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Influence of Macrophyte Types towards Agrochemical Phytoremediation in a Tropical Environment

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Abstract

The presence of agrochemicals waste water from agricultural fields poses major environmental and human health problems which may be solved by phytoremediation technologies. Phytoremediation is the use of plants to remediate contaminants in the environment. Batch experiments were conducted to evaluate the influence of four aquatic macrophytes *(Cyperus papyrus*, *Typha latifolia*, *Cyperus alternifolius* and *Phragmites mauritianus*) towards phytoremediation of agrochemicals from simulated wastewater in Arusha, Tanzania. The selected agrochemicals belonged to different categories namely heavy metal based (Cu, Fe, Mn and Zn) and pesticides (L-Cyhalothrin, Endosulfan and Permethrin). The change in mean concentration of the agrochemicals was described by first-order reaction kinetics. The results indicated that the removal rate constants were greater for the batch experiments planted with the macrophytes than for the control group. Furthermore, the rate of removal varied between the treatments for the different categories of agrochemicals. As far as heavy metals are concerned, *Cyperus papyrus* had a greater removal Cu and Fe with the k values of 0.338 d^{-1} and 0.168 d^{-1} respectively and *Typha latifolia* had a greater removal of Mn and Zinc with k values 0.420 d^{-1} and 0.442 d^{-1} respectively. On the other hand, the pesticides endosulfan and permethrin were greatly removed by *Cyperus papyrus* with k values 0.086 d^{-1} and 0.114 d^{-1} respectively. Lastly, L-Cyhalothrin was removed greatly by *Typha latifolia* with k value of 0.116 d^{-1}. Generally, the results demonstrated that aquatic macrophytes can influence the reduction of agrochemicals in wastewater.

Key words: wastewater,pesticides, heavy metals, agriculture, environment, batch reactor system, removal rate constant.

1. Introduction

1.1 Agrochemical pollution

The use of agrochemicals such as chemical fertilizers and pesticides are integral part in the current agriculture production system around the globe. Accordingly, their uses have been a common practice particularly in many nations in the tropical world [7]. In humid tropics of Africa, these agrochemicals have been extensively used to control pests and diseases affecting crop productivity and improve soil fertility. In Tanzania, the need to increase crop productivity has led to extensive use of pesticides, fertilizers and promotion of irrigation in horticultural practices [33]. However the excessive and indiscriminate uses of these agrochemicals create environmental problems such as contamination of soil and water resources[24].

Pollution by agrochemicals is one of the most significant threats to the integrity of the world's surface waters. In Tanzania, agriculture has been categorized as one of the most polluting industries releasing effluents containing agrochemicals[34]. The agrochemicals of main ecological concern are heavy metal based fertilizers, fungicides and pesticides because they are toxic and persistent in the environment and hence they can eventually bio-accumulate to higher levels that could affect human being [11] and other living organisms. Although heavy metals occur naturally in soils in small quantities but the major sources emanate from micro nutrients applied on agricultural fields as such as zinc, manganese, molybdenum, iron, nickel, phosphates, aluminium, selenium and copper.

These trace elements are essential for the growth and health of plants but they are highly toxic when the concentration exceeds certain limits.
Earlier information on the types of pesticides used in Tanzania revealed that different classes of pesticides are being used in agriculture like organochlorines (endosulfan); organophosphates (chlorpyrifos, dimethoate, profenofos, diazinon and fenitrothion); carbamates (carbofuran, mancozeb, carbaryl and metalaxy) and pyrethroids (permethrin, cypermethrin, deltamethrin and lambda-cyhalothrin [24; 25]. Due to the widespread, long term use and the chemical properties of these pesticides, their residues end up in the environment and are being detected in various environmental matrices including the biota.

Studies done in Tanzania and elsewhere have indicated significant agrochemical contamination of soil and water resources [25; 22; 32; 14]. Application of copper based fungicides has been reported to cause soil contamination by copper [31]. The application of phosphate fertilizers to the agricultural soil has led to increase in heavy metals like cadmium, copper, zinc and arsenic [46]. Although some farms in Tanzania treat their wastewater effluents in a suitable way, others lack convenient treatment systems thus discharging untreated or poorly treated wastewater into the natural environment [25]. The continual discharges of effluents containing these agrochemicals can increase the accumulation of toxic chemicals and thereby threatening the aquatic ecosystem and human health [38].

Due to their toxic properties and adverse negative effects on the environment, several strategies have been developed to remove contaminants from the environment. Conventional wastewater treatment techniques for removal of agrochemicals from agriculture runoff include physical and/ or chemical treatments such as isolation, containment, coagulation-flocculation, reverse osmosis, ion exchange, electrochemical treatment, etc. However, these technologies are impractical and expensive for developing countries like Tanzania and often require a large excess of chemicals and generate large volumes of sludge and hazardous by-products that require appropriate and costly disposal methods. Due to the above-mentioned constraints of conventional technologies, phytoremediation methods using aquatic macrophytes are the need for developing countries because they are environmentally friendly, effective and cheaper to establish and operate.

1.2 Phytoremediation using aquatic macrophytes

Macrophytes are aquatic plants and are regarded as important component of aquatic ecosystem due to their roles in oxygen production, nutrient recycling, controlling water quality, sediment stabilization and providing shelter for aquatic life [36]. Phytoremediation takes advantage of the natural processes of macrophytes and their roles in pollutant removal. These processes include water and chemical uptake, metabolism within the macrophytes, and the physical and biochemical impacts of root system. Aquatic macrophytes are more suitable for wastewater treatment than terrestrial plants because of their relatively fast growth rate and larger biomass production, higher capability of pollutant uptake and better purification effects due to direct contact with contaminants in water.

