

Ammoniacal Nitrogen Uptake by Macrophytes with Phytoremediation

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Review Article

Received date: 11/01/2017

Accepted date: 20/03/2017

Published date: 27/03/2017

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Keywords: Nutrient pollution, Nitrogen, Phytoremediation, Ammonia

ABSTRACT

Nutrient pollution from Nitrogen is one of the common environmental issues involving surface waters. Excess Nitrogen discharged into the environment lowers water quality, brought risks to humans, impend habitats and ecosystems, and leads to eutrophication phenomenon at the receiving waters. There are several current methods being used for the removal of the ammoniacal Nitrogen in wastewater. Presently, phytoremediation is a cheap and reliable technological solution utilized to eliminate ammoniacal nitrogen from wastewaters. Presently, phytoremediation is regarded as one of the most economically viable, sustainable and affordable technology. Phytoremediation utilized plants reduce pollutants. This paper aims to gather about ammoniacal nitrogen in wastewater sources and effects in the environment. It also describes about phytoremediation technologies, including the ammoniacal nitrogen removal mechanisms. Additionally, it discussed the factors affecting the uptake mechanisms, the advantages and disadvantages of this phytoremediation were also discussed. Some of the promising wastewaters for phytoremediation are also reported.

INTRODUCTION

Ammoniacal Nitrogen is one of the wastewater contaminant which can be found in many type of wastewater. Excessive ammoniacal Nitrogen in water body can lead to eutrophications. Eutrophications induces excessive plant and algal growth and decay and caused degradation of the water quality. This algal blooms limits light penetration. Eutrophications promote anoxia in the water body which kills fish and invertebrates and also leads to unpleasant and injurious gases.

There are several current methods being used for the removal of the ammoniacal Nitrogen in wastewater. Removing ammoniacal nitrogen through air stripping may remove 60 to 90% of the ammoniacal nitrogen, however, process requires time for pH control, hence, higher treatment cost and lime-related operating and maintenance problems. Ammoniacal Nitrogen can also be removed with Break-point chlorinations. It removes 90 to 100% of the ammoniacal Nitrogen present, however, it generates high chlorine residual and can be detrimental to the aquatic life. In addition, it requires careful control of pH to prevent the formation of nitrogen trichloride gas.

Currently, phytoremediation is regarded as one of the most economically viable, sustainable and affordable technology. Phytoremediation utilized plants-based systems and microbiological processes to reduce pollutants in nature ^[1]. It is an *in situ* remediation technologies are ecologically friendly and solar dependent clean-up technology. The economic success of phytoremediation is dependent on photosynthetic activity and the rate of growth of the plant ^[2].

Many species of macrophytes have been studied in removing Ammoniacal Nitrogen in various type of wastewater. The ammonium ions uptake by plants depends on several factors such as, sunlight, biomass, and plant type.

The objectives of this review journal is to discourse the possibility of the phytoremediation technology in remediating ammoniacal nitrogen polluted wastewater, compile some information about one of the wastewater contaminants which is ammoniacal nitrogen sources, effect and treatment. It also reviews about phytoremediation technology, with Ammoniacal

Nitrogen uptake mechanism, advantages of phytoremediation technology and factor affecting the removal mechanisms. Some recommended plant commonly used in phytoremediation and their capability to reduce Ammoniacal Nitrogen are also reported.

AMMONIACAL NITROGEN IN WASTEWATER: SOURCES AND EFFECT IN THE ENVIRONMENT

Ammonia is colourless gas and exhibits a pungent smell at ambient temperature and pressure. It is the main constituents of domestic wastewater concentrations which generally range from 10 to 50 mg/L. It is very soluble in water and in water it exists in equilibrium between ionized ammonia (NH_3) and ionized ammonia (NH_4^+) species. A number of studies indicated that total ammonia toxicity is caused by the effect of the unionized NH_3 [3]. Total ammonia is usually referred as the summation of ammonia and ammonium concentrations [4]. The ammonium ions is an important element which is needed in plants for growth.

