TREATMENT OF LEACHATE SAMPLE FROM KOK BEDOLLAH DUMPSITE USING *Scirpus validus*

by

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DECLARATION

I declare that this thesis entitled "treatment of leachate sample from Kok Bedollah dumpsite using *scirpus validus*" is the result of my own research except as cited in the references. The thesis has not been accepted for any degree and is not concurrently submitted in candidature of any other degree.

Signature : ________________________________

Name : ________________________________

Date : ________________________________

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LIST OF ABBREVIATIONS

COD	Chemical oxygen demand
BOD	Biological oxygen demand
DO	Dissolve oxygen
AN	Ammoniacal nitrogen
mg/l	Milligram per liter
HMs	Heavy metals
CERLIS	Comprehensive Environmental Response Compensation Liability Information System
HDPE	High Density Polyethylene
HR	High range
Ni	Nickel
Zn	Zinc
Cu	Copper
MSW	Municipal Solid Waste

Treatment Of Leachate Sample From Kok Bedollah Dumpsite By Using *Scirpus validus*

ABSTRACT

Phytoremediation is well established in treatment method to overcome the pollution in water, air and soil. Therefore, the alternative remediation can make cost-effective and green. Nowadays, phytoremediation treatment can use any significant plant either using trees or grassland. The mechanisms such rhizofiltration, phytoextraction, phytostabilization, phytovolatilization and phtodegradation are discussed. Ex-situ treatment are the method of application are described in this treatment. *Scirpus validus,* grass-like plant is the plant from scirpus family is used for this treatment in order to measure the parameter for wastewater leachate. This plant is a fresh water plant where it can be found at wetland, shallow water, lake side and wet meadows. For this aims, concetration of physicochemical parameter of wastewater (COD, BOD_5 and AN) are determined in raw leachate and th reduction rate of COD, BOD_5 and AN concentration after being treated with *scirpus validus*. This experiment is conducted for 15 days and the removal efficiency are analysed. This calculation of the removal efficiency shows that 11.20% of rmoving efficiency for COD, 30.90% for BOD_5 and 8.70% for AN. All of this parameters shows the reduction in concentration after being treated with *scirpus validus.*

Rawatan Sampel air sampah dari Tapak Pelupusan Sampah Kok Bedollah Dengan Menggunakan *Scirpus validus*

ABSTRAK

Fitopemulihan sangat berkesan dalam kaedah rawatan untuk mengatasi pencemaran di dalam air, udara dan tanah. Oleh itu, pemulihan alternatif ini boleh memberi kos efektif dan "hijau". Pada masa kini, rawatan fitopemulihan boleh dan mudah diaplikasikan pada mana-mana tumbuhan yang bersesuaian sama ada menggunakan pokok-pokok atau padang rumput. Mekanisme rhizofiltration itu adalah terdiri daripada *phytoextraction*, *phytostabilization*, *phytovolatilization* dan *phtodegradation* yang mana ia turut dibincangkan dalam kaedah fitopemuliharaan ini. Rawatan Ex-situ adalah kaedah yang diaplikasikan dalam fitopemuliharaan kali ini. *Scirpus validus* yang merupakan tumbuhan seperti rumput ini adalah tumbuhan yang berasal dari keluarga Scirpus yang digunakan untuk rawatan ini dalam usaha mengukur parameter untuk sisa air sampah. Tumbuhan ini adalah tumbuhan air tawar di mana ia boleh didapati di kawasan paya, kawasan air cetek, pinggiran tasik dan padang rumput basah. Kajian ini adalah bertujuan untuk mengukur kosentrasi parameter fizikal kimia air sisa (COD, BOD_5 dan AN) ditentukan dalam larut resapan mentah dan kadar pengurangan COD, BOD_5 dan kepekatan AN selepas dirawat dengan tumbuhan *scirpus validus*. Eksperimen ini dijalankan selama 15 hari dan kecekapan penyingkiran dianalisis. Pengiraan kecekapan penyingkiran menunjukkan bahawa 11.20% daripada pembuangan kecekapan untuk parameter COD, 30.90% bagi BOD_5 dan 8.70% bagi AN. Semua parameter ini menunjukkan keupayaan pengurangan kepekatan parameter yang diukur selepas dirawat dengan tumbuhan *scirpus validus.*

CHAPTER 1

INTRODUCTION

1.0 Background of study

The study of remediation technology is widely discussed nowadays in order to overcome or treat the contamination occur that contaminated the soil, water or even air. There are some examples of remediation technologies such microbial remediation and phytoremediation where microbial remediation is about microbs as the agent while phytoremediation is about the plants act as the agent.The increasing of antrophogenic activities and industrialization sectors increased the concentration of heavy metals (HMs) that exposed to the environment thus created various side effects to the human as well. Metallic elements with atomic is more than 63.5 g per mol is defined as heavy metals. The relation of human health to environment by the food chain as well as the environment health. This is due to sources of food that are come from environment such vegetables and meats from agriculture sector and drinking water from groundwater sources. When the plants is affected by the heavy metals consumed by the herbivors, the food enter to the food chain. Biomagnification of the heavy metals will be more toxic when consumed by the human because digestive system of human is not as same to animals. Therefore the needed of control the human activities that can contribute to release heavy metals to the environment and cleaning up the contaminated soil and water is recommended.

In this study, phytoremediation for remediation technology is used to treat the leachate from open dumping site. Phytoremediation defined as the use of green plants to treat the contaminated area from polluted the environment without harming (Raskin & Ensley, 1999). Phytoremediation as an old “new” technology that uses potential of higher plants remove, degrade, metabolize, immobilize, volatilize and vaporize soluble toxic substances from the soil, water or air through their natural plant systems (Nikolić & Stevović, 2015). This process takes place in the plants itself from the roots until the shoots. Generally, phytoremediation is well known as cost-effective green treatment method. This remediation technology is considered an economical and environmentally friendly method to extract heavy metal from contaminated soil (Wan *et al.*, 2015). The selection treatment of soil using various of remediation technique nowadays is needed to choose wisely in order to reduce the risk of unforeseen cost and minimising the overall reclamation cost to meet the sustainability concept (Day *et al.*, 1997). The use of plants that act as metal-accumulating plants can make the process is relatively cost-effective. Recently, there is a lot of researcher conducting this remediation method.

In this study, it is carried out in Tumpat, Kelantan at Kampung Kok Bedollah dumpsite under District Council of Tumpat located at (N06.19458^{o} , E102.13444^{o}) in geographical system. In this present study, *scirpus validus* choosen as the plant that are going to be use as a remediator. Plants provide renewable medium for microbial growth and a matrix to tyain solids. Root-induced changes can be many where can be changes in rhizosphere dissolve oxygen, pH and molecular weight. (Achintya N. Bezbaruah, 2004) .

Scirpus validus also called great bulrush. Great bulrush can growth into large colonies in muddy area or shallow water level area. Soil moisture is wet-wet mesic and the type of soil that suitable such clay, loam, peat and sand. The effectiveness of *scirpus validus* to treat the leachate from open dumpsite is measured based on a few of parameters in water quality . Chemical oxygen demand (COD), biological oxygen demand (BOD) and also the ammoniacal nitrogen (AN) are the parameters to be measured.

