS Fertilizer Kedah (PFK)



Figure 1.2: PETRONAS Fertilizer Kedah Company



Figure 1.3: PETRONAS Fertilizer Ammonia and Urea Plant

The ammonia and urea plants have a combined urea production capacity of 1.4 million metric tons per year. About 36 per cent of the output is sold locally, while the balance is exported. PETRONAS markets the product through its subsidiary Malaysian International Trading Corporation Sdn Bhd (MITCO), and currently supplies about 80 per cent of the domestic urea requirement. There is schematic of the company in Figure 1.3. The sample wastewater was treated by using kenaf (*Hibiscus Cannabinus*), a fiber tropical plant, and its ability was compared with reed plants

(*Phragmites Australis*). Kenaf plants have high biomass therefore the ability of kenaf to absorb N is high. In this experiment, the plants were planted on gravel to minimize the effect of other factors in N absorption for example to avoid the nutrients of soil absorb by the plant where might disturb the result of amount N removed. The initial pH of the nutrient solution adjusted to 6.3 and the solution added every four days to maintain the water level at the 9 cm below the gravel surface. At the end of the experiment the roots and shoots were dried at 60°C, weighed, and ground separately for determination of tissue N concentrations by Kjedahl method. At the end, kenaf showed a better N recovery compare to reed.

### CHAPTER 2 LITERATURE REVIEW

### 2.1 Introduction

Water pollution causes serious damages to environment, aquatic organisms and human health. (Halpern et al., 2007). In order to maintain sustainable management and protect fisheries and aquatic resources, control of aquatic pollution are really in demand. Excessive nutrients (e.g., nitrogen and phosphorus) in rivers is increasing concern worldwide (Pieterse et al., 2003; Edwards and Withers, 2008; Howden et al., 2013).

Water quality of groundwater, rivers, and seas is negatively influenced by high diffuse N and phosphorus discharge (Melanie Mewes, 2012). Nutrient pollution degrades riverine ecosystems and decreases the quality of water used for drinking, industry, agriculture, recreation, and other purposes. (Smith, 2009; Bowes et al., 2010; Houser and Richardson, 2010). There is usually a link between excessive nutrients and low O2 in deep water. This excessive biomass can cause 'harm' by sinking, decomposing and creating low oxygen conditions and could cause an impact on deep water organisms including commercially important fish species (Kedong Yin, 2011).

The treatment of wastewater with high levels of urea and ammonia-N is one of the problems faced by urea fertilizer plants (Islam et al., 2010). The major components in the effluents in a nutrient fertilizer plant are ammonia N(NH4<sup>+</sup>-N), nitrate N (NO3-N), and organic N (William, 1980). Total ammonia N is the combined concentration of the un-ionized (NH3) and ionized form (NH4<sup>+</sup>). The unionized form increasing in proportion with increase in pH and temperature. It is the un-ionized form (NH3) that is of concern due to its toxicity in the aquatic environment (Dave, 2013).

Technology which use accumulating plants to remove toxic from soil and water is cost-effectiveness to indicate sufficient measures to reduce nutrient (Alkorta et al., 2004; Kaja Kühl, 2010; Ilya Raskin et al., 1997; Melanie Mewes, 2012). Selection of plant is also under consideration of some researches. Herbaceous species, such as mustard, alfalfa, and grasses, and reeds can be used in the phytoremediation of contaminants. Hybrid poplars, willows, cottonwood, and other woody species that have rapid growth rates, deep roots, and high transpiration rates, can be in the phytoremediation of contaminants in groundwater or can be used to provide hydraulic control (Environmental Protection Agency 2011).

Common plants used for phytoremediation are reed (*Phragmites karka*), cattail (Typha angustifolia), softstem bulrush (Schoenoplectus tabernaemontani), sedge (Cyperus spp.) will not able to remove N effectively if they are not harvested regularly (Polomski et al., 2009) but kenaf is considered to be a nutrient demanding crop (Saba et al., 2015). Kenaf also known as a high biomass production rate plant and it demands high N and P absorption (Abe et al., 1998). Kenaf plant is an annual or biennial herbaceous plant growing to 1.5-3.5 m tall with a woody base. The stems are 1-2 cm diameter, often but not always branched. The leaves are 10–15 cm long, variable in shape, with leaves near the base of the stems being deeply lobed with 3-7 lobes, while leaves near the top of the stem are shallowly lobed or unlobed lanceolate. The fruit is a capsule 2 cm diameter, containing several seeds. The fibers in kenaf are found in the bast (bark) and core (wood). The bast constitutes 40% of the plant. These fibers are long 2 mm to 6 mm and slender. The cell wall is thick 6.3 µm. The core is about 60% of the plant and has thick  $\phi$  38  $\mu$ m but short 0.5 mm and thin walled 3  $\mu$ m fibers. Since the paper pulp is produced from the whole stem, the fiber distribution is bimodal. The pulp quality is similar to hardwood (University of Kentucky College of Agriculture, Food and Environment).