The word phytoremediation comes from the Greek word phyto which means plant and Latin word remediation which means to remove, which refers to a diverse collection of plant based technologies that use plants to clean contaminants[9]. Phytoremediation technology is relatively a new approach and has gained importance during the last two decades [10]. This technique can be applied to both organic and inorganic pollutants [13] present in solid substrates (e.g. soil), liquid substrates (e.g. water) and air [28]. Chemical substances that can be subjected to phytoremediation include metals (Pb, Zn, Cd, Cu, Ni, Hg etc), metalloids (As, Sb), inorganic compounds (NO^-_3, NH^+_4, PO^{3-}_4), radionuclides (U, Cs, Sr), petroleum hydrocarbons (BTEX), pesticides (atrazine, bentazone, chlorinated and nitroaromatic compounds), explosives (TNT, DNT), chlorinated solvents (TCE, PCE) and industrial organic wastes (PCPs, PAHs) and landfill leachates [20].

1.3 Phytoremediation mechanisms

There are several mechanisms by which phytoremediation can occur (Figure 1). Each of these mechanisms will have an effect on the volume, mobility, or toxicity of contaminants, as the application of phytoremediation is intended to do [12].

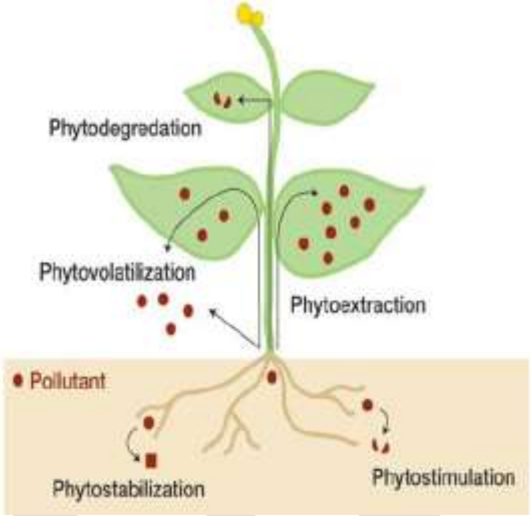

Figure1: Phytoremediation through the use of plants.

1.3.1 Phytodegradation or phytotransformation

Is the breakdown (degradation) of contaminants taken up by plants through metabolic processes within the plant, or the breakdown of contaminants surrounding the plant through the effect of enzymes produced by the plants [43]. Phytodegradation has been observed to remediate some organic contaminants, such as chlorinated solvents, herbicides, and it can address contaminants in soil, sediment, or water [12].

1.3.2 Rhizodegradation or phytostimulation

This refers to the breakdown of contaminants within the plant root zone, or rhizosphere through microbial activity. Microorganisms (yeast, fungi, and bacteria) are enhanced in the rhizosphere because the plant roots release natural substances like sugars, alcohols, acids, enzymes, and other compounds that contain organic carbon that is used as source of energy and food for microorganisms [8]. The roots also provide additional surface area for microbial growth and aeration. The rhizodegradation process has been investigated and found to be successful in treating a wide variety of mostly organic chemicals, including petroleum hydrocarbons, polycyclic aromatic hydrocarbons (PAHs), pesticides etc[12].

1.3.3 Phytoextraction or phytoaccumulation

Is the uptake of contaminants by plant roots and the translocation/accumulation (phytoextraction) of contaminants from the soil into the plants biomass (shoots and leaves). This process occurs when the sequestered contaminants are not degraded in or emitted from the plant rapidly and completely, resulting in an accumulation within the plant tissue [43]. The process involves the removal of contaminants (metals, radionuclides, and certain organic compounds) from the environment by direct uptake into the plant tissue.

1.3.4 Phytovolatilization

Phytovolatilization is the uptake and transpiration of a contaminant by a plant, with release of the contaminant or a modified form of the contaminant to the atmosphere from the plant through contaminant uptake, plant metabolism, and plant transpiration. Phytovolatilization has mainly been applied to groundwater, but it can be applied to soil, sediments, and sludges. Phytovolatilization may be applied to both organic and inorganic contaminants [12].

1.3.5 Phytofiltration of Rhizofiltration

Is used to remediate surface water, wastewater or groundwater and is defined as the use of plants to absorb, adsorb, concentrate and precipitate contaminants from polluted waters by their roots. The most appropriate plant for a rhizofiltration system is one capable of rapid growth, high root biomass, and has the ability to remove contaminants from the water in relatively high concentrations [44].

The most important factor in successful implementation of phytoremediation is the selection of appropriate plant which should have high uptake of both organic and inorganic pollutants, grow well in polluted environments and easily controlled [37; 42]. Careful selection of plant and plant variety is critical, first, to ensure that the plant is appropriate for the climatic and soil conditions at the site, and second, for effectiveness of the phytoremediation of the pollutant at hand [34]. Research experiences have demonstrated the feasibility of different macrophytes species for the removal of chemical pollutants from different types of wastewater. Amongst them include cattail (*Typha sp*) and common reed (*Phragmites sp*); vetiver grass (*Vetiveria zizanioides*) [6; 35]; water hyacinth (*Eichhornia crassipes*), rye grass (*Lolium multiflorium*), Duckweed (*water Lemna*) etc. However, majority of the documented work available on literature has been carried out in developed countries under temperate climatic conditions and their performance may differ in tropical conditions in Africa due to climatic factors. The potential for phytoremediation technology in the tropic environment is high due to the prevailing climatic conditions which favours plant growth and stimulates microbial activity [47].

Information on the capability of phytoremediation of agrochemicals removal is limited [23]. Tanzania lacks information on potential local plant species that may be used for phytoremediation [34]. Further studies in tropical countries like Tanzania, will add more information about the phytoremediation effectiveness of the locally available species. The objective of the study was to investigate the influence of different types of macrophytes towards agrochemical removal. The knowledge about the potential macrophyte plants towards agrochemical removal will provide insight into choosing appropriate macrophytes which may be suitable in wetland phytoremediation processes in agricultural environment.