1.1 Problem statement

Water pollution can cause various health problems as the water is very important in our daily life such for drinking, cooking, washing and bathing. One of the factor is the uncontrolled and untreated leachate from dumpsite area. Leachate can cause the changes of water quality as the chemical content is mixed with clean water. Phytoremediation with “green” technology is applied to the leachate from open dumpsite in Tumpat, Kelantan in order to treat the leachate wastewater. There are many remediation techniques such microbe technique, soil washing, soil flushing and others but this research will evaluate the effectiveness treatment of the implementation from the plant sources technique. High cost for waste treatment make phytoremediation technology rised up on demand and widely chosen in order to save cost and make cost-efficiency. Therefore, potential of *scirpus validus* plants for remediation is evaluated to treat the leachate sample from open dumpsite.

1.2 Research objectives are:

i. To determine the concentration of chemical oxygen demand (COD), biological oxygen demand (BOD) and ammoniacal nitrogen (AN) in raw leachate.

ii. To determine reduction rate of concentration chemical oxygen demand (COD), biological oxygen demand (BOD) and ammoniacal nitrogen (AN) in leachate after being treated with *scirpus validus*.

1.3 Significance of study

By doing this research, it will be able to trace the amount of concentration of ammoniacal nitrogen (AN), chemical oxygen demand (COD) and biological oxygen demand (BOD) of leachate treatment from *scirpus validus* that will be conducted soon. The rate of reduction of these parameter will be tabulated and determined after a period. Then, the results of changes in concentration within a period will show how far the effectiveness of this plant act as an agent in phytoremediation process. Other than that, it will able to prove that phytoremediation method is the best technique among other remediation's techniques that can give mutual benefit for both biological and economics aspect.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction to phytoremediation

A wide range of inorganic and organic compounds cause contamination, these include heavy metals, combustible and putriscible substances, hazardous wastes, explosives and petroleum products. Major component of inorganic contaminates are heavy metals they present a different problem than organic contaminants. Soil microorganisms can degrade organic contaminants, while metals need immobilisation or physical removal. Although many metals are essential, all metals are toxic at higher concentrations, because they cause oxidative stress by formation of free radicals. Another reason why metals may be toxic is that they can replace essential metals in pigments or enzymes disrupting their function. Thus, metals render the land unsuitable for plant growth and destroy the biodiversity.

Since the dawn of the Industrial Revolution, mankind has been introducing numerous hazardous compounds into the environment at an exponential rate. These hazardous pollutants consist of a variety of organic compounds and heavy metals, which pose serious risks to human health. Heavy metals are primarily a concern because they cannot be destroyed by degradation. Frequently, the remediation of contaminated soils, groundwater and surface water requires the removal of toxic metals from contaminated areas.

Eventhough several regulatory steps have been implemented to reduce or restrict the release of pollutants in the soil, water or air, they are not sufficient for checking the contamination. Metal contaminated soil and water can be remediated by chemical, physical and biological techniques. These can be grouped into two categories which are ex-situ method and in-situ method. Ex-situ method requires the removal of contaminated soil for the treatment on or of site and returning the treated soil to the resorted site. The conventional ex-situ methods applied for remediating the polluted soils relies on excavation, detoxification and/or destruction of contaminant physically or chemically, as a result the contaminant undergo stabilisation, solidification, immobilisation, incineration or destruction whereby in-situ method is different. In-situ method is a remediation without excavation of contaminated site.

Based on Reed (2000) defined in-situ remediation technologies as destruction or transformation of the contaminant, immobilisation to reduce bioavailability and separation of the contaminant from the bulk soil. In-situ techniques are favoured over the ex-situ techniques due to their low cost and reduced impact on the ecosystem. The generic term 'Phytoremediation' consists of the Greek prefix phyto (plant), attached to the Latin root remedium (to correct or remove an evil). This technology can be applied to both organic and inorganic pollutants present in soil (solid substrate), water (liquid substrate) or the air.

Industrial revolution created "Green Revolution" in the field of innovation cleanup technologies. There are a number of conventional remediation technologies which are employed to remediate environmental contamination with heavy metals such as solidification, soil washing and permeable barriers. But a majority of these technologies are costly to implement and cause further disturbance to the already damaged environment. Phytoremediation is evolving as a cost-effective alternative to high-energy, high-cost conventional methods.

Actually phytoremediation is not the new created technology in 21th century but this concept has been implemented for the past 300 years on waste water discharge (Henry, 2000). Phytoremediation has the potential to clean an estimated 30,000 contaminated waste sites throughout the US according to the EPA's Comprehensive Environmental Response Compensation Liability Information System (CERCLIS) and sites included in this estimate are those that have either been owned or contaminated by battery manufacturers, electroplating, metal finishing, and mining companies (Cheek, 1989). Also included in the estimate are producers of solvents, coated glass, paints, leather, and chemicals. The foundation of phytoremediation is built upon the microbial community, and the contaminated soil or water environment.

Complex biological, physical, and chemical interactions that occur within the soil allow for the remediation of contaminated sites. The major importance is the interaction that takes place in the soil adjacent to the roots, called the rhizosphere. It has been shown that the rhizosphere contains 10-100 times the number of microorganisms per gram than unvegetated soil.

Plants exudate from their roots a variety of organic compounds that support the microbial community and facilitate the uptake of some metals.

2.2 Mechanisms used for the phytoremediation in remediate contaminant

2.2.1 Rhizofiltration

Rhizofiltration is defined as the use of plants, both terrestrial and aquatic to absorb, concentrate, and precipitate contaminants from polluted aqueous sources with low contaminant concentration in their roots. Other definition of rhizofiltration is the technique of utilizing plant roots to absorb, concentrate and precipitate toxic metals from contaminated ground water or polluted effluents (Rawat, 2012). Rhizofiltration can partially treat industrial discharge, agricultural runoff, or acid mine drainage. It can be used for lead, cadmium, copper, nickel, zinc and chromium, which are primarily retained with in the roots. Rhizofiltration mechanism have been proved its potential not only absorb the common heavy metal but can remove uranium from culture medium. Roots many hydroponically grown terrestrial plant such Indian mustard and sunflower (Susan Eapen, 2003).

Rhizofiltration is primarily used to remediate extracted groundwater, surface water, and wastewater with low contaminant concentrations. It is defined as the use of plants, both terrestrial and aquatic, to absorb, concentrate, and precipitate contaminants from polluted aqueous sources in their roots. Rhizofiltration can be used for Pb, Cd, Cu, Ni, Zn, and Cr, which are primarily retained within the root. Sunflower, Indian mustard, tobacco, rye, spinach, and corn have been studied for their ability to remove lead from water, with sunflower having the greatest ability. In one study, after only one hour of treatment, sunflowers reduced lead concentrations significantly. Indian mustard has a bioaccumulation coefficient of 563 for lead and has also proven to be effective in removing a wide concentration range of lead (4 mg/ L-500 mg/L). The advantages associated with rhizofiltration are the ability to use both terrestrial and aquatic plants for either in-situ or ex-situ applications. Another advantage is that contaminants do not have to be translocated to the shoots. Thus, species other than hyperaccumulators may be used.

