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The Role of Duckweeds as a Sustainable Technology for the Remediation of Water Pollution

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Abstract
Pollution is a global environmental and public health problem in modern society. Water pollution is the second leading causes of death after air pollution. Freshwater resources in Nigeria are rapidly declining as a result of municipal and industrial pollution. Industrial activities mainly from agriculture, manufacturing, chemical and paints, breweries, pulp and paper, tourism and hospitality, leather and textiles, electronics, maritime and shipping, mining of solid minerals and from the oil and gas industry are affecting rivers, streams, wetlands and coastal regions across Nigeria. Oil spill resulting from accident, poor maintenance culture, corrosion of oil facilities and sabotage have led to the degradation of the natural environment, pollution of water resources, reduction in biodiversity and significant impact on the social, economic and health of local people. Oil spill in aquatic environment results in death (lethal) of aquatic life. Even when plant and animals survive, some may fail to reproduce (sub-lethal effect) due to irreversible damage to tissues and organs leading to long-term habitat disruption. Treatments technologies using chemicals, enzymes, microbes and plants have been developed over time for the treatment of water pollution. Among the various technologies available for the treatment of water pollution, the application of duckweeds has been proven effective as a sustainable and ecological friendly solution for the removal of organic pollutants, heavy metals, agrochemicals, pharmaceuticals and hydrocarbons from the aquatic environment.

Keywords: *Water pollution; Duckweed; Remediation; Heavy metals; Agrochemicals; Pharmaceuticals; Petroleum hydrocarbons*

1. Introduction

Water is very essential and priceless natural resources to life and human society. Apart from air, it is the second most crucial component needed by all living organisms. Water makeup 71% of the Earth, with about 97.5% as saltwater and only 2.5% is freshwater. About 69% of the freshwater is frozen in polar ice caps and in glaciers, while about 30% is below ground as groundwater. Only about 1.2% is available as surface waters in rivers, streams, lakes, wetlands, swamps, springs, etc (USGS, 2016). In Nigeria, the eight major rivers make up about 11.5% of the total surface area, which is approximately 10,812,400 hectares (Ita, 1993). Apart from the Lake Chad basin, all other basin system drains into the Atlantic Ocean, especially in the Niger Delta region. As the world population increases, there will be more demands for the use of freshwater resources. As of 2000, the human population was estimated to be about 6.2 billion. The United Nations projected that by 2050, an additional 3.5 billion people will be born into the earth making the world population about 9.1 billion with most of the growth coming from developing countries with water resources challenges (United Nations, 2005). The increase in population will lead to increased demand for water resources and increasing shortage of water-stressed regions. In 2025, water shortage is expected to be more pronounced in low income economies where resources are scarce and population growth is expanding, such as the Middle East, Africa, and parts of Asia. The *Freshwater Strategy 2017-2021* report by the United Nations Environment stressed the need to meet the strategic targets related to global water quality enlisted in the sustainable development goals for the effective management of freshwater resources for modern society (United Nations, 2017). Failing to meet these targets would create a critical challenge for meeting the water needs of the human population especially in developing countries as we move into the future.

2. Environmental and economic burden of water pollution

Pollution is a global environmental and public health problem in modern society. According to a recent publication by the *Lancet* Commission on Pollution and Health 2017, pollution was reported to be responsible for a significant level of diseases and deaths worldwide. Diseases from pollution were responsible for about 9 million untimely deaths in 2015, which is estimated to be 16% of all death recorded worldwide. About 92% of such deaths occur in developing countries among minorities and marginalized populations with children and elderly bearing the greatest burden (Landrigan *et al*., 2017). Economically, diseases related to pollution resulted in a huge loss in productivity reducing the gross domestic product in developing countries by up to 2% annually and about 7% of health cost. Welfare losses due to pollution are estimated to amount to US$4.6 trillion per year: 6.2% of global economic output (Landrigan *et al*., 2017). Water pollution is a serious cause of death besides air pollution. Improved analytical techniques have allowed identification of hundreds of industrial chemicals, pharmaceuticals, and pesticides in water systems, some of the worst biological and chemical pollution of drinking water is seen in rapidly urbanizing and industrializing countries, where local waterways and groundwater are heavily polluted and serious health conditions are widely reported (Landrigan *et al*., 2017). According to the *Lancet* report water-related diseases linked to unsafe water supply, poor sanitation affects over a billion people in developing countries of the world (Landrigan *et al*., 2017). A high proportion of deaths occur in children below 5 years old. Increased numbers of deaths are also reported with adults older than 60 years of age (Landrigan *et al*., 2017). Global estimates of the number of deaths from water pollution are highest in sub-Saharan Africa and Southeast Asia (Landrigan *et al*., 2017).