2.0 Materials and Methods

2.1 Site of the study

The research study was conducted between October 2013 and March 2014 in a ventilated greenhouse located at the premises of Nelson Mandela African Institution of Science and Technology (NM-AIST) in Arusha, Tanzania. The site is at an altitude of 1204 m above sea level and at a geographical location of coordinates S 03^0 23. 945´and E 036^0 47.671´. The dominant climate is tropical – savannah type of climate with clearly rainy and dry seasons.

2.2 Preparation of wastewater

Analytical grade heavy metal salts of copper sulphate ($CuSO_4.5H_2O$), zinc sulphate ($ZnSO_4.7H_2O$), manganese sulphate ($MnSO_4.4H_2O$), iron sulphate ($FeSO_4.7H_2O$), aluminium sulphate ($Al_2(SO_4)_3.16H_2O$) and formulated pesticides endosulfan, lambda cyhalothrin and permethrin were used to prepare the artificial wastewater by diluting with tap water to a final concentration of 5 ppm. These initial concentrations were to simulate typical concentrations reported in runoff from horticultural farms and were also at concentration levels capable of being detected by analytical instruments.

2.3 Experimental setup and operation

The experimental system was bucket-reactor based and consisted of 15 plastic buckets and a 500 L bulk tank for wastewater storage. The plastic bucket reactors had a capacity of 100 litres and were filled with gravel of porosity of 0.3, giving a total working volume of 30 L. Healthy young seedlings of *Cyperus papyrus*, *Typha latifolia*, *Phragmities mauritianus* and *Cyperus alternifolius* that had similar biomass were collected from natural wetlands in Arusha and were planted into 12 buckets while 3 unplanted buckets were set as controls (Figure 2). The experiment was conducted in triplicates. These macrophytes were selected on the basis of local availability and they also grow well in tropic regions. The macrophytes were watered on daily basis with tap water and occasionally enriched with Hoagland solution as source of nutrients. The acclimatization period observed was 3 months during which the plants appeared green, healthy and with new grown shoots (Figure 3). Prior to the start of the experiment, sewage with water addition (1:1) and glucose 22.5 ppm was applied to the system for seven days to establish bacterial inoculation and generation of biofilms on the surface of the gravel. Thereafter, artificial wastewater from the 500 L storage tank was fed into the system at the start of the batch experiment. During the whole experimental period, the water volume was kept constant by adding tap water to compensate for water lost through evapotranspiration [41].

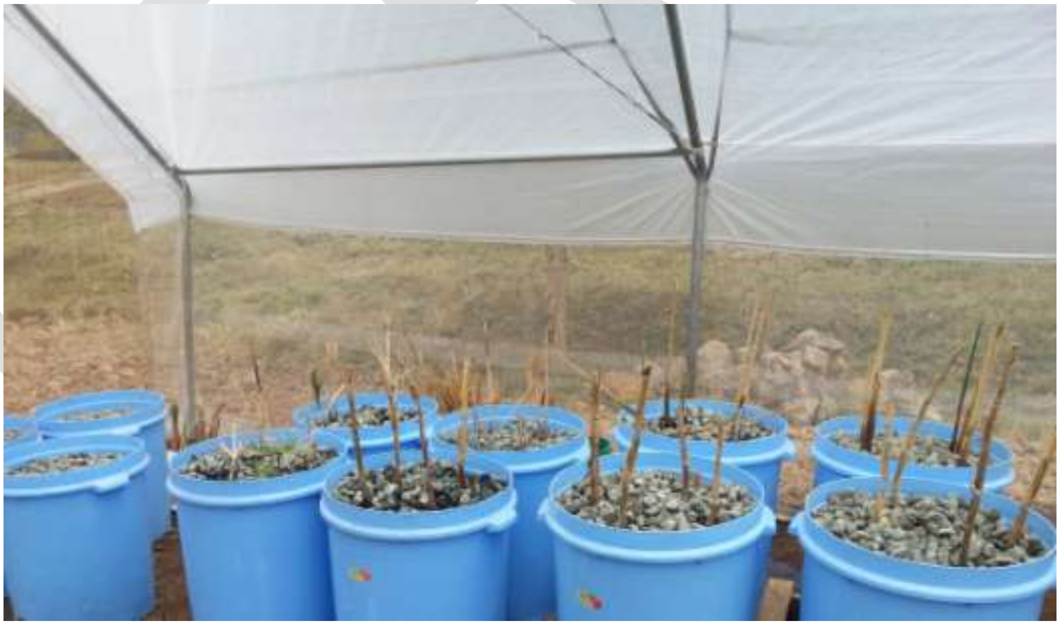

Figure 2: Planting duration in October 2013.

Figure 3: After three months of macrophyte establishment in January 2014

2.4 Sampling and measurement

2.4.1 Heavy metal based agrochemicals

Sampling was done as per standard methods specified in [3]. The waste water was collected by using a 250 mls. polyethylene sampling bottles at 9 am on every sampling day. The sampling was done at initial start-up (day 0), day 1, day 4, day 8, day 12 and finally day 16. All samples were filtered using 0.45 µm filters (Whatman filter papers) and preserved by acidifying with analytical grade HNO_3 to pH < 2 and kept at 4 ^{0}C. The concentrations of heavy metal based agrochemicals in the waste water samples were analysed by Inductively Coupled Plasma Optical Emission (ICP-OES) (manufactured by Horiba Jobin Yvon, France) with detection limits of 0.01 ppm for Al, Cu, Zn, Mn and Fe respectively.