Ammonia enters the environment due to the municipal, agricultural, industrial and also natural activities. Ammonia that enters the environment from the natural sources due to the degradation of organic waste matter, gas exchange with atmosphere, animal waste and nitrogen fixation. They are two types of sources how ammonia enters the environment which include point sources and non-point. Point source of ammonia are from the emissions and effluent from various types of industrial plants. Whereas, the non-point sources of ammonia are from agricultural, residential, municipal and atmospheric releases.

The presence of ammoniacal Nitrogen in water leads to environmental problems such as eutrophication of surface water, changes in ecosystems and acidifications. The ammoniacal nitrogen's part in aquatic eutrophication is as a source of nitrogen needed for the production of nitrates. The high concentration of nitrates and ammonia in a water body resulted in a toxic environment and may cause to oxygen deficient conditions from the nitrification process. In a severe eutrophication, a hypoxic condition creates a dead zone where no aquatic life can survive [5].

PHYTOREMEDIATION TECHNOLOGY

Phytoremediation is the utilization of plant for the *in situ* removal, degradation, or control of contaminants in soils, sludges, sediments, surface water and ground water [6]. It is a cheap, solar dependent and environmentally friendly technology in relative with the conventional contaminants cleanup technology (USEPA). The application of phytoremediation in a contaminated site is attractive due to its cost-effectiveness and brought a relatively low environmental impact [6]. Phytoremediation cover several technologies, these technologies include Phytoextraction, Rhizofiltration, phytodegradation, phytovolatilization, rhizosphere bioremediation, Uptake and metabolism of pollutants in plants.

Phytoextraction

Phytoextraction is the removal of metal with plants in the soil to the upper parts of the plants. Phytoextraction can be used to treat contaminated soils (EPA). The removal of metal contaminants is done by the plant through absorption, concentrate and precipitate to the shoots and leaves of the plant. The type of plants which have the relatively high capability is known as Hyperaccumulator. The processes of hyperaccumulation of metals by plants are usually comprised of three processes. These processes are via adsorption, transport and translocation which require large sinks to accumulate the contaminants (EPA).

The disadvantages of the phytoextraction is the plant species usually have slow growth and possess low biomass [7]. Ideal plants for phytoextraction include ability to grow outside its area of collection, fast growth, high biomass, easy harvesting and accumulation of a range of heavy metals in their harvestable parts [8].

Rhizofiltration

Rhizofiltration is typically exploited in groundwater (either *in situ* or extracted), surface water, or wastewater for removal of metals or other inorganic compounds (EPA). The Rhizofiltration process utilized plant roots to absorb, concentrate, and precipitate contaminants. Rhizofiltration decrease the mobility of contaminants and circumvent migration to ground water thus decreasing the bioavailability for access into the food chain [9].

The mechanisms of rhizofiltration are governed by the physical and biochemical impacts of plant roots in waste water treatment. The efficiency of the mechanism is influenced by the ability of the roots to produce specific metals which will cause the heavy metals to rise in plant body. In which, the plant root exudates and changes in rhizosphere, the pH surrounding the roots of the plant can potentially cause metals to precipitate onto the roots surfaces. When the roots become saturated with heavy metals contaminants, either the roots or the whole plant are harvested for disposal [9].

Phytodegradation

Phytodegradation involves the degradation of complex organic molecules to simple molecules or the combination of these molecules into plant tissues. Plants contain enzymes (complex chemical proteins) which speed up and chemical reactions. In the phytodegradation, pollutants are broken down by the enzymes and after that taken up by the plant (EPA). Phytodegradation has been successful to treat some organic contaminants, such as chlorinated solvents, herbicides, and munitions, and it can be used to remove contaminants in soil, sediment, or groundwater (EPA).

Phytovolatilization

Phytovolatilization is the plant uptake and transpiration of pollutants by the release of the pollutants or altered form of the contaminants from the plant to the atmosphere [6]. This technology involves pollutants being absorbed into the tissues of the plant as a volatile form or volatile degradation product is transpired with water vapor from the leave [10].

Mercury is one of the example which uses Phytovolatilization for remediation. Other contaminants include organic molecules (trichloroethane) and inorganic chemicals which are volatile (selenium, arsenic) (EPA). The volatilization can be induced by the use of phreatophytes species with high transpiration rates and can overcome stomatal closure through sufficient irrigation [7]. These processes transform the contaminants and convert it into a less toxic substance. However, this technology is likely to be recycled by precipitation and redeposited back into lakes and ocean (EPA).

