REMOVAL OF POLLUTANTS IN AMMONIA RICH SYNTHETIC WASTEWATER USING MICROALGAE MEMBRANE BIOREACTOR

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ABSTRACT

An ammonia-urea fertilizer plant with 1.2 million tons of annual production capacity is to be opened in Sabah commencing in 2015. The discharge from this ammonia-urea fertilizer plant will impose a threat to Sabah's natural aquatic ecosystem. An alternative treatment for ammonia-urea fertilizer plant wastewater was researched by using microalgae to utilize the nutrient content and to provide microalgae biomass for other industrial usage. Locally isolated microalgae of *Chlorella* sp., *Scenedesmus dimorphus* and *Scnedesmus quadricauda* were compared in their nutrient removal rate. *Chlorella* sp. displayed highest performance (>55% of NH_3, >15% of PO_4^{3-}) after 3 days operation and therefore was incorporated in the microalgae membrane bioreactor treatment system. Sample with high concentration and low concentration were used and two retention time (RT) were applied (2 and 3 days RT). Results show that microalgae are preferable to low concentration (>80% of NH_3, >20% of PO_4^{3-}) compared to the high concentration wastewater feed (<30% of NH_3, <20% of PO_4^{3-}) for both RT. The highest efficiency was achieved in operation with low concentration wastewater sample in 2 days RT (81.9% of NH_3 and 25.5% of PO_4^{3-} removal). Ultrafiltration membrane was able to simultaneously remove the chemical oxygen demand (COD) (<12 mg/L for low concentration feed) and biological oxygen demand (BOD) (<5 mg/L for low concentration feed) content in the effluent. Low turbidity reading (<6 Fau) was also recorded for all permeate samples. A highest biomass growth rate of 0.512 x 106 cell/mL.day for high concentration sample in batch operation and 0.681 x 10^6 cell/mL.day for the 2 days RT with low concentration feed were attained, showing a high volume biomass production was not achieved.

ABSTRAK

PENYINGKIRAN BAHAN PENCEMAR DALAM AIR SISA SINTETIK KAYA AMMONIA MENGGUNAKAN MIKROALGA MEMBRANE BIOREAKTOR

Pembinaan sebuah kilang baja ammonia yang bakal menghasilkan 1.2 juta tan produk setahun sedang berjalan di Sabah dan dijangka akan siap pada tahun 2015. Dengan adanya kilang tersebut, ekosistem hidupan laut di Sabah akan terancam oleh sisa air buangan. Oleh itu, satu rawatan alternatif bagi merawat sisa air buangan kilang baja ammonia-urea menggunakan mikroalga bagi mengurangkan kandungan nutrien telah dijalankan. Perbandingan kadar penyingkiran nutrien tiga spesis mikroalga tempatan (Chlorella sp., Scenedesmus dimorphus dan Scnedesmus quadricauda) telah dikaji. Chlorella sp. telah menunjukkan kadar penyingkiran tertinggi (>55% bagi NH_3, >15% bagi PO_4^3) selepas 3 hari rawatan dan ianya telah digunakan dalam operasi mikroalga membrane bioreaktor. Dua sampel air buangan dan dua retention time (RT) (2 dan 3 hari) telah dikaji dalam operasi mikroalga membrane bioreaktor. Keputusan menunjukkan, kadar penyingkiran nutrien dalam penggunaan sampel berkepekatan rendah adalah lebih tinggi (>80% bagi NH_3, >20% bagi PO_4^{3-}) berbanding dengan sampel berkepekatan tinggi (<30% bagi NH_3, <20% bagi PO_4^{3-}) bagi kedua-dua RT. Kadar penyingkiran tertingggi ialah 81.9% bagi NH_3 dan 25.5% bagi PO_4^{3-} dalam operasi mikroalga membrane bioreaktor dengan sampel air buangan berkepekatan rendah dengan RT 2 hari. Membran ultrafiltration yang digunakan telah sekaligus menyingkirkan kandungan chemical oxygen demand (COD) (<12 mg/L bagi sampel berkepekatan rendah) dan biochemical oxygen demand (BOD) (<5 mg/L bagi sampel berkepekatan rendah). Bacaan kekeruhan air yang rendah (<6 Fau) juga didapati. Kadar pertumbuhan biomas tertinggi 0.512 x 10^6 cell/mL.hari telah direkodkan dalam operasi batch dan 681 x 10^6 cell/mL.hari dalam operasi mikroalga membrane bioreaktor bagi sampel berkepekatan rendah dengan RT 2 hari. Ini telah menunjukkan penghasilan biomas yang tinggi tidak dapat dicapai.