2.4.2 Pesticide agrochemicals

Effluent water samples were collected using standard methods as described by [2]. Effluent water was sampled before the start of the experiment (day 0), day 1 and every four days at about 9 am on every sampling day. Upon reaching the laboratory, the samples were immediately extracted by liquid-liquid extraction (LLE) method [40]. The 1-L unfiltered water sample was quantitatively transferred in a 2-L separating funnel and the sampling bottle rinsed with 60 ml hexane:acetone 1:1. The rinsate was then mixed with the sample in the separating funnel. The combined contents were extracted successively with hexane:acetone 1:1 (3x60 ml). The organic phase was filtered through a plug of glass wool containing anhydrous sodium sulphate (ca. 20 g) for drying and drawn into an erlenmeyer flask. The aqueous layer was repeatedly extracted with a mixture of hexane:acetone (1:1 v/v, 60 ml) as above. After the extraction procedure, the volume of the extract was concentrated to 2 mls using a rotary evaporator at 40 ^{0}C and the final volume adjusted by evaporating under gentle stream of nitrogen gas to 1 ml. The water extracts appeared clean and were not subjected to further clean up, and hence was stored at -5 ^{0}C freezer ready for GC/MS analysis. Analysis of pesticides was done using gas chromatography (Agilent Technologies, 7890A GC System with auto sampler 7683B series injector) coupled with mass spectrometer (Agilent Technologies, 5975C inert XL EI/CIMSD with Triple-Axis Detector). The GC/MS analysis parameters and operating conditions were as follows: Helium was used as a carrier gas at a flow rate of 1.2 mls/min; the oven temperature programme was 50 ^{0}C held for 1 min at a rate of 10 ^{0}C /min to 160 ^{0}C then held for 5 minutes and finally by 3 ^{0}C /min to 300 ^{0}C and held for 18.5 min. The temperature of the injection port was 250 ^{0}C. The MS detector temperature was 250 ^{0}C (transfer line temperature) and 230 ^{0}C (ion source). Pesticide residues were identified and quantified by comparing their retention times and peak heights with respect to external reference standards.

2.5 Statistical Analysis

Descriptive statistics (mean and standard deviation) of the results was determined using Origin 8.0 software (Origin Lab Corporation, Northampton, MA, USA). The data obtained were analysed using SPSS 16.0 for windows package (SPSS, Inc., Chicago, IL, USA). The data was subjected to a one-way analysis of variance (ANOVA) to test the overall variations and differences in mean concentrations of agrochemicals in wastewater in the batch reactor systems. Furthermore, post hoc Tukey test was used to assess the significant differences between the planted batch treatment groups relative to control. Differences at $p<0.05$ were considered statistically significant.

3.0 Results and Discussion

3.1 Heavy metal removal

Figure 4 shows the performance of the different types of macrophytes towards removal of metals from wastewater. The data analysis revealed significant differences ($P < 0.05$) in the removal of heavy metals between the planted batches as compared to the control. Figure 4 shows that the concentration of heavy metals decreased with time, however a rapid drop in concentration levels was observed during day 1. This could be a result of dilution in the batch reactor system because it is not completely dry at start of the experiment. Similarly, this might be associated to the different multiple mechanisms taking place in the batch reactors such as adsorption, precipitation, co-precipitation, complexation and ion exchange [30]before attaining equilibrium.

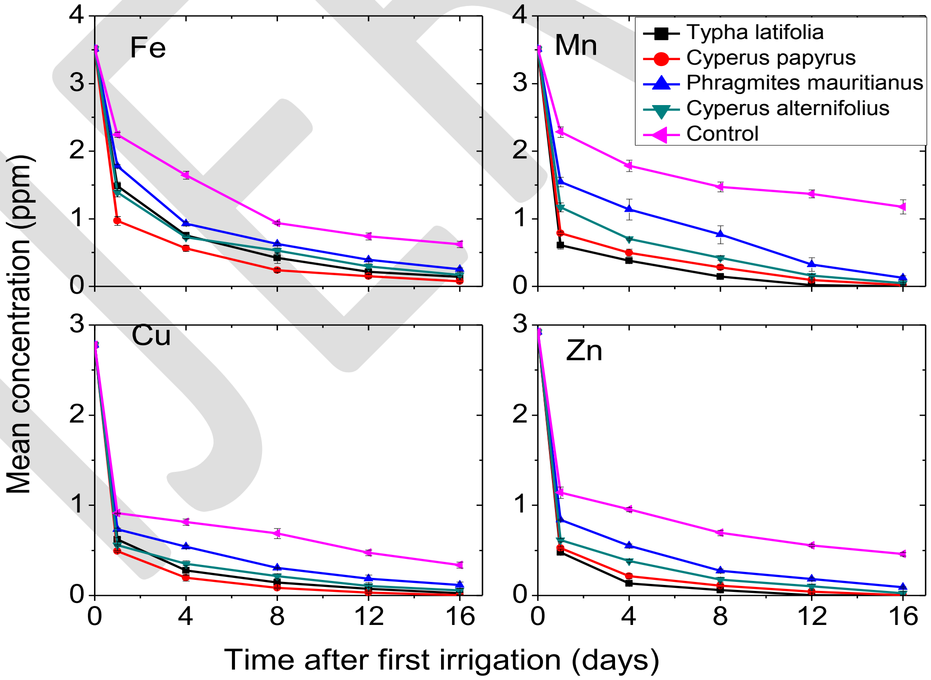

Figure 4: Variation of heavy metal removal in wastewater in planted treatments and control.