### 2.1 Critical Review of Literatures

"Phytoremediation is a biological treatment process that utilizes natural processes stimulated by plants to enhance degradation and removal of contaminants in contaminated soil or groundwater" (Alvarez & Illman, 2006). Phytoremediation capitalizes on the natural processes of plants. These processes include dihydrogen monoxide and chemical uptake, metabolism within the plant, exudate release into the soil that leads to contaminant loss, and the physical and biochemical impacts of plant roots (Suthersan and Payne, 2004).

Magnification of plants depends on photosynthesis, in which dihydrogen monoxide and carbon dioxide are converted into carbohydrates and oxygen, utilizing the energy from sunlight. Roots are efficacious in extracting dihydrogen monoxide held in soil and water, even dihydrogen monoxide held at relatively high matric and osmotic negative dihydrogen monoxide potentials; extraction is followed by upward convey through the xylem (Figure 2.1).



Figure 2.1: Process of phytoremediation (Kansas State University Agricultural Experiment Station and Cooperative Extension Service)

Transpiration (dihydrogen monoxide vapor loss from plants to the atmosphere) occurs primarily at the stomata (apertures in leaves and stems where gas exchange occurs), with supplemental transpiration at the lenticels (gas exchange sites on stem and root surfaces) (Donal, 1970). The phytoremediation of N in plants is related to plant species, element species, chemical and bioavailability, and a number of environmental conditions such as pH, dissolved oxygen and temperature (Cheng, 2003; Weis, 2004). plants tolerate and accumulate N are depends on various physiological factors such as uptake and leakage of metal ions by roots, root cation exchange capacity (CEC), phytochelatin production, antioxidative stress, carbohydrate production and utilization (Suresh and Ravishankar, 2004). Some experiment had been conducted previously of phytoremediation process by several researchers using different type of plants and concluded the finding results. *Canna generalis* able to remove 44% of N of domestic wastewater.

In other studies highlighted that different concentration of N fertilizer did not result in any significant difference in plant growth, biomass and foliage production at the rate of 100N: 200P kg/ha showed significant positive effects on yield and growth of kenaf plants (Mohd Hadi Akber Basri et al., 2014). An experiment conducted by (Mun et al., 2008) with kenaf (*Hibiscus cannabinus* L.) for phytoremediation of sand tailings. (Thawale et al., 2006) conducted an experiment of High Rate Transpiration System (HRTS) using *Bamboo, acacia* and *Eucalyptus* to transpire water equivalent of 7 to 13 times the potential evapotranspiration from the soil matrix alone for 2 years. Where else, (Huett et al., 2005) used *Phragmites australis* to removal 96% of 10 mg  $L^{-1}$  N of nursery runoff for 19 months. Akratos and Tsihrintzis (2007) used *P. australis* to remove N from municipal wastewater contaminated with 21.1 mg  $L^{-1}$  N and showed a 66.8% removal of the pollutions. In other study, Abe and Ozaki (2007) used *H. cannabinus* as phytoremediator and found the removal percentage of 34.65 % of domestic wastewater containing 8 mg  $L^{-1}$  N.

Phytoremediation has been considered as a promising approach to remove metals from contaminated soils. Hence after harvest disposal of remedial plant materials is an unsolved problem (Sas-Nowosielska et al., 2004). Several methods such as composting, compaction, incineration, ashing, pyrolysis, direct disposal and liquid extraction are used for the disposal of the contaminated plant materials after phytoextraction process (Salt et al., 1995; Garbisu and Alkorta, 2001; Mulligan et al., 2001).