Terrestrial plants are preferred because they have a fibrous and much longer root system, increasing the amount of root area. Disadvantages and limitations include the constant need to adjust pH, plants may first need to be grown in a greenhouse or nursery, there is periodic harvesting and plant disposal tank design must be well engineered and a good understanding of the chemical speciation or interactions is needed. The cost of remediation by rhizofiltration has been estimated to be $2-$6 per 1000 gallons of water. Rhizofiltration is the combination of phytoextraction and phytostabilization. This process refers to the absorption, concentration and precipitation of contaminates from polluted water in plants'roots. Absorbed and concentrated contaminantsplants precipitate as carbonates and phosphates.

It was observed that besides metals, rhizofiltration is suitable to remove organics such as tetrachloroethane, trichloroethylene, metachlor, atrazine, nitrotoluenesanilines, dioxins and various petroleum hydrocarbons (Nikolić, 2015). Since the advantages of rhizofiltration include in-situ or ex-situ plant applications, both terrestrial and aquatic plants other than hyper-accumulators may be used. Because of the fibrous and much longer root systems, terrestrial plants are more suitable for the rhizofiltration application.

Rhizofiltration disadvantages include periodical harvest and disposal of plants included in the process. Rhizofiltrationis suitable to clean contaminated water such as groundwater or waste stream

2.2.2 Phytostabilization

Phytostabilisation is mostly used for the remediation of soil, sediment and sludges and depends on roots ability to limit contaminant mobility and bioavalability in the soil. Phytostabilization can occur through the sorption, precipitation, complexaction, or metal valence reduction. Commonly, in situ metal immobilization can be used in combination with phytostabilization approaches. Sorption or precipitation reactions induced by the soil amendments decrease the concentration of contaminant mobile pools in the amended soil. A reduction in the plant available metal fraction allows revegetation and ecosystem restoration on heavily contaminated sites. The vegetation reduces or even prevents the dispersion of the contamination through wind and water erosion, and improves the aesthetic value of formerly bare areas (Ruttens et al., 2006).

The main role of plants in this technology is to immobilize contaminants in the soil and groundwater through accumulation and adsorption on roots or precipitation within the root zone (rhizo-sphere) (Mirza et al., 2014). The main purpose of phytostabilization is sequestration of pollutants in the soil near the roots, but not in the plant tissues. Through this process contaminantsare immobilized in the soil, prevented from migration to the groundwater, their bio-availability into the food chain is reduced (Sharmaand Pandey,2014) and the disposal of biomass is not required (Gill,2014). However, the short coming of this method is that contaminants remain in the soil, and their regular monitoring is necessary.

Phytostabilization, also referred to as in-place inactivation, is primarily used for the remediation of soil, sediment, and sludges. It is the use of plant roots to limit contaminant mobility and bioavailability in the soil. The plants primary purposes are to decrease the amount of water percolating through the soil matrix, which may result in the formation of a hazardous leachate, act as a barrier to prevent direct contact with the contaminated soil and prevent soil erosion and the distribution of the toxic metal to other areas. Phytostabilization can occur through the sorption, precipitation, complexation, or metal valence reduction

2.2.3 Phytoextraction

Phytoextraction is the best approach to remove the contamination primarily from soil and isolate it, without destroying the soil structure and fertility. It is also referred asphytoaccumulation (Ghosh, 2005). The process of phytoextraction generally requires the translocation of heavy metals to the easily harvestable shoots (Kumar et. al ,1995). As the plant absorb, concentrate and precipitate toxic metals and radionuclide from contaminated soils into the biomass, it is best suited for the remediation of diffusely polluted areas, where pollutants occur only at relatively low concentration and superficially. The degree of accumulation of metals such as Ni, Zn and possibly Cu in these plants, called hyperaccumulators, often reaches 1–5% of the dry weight. This is an order of magnitude greater than concentration of these metals in non-accumulating plants growing nearby.

The suggestion that hyperaccumulating plants can be used for metal remediation was first published in the 1980s however, the very low biomass of known metal-accumulating plants, the lack of technology for their large-scale cultivation and a deficiency in understanding biological and environmental factors involved in metal hyperaccumulation prevented the development of phytoextraction for a long time. Thus, the research emphasis shifted to evaluating the metal accumulation capacity of high biomass plants that can be easily cultivated using established agronomic practices. Particular emphasis has been placed on the evaluation of shoot metal-accumulation capacity of the cultivated *Brassica* (mustard) species because of their relation to wild metal-accumulating mustards (Raskin & Ensley, 1999)

2.2.4 Phytovolatilization

Phytovolatilization is involves the use of plants to take up contaminants from the soil, transforming them into volatile form and transpiring them into the atmosphere. Phytovolatilization occurs as growing trees and other plants take up water and the organic and inorganic contaminants. Some of these contaminants can pass through the plants to the leaves and volatilise into the atmosphere at comparatively low concentrations. In phytoremediation of organics, plant metabolism contributes to the contaminant reduction by transformation, break down, stabilisation or volatilising contaminant compounds from soil and groundwater (Ghosh, 2005). In example in oxygenated gasoline impacted of groundwater, phytovolatilization processes remove a substantial quantity of gasoline oxygenates from groundwater, partly due to the high transpiration demand relative to the natural groundwater flow rate. Transpiration is believed to be the primary removal process facilitated by possible diffusion to ambient air through tissues (Arnold et. al , 2007).

2.2.5 Phytodegradation

Phytodegradation also one of the process in phytoremediation in which the breakdown of organics taken up by the plant such *Chromolaena odorata* to simpler molecules that are incorporated into the plant tissues (Ghosh, 2005). As we know, plants contain various of enzymes and this phytodegradation process use plant enzyme to breakdown and convert ammunition wastes, chlorinated solvents such as trichloroethylene and other herbicides. The enzymes are usually dehalogenases, oxygenases and reductases.

2.3 Challenges in phytoremediation treatment

Phytoremediation is an attractive option for soil heavy metals removal but it also has some challenges (Gomes, 2012):

- Needed for soil remediation is up to several years.
- Phytoextraction efficiancy of most metal hyperaccumulator plants are generally restricted by their low biomass and slow growth rate.
- Correct disposal of the polluted biomass (as dangerous waste) needed following phytoextraction.
- The accumulation capacity of some plants may be compromised and ineffective due to pests and disease attack in climate affected tropical and sub-tropical regions.
- Hard to mobilize more tightly bound fraction of metal ions from soil i.e., limited bioavailability of the contaminants in the soil.
- Must avoid the introduction of invasive plant species as hyperaccumulator which may affect the indigenous floral diversity.
- Agronomic practices and soil amendments may negatively influence the mobility of contaminants.
- Sustainable phytoremediation depends mainly on the climatic and weather conditions
- Phytoremediation is an applicable approach for sites which have low to moderate levels of metal pollution due to unsustainable plant growth in highly contaminated soils.

- Accumulated metals can be transfer into food chain incase of mishandling of biomass.

2.4 Physico-chemical and toxicology characteristics of leachate from MSW Landfill

Leachate can be any a liquid that has dissolved or entrained environmentally harmful substances that may then enter the environment. It is most commonly used in the context of land-filling of putrescible or industrial waste. The elimination of the hazard is related to the pollution of the ground and surface water. Leachate can be found as a result of the infiltration process of the precipitation at the landfill. According to the Johnson and Carlson, the factor affecting are solid waste composition, operaation the mode of a landfill, moisture, temperature and the age of the landfill. All leachate samples were found to contain high concentrations of nitrogen, mainly in the form of ammonium (NH_4 -N).