3.1.1 Influence of different types of macrophytes in iron (Fe) removal.

According to Figure 4, the results showed that macrophytes are capable in removing Fe from the wastewater. After 16 days retention in the wastewater, a significant difference ($P<0.05$) in mean concentration of Fe was observed in all the macrophytes relative to control. Among the various types of macrophytes, the highest removal capability was observed in planted batch reactor with *Cyperus papyrus* and *Typha latifolia*, and then followed planted batch reactors with *Cyperus alternifolius* and *Phragmites mauritianus* where the initial concentration of iron (3.515 ppm) dropped to 0.077(±0.021) ppm, 0.142(±0.015) ppm, 0.170(±0.042) ppm and 0.252 (±0.026) ppm respectively. This observation revealed that macrophytes have different capabilities influencing the magnitude of Fe removal from wastewater. According to [16; 29; 21], have highlighted that the mechanisms involved in Fe removal from wastewater are rhizofiltration and chemical processes such as precipitation. Similarly, macrophytes can play an important role in metal removal through adsorption and uptake by plants [19]. However, in the control reactors, the decrease in the mean levels of iron to 0.624(±0.048) ppm can be related to other non phyto mechanisms for heavy metal removal such as adsorption to substrates (e.g. gravel, particulates and soluble organics), by cation exchange and chelation, and precipitation as insoluble salts as explained by [18].

3.1.2 Influence of different types of macrophytes manganese (Mn) removal.

There was a significant ($P<0.05$) decrease in the mean concentration of manganese in the wastewater during the 16 day retention time for the planted batch reactors with macrophytes relative to control (Fig. 4). The levels of manganese concentration decreased from 3.508 ppm to 0.001(±0.001) ppm, 0.017(±0.006) ppm, 0.045(±0.012) ppm, and 0.127(±0.033) ppm, for the plated batch reactors with *Typha latifolia*, *Cyperus papyrus*, *Cyperus alternifolius* and *Phragmites mauritianus* respectively. The highest removal capability was influenced by *Typha latifolia* and *Cyperus papyrus* causing a reduction of manganese in wastewater to almost completion. The control group also showed a decrease in levels of manganese to 1.177(±0.104) ppm over the 16 day retention time. This decrease in the control group could be attributed to adsorption to substrate, chemical precipitation and microbial interactions as explained by [19]. Generally, the overall results indicated that aquatic macrophytes were very effective in phytoremediation of manganese. According to [15], plants possess mechanisms which are able to stimulate metal bioavailability in the rhizosphere and enhance adsorption and uptake into their roots.

3.1.3 Variations among macrophytes in zinc (Zn) removal.

As shown in Figure 4, the planted batch reactors affected significantly ($P<0.05$) the mean concentration levels of zinc relative to control during the 16 day retention time. Likewise, the planted batch reactors with macrophytes caused a reduction of zinc levels from initial concentration of 2.921 ppm to 0.001(±0.001) ppm, 0.001(±0.001) ppm, 0.091(±0.007) ppm and 0.025(±0.022) ppm for the plated batch reactors with *Typha latifolia, Cyperus papyrus*, *Phragmites mauritianus* and *Cyperus alternifolius* respectively. The greater removal occurred in the treatments planted with with *Typha latifolia* and *Cyperus papyrus*, where the levels of zinc almost reached to completion on day 16 retention time. The control group also showed a reduction in the mean concentration of zinc to 0.459(±0.019) ppm. This reduction in unplanted control system can be due to sorption onto particulates and settlement. Similar studies indicated that more than 50% of the heavy metals can be easily adsorbed onto particulate matter in the wetland and thus be removed from the water column by sedimentation [39].

3.1.4 Variations among macrophytes in copper (Cu) removal.

The results shown on Figure 4 indicate that the mean concentrations of copper in wastewater decreased with the retention time. A sharp decrease in concentration was observed during day 1 exposure perhaps owing to the multi mechanisms for heavy metal removal in the batch reactor systems. As far as heavy metals are concerned, generally for the batch reactor systems, most removal takes place during the initial stages, and the rate slows after wards. This phenomenon has been observed by other authors [26; 1]. As shown in the figure, the batch reactors planted with macrophytes significantly affected the reduction in copper concentration (P<0.05) as compared to control. On the other hand, *Cyperus papyrus* and *Typha latifolia* achieved the greatest reduction in mean levels of copper from initial concentration of 2.778 ppm to 0.001(±0.001) ppm and 0.023(±0.013) ppm respectively, followed by *Cyperus alternifolius* 0.055(±0.022) ppmand *Phragmites mauritianus* 0.0116(±0.035) ppm. The mean levels of copper observed in the control was 0.338±(0.033) ppm. The significant reduction in levels of copper in the planted batch reactors with the macrophytes relative to control may be influenced by plant uptake and filtration effect of the roots system. Statements that of [19; 7]may confirm that macrophytes can contribute directly through uptake, sedimentation, adsorption and other mechanisms in the rhizosphere.

3.2 Pesticide removal

According to Figure 5, the data obtained during the study revealed that all the batch reactors panted with macrophytes caused a reduction in the mean concentration of the pesticide levels from the wastewater during the 12 days experimental period. However, it appeared that there was no statistical significant difference between the planted batch treatments relative to control group at α = 0.05 level. The variation of pesticide removal in wastewater in the planted reactors and control is shown in Figure 5.