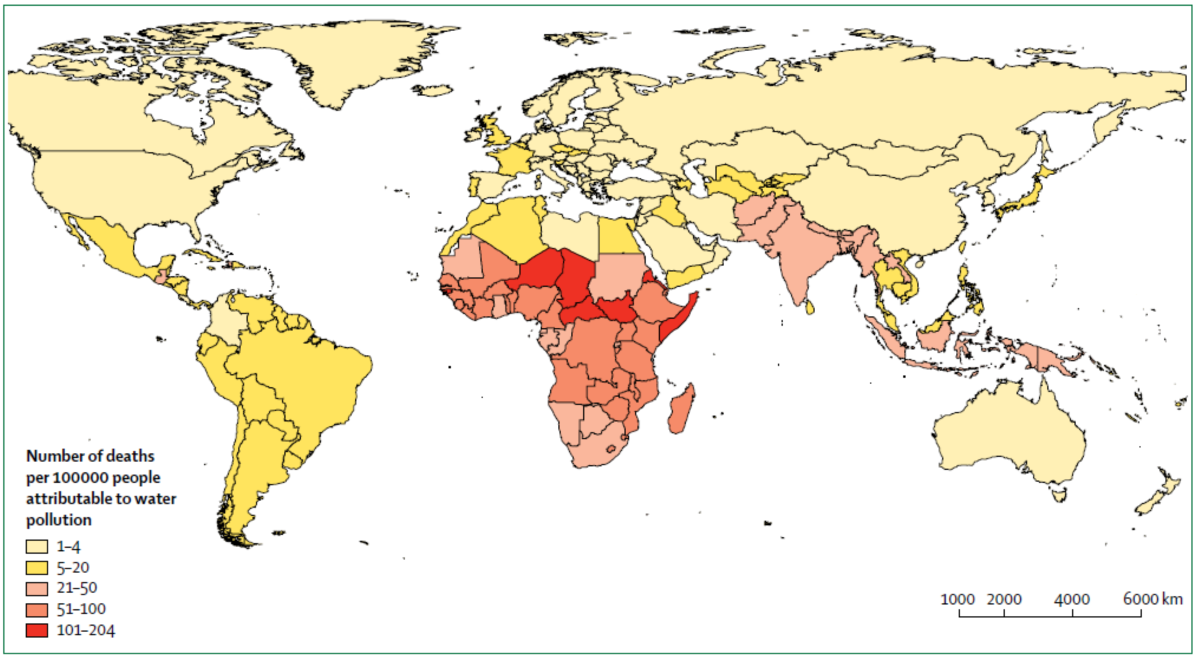

Fig 1: Number of deaths per 100,000 people due to water pollution in 2015 (Landrigan *et al*., 2017)