# CHAPTER 3 METHODOLOGY

### 3.1 Introduction

In this research, phytoremediation technique is been used for removing nitrogen (N) from influents discharged from urea fertilizer factory which contain high N concentration. Through the experiments, the growth and remediation potential of kenaf, a fiber plant, has been evaluated and compared with reed as a common wetland plant for 8 weeks. Since kenaf plants have high biomass therefore the ability of kenaf to take up N is high. To make sure the kenaf plant absorb the nutrient from the influent sample, this experiment was conducted in open space but under the shade where the plant can receive enough sun lights for photosynthesis process. The plants were planted on gravel in this experiment to minimize the effect of other factors in N absorption for example to avoid the nutrients of soil absorb by the plant where might disturb the result of amount N removed. The initial pH of the nutrient solution adjusted to 6.3 and the solution added every four days to maintain the water level at the 9 cm below the gravel surface. At the end of the experiment the roots and shoots were dried at 60°C, weighed, and ground separately for determination of tissue N concentrations by Kjedahl method.

### 3.2 Experiment Methodology

#### **3.2.1** Wastewater Collection and Composition Determination

Wastewater samples were collected from Petronas Fertilizer Kedah (PFK) urea manufacturing influents and stored in the laboratory at 4°C before starting the experiment. Total organic carbon (TOC) determined from the influent sample using a TOC-L Shimadzu apparatus, chemical oxygen demand (COD) according to HACH method (Method 8000), pH by a portable pH meter (Model EW 53013, HACHSension), total N using the HACH Test'N Tube tests, orthophosphate ( $PO_4^{-3}$ ) by PhosVer 3 Method (HACH, Method 8190) and potassium (K), iron, zinc, by atomic absorption spectroscopy, AAS (Model AA 6800 Shimadzu) (HACH, 2002).

#### 3.2.2 Experimental System Design

Two polyethylene pots of different sizes was prepared. The smaller pots are placed on the bigger pots for experiment purposes. The dimension of the smaller pot was (200 mm rim diameter, 160 mm bottom diameter, 150 mm high), which filled with pea gravel. The dimension of the bigger pot is (202 mm rim diameter, 170 mm bottom diameter, 190 mm high). Swater depth of 90 mm below the surface of the stone pebbles in a vase. Schematic layout of the experiment is shown in Figure 3.1.



Figure 3.1: The schematic of the experimental laboratory scale wetland

### 3.3 Proposed Acclimation Procedure

### 3.3.1 Kenaf Plant

Three weeks before the initiation of the experiment, 22 kenaf seedlings were transplanted into the experimental systems for acclimatization. Kenaf seeds were planted in wet cotton and store at room temperature for seven days as shown in Fig 3.4. Kenaf seeds will plant 1.25 to 2.5 cm deep in the pot fill of gravel as shown in Fig 3.5. Normally the plant emerges within two to four days after planting. During acclimatization process, <sup>1</sup>/<sub>4</sub> Hogland solution prepared as fertilizer, since the seedlings transplanted in pot filled with gravel where there is no nutrient source for them to grow. This is made essentially according to the following reference: D.R. Hoagland and D.I. Arnon, as shown in Table 3.1. The water-culture method of growing plants without soil.



Figure 3.2: Kenaf seed starts to grow



Figure 3.3: Kenaf plant transplanted in pot

### 3.3.2 Reed Plants

Reed with average 1 feet height chosen from Seri Iskandar area. These plants took up with the root from rooting system. The root of reed washed to remove the sands and clay. Reed then planted in the pot filled with gravel. Two weeks before the initiation of the experiment, 20 reed plants were transplanted into the experimental systems for acclimatization. During acclimatization process, <sup>1</sup>/<sub>4</sub> Hogland solution prepared as fertilizer, since the seedlings transplanted in pot filled with gravel where there is no nutrient source for them to grow.



Figure 3.4: Reed cleaned with deionized water



Figure 3.5: Reed transplanted into the pot

16.3744 g	
3.4035 g	
4.368 g	
16 g	
83.2 mg	
240 mg	
121.6 mg	
11.2 mg	
4.48 mg	
4.48 mg	

Table 3.1: Preparation of <sup>1</sup>/<sub>4</sub> Hogland solution for 80 liter

Table 3.1 shows the method to prepared <sup>1</sup>/<sub>4</sub> Hogland solution for the plant. All the elements were is powder form, therefore the powders is measured by used weighing machine and mixed them together (Figure 3.6). The mixed elements were add to 80 liter water and stirred before supplied to the plants.