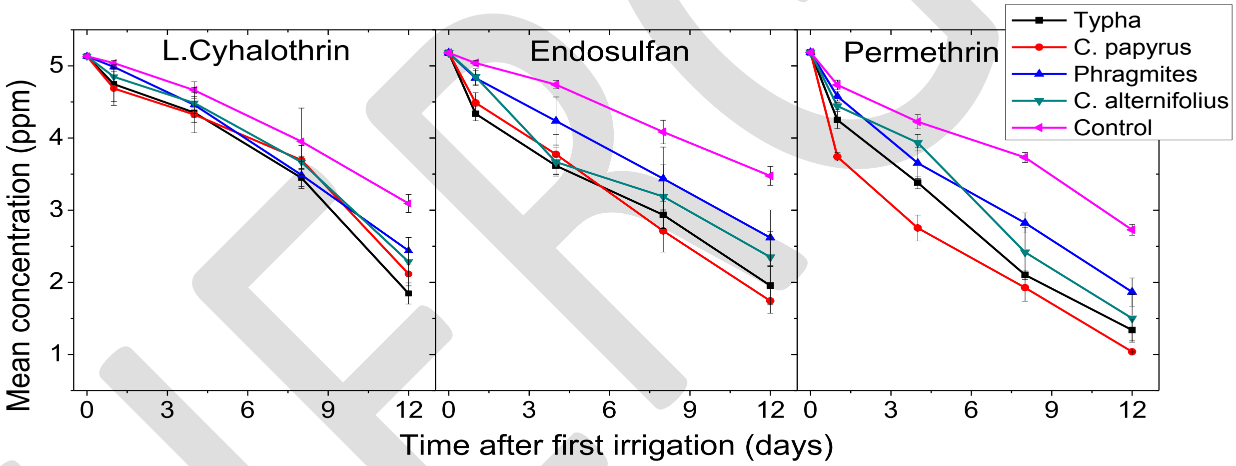

Figure 5: Variation of pesticide removal in wastewater in planted treatments and control.

3.2.1 L. Cyhalothrin removal

The variation of pesticide removal in wastewater in the reactors planted with macrophytes (treatments) and control is shown in Figure 5. Stististical analysis showed that there were no observed significant differences in L. Cyhalothrin removal between the treatments at α = 0.05. However, the study has observed that over the 12 days experimental period, *Typha latifolia* showed the greatest reduction of L. Cyhalothrin in wastewater from initial concentration of 5.132 to 1.184(±0.147) ppm, followed by *Cyperus papyrus*, *Cyperusalternifolius* and *phragrmites mauritianus* with mean concentrations of 2.116(± 0.290) ppm, 2.285(± 0.186) ppm and 2.437(±0.186) ppm respectively. Meanwhile, the mean concentration of wastewater in the control group was 3.093(±0.126) ppm. These results demonstrate that the planted batch treatments had a better removal of L. Cyhalothrin in wastewater as compared to the control. Macrophytes can increase pollutant removal including pesticides either directly through uptake or indirectly through enhanced rhizosphere degradation [32]. Though, the reduction in the control group could be explained by the lipophilic nature of the pesticide. The pesticide L. Cyhalothrin is a pyrethroid insecticide and their molecules rapidly dissipate from the water column and are strongly adsorbed to particulates and other aquatic organisms. Reference [26] observed that L. Cyhalothrin residues in water decrease rapidly if suspended and/or aquatic organisms (algae, macrophytes or aquatic animals) are present. The better performance in planted batch treatments is influenced by the macrophytes which serve as sites for adsorption, absorption and degradation of the pesticide.

3.2.2 Endosulfan removal

The difference observed in the removal trends (Figure 5) was found to be not statistically significant at α = 0.05 level between the planted batch reactors. Likewise, there was no observed statistical significant difference between the planted batch reactors and the control group. However, the analysis of wastewater measured daily for 12 days in the reactors showed that the initial concentration of endosulfan (5.180 ppm) decreased with time (Figure 5). Among the planted batch treatments, *Cyperus papyrus* and *Typha latifolia* showed highest reduction of endosulfan in wastewater to mean levels of 1.742(±0.171) ppm and 1.954(±0.265) ppm respectively, followed by *Cyperus alternifolius* and *Phragmites mauritianus* where the mean concentration levels dropped to 2.349(±0.383) ppm and 2.349(±0.358) ppm respectively. Meanwhile, the mean concentration of endosulfan in wastewater dropped to 3.475(±0.131) ppm in the control group. The results demonstrated that slightly better endosulfan removal was affected by the planted batch reactors as compared to unplanted control group. The results were indicative that macrophytes may influence the removal of endosulfan through several phytoremediation mechanisms such as plant uptake, phytodegradation, and sorption through the root system (rhizosphere). Pesticides that are sorbed are more likely to remain in the root zone where they may be available for plant uptake and microbial or chemical degradation. However, the decrease in the control group may be influenced through sorption and bioremediation mechanisms due to the presence of biofilm, gravel and organic matter in the reactor system [4].

3.2.3 Permethrin removal

There was no observed statistical significant differences in permethrin removal between the planted batch reactors at α = 0.05 level during the 12 day operation of the system. Likewise, no statistical significant difference was noted between the planted batch reactors and the unplanted control group. However, the analytical results of the levels of permethrin in the wastewater decreased with time. Among the planted batch reactors planted, *Cyperus papyrus*, *Typha latifolia* and *Cyperus alternifolius* had a higher removal ability of permethrin from initial concentration of 5.187 ppm to 1.037(±0.005) ppm, 1.338(±0.151) ppm and 1.500(±0.330) ppm respectively, followed by *Phragmites mauritianus* where the mean concentration levels dropped to 1.865 (±0.196) ppm. The least removal ability was observed in the control group with a reduction of permethrin to mean concentration of 2.728(±0.076) ppm. The decrease in pesticide in control group can be explained by adsorption to substrates such as gravel and other particulates in the reactor. However, it appeared that the macrophytes in the planted batch reactor have shown a higher removal capability towards permethrin in the wastewater. This phenomenon may be influenced by several mechanisms such as phytodegradation, rhizofiltration, or uptake by plants as explained by[5; 17; 45].