3. Water pollution in Nigeria

Nigeria with a population of over 186 million people is the most populous nation in Africa and the 7th most populous country in the world (World Fact Book, 2014). According to the UN, Nigeria has been undergoing exponential growth in human population with one of the highest fertility rates in the world. By 2100 the UN estimates that the Nigerian population will be between 505 million and 1.03 billion people (United Nations, 2010). In 2015, Nigeria was reported as the 20th largest economy in the world with a net worth of more than $500 billion and $1 trillion in relation to nominal GDP and purchasing power parity respectively. Nigeria surpasses South Africa to become Africa's largest economy in 2014 (Bloomberg, 2014). Nigeria is considered to be an emerging market by the World Bank. Nigeria is recognized as a regional power bloc on the African continent, a middle power player in international affairs (Cooper *et al*., 2007) and as an emerging global power (www.bbc.com) in the world stage. Nigeria is blessed with abundant natural resources spread across the different states of the federation. Nigeria is known to have over 23 billion barrels of crude oil reserves, 160 trillion cubic metres of gas reserves, over 40 million tonnes deposits of talc, over one billion tonnes of gypsum, over 3 billion metric tonnes of iron ore, estimated 10 million tonnes of lead/zinc, 7.5 million tonnes of baryte, 700 million tonnes of bentonite, 42 billion tonnes of bitumen, 3 billion tonnes of kaolin clay, nearly 3 billion tonnes of coal and large deposits of gold, rock salt and gemstones such as sapphire, ruby, aquamarine, emerald, tourmaline, topaz, garnet, amethyst, zircon and flourspar which are among the world's best (www.nigeria.gov.ng). Despite these achievements, Nigeria is undergoing serious environmental pollution and rapid deterioration of water resources especially from activities in several sectors such as agriculture, manufacturing, maritime, solid minerals and the oil and gas industry. There is a lack of proper waste management practices in Nigeria, with many of the waste generated ending up in water resources directly or indirectly from the point of generation. In almost all coastal and riverine communities in Nigeria untreated waste and sewage are deposited directly into water bodies. In major cities across the nation, untreated waste and other solid materials are thrown into drains that end up reaching rivers, streams and lakes. Indiscriminate disposal of waste, dumping of waste into the canals, sewerage systems that are channelled into water resources lead to increase in the burden of water pollution on water resources of Nigeria. According to the Food and Agriculture Organization of the United Nations, Nigeria has one of the highest rates of deforestation in the world. It is estimated that between 1990 and 2000, Nigeria lost an average of 409,700 hectares of forest each year, which is equivalent to an average annual deforestation rate of 2.38% (FAO, 2010). The rapid decline in forest cover due to exploitation of resources and increased urbanization has led to a significant erosion and flooding issues carrying several categories of waste into aquatic ecosystems across the nation. The Agricultural sector is the largest sector in Nigeria, employing over 30% of the Nigerian population as at 2010 (NBS, 2010; Ake 1996) Major cash crops include cocoa, groundnut, palm oil, corn, cassava, beans, rice, sesame, cashew nuts, gum, kolanut, melon, millet, palm kernels, plantains, rubber, sorghum, soybeans and yams. The Nigerian industrial sector with activities from manufacturing, chemical and paints, breweries, pulp and paper, tourism and hospitality, leather and textiles, electronics, etc. Many of these industries release untreated or poorly treated wastewater into rivers, streams and coastal regions in Nigeria. The maritime or shipping industry also releases waste or polluting substances into the coastal or navigable waters in Nigeria. The poor regulation in the maritime industry plays a factor in the pollution of water resources in Nigeria. The mining of solid minerals especially by artisanal and small-scale miners is also a contributor to water pollution in Nigeria. Nigeria is the 12th largest producer of crude oil in the world and the 8th largest exporter and has the 10th largest proven reserves (Williams, 2008) with a total of 159 oil fields and 1,481 wells in operation according to the Department of Petroleum Resources (NDES, 1997). The Nigerian oil and gas industry is a major polluter of water resources in Nigeria. Nigeria is listed as one of the top ten polluted regions in the world, due largely to the over a century of unabated crude oil pollution in the Niger Delta region. Oil spill results from accident, poor maintenance culture, corrosion of oil pipelines and oil facilities and sabotage. A study carried out on the natural resources and damage assessment in the Niger Delta indicated that an estimated 9 – 13 million barrels of crude oil have spilled into the Niger Delta habitat over the past 50 years, which is equivalent to be about 50 times the estimated volume spilled in the Exxon Valdez Oil Spill in Alaska in 1989 (Obot *et al*., 2006). In addition to oil spills, upstream and downstream operations have resulted in deforestation, dredging, gas flaring, waste discharge and migration to the region thereby increasing population pressure (Obot *et al*., 2006). Also, the Environmental Assessment of Ogoni Land by the United Nations Environment Programme indicated extensive damage of the environment including water resources, biodiversity, social, economic and health impact of the local people (UNEP, 2011). Oil spill in the coastal environment reaches the shore within 72 hours in high tide and spread into distributaries, rivers, streams, creeks in no time due to poor or slow response from oil operators and industry regulators. Oil spill in aquatic environment results in death (lethal) of aquatic life. Even when plant and animals survive, some may fail to reproduce (sub-lethal effect) due to irreversible damage to tissues and organs leading to long-term habitat disruption.