Figure 3.6: Prepare <sup>1</sup>/<sub>4</sub> Hogland fertilizer



Figure 3.7: Supply ¼ Hogland fertilizer to plants

### 3.4 Proposed Solution Procedure

The data set was tested to find the influent characteristic of urea plant of PFK. Four test solutions were prepared by collected wastewater of the urea production plant with different levels of N concentration; T1: wastewater alone; T2: T1+50 mg  $L^{-1}$  NH<sub>4</sub>NO<sub>3</sub>; T3: T1+100 mg  $L^{-1}$  NH<sub>4</sub>NO<sub>3</sub>; T4: T1+150 mg  $L^{-1}$  NH<sub>4</sub>NO<sub>3</sub> (Table 3.2).

T1	T2	Т3	T4
Raw Wastewater	T1+ 50 mg.L <sup>-1</sup>	T1 + 100 mg.L <sup>-1</sup>	T1 + 150 mg.L <sup>-1</sup>
	NH4NO3	NH4NO3	NH4NO3

Table 3.2: The concentration of waste water prepared



Figure 3.8: Preparing solution for plants

### 3.5 **Proposed Experiment Procedure**

The procedures for the experiment were as follows:

- Plants were lifted from their aquatic containers, flushed with deionized water, and then returned to aquatic pots that had been emptied and rinsed with deionized water.
- 2) Pots were prepared and seedlings were planted in the pots.
- 3) The test solution been batch-loaded into the pots until it started to escape from the overflow valve.
- The test solution PFK treatment plant wastewater with four levels of N concentration to investigate the plants tolerance.
- The initial pH of the nutrient solution were adjusted to 6.3 with 2 N H2SO4 or 10 N NaOH.
- 6) The solution were added every four days to maintain the water level at the9 cm below the gravel surface.
- During the eight-week experiment volumes of nutrient solution were supplied to each container recorded.
- Water samples from the pots were filtered and analyzed for measurement of NO3-N, NH4-N and TKN and TN.
- 9) The percentage of recovered N determined using Eq.1.

10) 
$$R = \left(\frac{(Ci-Cf)}{Ci}\right) x \ 100$$
 Eq. 1

- a. \*Where  $C_i$  is the initial amount of N and  $C_f$  is the remaining amount of N
- 11) The above- and below-ground portions of each plant removed from the containers and weighed.
- 12) The roots and shoots were dried at 60°C, weighed, and ground separately for determination of tissue N concentrations by Kjedahl and the P and K concentrations by a spectrophotometer.
- 13) To normalize differences in nutrient concentrations as a result of growth differences between treatments, plant tissue N content were calculated by multiplying plant part dry weight by N concentration.
- 14) Whole plant N content were derived by adding above- and below-ground N content.

#### 3.6 Measuring Method

The effect of N concentration treatments on plant growth was evaluated by weekly monitoring of plant height from gravel surface to the tallest plant part (Cornelissen et al., 2003). As an indication of chlorophyll content, the greenness of new fully expanded leaves determined using a SPAD-502 Chlorophyll Meter. After termination, plants were harvested and separated into leaves, stems and roots.

All plant parts separately were oven dried for approximately 24h at  $60^{\circ}$ C and weighed and ground in Mortar grinder (Rocklabs, NZ) to pass through a 40-mesh (0.425-mm) screen. N concentration determined using 1 g of dried tissue and assayed by Kjeldahl method (Nelson and Sommers, 1980). The N content calculated using equation 3 to normalize the differences in N concentrations as a result of growth differences between treatments (Polomski et al., 2009).

The growth of the plant was monitored weekly by measuring the height of the plant and the number of the leaves to evaluate the growth of the plant with the concentration of the N (Table 3.3).

DATA COLLECTION	METHOD	EQUIPMENTS/FORMULA	REMARKS
Growth of Plants	Measure the Height of the Plants	Measuring tape	Weekly
Growth of Plants	Number of Leaves	Count	Weekly
Indication of Chlorophyll Content	Greenness of New Fully Expanded Leaves	SPAD-502 Chlorophyll Meter	Weekly
Solution Volumes Supplied	Percentage of Recovered Nitrogen	$R = \left(\frac{(Ci - Cf)}{Ci}\right)$	End of Experiment
N Content	Measure the Dry Weight of Each Plant After Dried for 24 Hours In Oven for 60°c	N Content= Plant Dry Weight ×N Concentration	End of experiment
Concentration of Sample Wastewater	Kjeldahl Method		Beginning and End of Experiment

Table 3.3:	Summary	of data	collection
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# CHAPTER 4 RESULTS AND DISCUSSION

### 4.1 Wastewater Characteristic

The type of data used for this project is the influent of urea plant of PFK. Table 4.1 shows the result of data set that were used in this experiment.