MECHANISMS OF AMMONIACAL NITROGEN UPTAKE BY PLANT

The plant utilization of nitrogen involves few steps which include uptake, assimilation and translocation [11]. Plant take up mainly three form of nitrogen. These two form of nitrogen include nitrate ions, urea and ammonium ions. Once ammonia is present in the plant cell, it is incorporated into proteins and other organic combination through a biochemical reaction. However, only the ammonium ion is assimilated into the organic molecules in the plant tissues by enzymatic process.

The ammonium ions can be directly absorbed by plant roots or as a result of nitrate ion reduction, is further assimilated into the amide amino group of glutamine by the glutamine synthetase and subsequently into glutamic acid by the glutamate synthase. These two enzymes results in the assimilation of most of the ammonium ions [11]. The ammonium ions is toxic and not permitted to be stored in a plant. Hence, the ammonium ions is either oxidized nitrates ions, assimilated to produce amino acids or converted to amides [12].

When the plant takes up ammonium ions, it releases one hydrogen ion in the medium solutions. Over time, the uptake of the ammoniacal nitrogen will increase the hydrogen ions concentration and hence decreasing the growing medium pH. However, an increase of ammonium uptake in plants and storage will results in cell damage and will progressed to cell death [13]. The plant transformation of Nitrogen is shown in **Figure 1**.

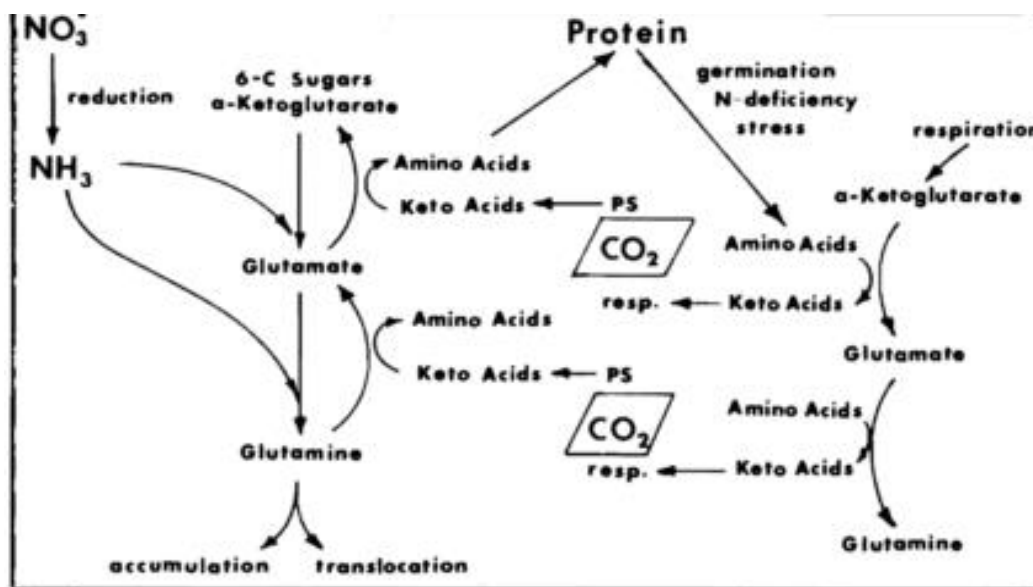


Figure 1. N-transformation in plants.

As illustrated in **Figure 1**, the excess ammonia in the plant tissues either accumulated or translocated.

The ammonium ions are taken up by the plants from root uptake. The Nitrogen uptake by the root system depends on the nitrogen demand of the entire plant and is depends on the Nitrogen requirement for growth. Nitrogen starvation of plants for several days lead to increased capacity for ammonium uptake [13].

FACTORS INFLUENCING THE AMMONIACAL REMOVAL MECHANISM

Few factors affecting the plant’s ammonium uptake mechanims as depicted in **Figure 2**. The uptake performance can be enhanced by considering these factors into account.