4. Treatment technologies for water pollution

Over the years, various technologies have been developed for the treatment of surface water pollution in rivers, streams, wetlands, swamps and lakes. Treatment technologies vary across different regions of the world and are applied based on several prevailing conditions present in the aquatic environment where water pollution occurs. Basically, physical, chemicals and biological methods are broadly applied for the treatment of water pollution. Physical treatment involves the use of physical devices or tools to create barriers in order to stop the spread of pollutants in water. Physical barriers are usually deployed at the early stages for the treatment of water pollution. Physical barriers include the use of booms and other floating devices to contain water pollution to facilitate the recovery of pollutants. This is the regular application during oil spill cases worldwide. Physical treatments only minimize the level or concentration of pollutants in water bodies. It does not remove completely the pollutants from aquatic environment. Several chemicals have been produced for the remediation of pollutants in water bodies. Most of these chemicals bind, coagulate or breakdown pollutants in water by attacking the chemical bonds in pollutants. Corexit is one of the major chemical series used for the control of oil pollution in water bodies. There have been reports of successful clean-up of several pollutants from water bodies with the use of several brands of Corexit. There has also been controversy regarding the use of Corexit. In many studies, Corexit has been reported to be detrimental to aquatic organisms especially bottom-dwelling organisms because the chemical has been reported in sediments where it is shown to be toxic to several organisms found in bottom sediments. Biological treatments involve the use of biological resources such as extracts, enzymes, and living organisms especially microbes, plants, etc. for the treatment of water pollution. Extracts and enzymes produced from biological organisms have been reported to be very successful in the remediation of water pollutants. The production of extracts and enzymes are sometimes very complicated and cost-intensive hence their regular application is limited. Microbial population have been long applied for the remediation of aquatic pollution especially in marine and coastal environment. Several developing countries and regions lack the resources for the extraction, culture, identification, purification and mass production of favourable microbial strains needed for the remediation of water pollutants. Several species of aquatic plants or macrophytes have been identified, applied and found very successful for the remediation of a wide range of aquatic pollutants (Ekperusi *et al.*, 2018). The abundance of aquatic plants in the natural environment, the low cost of culture and application makes aquatic plants very attractive for the remediation of pollutants in water. The mechanisms by which aquatic plants carry out remediation of pollutants include phytoextraction, phytovolatilization, phytodegradation, rhizodegradation and rhizofiltration, phytostabilization.

5. Duckweeds (*Lemnaceae*)

Duckweed is the general name of the simplest and smallest angiosperm that grows sporadically on fresh or polluted waters throughout the world. Duckweeds are small, fragile, free-floating aquatic plants that grow exponentially in water bodies. The plant reproduces by dividing vegetatively and sexually. Flowering in duckweed occurs very quickly and unpredictably. The plant reproduces approximately within 1-2 days and can cover a large area of water body forming a floating mat of duckweed on the water surface. The plant is simply made up of fronds or leaves with fragile roots without stem. In the presence of nutrients, daughter fronds are produced sporadically. As each frond mature, as they mature, may remain attached to the mother frond and then divide to produce more daughter cells. In all the genera each mother frond produces a considerable number of daughter fronds during its lifetime. However, after six generations of producing daughter fronds, the mother frond tends to die out (Leng, 1999).

Duckweeds are found in all continents except in Antarctica, but they are mostly distributed in tropical and subtropical regions of the world. They are found in standing and slow-moving freshwater bodies laden with nutrients worldwide. Some species are known to tolerate saline waters and can survive in a brackish or coastal environment. Duckweed can persist for a longer period during dryness or drought until conditions return that can support growth.