INFLUENT OF UREA PLANT			
pH	9.02		
TSS	9.5 mg L <sup>-1</sup>		
COD	11.33 mg L <sup>-1</sup>		
TOC	0 mg L <sup>-1</sup>		
TN	190 mg L <sup>-1</sup>		
PO4 <sup>-3</sup>	1.13mg L <sup>-1</sup>		
K	1.81 mg L <sup>-1</sup>		
Zn	0 mg L <sup>-1</sup>		
Fe	0 mg L <sup>-1</sup>		

Table 4.1: Characteristic of PFK influents wastewater

Table 4.2: Standard effluent discharged concentration

PARAMETER	UNIT	STANDARD
Temperature	С	40.00
pH Value	-	5.5-9.0
BOD, at 20°C	mg.L <sup>-1</sup>	50.00
Suspended Solids	mg.L <sup>-1</sup>	100.00
Mercury	mg.L <sup>-1</sup>	0.05

Cadmium	mg.L <sup>-1</sup>	0.02
Chromium Hexavalear	mg.L <sup>-1</sup>	0.05
Chromium Trivalent	mg.L <sup>-1</sup>	1.00
Arsenic	mg.L <sup>-1</sup>	0.10
Cyanide	mg.L <sup>-1</sup>	0.10
Lead	mg.L <sup>-1</sup>	0.50
Copper	mg.L <sup>-1</sup>	1.00
Maganese	mg.L <sup>-1</sup>	1.00
Nickel	mg.L <sup>-1</sup>	1.00
Tin	mg.L <sup>-1</sup>	1.00
Zinc	mg.L <sup>-1</sup>	2.00
Boron	mg.L <sup>-1</sup>	4.00
Iron	mg.L <sup>-1</sup>	5.00
Silver	mg.L <sup>-1</sup>	1.00
Aluminium	mg.L <sup>-1</sup>	15.00
Selenium	mg.L <sup>-1</sup>	0.50
Barium	mg.L <sup>-1</sup>	2.00
Fluoride	mg.L <sup>-1</sup>	5.00
Formaldehyde	mg.L <sup>-1</sup>	2.00
Phenol	mg.L <sup>-1</sup>	1.00
Free Chlorine	mg.L <sup>-1</sup>	2.00
Sulphide	mg.L <sup>-1</sup>	0.50
Oil and Grease	mg.L <sup>-1</sup>	10.00
Ammoniacal Nitrogen	mg.L <sup>-1</sup>	20.00
Colour	ADMI*	200.00

Based on the Table 4.1, this influent contains a large concentration of total nitrogen (N) 190 mg.L<sup>-1</sup> which mainly originated from urea and ammonium compounds. It has also an alkaline pH due to the present of unreacted ammonia in the wastewater remaining from the urea synthesis (Williams, 1970). The other characteristics of wastewater are in the below range according to Table 4.2 (Environmental Quality Act 1974) such as zinc and iron. Therefore N is the main

compound for the acclimation of the plants compare to the other compounds which shows minimum value compare to the range provided.

### 4.2 Results and Discussion

Figure 4.1 and Figure4.2 shows the total nitrogen (N) recovery by kenaf and reed plants. Graph below compares the request of reed and kenaf plants from different experimental sets for urea wastewater solution. Based on the table, kenaf plants have more tendency to wastewater solution up taking compared to reed in every type of solutions. Plants supplied with higher concentrations of N (T4) required more wastewater compared to T1, T2 and T3 which indicates better acclimatization of plant in accepting N in higher concentration.