Leachates generated in the initial period of waste deposition (up to 5 years) on landfills have pH 3.7- 6.5 that reflects the presence of carboxylic acids and bicarbonateions. With time the leachates become neutral or weakly lkaline (pH 7.0-7.6). Landfills exploited for a long period of time give rise to alkaline leachates (pH 8.0-8.6). Based on Szpadt other than in the case of foreign landfills, leachates from polish. Ones usually do not show an acidic pH, even in the course of acidogenic fermentation, this being due to the high alkalinity of municipal wastes that contain ashes and slag from the combustion of stone coal and coke in household furnaces.

According to Artiola-Fortuny and Fuller over 60% of COD content in anaerobic leachates was accounted for by components with structure resembling that of humic compounds. These authors also suggested that fulvic acids are formed before humic acids. Hence, the ″ageing″ of leachates and their dilutionis accompanied by a change in the ratio of humic acids to fulvic acids from below one to above (B. Słomczyńska, 2004)

Table 2.4: Leachate analysis from some landfills in Norway and the Pacific Northwest, USA (B. Słomczyńska, 2004)

	Parameter \ Fill		Norway						USA	
			Gronmo	Brånåsdalen	Yggeseth	Isi I	Isi II	Taranrod	Cedar Hills	Kent Highland
Dry weather analysis	COD	mg O_2/l	470	1080	9425	825	110	3455	38800	3800
	BOD total	mg O_2/l	320	870	5250	590	50	2300	24500	2460
	TOC	mg C/l	100	250	1700	180	30	800		
	Total N	mg N/l	182	254	250	155	16.6	156	630	56
	NH_4-N	mg N/l	120	225	227	141	10.2	84		
	NO_3-N	mg N/l	0.04	0.01	0.04	0.02	0.79	0.68		
	Organic N [1]	mg N/l	62	29	23	14	6	71		
	Total P	mg P/l	0.6	1.7	7.7	3.3	0.1	1.6	11.3	5.9
	Suspended solids	mg/l	140	397	466	270	68	1079	310	220
	Volatile suspen. solids	mg/l	85	98	182	229	11	602	170	90
	Total solids	mg /	2960	2730	4160	3880	610	3160		
	Total volatile solids	mg/l	760	1005	2180	890	145	1670		
	pH		6.8	6.9	5.9	7.0	6.4	6.2	5.4	6.4
	Alkalinity	meq/l	30	41	39	31	6.2	21.6	130	26
	Spec. conductance	mS/cm	3310	3210	3380	3050	655	2370		
	Ca	mg Ca/l	188	198	400	173	99	218		
	Mg	mg Mg/l	66	96	54	58	13	40		
	Na	mg Na/l	462	229	206	312	34.8	197		
	K	mg K/l	200	172	187	219	21.3	214		
	Chloride	mg Cl/l	680	280	370	590	68	340		
	Sulphate	mg SO_4/l	30	10	100	37	41	100		
	Fe	mg Fe/l	67.6	78.0	234	37.7	11.5	68.9	810	245
	Zn	mg Zn/l	0.055	0.095	0.65	0.085	0.12	2.65	155.0	5.3
	Cr	mg Cr/l	0.023	0.035	0.06	0.027	0.002	0.17	1.05	0.05
	Ni	mg Ni/l	<0.1	0.02	0.03	0.015	0.005	0.12	1.20	0.10
	Cu	mg Cu/l	0.085	0.011	0.022	0.009	0.008	0.021	1.30	0.18
	Cd	mg Cd/l	0.0005	0.0001	0.0009	0.002	0.0005	0.0008	0.03	0.01
	Pb	mgPb/l	0.004	0.001	0.01	0.001	0.001	0.015	1.40	<0.1
	Co	mg Co/l	-	0.009	0.07	0.018	0.004	0.033	-	-
Wet weather analysis	COD	mg O_2/l	520	825	9730	215	145	245	9100	455
	Total N	mg N/l	155	255	305	80	12	24	172	31
	Fe	mg Fe/l	84.3	42.7	258	10.2	6.8	10.3	215	38

2.5 *Scirpus validus* plant

Scirpus validus is a rhizomatous cool season perennenial with tall dark green with triangular culms. Leaf sheats wrap the culm but blades are insignificant or absent. The stems are topped by pendolous reddish brown umbels. Thin kind of plant usually in wetland and many distributed through most of North America and in Rurasia.

According to New Moon Nurseries (2016) *scirpus validus* is unbranched perennial sedge that form dense colony from strong rhizomes. For the size, this plant are 8' tall, spongy and triangular green culms. No obvious leaf blades. Culms terminate in a 6" wide compound umbel. The umbel consists of ¼" ovoid rusty brown pubescent an scaly spikelets. Each has a single basal bract less than 3" long that appears to be an extension of the culm. The umbel rays are spreading and usually droping.

Table 2.5: *Scirpus validus* characteristics (New Moon Nursery, 2016)

CHARACTERISTICS	
Exposure	Full sun to partial shade
Attributes	Clay soil Coastal Bog Rain garden Naturalizing East-coast native Rain garden Interesting folliage
Flowering month	June to October
Attract wildlife	Songbirds Pollinators
Soil miosture preference	Wet Wet to moist
Salt tolerence	Medium
Season of interest	Spring Winter Fall Summer

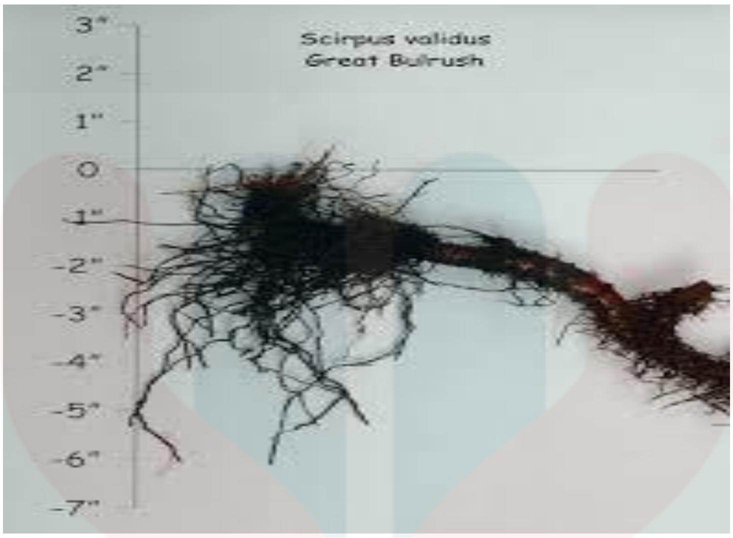


Figure 2.5: *Scirpus validus's* root

Figure 2.5.1: *Scirpus validus's* flower

2.6 Preliminary regression model for removal DOB and COD from landfill leachate.

Preliminary models for first-order rate constants for BOD and COD removal from leachate were developed. The models represent a first step to estimate BOD and COD concentrations over time for any conventional municipal solid waste landfill. Data of BOD and COD is in between time. Based o the experiment, The maximum BOD concentrations in all reactors ranged between 856 and 46,134 mg/l. These peak values were recorded within the first 100 days of the reactor operation. The maximum COD concentrations ranged between 2,458 to 64,032 mg/l. This wide range emphasizes the significance of temperature, rainfall rate, and waste composition in the MSW stabilization phase of landfills. Increasing rainfall rate and temperature leads to higher BOD and COD concentration in leachate, which translates into faster waste decomposition. The K_{COD} model suggested that paper and textile waste contributed towards COD concentration. (Bhatt & Bhatt, 2016)

2.7 Restoration of polluted waters by phytoremediation using Myriophyllum aquaticum (Vell.) Verdc., Haloragaceae

Based on the literature review, in water quality parameter, there are many thing to be monitored . There are chemical oxygen demand (COD) by colorimetry with ammonium dichromate; biochemical oxygen demand (BOD) by the Winkler method ammoniacal nitrogen (AN), and total kjeldahl nitrogen (TKN) by the Kjeldahl method. Organic nitrogen (ON) was calculated as the difference of TKN and AN.