3.3 Kinetics of agrochemical removal

The change in mean concentrations of the selected agrochemicals in the batch experiments was described by first-order reaction kinetics and mathematically expressed as:-

$$r = -kC$$

$$\frac{dC}{dt} = -k\,C$$

$$\frac{dC}{C} = -k\,dt$$

$$\int_{C_0}^{c} \frac{dC}{C} = -k \int_{t0}^{t} dt$$

$\ln \frac{C}{C_0} = -kt$ ------------------------------ (Eq. 1)

Where C was the concentration of the respective agrochemicals (mg/l) at time t (d), C_0 being the initial concentration (mg/l) and *k*, the first – order rate constant (t^{-1}). A graph of ln C/C_0 versus time was produced and the slope k determined. The value of *k* was used to determine the removal of the agrochemicals with respect to the batch treatment planted with different types of macrophytes relative to the control. A higher removal rate constant implied a reduction of the concentration levels of the respective agrochemicals.

3.3.1 Kinetics of heavy metal removal

When ln C/C_0 was plotted against t, linear relationships were obtained and the rate constants *k* was obtained as the -slope of theline. All samples observed a linear fit with $R^2 \geq 0.9$ (Figure 6). The results obtained have shown that the magnitude of *k* values was greater for the planted batch reactors than for the control. Furthermore, the rate of removal varied between the planted batch reactors for the different types of heavy metals. Among the planted batch reactors, *Cyperus papyrus* had a greater removal Cu and Fe with the *k* values of 0.3385 d^{-1} and 0.1679 d^{-1} respectively and *Typha latifolia* had a greater removal of Mn and Zinc with *k* values 0.4197 d^{-1} and 0.4423 d^{-1} respectively. The findings have also revealed that macrophytes differ in their affinity towards different types of heavy metals. Similarly, the rate of removal of heavy metals were much higher that the pesticides.

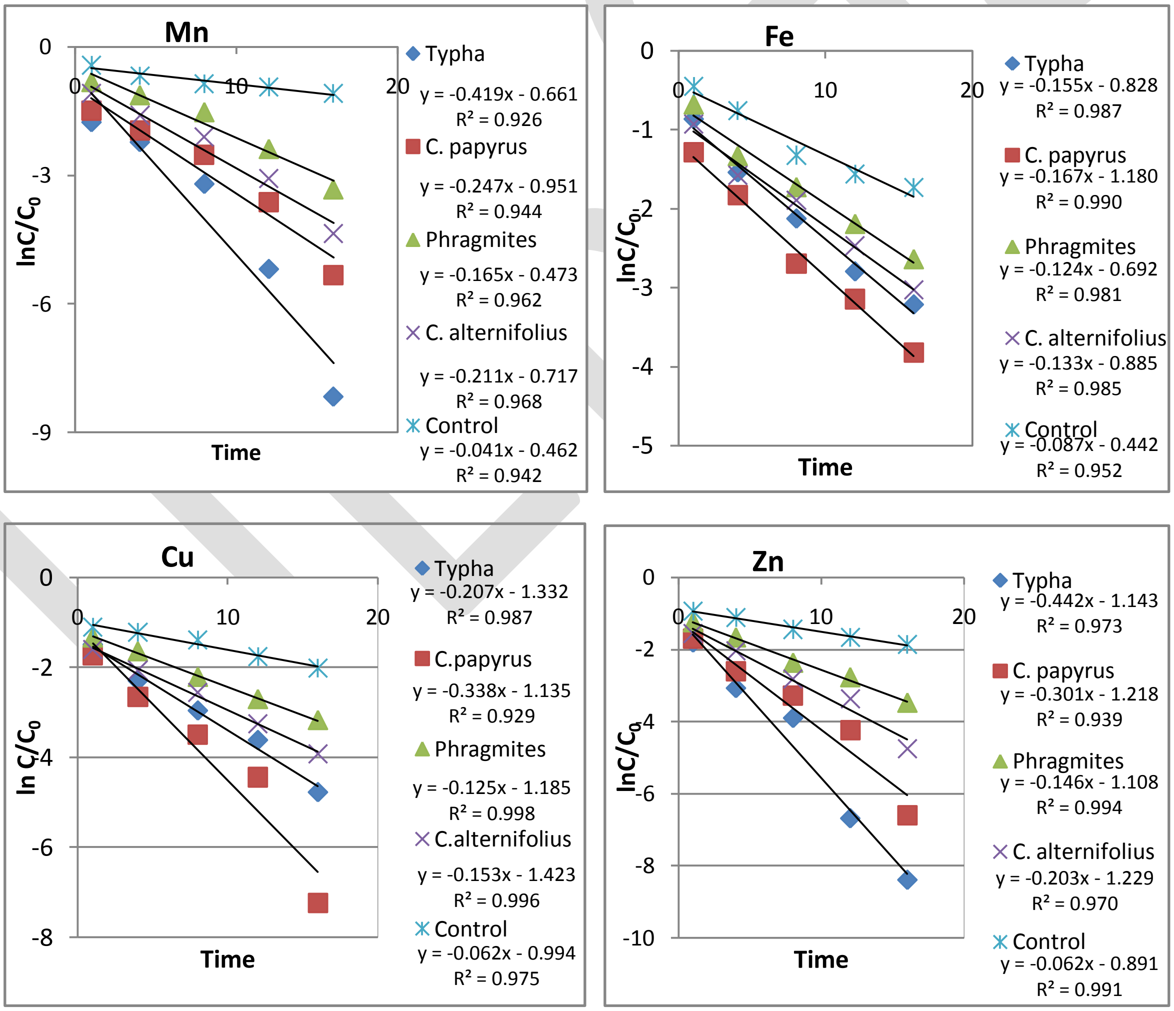

Figure 6: Determination of first-order kinetic constant (k) for heavy metal removal