Figure 4.1: Concentration of total N vs percentage of N recovery in Kenaf

KENAF	TN Supplied (lit)	TN Remained (lit)	% N Recovery
K1	1388.710	367.605	73.53%
K2	1832.400	660.960	63.93%
K3	2519.230	913.680	63.73%
K4	3077.340	1138.500	63.00%

Table 4.3: Percentage of N Recovery by Kenaf



Figure 4.2: Concentration of total N vs percentage of N recovery in Reed

REED	TN Supplied (lit)	TN Remained (lit)	% N Recovery
<b>R</b> 1	842.270	322.320	61.73%
R2	1292.160	555.300	57.03%
R3	1414.040	869.175	38.53%
R4	1652.740	1076.075	34.89%

Table 4.4: Percentage of N recovery by reed

SAMPLE	REED	KENAF	BLANK	
T1	61.73%	73.53%		
T2	57.03%	63.93%	27.21%	
Т3	38.53%	63.73%		
T4	34.89%	63.00%		

Table 4.5: Comparison of kenaf and reed plant in % of N recovery

Table 4.4 shows the comparison N recovery of reed and kenaf plant with different concentration of N. Nitrogen recovery for reed is high for T1 which is 61.73% and low for T4 which is 34.89%. Same goes to kenaf where T1 recover more N 73.53% and T4 recover low N 63.00%. For both plant T1 recover more N compare to T2, T3 and T4. Moreover N recovery for blank is 27.21%.there is no plant in the blank pot and the N recovery happen because of evaporation process.

Weekly monitoring of the height of kenaf plant indicated that the pattern of growth is an increasing trend throughout the experimental period in the all investigated plants. Based on the graphs, T4 shows the greatest growth compared to T1, T2 and T3 which indicates better acclimatization of plant in accepting N in higher concentration. Plant height during the experimental period showed significant differences among the treatments with regards to the level of nutrient concentrations (Hossain et al, 2010).



Figure 4.3: Height of plant growing duration in the form of four different N concentration

Weekly monitoring of the height of reed plant indicated that the pattern of growth is an increasing trend throughout the experimental period in the all investigated plants. Based on the graphs, T4 shows the greatest growth compared to T1, T2 and T3 which indicates better acclimatization of plant in accepting N in higher concentration.



Figure 4.4: Height of plant growing duration in the form of four different N concentration



Figure 4.5: Height kenaf and reed plant

Figure 4.5 above shows the height of both plants where T4 has high potential to grow compare to T1, T2 and T3. Height of reed plant is higher than kenaf plant because kenaf able to grow 1.5-3.5 m within 2 years where else reed able to grow 5m tall within 4 to 5 months. Therefore the reed plant grow fast compare to kenaf plant. The growing process happens very fast in short duration for reed plant. Kenaf need more time to grow tall.



Figure 4.6: No of kenaf leaves growing duration in the form of four different N concentration

Weekly monitoring of the number of plant leaves indicated that the pattern of growth is an increasing trend until week four. The number of leaves start to fall slightly after week four. Based on the studies, plants need sufficient nutrients to grow healthy such as Calcium, magnesium and sulfur are required in somewhat lesser amounts and the micronutrients (iron, manganese, copper, zinc, boron, molybdenum) in considerably littler sums. But each nutrient is essential and if just one is lacking the plant will grow poorly (Shanyn & Lucy, 1999). Based on the graphs, T4 shows the greatest growth compared to T1, T2 and T3 which indicates better acclimatization of plant in accepting N in higher concentration.



Figure 4.7: No of reed leaves growing duration in the form of four different N concentration

Weekly monitoring of the number of plant leaves indicated that the pattern of growth is an increasing trend throughout the experimental period in the all investigated plants. Based on the graphs, T4 shows the greatest growth compared to T1, T2 and T3 which indicates better acclimatization of plant in accepting N in higher concentration.



Figure 4.8: Number of leaves of kenaf and reed plants

Figure 4.5 shows the growth of number of leaves for kenaf and reed plant with T1, T2, T3 and T4 which is raw wastewater with 190 mg L<sup>-1</sup>, 240 mg L<sup>-1</sup>, 290 mg L<sup>-1</sup> and 340 mg L<sup>-1</sup> of nitrogen respectively. Kenaf plant showing a rapid growth of the number of leaves for 20 days. As the kenaf plant growing and extra leaves are produced, the leaves begin to differentiate into the leaves shape characteristic for that specific cultivar (Webber C.L., Harbans L.B., and Venita K.B., 2002). After 20 days to 42 days the leaves start to drop because nutrient inadequacy manifestations for the most part show up on the base leaves first. In extreme cases, the lower leaves have a "fired" appearance on the tips, turn colour, for the most part deteriorate, and fall off (M. Ray, 1999) as shown in Fig 4.6 and Fig 4.7. Where else number of leaves for reed is slow growing and remain with the same number of leaves after 35 days. Reed is a highly competitive plant that is fit for rapid growth and spread.