The efficiency can be measured by calculation. Equation (1) was used to determine the removal efficiency (%) on days 15 and 30 based on the replicate averages of CG and PTG of the COD, BOD, AN, ON, TKN, and TP analyses

$$RE = \frac{(\mathrm{WC} - \mathrm{C})}{(\mathrm{WC})} \times 100$$

where:

RE = removal efficiency (%),

WC = initial value of water quality parameter (day 0)

C = value of water quality parameter on day 15 or 30.

CHAPTER 3

MATERIAL AND METHOD

3.1 Treatment Preparation

3.1.1 Collection of leachate sample

The leachate sample are collected at leachate reservoir in the dumpsite. The dumpsite is located in Tumpat, Kelantan at Kampung Kok Bedollah (N06.19458^{o} , E102.13444^{o}). The leachate sample are collected in four High Density Polyethylene (HDPE) with 10 liter each means that 40 liter in total where the amount of leachate sample is enough to fill all 15 pot.

3.1.2 Preparation of nursery

Matured s*cirpus validus* plant and its soil are taken from its original site at wet meadow and transferred to each pot respectively for ex-situ treatment. Its soil are excavated using hand-scooping about 10 cm in depth and width. The matured *scirpus validus* are chose at 20 cm of height. All plants are nursed properly to ensure they keep alive for treatment. *Scirpus validus* are placed at flat area and covered with black net to ensure there are no disrupter that can disrupt the plant growth such directly rainfall, windy weather and animals. The plants are placed in a square area for 5 meter width and 5 meter length. This area is to ensure that the samples are arranged in properly and ease to collect the leachate sample.

3.2 Treatment process

3.2.1 Number of treatment

The total amount of treatment sample are 15 where the experiment are performed in surrounding temperature. The plants are divided into 3 batch. Every 5 pot are assigned as batch where first batch, second batch and third batch. Each batch represent 5 days, 10 days and 15 days respectively. Each of pots will be analyse the amount of concentration of chemical oxygen demand (COD), biological oxygen demand (BOD) and ammoniacal nitrogen (AN) after a period. The earlier data of raw leachate are recorded before treated with *scirpus validus*.

3.2.2 Sample collection

The samples are collected with 3 consecutive times in 15 days where after 5 days treated, 10 days treated and 15 days treated. For the first 5 days, 5 pots assigned as first batch were selected and the sample of leachate from that selected pots were taken out to be analyzed. The area of each pot is divided into a quadrant (four sections) equally and the sample is taken out from each of these quadrant from the bottom side of the pot, not the surface.

The sample from each quadrant collected was mixed together to form one sample from respective pots. The same method applied to other pots in order to ensure equally distributed sample in each pot is taken. The 5 pots in the first 5 days are marked, so that the sample will not be taken from the same pot for the next and following time.

3.3 Sample analysis

3.3.1 Chemical oxygen demand (COD) analysis

COD of the treated sample will be determined using colorimeter (HACH DR 900). High range reagent is used to identify the COD. The treated leachate sample is taken for 2.0 mL using pipette and mixed up in the vial that contain high reagent sample. Preheated the DRB200 spectrometer at 150^{o}C for a few minute. The mixture is inverted gently for several times with holding by the cap over the sink. The mixed is placed into the DRB200 for two hours. As beep sound heard, the time is up and turn off the reactor. The sample is cooled for 20 minutes until the temperature dropped to 120^{o}C.

The vial is inverted upside down while it still hot then placed it at tube rack to cool to room temperature. Colorimeter is on and the programme is selected to 435 COD HR code. The blank sample is placed to get zero reading then, the sample in th vial is placed in the colorimeter after being cleaned thoroughly the oustside of the vial. The reading is appear in mg/l and recorded.

3.3.2 Ammoniacal Nitrogen (AN) analysis

Stabalize the pH of the sample to pH 7 with 5.0 N sodium hydroxide standard solution. The sample is placed in room temperature before start the analysis. The colorimeter is set up to 385 N, Ammonia, Salic. programme. Blank sample is prepared by filled in with 10ml of deionized water and 10ml treated leachate sample also filled in the second sample cell. The content of ammonia salicylate is added to both of the sample cell. The sample was shaked to dissolve the reagent and the timer is started for three minutes reaction. Ammonia Cyanurate is added after that for the same sample.

The sample is placed again into it for the 15 minutes reaction. The result appear after 15 minutes in period in mg/l. The data is recorded and tabulated.

3.3.3 Biological oxygen demand (BOD) analysis

Sample dilution water is prepared using a BOD Nutrient Buffer Pillow. Pipet is used to measure a graduated series of at least four, but probably five or six portions of well-mixed sample and transfer to separate, glass-stoppered, 300-mL BOD bottles. The sample is stirred with the pipet before pipetting each portion. Separate BOD bottle is prepared with sample dilution water only. This will be the dilution water blank. Each bottle is filled to just below the lip with seeded or unseeded dilution water. When adding the water, allow it to flow slowly down the sides of the bottle to prevent bubbles from forming.

The stopper is put to the bottle and carefully for not to trap the air bubbles. The stopper is pressed with finger, then invert several times to mix. A plastic over cap was put over the lip of each bottle and the bottles are placed in chiller at 20 ±1 °C in the dark for five days. After the 5 days incubation period was completed, the dissolved oxygen content (mg/l DO remaining) was determined in each bottle. (Klein & Gibbs, 1979)

3.4 Data analysis

The data is obtained from the data tabulated. Removal effeciency (RE) is used for COD, BOD and AN to demostrate the removal efficiency during 15 days. For the removal efficiency, (%) calculation, used :

$$RE = \frac{(\mathrm{WC} - \mathrm{C})}{(\mathrm{WC})} \times 100$$

where:

RE = removal efficiency (%)

WC = initial value of water quality parameter (day 0)

C = value of water quality parameter on day 5, 15 or 30.