3.3.2 Kinetics of pesticide removal

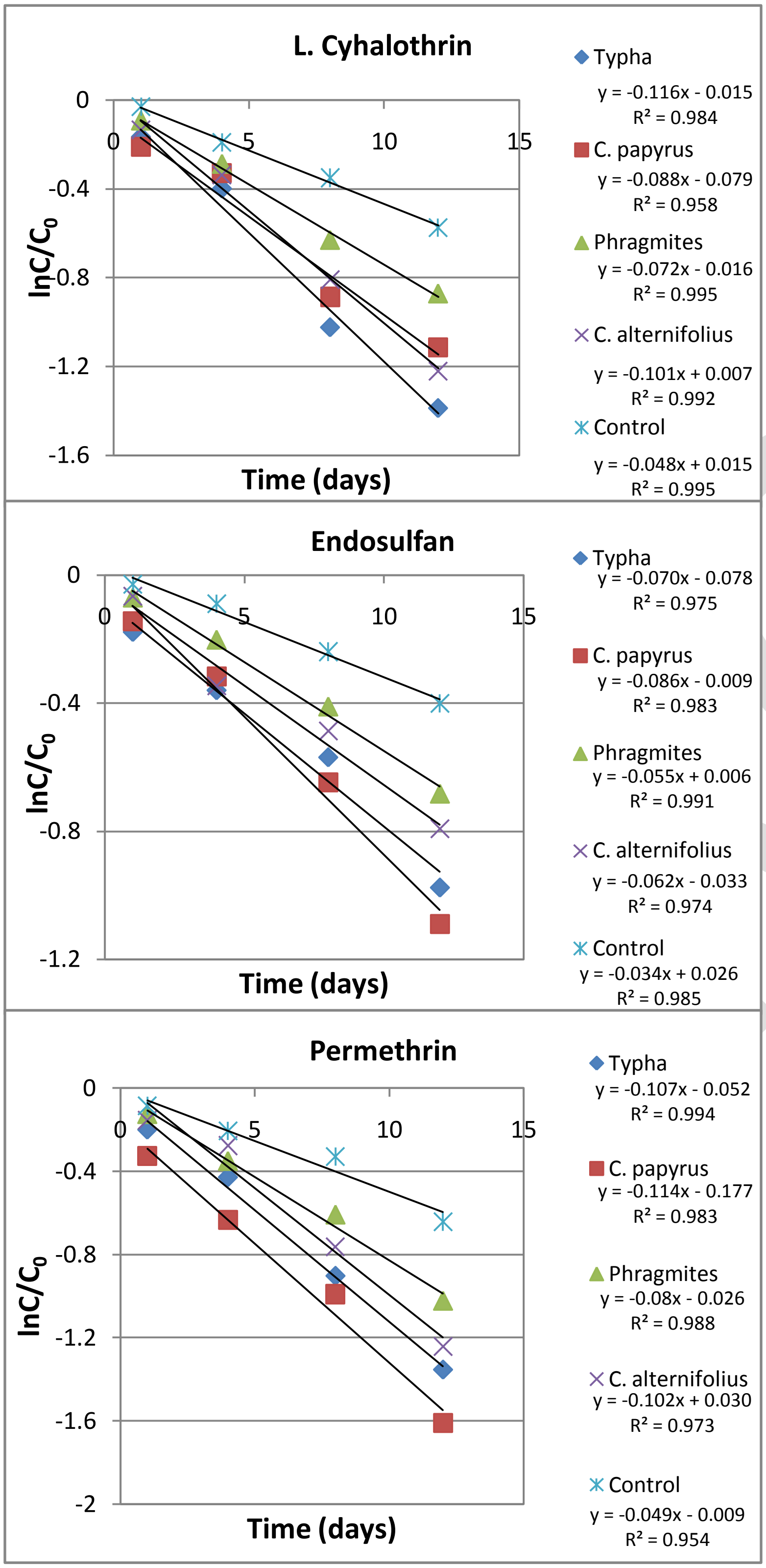

Figure 7: Determination of first-order kinetic constant (k) for pesticide removal

The results for the kinetic parameters for the pesticides (Figure 7) indicated that all samples observed a linear fit with $R^2 \geq 0.9$. The amount of k values was greater for the planted batch treatments than for the control. Furthermore, the rate of removal varied between the planted batch reactors for the different types of pesticides. Among the planted batch treatments, *Cyperus papyrus* showed the highest *k* value for both endosulfan and permethrin removal with *k* values of 0.086 d^{-1} and 0.114 d^{-1} respectively. Likewise *Typha latifolia* had the highest k value of 0.116 d^{-1} for the removal of L-Cyhalothrin.

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4. Conclusion and Recommendation

Water pollution by agrochemicals from agricultural runoff is a serious environmental problem in many parts of the world including Tanzania. Agrochemicals cannot be degraded easily and thus require a preventative approach for a successful outcome. In this study, the influence of four aquatic macrophytes *Cyperus papyrus*, *Typha latifolia*, *Cyperus alternifolius* and *Phragmites mauritianus* towards agrochemical phytoremediation in wastewater were investigated. The results revealed that planted systems work better than unplanted systems in the removal of agrochemical residues from wastewater. These results prove their suitability for use in phytoremediation of agrochemicals. Furthermore, the study has demonstrated that plant type has influence on the removal of agrochemicals where in this study, *Cyperus papyrus* and *Typha* latifolia showed higher removal capability for most agrochemicals, followed by *Cyperus alternifolius* and *Phragmitesmauritianus*. The findings have also shown that the rate of removal of heavy metals were much higher than the pesticides. Therefore, in designing wastewater treatment systems for agricultural and industrial lands, removal of pesticide should be used to size the systems. It is recommended that the experiment conducted in this research could be up-scaled to include treatment of actual wastewater from agricultural industries to establish their long term characteristics under various environmental conditions like organic loading and velocity.

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