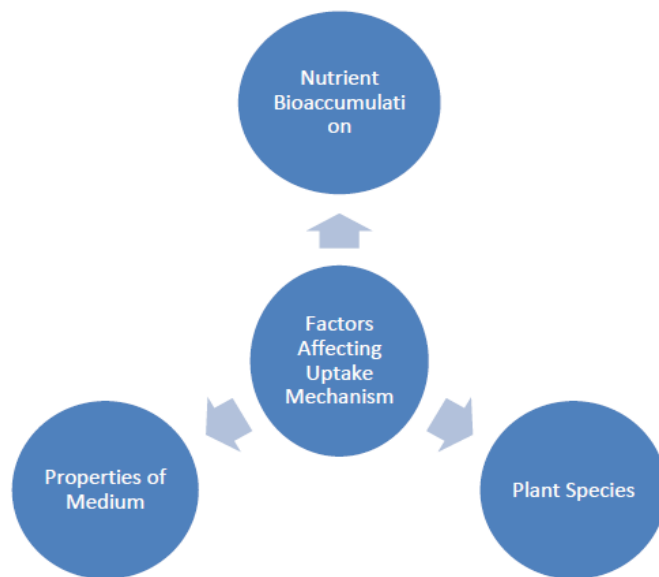


Figure 2. Factors affecting the plant's uptake mechanism.

Nutrient Bioaccumulations

Nutrient bioaccumulation by plant is the uptake of nutrient by biota. Aquatic macrophytes nutrient bioaccumulation capability is key in wastewater treatment. Capacity of the nutrient uptake is restricted to growth and the nutrients availability in the plant (Figure 3).

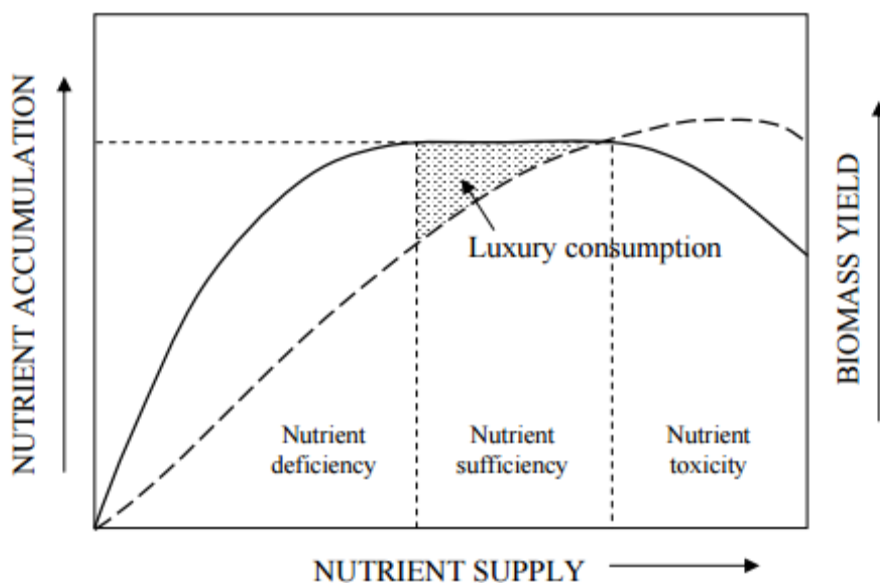


Figure 3. Nutrient supply against nutrient accumulation and biomass production.

According to Greenway [14], Nutrient content varies with the plant and age. Younger plants and leaves have more nitrogen content. However, when plant grows, the nutrient become lesser. Nevertheless, plant biomass increases with as the plant gets older. Hence, total nutrient accumulation becomes higher.

Plant Species

According to Greenway [14], the rate of ammonium uptake and the assimilation of the nutrients into the plant is key in determining the potential of macrophyte species to be utilized for phytoremediation. The generated plant can utilized as to approximate the nutrient take up by the plant. Macrophytes species with potential ammoniacal nitrogen removal potential were chosen. The rate of ammonium uptake by plants is influence by type of plant. Hence, efficiency of reduction of ammoniacal nitrogen in wastewater depends on the plant tolerance on higher ammoniacal Nitrogen concentrations, low oxygen content (caused by BOD and COD loads), high turbidity.