CHAPTER 4

RESULT AND DISCUSSION

4.1 Outline of the chapter

This chapter represents the result and discussion for efficiency of *scirpus validus* for treatment of leachate sample where the indicators are chemical oxygen demand (COD), biological oxygen demand (BOD) and ammoniacal nitrogen (AN). The leachate sample were collected from Kok Bedollah dumpsite located in Tumpat, Kelantan and analysed in laboratory after being treated by *scirpus validus* for a period of 15 days. The treatment that applied in this research is ex-situ method. The leachate sample is analyzed using colorimeter and BOD measure instrument

4.2 Physico-chemical characteristics of leachate from Kok Bedollah dumpsite

Leachate is consider as one of the wastewater where it contain of physical and chemical characteristics. Based on Table 4.1, there are some parameter that had been analyzed. For raw leachate chemical characteristics, there are biological oxygen demand (BOD), chemical oxygen demand (COD) and ammonical nitrogen (AN). The values recorded for BOD is 132 mg/l, COD is 515 mg/l and AN is 239 mg/l. The temperature and pH are considered as physical characteristics and the value of pH recorded is very acidic where 3.63. According to Kladec and Knight (1996), the abundance of macrophytes and high decomposition if organic matter able to proof low values of pH water in between 3.5 – 5.5 (Fernanda Aguiar Souza, 2013). The decline of pH value can be due to the presence of facultative bacteria which help to disintegrate waste and favour the growth of methagonic microorganism, acidogenic bacteria and another chemical content or formation due to hydrolysis and biodegradation process (Bikash, 2014).

Table 4.1: Physico-chemical characteristics of leachate

Characteristics	Values
Temperature	27.5 ºC
pH	3.63
Biological Oxygen Demand (BOD)	132 mg/l
Chemical Oxygen Demand (COD)	5I5 mg/l
Ammoniacal Nitrogen (AN)	239 mg/l

4.3 Influence of *scirpus validus* on sample leachate treatment

4.3.1 Changes concentration value in data collected

The pots are divided into 3 batch where the number of pots for each batch are 5 respectively. As shown in Table 4.3, the changes of concentration in every single parameter in first batch (FB_5) are not drastically changes compared to second batch (SB_{10}) and third batch (TB_{15}).

The plants, *scirpus validus* need to adapt to its new environment and the process of phytoremediation take place. In this remediation technology, phytopumping involved where this mechanism can be used to remove and minimize the migration of the contaminant. Phytopumping pumps large amount volume of contaminated water for transpiration process. This can reduce the amount of contaminant in water and large potential uptake (Sridhar Susarla, 2002).

Table 4.2: Data of reduction in concentration of AN, BOD and COD over 15 days

Number of pots	Parameters		
	Ammoniacal nitrogen (mg/l)	Biological oxygen demand (mg/l)	Chemical oxygen demand (mg/l)
FIRST BATCH (FB_5)			
1	237.50	130.00	513.42
2	235.70	128.40	509.49
3	238.40	131.45	514.90
4	235.90	129.18	509.86
5	238.70	130.11	513.45
SECOND BATCH (SB_{10})			
6	235.87	104.32	483.49
7	235.77	97.45	479.32
8	233.00	96.89	476.75
9	227.48	96.72	475.77
10	225.45	95.87	473.19
THIRD BATCH (TB_{15})			
11	220.70	100.78	469.76
12	218.88	90.38	460.94
13	217.35	89.89	449.87
14	214.80	87.54	445.88
15	219.87	87.51	461.14

4.4 Effect on biological oxygen demand (BOD) concentration.

Biological oxygen demand (BOD) is used to measure waste loads to treat plants, determination of plant efficiency in terms of BOD removal, control plant processes and also used to determine the effects of discharges on receiving waters. The effects of potential *scirpus validus* on the BOD in leachate wastewater in 15 days were analyzed and the results of changes are given in Figure 4.1

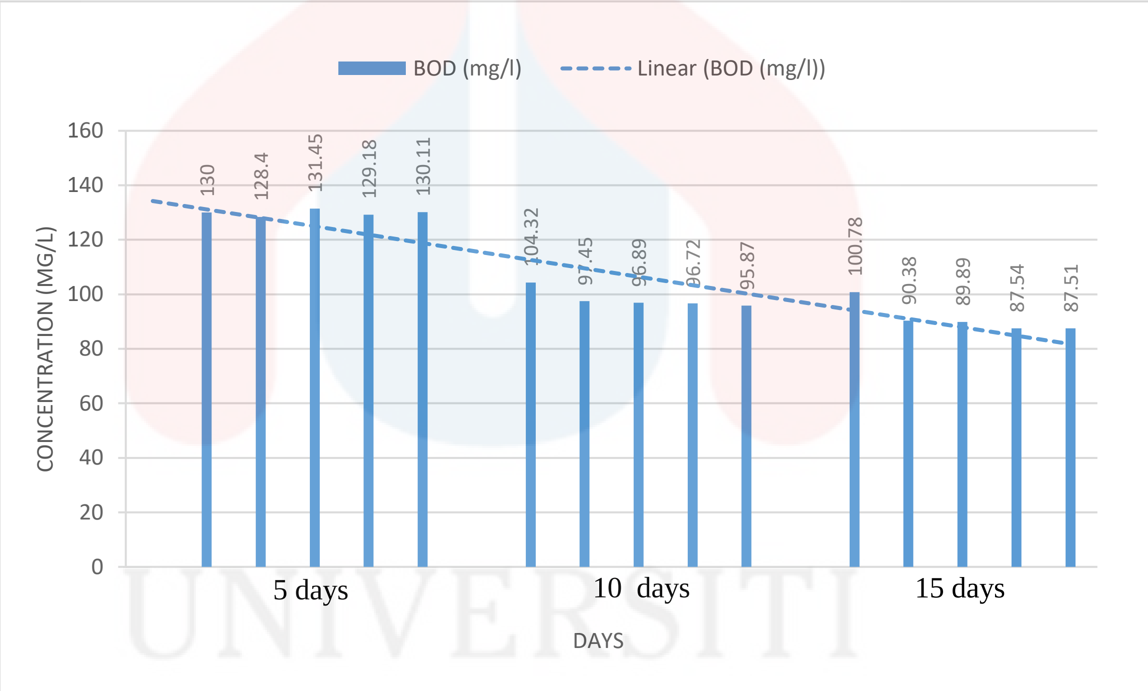


Figure 4.1: Concentration of BOD against time

For the first 5 days, the concentration of BOD in first batch are very high compared to second batch (10 days) and third batch (15 days). Five days duration are not enough to make the concentration of BOD to decrease as the plants need times to absorb, uptake and degrade the contaminant in the leachate sample. Based on Figure 4.1, for 5 days treatment, most of the result are above 120.0 mg/l. When compared to the raw leachate reading for BOD concentration, only small differences achieved about 10% of decreasing. In first batch, the highest reading of BOD concentration is recorded at pots number 3 with 131.45 mg/l and the lowest reading of BOD concentration is recorded in pot number 2 with 128.40 mg/l. In average, the results for BOD concentration in first batch is 129.83 mg/l. The reduction of BOD also due to aerobic and anaerobic process. The more anaerobic the aquatic environment, fostering the decomposition.

For the second batch, where after 10 days treatment, Figure 4.1 shows that decreasing in concentration of BOD due to phytoremediation process take place. High reading recorded at pot number 6 where 104.32 mg/l and the lowest recorded at pot number 10 where 95.87 mg/l . The average data that achieved in secod batch is 98.25 mg/l. This shows slightly decreasing from first batch to second batch about 32% decreasing. Compare to the third batch after 15 days treatment, it gives about 91.22 mg/l for average concentration. Lowest reading for BOD recorded at pot 15 where 87.51 mg/l.