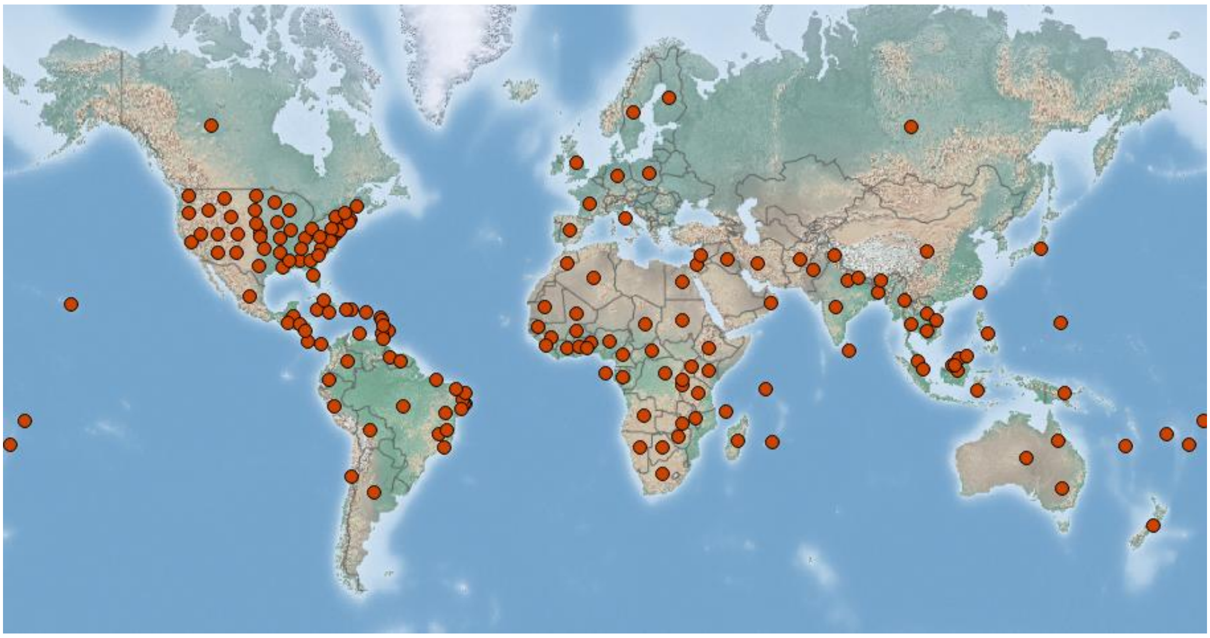

Fig. 2: Global distribution of *Lemna perpusilla* (www.cabi.org)

About 40 species of duckweed have been described worldwide and belong to five genera: *Landoltia*, *Lemna*, *Spirodela*, *Wolffiella* and *Wolffia* (Les *et al*., 2002). There is still an ongoing debate if the *Spirodela* and *Landolta* are the same and should be classified under *Spirodela*. For over 2000 years, the taxonomy of duckweeds was complicated due to the minuteness of the group. The advancement in molecular studies shed more light on the various genera making the group (Cabrera *et al*., 2008). To elucidate the different duckweed genomes a molecular identification system was created using seven plastid-markers by the Barcode of Life group (Hollingsworth *et al*., 2009). The classification of duckweed is shown below:

Kingdom: Plantae
    Clade: Angiosperms
        Clade: Monocots
            Order: Alismatales
                Family: Araceae
                    Subfamily: Lemnoideae
                        Genera:
                        Landoltia
                        Lemna
                        Spirodela
                        Wolffia
                        Wolffiella

Below is the global list of all species of duckweeds that has been described so far:

Landoltia:
- Landoltia punctata (Meyer)

Lemna:
- Lemna aequinoctialis Welwitsch
- Lemna disperma Hegelmaier
- Lemna ecuadoriensis Landolt
- Lemna gibba Landolt
- Lemna japonica Landolt
- Lemna minor Landolt
- Lemna minuta Kunth
- Lemna obscura (Austin)
- Lemna perpusilla Torrey
- Lemna tenera Kurz
- Lemna trisulca Landolt
- Lemna turionifera Landolt
- Lemna valdiviana Philippi
- Lemna yungensis Landolt

Spirodela:
- Spirodela intermedia (Koch)
- Spirodela polyrrhiza (Schleiden)
- Spirodela sichuanensis (Liu & Xie)

Wolffia:

Wolffia angusta (Landolt)
Wolffia arrhiza (Wimmer)
Wolffia australiana (Bentham)
Wolffia borealis (Landolt)
Wolffia brasiliensis (Weddell)
Wolffia columbiana (Karsten)
Wolffia cylindracea (Hegelmaier)
Wolffia elongata (Landolt)
Wolffia globosa (Hartog & Plas)
Wolffia microscopica (Kurz)
Wolffia neglecta (Landolt)

Wolffiella:

Wolffiella caudata (Landolt)
Wolffiella denticulata (Hegelmaier)
Wolffiella gladiata (Hegelmaier)
Wolffiella hyalina (Delile)
Wolffiella lingulata (Hegelmaier)
Wolffiella neotropica (Landolt)
Wolffiella oblonga (Hegelmaier)
Wolffiella repanda (Hegelm)
Wolffiella rotunda (Landolt)
Wolffiella welwitschii (Hegelmaier)

Several research groups and international organizations have been created due to the many potentials of duckweed in modern society. Prominent research centres have been established in Israel, United States, China and Europe for the advancement of research in duckweed application. Key areas of interest include the application of duckweeds for biofuel, animal feeds, food, toxicity testing, medicine and removal of pollutants especially organic pollutants, heavy metals, agrochemicals, etc. from the aquatic environment and wastewater effluents.