The following **Table 1** shows the plant species, biomass, nutrient content, and nutrient storage in several types of macrophytes.

Table 1. Nutrient storage capacity with different types of macrophytes.

Species	Period	Biomass (G/M ²) Mean + Sd	N Content (Mg N/G)	Reference
<i>Typha Orientalis</i>	12 months	4000	53.7	Greenway ^[14]
<i>Duckweed</i>	30 days	500 ± 50	-	Shah et al. ^[15]
<i>Water lettuce</i>	30 days	650 ± 50	-	Shah et al. ^[15]
<i>Water Hyacinth</i>	30 days	800 ± 50	-	Shah et al. ^[15]
<i>Phragmites Australis</i>	12 months	6700	127.0	Greenway ^[14]

EXTERNAL FACTOR

The performance of the ammonium uptake by plants is also affected by the properties of the external factors. This includes salinity and temperature.

Temperature

According to Shah et al. ^[15], temperature has a significant effect on the contaminants uptake of the aquatic macrophytes. The plants which are sensitive to temperature show no growth and pollutant removal at 10°C. **Figure 4** shows that the BOD contaminant uptake by plant is the most suitable from 15°C to 35°C for municipal wastewater treatment ^[15]. However, the optimal water temperature for the aquatic plants growth is from 28°C to 30°C. The temperature above 30°C will disrupt the growth of the aquatic plants.

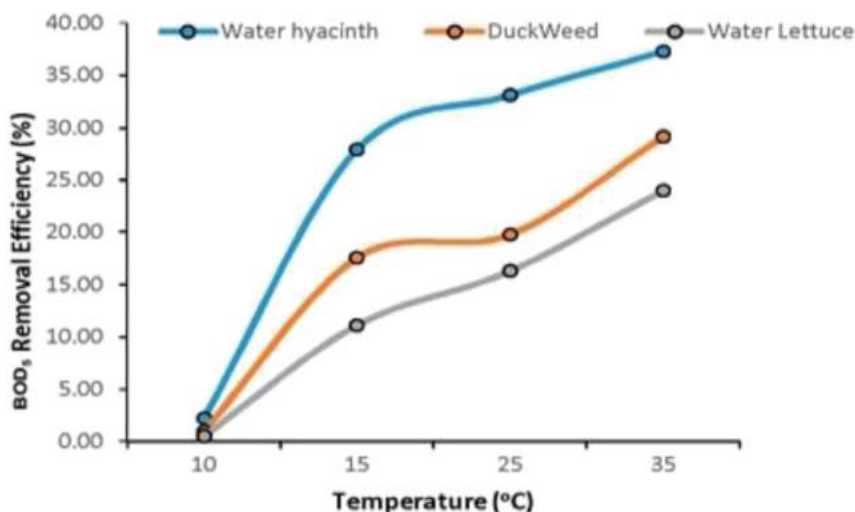


Figure 4. Effect of temperature variation on the macrophytes performance in municipal wastewater ^[15].

Salinity

Effect of salinity stress on aquatic macrophytes can greatly affect the growth and reproduction of the aquatic plant which can be seen in **Table 2**. Different types aquatic macrophytes species have different tolerance ranges as shown in **Table 2**. These effects include reduced growth and reproduction. The effects of high salinity observed in the aquatic macrophytes are leaf margin became chlorotic and twisted leaves ^[16]. According to it, the acceptance of aquatic macrophytes towards salinity will disturb the efficiency in water remediation due to the reduction of uptake of water with higher level of salt and mortality.

Table 2. Salinity tolerance of selected aquatic macrophytes.

Species	Reduction in biomass (S cm ⁻¹)	Mortality salinity (S cm ⁻¹)
<i>Eichornia Crassipes</i>	1220	3600
<i>Pistia Stratiotes</i>	2500	4900
<i>Typha domingensis</i>	4300= slight 8600=severe	22000 =75% mortality
<i>Salivina rotundifolia</i>	9800	-
<i>Phramites australis</i>	14700	33100=88% mortality (for seedlings)
<i>Lemna Minor</i>	14700	-
<i>Triglochis procera</i>	1500	10300
<i>Hydrilla Verticullata</i>	9700	14700

According to a study by Izuangbe ^[17], the remediating efficiency of the aquatic macrophytes will be affected by the salinity of the medium ^[17].