Biochemical oxygen demand (BOD) as we know that the amount of the oxygen required for microbes metabolism of the organic compound in water. The BOD is similar functon to COD but COD is less specific. According to ReVelle (1988), BOD is refers to the amount of oxygen that would be a consumed if all organics in one liter of water were oxidized by bacteria and protozoa. According to the Center for Innovation Engineering and Science Education (CIESE) (2016), Biological Oxygen Demand (BOD) is a measure of the oxygen used by microorganisms to decompose this waste. If there is a large quantity of organic waste in the water supply, there will also be a lot of bacteria present working to decompose this waste. In this case, the demand for oxygen will be high (due to all the bacteria) so the BOD level will be high. As the waste is consumed or dispersed through the water, BOD levels will begin to decline. Nitrates and phosphates in a body of water can contribute to high BOD levels. Nitrates and phosphates are plant nutrients and can cause plant life and algae to grow quickly. When plants grow quickly, they also die quickly. This contributes to the organic waste in the water, which is then decomposed by bacteria. This results in a high BOD level. When BOD levels are high, dissolved oxygen (DO) levels decrease because the oxygen that is available in the water is being consumed by the bacteria. Since less dissolved oxygen is available in the water, fish and other aquatic organisms may not survive. The result that represented gives the decline of BOD concentration, but there are not really shows the efficiency of declination as expected. This must be considered the adaptation of the plants toward the soil use and the environment. Eventhough the amount of reduction is not big enough, it quite good. This plant might need a long time to remediate more.

4.5 Effect on chemical oxygen demand (COD) concentration

The chemical oxygen demand (COD) test is based on the chemical decomposition of organic and inorganic contaminants, dissolved or suspended in water. The result of a chemical oxygen demand test indicates the amount of water-dissolved oxygen (expressed as parts per million or milligrams per liter of water) that consumed by the contaminants. The higher the chemical oxygen demand, the higher the amount of pollution in the sample.

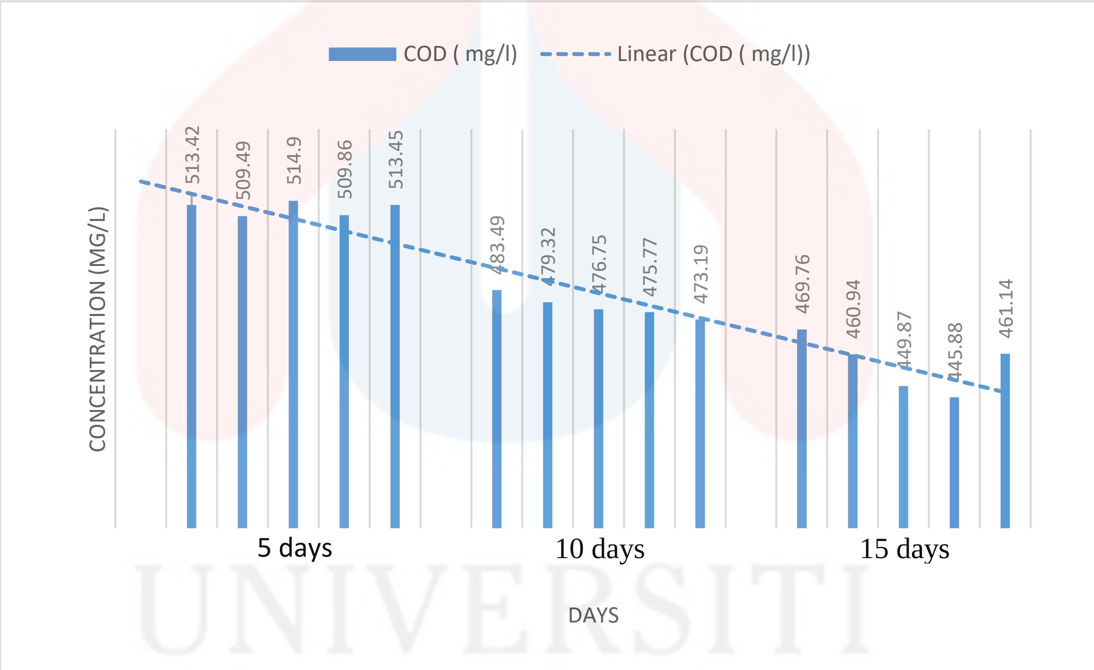


Figure 4.2: Concentration of COD against time

The first batch analyse after 5 days give out the small improvement in reduction rate. The highest reading recorded for pot number 3 with 514.90 mg/l. This means, highest number of contaminant among the others pot. Meanwhile lowest reading recorded in pot 2 where 509.49 mg/l. The average recorded for the first batch is 512.22 mg/l of COD concentration.

As shown in Figure 4.2, graph demostrate the reduction in concentration of COD starting after 5 days treatment until 15 days treatment. Compared to another batch after 10 days and 15 days, there are increasing in decline of COD concentration. The longer the time taken, the lower the concentration. For the average for second batch, it gives 477.70 mg/l meanwhile the third batch with 15 days treatment, gives out 457.52 mg/l.

There are not much differences of reduction rate between 3 batch. The factor that can contribute to the reduction of COD might be the precipitate or dissolved like the heavy metals or the suspended solid. Increasing dissolved heavy metals that come from the soil will be toxic to bacteria and inhibit the COD.

4.6 Ammoniacal nitrogen (AN) concentration

Ammoniacal nitrogen (NH_4-N) is a measure for the amount of ammonia, a toxic pollutant often found in landfill leachate. Other than that, it also can be measure the health of water in natural water bodies. Ammonia is very dangerous to human health and many human are affected especially when drinking the water. Sequencing batch reactor can lowered the level of ammoniacal nitrogen level.

Based on Table 4.2, the highest concentration of ammoniacal nitrogen recorded in pot 5 where 238.70 mg./l while the lowest reading recorded in third batch at pot 14 where 214.80 mg/l. Figure 4.6 shows that the linear line that represent the decreasing pattern of AN concentration over 15 days. Average reading recorded for the first batch is 237.25 mg/l while the second batch gives 231.51 mg/l and the third batch gives 218.32 mg/l. The process of biomass assimilation might play the significant role in the removal of ammoniacal nitrogen other than removal by the growth and the respiration process of microorganism.