6. Application of duckweed for the remediation of water pollution

Several species of duckweed have been applied for the removal of a wide range of pollutants from aquatic environment. The sporadic growth potentials of duckweed and the ability to survive in nutrients rich or polluted environment have been exploited for research in phytoremediation of pollutants in water. Duckweeds have been applied successfully in the remediation of organic wastes, heavy metals, agrochemicals, pharmaceuticals, radioactive wastes and petroleum hydrocarbons.

6.1. Remediation of organic pollutants

Yilmaz and Akbulut (2011) investigated the phytoremediation of organic pollutants using two species of duckweeds (*L. gibba* and *L. minor*) in simulated laboratory wastewater effluents in Turkey. They reported that both plants resulted in the removal of about 85.3 - 88.2% and 59.6 - 66.8% for BOD_5 and COD respectively within 10 days of study. Both plants have the potentials to degrade organic pollutants through their metabolic pathways. They concluded that *L. gibba* was more efficient than *L. minor* in the removal of pollutants in the wastewater. Zhao *et al*. (2014) carried out a study on the potentials of duckweeds to remove pollutants from swine wastewater in China. They reported that the three species of duckweeds were very successful in the removal of pollutants from swine wastewater. *L. minor* had the highest ammonium nitrate and phosphate removal, followed by *L. punctata* and *S. polyrhiza*. Most of the organic pollutants were removed from wastewater within 6 and 9 days of the study. They reported that within the first 3 days no differences were observed between separate application and combination of both duckweed species in the removal of ammonium nitrate. On the 4th day upward there was a sharp difference in the removal for mixed culture compare to separate culture. Removal of pollutants did not occur within the first 2 days but accelerated after 2 days. After 12 days the removal rate of ammonium nitrate and phosphate for *S. polyrhiza*, *L. minor* and *L. punctata* in combine culture were higher than separate culture. Nitrate removal occurred earlier than phosphate removal, but phosphate removal was faster than nitrate removal. Zhao *et al*. (2014) investigated the removal of organic pollutants by *Lemma aequinoctialis* from pilot-scale wastewater system in China. They reported increase biomass and protein contents in duckweed exposed to the pollutants after 4 days. The duckweed achieved a removal rate of 66.16, 23.1, 48.3 and 76.52% for ammonium nitrate, total nitrogen, total phosphorus and turbidity respectively. In addition, there was an increase in dissolved oxygen in the media. It has been suggested in some quarters that local macrophytes may outperform introduced species in the removal of a pollutant from wastewater. Van Echelpoel *et al*. (2016) carried out a study to test the hypothesis if local duckweed species outperform imported species for the removal of pollutants in wastewater. They reported that after 4 days, a significant amount of nutrients was removed by *L. minor* and *L. minuta* although significant differences among both species were only observed at lower nutrient concentrations with higher nutrient removal exerted by *L. minor*. Removal of pollutants ranges from 93 to 99% for nitrogen and 95 to 98% for phosphorus. In all cases, *L. minor* outperforms *L. minuta* for nutrients removal and biomass. They concluded that the introduced *L. minuta* did not show any competitive edge over the native *L. minor*.