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LIST OF ABBREVIATIONS

ASEAN	Association of South-East Asian Nations
BOD	Biochemical oxygen demand
BOD_5	5 days Biochemical oxygen demand
C.	*Chlorella*
COD	Chemical oxygen demand
Conc.	Concentration
DOE	Department of Environment
EQA	Environmental Quality Act
RT	Hydraulic retention time
MBR	Membrane bioreactor
MF	Microfiltration membrane
N:P	Nitrogen to phosphorus ratio
OD_{680}	Optical density at 680 nanometer wavelength
PETRONAS	Petroliam Nasional Berhad
S.	*Scnedesmus*
Sdn. Bhd.	Sendirian Berhad
sp.	Species
TMP	Transmembrane pressure
TSS	Total Suspended Solids
UF	Ultrafiltration membrane

LIST OF SYMBOLS

µm	micrometer
cell/mL	cell per mililiter
CO_2	Carbon dioxide
h	hour
kDa	Kilo Dalton
L	Liter
Mpa	Megapascal
mg/L	milligram per liter
W/m^3	Watt per meter cube
N	Nitrogen
P	Phosphorus
H_2O	Water
NH_3	Ammonia
NH_4	Ammonium
NO_3-	Nitrate
NO_2-	Nitrate
PO_4^{3-}	Phosphate
NaOH	Sodium Hydroxide
NaClO	Sodium Hypochlorite
Na_2HPO_4	Disodium phosphate
$CaCl_2$	Calcium chloride
$MgSO_4.7H_2O$	magnesium sulphate heptahydrate
$Na_2HPO_4.2H_2O$	Disodium hydrogen phosphate dihydrate
$FeCl_3$	Iron (lll) chloride
KH_2PO_4	Potassium hydrogen phosphate

K_2HPO_4	Dipotassium phosphate
$CaCl_2.2H_2O$	Calcium Chloride Dihydrate
$NaNo_3$	Sodim nitrate
NaEDTA	Disodium EDTA
KOH	potassium hydroxide
$FeSO_4.7H_2O$	Ferrous Sulfate Heptahydrate
H_2SO_4	Sulphuric acid
$MnC_{l2}.4H_2O$	Manganese (ll) Chloride Tetrahydrate
$ZnSO_4.7H_2O$	Zinc Sulfate Heptahydrate
$CuSO_4.5H_2O$	Copper (ll) Sulfate Pentahydrate
$CO(NO_3)_2.6H2O$	Cobalt (II) Nitrate Hexahydrate

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CHAPTER 1

INTRODUCTION

1.1. Overview

Sabah the most eastern state of Malaysia is recognized for its natural tropical beauty, a far reaching history and its art culture. Being awarded as the most beautiful diving spot in 2009, its coral reef is best known to be the home of the largest, most varied communities of marine life on earth. Apart from the biological significance, these reefs encompass numbers of exotic islands which have become important centres reserved for marine research and conservation.

Therefore, preserving the vulnerable aquatic ecosystem of which Sabah contains, as well as to avoid depletion of natural resources and implication of unnecessary cost in the future is a fundamental goal. However, achieving this goal has become more challenging, especially with increasing human population, which arises with the demand and necessity for industrialization. Industrial development will essentially lead to industrial by-products and wastes that could potentially impose threat the environment. Among other wastes produced, industrial wastewater is one of the main contributors in water pollution.

To cater the increasing demand in food supplies, the agricultural industry requires fertilizers in good amount and quality. This necessity has called for more fertilizer plants to be constructed in order to cater the escalated demand, not only within Malaysia, but also in the neighbouring countries. However, concerns from these plants in the form of pollution are significant especially the wastewater discharge. In every ton of produced urea, 0.3 tons of wastewater will be formed (Rahimpour *et al.,* 2010a) and it may contain 2-9 wt. % ammonia, 0.8-6 wt. % carbon dioxide and 0.3-1.5 wt. % urea (Ljubica *et al.*, 2010; Rahimpour *et al.*, 2010a). Therefore the fate of Malaysian waterbodies is at stake as the discharge of effluent from the plant is a definite consequence. An efficient wastewater treatment

shall be implemented in order to avoid discharge of polluted wastewater that may endanger the beauty and diversity Malaysian waterbodies.

Over the years, the wastewater treatment sector has been researching and developing various technologies in order to serve the increasing demand in wastewater treatment and to optimize cost of operation. As discussed in several literature, the treatment of wastewater containing high amount of nutrients (urea and ammonia) can be done by biological and chemical means which by using nitrification and denitrification or stripping of ammonia by using hydrolysis. Another method that is vigorously being researched into and highly potential is by using microalgae.

Microalgae and its benefits have been explored all over the world and have been recorded to present significant contributions in many industries. As a photosynthetic microorganism, microalgae has seen to contribute to the production of biofuel, wastewater treatment by nutrient removal primarily nitrogen and phosphorus (Richmond, 2004), removal of CO_2 from industrial flue gas (Yun *et al.,* 1997) and production of other consumer products such as food and food supplements (Harun *et al.,* 2010). Even though nutrient removal can be accomplished via other processes as mentioned in the previous paragraph (biological and chemical), microalgae are able to serve the same objective in a lower net cost by dual objectives in a single cultivation. In cultivation of microalgae in nutrient rich wastewater, the nutrients become feed for the algae, which can become either source of biofuel, a food source for fish or livestock (Kryder, 2001) or even further processed to produce consumer products.