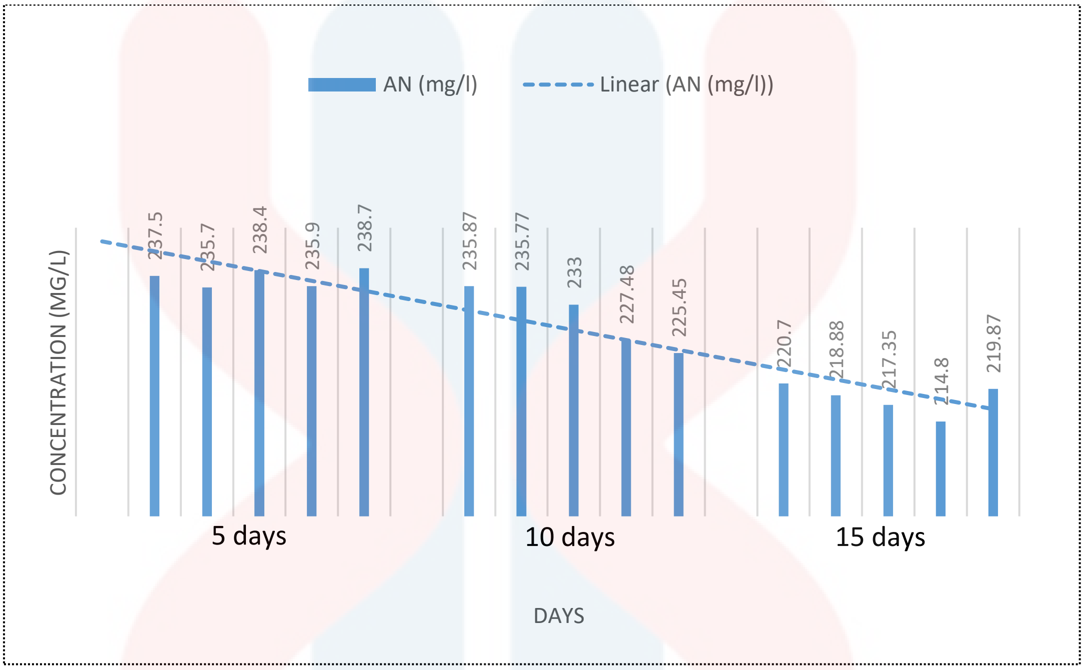


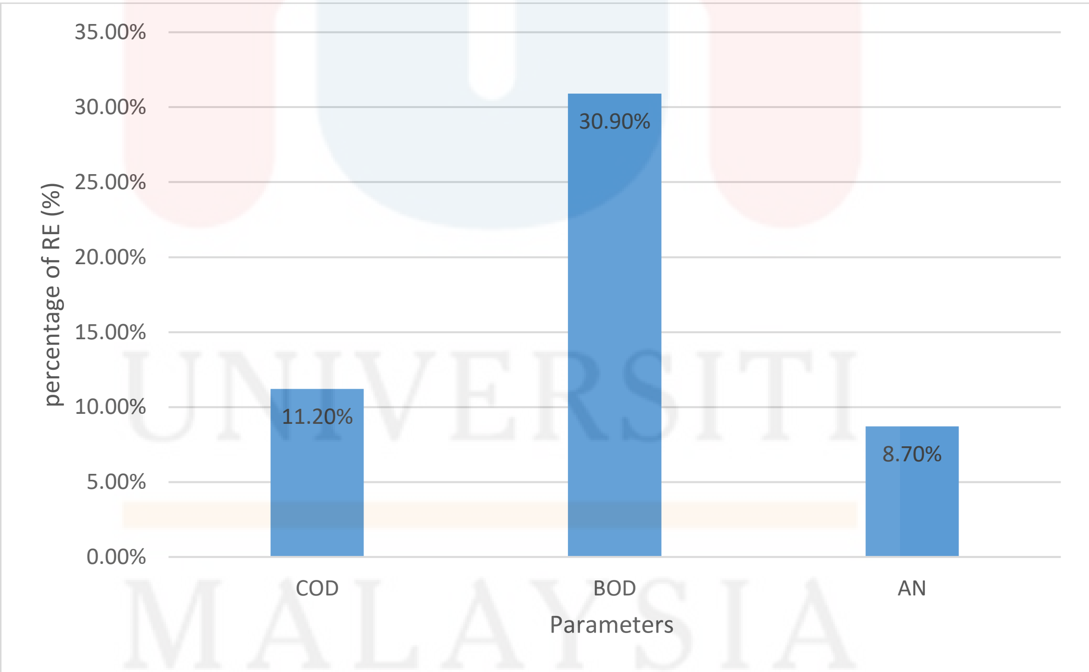
Figure 4.6: Concentration of ammoniacal nitrogen against time

The large amount of differentation in average concentration between second batch and third batch make sense. If we can see, some factor influence the amount of ammoniacal nitrogen such the decaying of plant, animal waste, agriculture ruimnoff, and also the atmospheric nitrogen. The result just now gives that the decreasing of ammoniaum level, this means, the leachate become less toxic. This gives good impression for the *scirpus validus* in order to reduce the ammoniacal nitrogen nthat can be toxic if exceed the minimal amount. Biological and chemical history of the soil treatment may be the one of the factor contribute to the variation of results. The soil and the microbs may take several days for nitrifying bacteria to gain to optimum level. Many microbial changes and adaptation occur in the soil when the first time recieving leachate. Chemicals may accumulate in the soil and influences the microbial degradation process.

4.7 Removal efficiency

Based on data collected from BOD concentration, COD concentration and AN concentration, it shows the decreasing of concentration for each of these parameters . Removal efficiency formula is used to show the percentage of removal value of each parameters. As the time increase following the phytoremediation process, the removal efficiency is corresponding increasing. Table 4.4 shows the percentage of efficiency for each parameters. the percentage of removal efficiency for BOD is higher compared to COD and AN with 30.9%. This data represent the *scirpus validus* very efficient in controlling BOD concentration rather than COD and AN. For AN, it recorded only 8.70% of removal efficiency meanwhile COD represent 11.20%

Table 4.4: Percentage of removal efficiency after 15 days



Various value of remval efficiency obtained in this studies. Generally, all the parameters in this experiment reduced from 8% - 30% by the treatment of wastewater leachate using *scirpus validus*. High removal rates that occur among the parameter may be attributed to the plant tendecies to absorb into the soil through pytoremediation mechanism.

CHAPTER 5

CONCLUSION AND RECOMMENDATION

5.1 Conclusion

Based on the result. The results showed the significant data of reduction rate in BOD_5, COD and AN after been 15 days treated. This study proved that this scirpus could be the alternative for reducing the nutrient and organic matter in leachate when applied in phytoremediation when the reduction rate is proved using removal efficiency formula. The RE for BOD is 30.9%, COD is 11.2% and AN is 8.7%. Among these three parameter, the rate of ammoniacal nitrogen was found lower compared to COD and BOD. Although, it is possible due to the properties of the soil, microbes, nitrifying bacteria to adapt the changes as a first time for the soil recieve landfill leachate. The efficiency of removal is depends on the composition of that plant and its abilities. A combination of chemical from the laechate and the biological process is likely to govern the fate of nitrogen in that system. Other than that, the external factor also influence the result such the amount of precipitation and temperature. High temperature can disrupt the microorganism activity and the properties. Preparation of nursery plays an important role in order to make them well prepared to undergo treatment. In-situ technique could be the best way rather than ex-situ method because the plant can easily adapt to the environment and the biological changes.

5.2 Recommendation

Present study recommends that preparation of nursery should be more concern for the plants to get more comprehensive results of the leachate sample. The preparation of nursery can be able for the plant to growth, strong and adapt to the new environment as ex-situ method is applied. This is due high potential of loss of soil nutrient for the plant to keep alive plus, scirpus family's plant are tall thus difficult for the researcher to bring back . Present study can be added more parameter as stated in wastewater treatment to find out more results to be discussed hence created more informations of sample. Exploration of another species is recommended thus can create more comparison of each plants in phytoremediation technology. Other than that, present study also recommended to explore data of the heavy metal that accumulated in the plant. This recommendation can be able to know how much heavy metal uptake by that plant species thus easy to know the efficienciness of each plants for the future study. For present study can be extended to find out more potential plant for phytoremediation technology.

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