6.2. Remediation of heavy metals

Yilmaz and Akbulut (2011) conducted a study on the phytoremediation of heavy metals using two species of duckweeds (*L. gibba* and *L. minor*) in simulated laboratory wastewater effluents in Turkey. They reported that both plants were very successful in the removal of heavy metals from the media within 10 days. *L. gibba* removed about 50±2.01, 60±4.7, 62±2.7 and 57±3.4% of nickel, lead, manganese and copper, while *L. minor* removed about 68±2.7, 62±1.7, 76±2.6 and 58±3.8% of nickel, lead, manganese and copper respectively. The heavy metals removed are reflected in tissues of both plant biomasses. In *L. gibba* the maximum accumulation of nickel, lead, manganese and copper includes 35, 6.75, 120.6 and 18 mg/g dry weight while in *L. minor* the maximum accumulation includes 33.57, 5.93, 47.1 and 7.62 mg/g dry weight respectively. The authors reported that the combination of both duckweeds was more effective than the separate application of duckweeds species. Zhao *et al*. (2015) investigated the influence of duckweed species on copper removal from effluents in China within 7 days. They reported that *L. punctata* and *L. minor* were able to remove copper at moderate concentrations. As the copper concentration increases, the duckweed under mixed culture limits their copper uptake to prevent toxicity and damage. The rate of chlorophyll pigments and crude proteins decreased due to exposure to high copper concentrations. Combination of duckweeds did not show a significant difference compared to a single or separate application. *L. minor* is more resistant to copper compared to *L. punctata* which is more sensitive and show more signs of toxicity than *L. minor*. When both species of duckweed (*L. punctata* and *L. minor*) were combined at moderate metal concentrations, their inherent advantages can enhance the performance of the system in order to respond properly in the presence of stress in the environment through increasing the antioxidant enzyme activity of each other. Lahive *et al*. (2011) evaluated the phytoaccumulation of zinc by three duckweed species. The three species accumulated zinc preferentially. *L. gibba* accumulated a high level of zinc, *L. minor* had higher zinc levels in roots compared to fronds while the opposite was the case for *L. punctata*. In general, *L. punctata* and *L. minor* had higher levels of zinc accumulation than *L. gibba*. This study indicated that when exposed to the same concentration of environmental stress or pollutant, species of duckweed respond differently. Vardanyan and Ingole (2006) investigated the potentials of 45 aquatic plants including duckweed for the remediation of heavy metals from a lake. They observed that all macrophytes exhibited the same pattern in the accumulation of metals. Metals such as calcium, iron, aluminium, chromium, copper, barium, titanium, cobalt and lead were higher in the roots, manganese, zinc and magnesium were more in the stem or fronds while calcium was more in the leaves. They further observed that accumulation of essential metals (calcium, iron and manganese) was higher than non-essential metals (chromium, cadmium, lead and nickel) in macrophytes.

6.3. Remediation of agrochemicals

Dosnon-Olette *et al*. (2010) investigated the removal of dimethomorph by two species of duckweeds from polluted water. Both macrophytes were reported to remove the agrochemical from wastewater. *L. minor* was more successful in the removal of dimethomorph than *S. polyrhiza* at the prevailing conditions. Burns *et al*. (2015) reported a significant inhibition for *L. gibba* and *L. minor* exposed to the herbicide, diuron within 7 days period. It is probable that the concentration of the herbicide exceeded the tolerance threshold for both species of duckweed.

6.4. Remediation of pharmaceuticals and personal care products (PPCPs)

Reinhold *et al*. (2010) compared the phytoremediation of emerging organic pollutant with two species of duckweeds. They reported that *L. minor* and *L. punctata* showed similar remediation pattern for ibuprofen, fluoxetine, triclosan and 2,4-D (2,2,4-dichlorophenoxy acetic acid) within 9 days. Both plants were able to remove about half of the pollutant in the constructed wetlands. Nunes *et al* (2014) reported that *L. minor* and *L. gibba* were effective in the removal of acetaminophen, but the drug was significantly toxic when the dosage exceeded the detoxification potentials of both duckweed species. The two duckweeds showed different adaptive strategies for the removal of the pollutant.

6.5. Remediation of petroleum hydrocarbons

Several authors have reported the application of macrophytes for the remediation of petroleum hydrocarbons (Machate *et al*., 1997; Agbogidi and Bamidele, 2007), but there is quite few literatures involving the application of duckweed for oil-contaminated waters. Many of the reports did not show the appreciable success of the application of duckweed for hydrocarbon remediation. Studies by Agbogidi and Bamidele (2007) with the application of water lettuce (*P. stratiotes*) and lesser duckweed (*Spirodela polyrrhiza*) for hydrocarbon remediation did not yield a significant removal rate for hydrocarbons. Another report by Reinhold *et al*. (2011) using duckweed species such as *L. punctata* and *L. minor* indicated a good performance for the removal of phenol.

7. Conclusions

The paucity of reports or investigation with the role of duckweed in the remediation of petroleum hydrocarbon deserves further attention from researchers. This is paramount to develop ecologically acceptable methods for the remediation of water pollution especially from the petrochemical industry for the sustainable management of environmental resources.

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