Figure 4.9: Dried Kenaf plant



Figure 4.10: Dropped Kenaf leaves

# CHAPTER 5 CONCLUSION AND RECOMMENDATION

As a conclusion, this project is important as it deals with alternative ways of removing N in urea fertilizer waste water before discharge to the river. Phytoremediation is believed to be one of the effective ways to encounter the current problem with the conventional ways of using kenaf plant to derive the phytoremediation. Yet the side effects and indications of inconvenience in plants, potentially the most ignored are supplement insufficient. The interrelationship between a supplement's accessibility and pH value, temperature, available moisture and absents of other nutrients. Therefore something needs to be add to replace those lost nutrients (Shanyn & Lucy, 1999).

Over two-month period kenaf seedlings fed with urea manufacturing influents in gravel- based bench-sized subsurface constructed wetlands. Kenaf plant are known as grow faster, high evaporation rate, and high biomass accumulation therefore will have high efficient to remove the high load of N from fertilizer factory wastewaters. Significant efficiency of kenaf plants to N uptake represents the fact that phytoremediation can be used for remediating high loads of N pollution. Therefore N uptake capacity enhanced by providing a proper balance of plant required elements. Kenaf thrive well in tropical rainforests and propagate easily by seeds and establish rapidly. Hence, they can consider as a proper alternative plant for phytoremediator grasses which not only compensate the cost of harvest but also their fiber is industrially important.

Over a two-month period kenaf seedlings fed with urea manufacturing influents in gravel-based, bench-sized subsurface constructed wetlands showed a considerable potential for removing N as high as 73% when they were supplied with up to 3 g N in solution. However, this efficiency was obtained in condition which plant growth was limited by micronutrients and P deficiency. Therefore N uptake

capacity likely can be enhanced by providing a more proper balance of elements required by the plant. Future research should investigate the relationship between N, P and micronutrients, in order to minimize the nutrient imbalances and possibly increase of N concentrations in wastewater influents.

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### **APPENDIX A**

ACCEPTABLE CONDITIONS FOR DISCHARGE OF INDUSTRIAL EFFLUENT OR MIXED EFFLUENT OF STANDARDS A AND B					
-Challed and	Parameter	Umt	Standard		
			A	В	
	(1)	(2)	(3)	(4)	
(1)	Temperature	°C	40	40	
(11)	pH Value		6.0-9.0	5.5.9.0	
(iii)	BOD, at 20°C	mg/L	20	50	
(m)	Suspended Solids	me/L	50	100	
(*)	Mercury	mg/L	0.005	0.05	
(vi)	Cadmum	mg/L	0.01	0.02	
(711)	Chromium, Hexavalent	mg/L	0.05	0.05	
(vm)	Chromium, Trivalent	mg/L	0.20	10	
(ix)	Arsenic	mg/L	0.05	0.10	
(x)	Cyanide	mg/L	0.05	0.10	
(XI)	Lead	mg/L	0 10	0.5	
(xii)	Copper	mg/L	0.20	1.0	
(1111)	Manganese	mg/L	0,20	1.0	
(XIV)	Nickel	mo/L	0.20	10	
(vz)	Tin	mg/L	0.20	1.0	
(xvi)	Zinc	mg/L	2.0	2.0	
(nvx)	Boron	mg/L	10	4.0	
(xviii)	Iron (Fe)	me/L	10	5.0	
(xix)	Silver	mg/L	0.1	1.0	
(XX)	Aluminium	mg/L	10	15	
(17.1)	Selenium	mg/L	0.02	0.5	
(xxii)	Barium	mg/L	1.0	2.0	
(xxm)	Fluoride	mg/L	2.0	5.0	
(xxiv)	Formaldehyde	mg/L	1,0	2.0	
(xxv)	Phenol	mg/L	0.001	1.0	
(xxvi)	Free Chlorine	mg/L	1.0	2.0	
(1722)	Sulphide	mg/L	0.50	0.50	
(XXVIII)	Oil and Grease	mg/L	1.0	10	
(XXIX)	Ammoniacal Nitrogen	mg/L	10	20	
(777)	Colour	ADMI*	100	200	

Standard Effluent Discharged Concentration

### **APPENDIX B**

 Random plants were chosen to observe the growths at beginning and ending of project:



Kenaf





Reed



Kenaf



Ending

Reed

2) Growth of kenaf plants at the end of project:



K1







K2



K4

3) Growth of reed plants at the end of project:



**R**1







R2



R4