According to Eaton ^[18], the decrease in transpiration and total dry weight are the common responses of plants exposed to increasing salinities.

According to Tisdale et al. [19] terrestrial plants varies in its acceptance to salinity as shown in **Table 2**. According to this, large-leaved floating species are most vulnerable to salinity, submerged species can tolerate high level of salinity. This high salinity level prevents the plant from taking up water by reducing the osmotic pressure.

According to water lettuce and water hyacinth can be significantly affected by lower salinities around 10% and 13.32% respectively. Qin Lu [20] observed that, the water lettuce production was reduced about 30% with salinity 1766 $\mu\text{S cm}^{-1}$ and inhibited biomass production at higher salinity as founded by Pascale et al [21].

ADVANTAGES AND DISADVANTAGES OF PHYTOREMEDIATION

Phytoremediation is driven by the energy from the sun and more environmentally friendly [22]. The advantages of phytoremediation include phytoremediation treatment can be carried out *in situ* (USEPA). No Expensive equipment and highly skilled personnel is not needed. It is cost effective for large volume of wastewater with content of contaminants [23].

Phytoremediation has lower capital and operational cost. The operational cost is mainly on harvesting, disposal of contaminated plant mass and repeating the plant growth cycle [24]. Besides that, phytoremediation also indirectly enhance the nearby water quality through nutrient uptake by plants and Enhances the site landscape [24]. Last but not least, No specific design life duration is allocated for treatment wetlands [25].

The disadvantages of phytoremediation include large surface area of land is needed for the same or lower level of treatment by the conventional system [25]. Not only that, the Process dynamics is not well understood, hence, resulting in uncertainties in the design and operating factors [25] and Pest control is needed to avoid mosquitoes and other insects or pests from breeding in the system [25].

Besides that, phytoremediation with an outdoor system with large surface area is subjected to variability in efficiency due to temperature variations, wind, storm and floods [25] and the remediation with the utilization of plant is time consuming than the convelial remediation technology. Last but not least, Plants need to be tolerant of contaminants and limited by the depth of the roots [26]. **Figure 5** summarizes the advantages and disadvantages of phytoremediation.

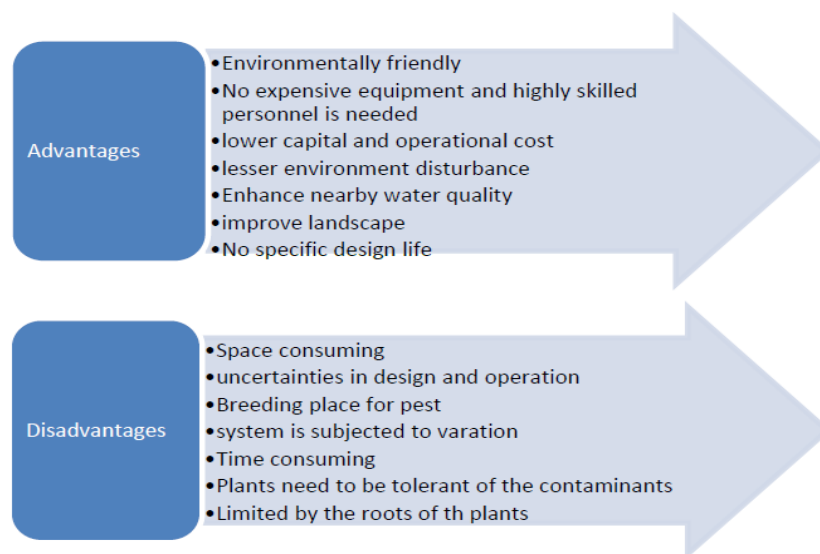


Figure 5. Advantages and disadvantages of phytoremediation.

PROMISING WASTEWATER FOR PHYTOREMEDIATION TREATMENT

Various type of study has been carried out by researchers on the phytoremediation of different types of wastewater. **Table 3** shows various type of wastewater used for phytoremediation by researchers.