The purpose of this study was to determine the potential in application of microalgae in removing the nutrient content in a synthetic ammonia-urea fertilizer production wastewater as an alternative of the current application of biological and chemical treatment. The experiment combines the microalgae treatment with ultrafiltration membrane as a downstream process to separate the microalgae biomass from treated water to become a microalgae membrane bioreactor.

This project is seen as important as it can contribute to wastewater treatment process intensification for an energy efficient, shorter time and smaller treatment plant scale. This project is also able contribute for a cost minimization as the cultured microalgae can be further used for other purpose such as biofuel production and other consumer products.

1.2. Problem Statement

In fertilizer plants that produces ammonia rich wastewater, there are two common applied wastewater treatments which are using physical and biological treatment. The physical treatment is by using desorption and hydrolysis, involving the decomposition of urea into ammonia and carbon dioxide. It allows recovery of ammonia and urea (Rahimpour *et* al., 2010b; Egyptian Environmental Affairs Agency, 2002). However, the effluent from this treatment will need to be discharged to a sewage system. This is because of the effluent quality of the physical treatment is not enough to be used in utility unit or in other unit. So in order to reuse or discharge this wastewater, residual urea, ammonia and carbon dioxide must be removed (Rahimpour *et al.,* 2010a).

On the other hand, the biological treatment is by using bacterial degradation based on three steps ammoniafication, nitrification and denitrification (Metcalf and Eddy, 2003; Setiadi *et al.,* 1995). This treatment is able to remove almost all of the ammonia content. However, besides the large area and a longtime requirement for the treatment, the aeration cost is very high as the treatment works best in an aerobic condition. Post treatment sludge management is also required and will impose an extra cost for this type of treatment (Singh and Thomas, 2012).

1.3. Objectives

The objective of this project is to investigate the efficiency of the microalgae membrane bioreactor in treatment of wastewater derived from the production of ammonia-urea fertilizer as an alternative of biological and chemical treatment. The specific objectives of the project are;

i. To identify which microalgae species (*Chlorella* sp., *Scenedesmus quadriqauda*, *Scenedesmus dimorphus*) that has the most efficiency in nutrient removal (NH_3 and PO_4^{3-}) in synthetic ammonia rich wastewater;

ii. To identify the percentage of nutrient removal by microalgae membrane bioreactor in different concentration of nutrient and short retention time (2 and 3 RT);

iii. To determine the effectiveness of membrane filtration unit as solid-liquid separation method for microalgae; and

iv. To identify the potential of using a microalgae membrane bioreactor for dual application of wastewater treatment and microalgae culturing.

1.4. Scope of Study

The efficiency of three microalgae species i.e *Chrollera* sp., *Scenedesmus quadricauda* and *Scenedesmus dimorphus* to remove pollutants from ammonia rich synthetic wastewater was studied in a laboratory scale batch reactor. The percentage removal of ammoniacal nitrogen (NH_3), phosphate (PO_4^{3-}), chemical oxygen demand (COD), biochemical oxygen demand (BOD) and turbidity by each of microalgae species were measured and compared. The species with highest removal rate was incorporated in batch and microalgae membrane bioreactor operation for semi-batch operation. Two different concentrations of the synthetic wastewater were used to study the reaction of microalgae wastewater treatment in different concentration. To determine the potential of using microalgae membrane bioreactor system in a short period, two short retention (RT) time were applied, 2 and 3 days RT. A commercial ultrafiltration membrane with 50kDa molecular cutoff was used to remove microalgae biomass from the treated water to produce clean permeate. The microalgae biomass concentration was also monitored to investigate the potential of dual application of wastewater treatment and microalgae cultivation.

1.5. Thesis Organization

Chapter 1 starts off with a basic overview of the problem of wastewater treatment, especially in the fertilizer industry sector and the potential of using microalgae for treatment. This chapter also covers the problem statement, objectives and scope of work for this study.

Chapter 2 presents the literature review of the ammonia-urea production wastewater and the regulations stated in Malaysia for wastewater discharge. The chapter also explains the nature of microalgae, the nutrient removal by microalgae, cultivation techniques and factors affecting microalgae growth and downstream processing of microalgae cultivation. Finally, the chapter covers the membrane filtration that will be used as the harvesting method in the project.

Chapter 3 presents the materials and methodologies used in conducting the investigation of feasibility in using microalgae as the medium for wastewater treatment that was conducted in a laboratory scale.

Chapter 4 encloses the data obtained during experimental operation followed by the discussion of the efficiency and feasibility of the treatment system.

Finally, Chapter 5, conclude the performance and applicability in utilizing microalgae in treatment of ammonia-urea production wastewater. The chapter also concludes of the performance of the entire treatment system as a semi-batch wastewater treatment to be utilized in the industrial scale.