According to a study Hadiyanto [27], water hyacinth is more effective in remediating palm oil mill effluent as compared to water lily. After 8 days pf remediation, the water hyacinth lowers the COD up to 50%, total nitrogen up to 88% and total phosphorus up to 64% whereas, the water lily less reduction with COD reduction of 44.51%. Total nitrogen up to 83.74% and total phosphorus up to 58%.

Karim [28] used water hyacinth system to remediate a glove factory effluent treatment and observed that highest removal efficiencies achieved for total nitrogen and ammonium nitrogen were 55% and 43%, respectively. These removals were obtained at loadings of 2.6 g total nitrogen/m²/day and 1.65 g ammonium nitrogen/m²/day.

Kutty et al. [29] observed 99% ammonia removal efficiency with plants and 68% without plants, 72% phosphorus removal and 81% nitrate removal in municipal wastewater (secondary treatment plant effluent).

Akinbile and Suffian [30] observed that water lettuce root system provides extensive surface area to promote physical, chemical and microbial processes for absorption of nutrients and nitrification processes. The phytoremediation treatment with water lettuce resulted reduction in the nutrient levels of the aquaculture wastewater. According to Akinbile and Suffian [30], to achieve efficient water purification, grown up biomass of aquatic macrophytes must be harvested from water bodies to keep an optimum plant density. The huge amount of the nutrients that have been incorporated into the plant tissue will be returned back to the water by decomposition process if not harvested.

Table 3. Various study on phytoremediation of different types of wastewater.

Type of Waste water	Wastewater Characteristics	Type of plant	Remediation Outcome	References
Palm oil mill effluent	pH: 7.5 COD: 1640 mg/L BOD: 809 mg/L TN: 97.22 mg/L TP: 8.73 mg/L	Water hyacinth and water lily	COD: 50% removal Total Nitrogen: 88% removal Phosphorus: 58% removal	Hadiyanto et al. [27]
Glove Factory effluent	pH: 7.8 COD: 2010 mg/L BOD: 1020 mg/L Ammonium Nitrogen: 100 mg/L	Water Hyacinth	BOD: 96% removal at loading rate of 17 g BOD/m ³ /day COD: 80% removal at loading rate 35 g COD/m ³ /day Ammonium Nitrogen: 55% at loading rate of 1.65 g ammonium N/m ² /day	Karim [28]
Municipal Wastewater (Secondary Treatment plant Effluent)	COD: 58 mg/L Ammonia: 12 mg/L Phosphorus: 5 mg/L Nitrate: 7 mg/L	Water Hyacinth	Ammonia: 99% ammonia removal efficiency with plants and 68% without plants. Phosphorus: 72% phosphorus removal efficiency with plants and 55% without plants Nitrate: 81% nitrate removal with plants and 75% removal without plants	Kutty et al. [29]
Aquaculture Wastewater	pH: 4-6 COD: 205 mg/L Nitrate: 30.17 mg/L	Water Lettuce	Turbidity: 92.70% reduction (non-aerated) and 93.69% reduction (aerated) COD: 53.82% reduction (non-aerated) and 56.91% (aerated) Ammonia-Nitrogen: 83.34% (non-aerated) 91.82% (aerated) Phosphate-phosphorus: 69.64% (non-aerated) and 72.82% (aerated)	Akinbile and Suffian [30]

ACKNOWLEDGMENT

The authors would like to thank Centre of Renewable Energy (Coere) Unimas for funding this research and University Malaysia Sarawak for the research facilities provided.

CONCLUSION

Ammoniacal Nitrogen reduction by plants using phytoremediation technology can be a sustainable way to remediate ammoniacal nitrogen from various types of wastewaters. It has some advantages compared with the conventional technologies. However, several factor must be taken account in to increase the efficiency of the remediation. Among the important factors affecting the efficiency of phytoremediation is the nutrient bioaccumulation, properties of medium and plant species. Although phytoremediation appears to be a good choice for sustainable technology, it also has some drawbacks. More study is needed to overcome this drawbacks in order to implement this technique effectively.

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