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Sequestration Rate of Heavy Metal Contaminants Using *Riccia Fluitans* as Potential Phytoremediation Agent in Polluted Aquatic Ecosystem

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ABSTRACT

The application of green technology is the combination of the environmental science and technology in which helps the improvement and application of products, apparatus as well as the system to safeguard the natural resources and the environment. Aquatic plants have been increasingly being utilized as remarkably efficient and responsive apparatus for diagnosing and predicting environmental stresses. Thus, this research aimed to assess *Riccia fluitans* capability and potential as a phytoremediation agent to remediate heavy metal contamination in an unhealthy aquatic ecosystem. Subsequently, *Riccia fluitans* was exposed to three types of heavy metals (Mn, Zn and Pb) at three different concentrations (1.0, 2.0 and 5.0 mg l^{-1}) at four different periods of time (week 1 to week 4). All heavy metals were analyzed through HACH DR5000 spectrophotometer. As a result, among five heavy metals tested, *Riccia fluitans* revealed as a good agent to sequester Mn, Zn and Pb at 3.75mg/L, 4.8mg/L and 0.3mg/L respectively. The analysis affirmed the accumulation of different metals within the plant and an equally lessen of metals in the water. An eloquent equivalence between type of heavy metals and concentration, period of time and *Riccia fluitans* were attained. As a conclusion, *Riccia Fluitans* is proven to be a potential biosequester agent for polluted aquatic environment.

Keywords: Green technology, Phytoremediation, Heavy metals, Aquatic ecosystem, Biosequester agent.

1. Introduction

An increase in industrial activities is giving birth to a severely injured of environmental pollutions and corroded some aquatic ecosystems correlated with heavy metal accumulation in biota and flora (Uka et al., 2013). Since the beginning of the industrial revolution, toxic metal pollution of the biosphre has become more exacerbated until causing greater environmental and health problem. Usability of freshwater runoff had reached nearly 50% and expected to increase another 20% by 2025 (Harris H. and W. Omar W.A. 2008). Beneficial of river has levelled off in the environment due to a poor planning. The monitoring of river water quality is under the responsibility of the Department of Environment Malaysia (DOE 1998). Declination shown in the aquatic environment is particularly due to dam construction, river diversions, heavy pollution loads and other habitat changes (Postel et al., 1996).

In fact, Malaysian waters suffered with 30 to 100 times more phatogens, heavy metals and poisons from industry and agriculture above than government standards permit (Hinrichsen et al., 2002).

Macrophytes species are undeniably fitting as an ideal biomonitor organism based on the criteria listed. They are motionless, visible to the naked eye, easy to handle and collectible, easy to find on the site, accumulate and mobilize contaminants and nutrients in their tissues and signifies environmental stresses (Milan et al., 2006). Furthermore, some of aquatic plant species have an outstanding ability in bioconcentration which, hence elevates more nutrients and heavy metal accumulations. In some cases, plant tissues are able to concentrate high amounts in their tissues, resulting in the significant availability of those elements in the surrounding environment (Milan et al., 2006). Thus, macrophytes are applicable as a biosequester agent in aquatic environments. Through a right selection of wetland plant species benefits in greater removal trace element.

Free floating plants are one of the aquatic plant species categories. Like other categories, free floating plants are also capable to accumulate and uptake metal from waste water. One of the family floating plants that assuring results in removing metal from industrial waste matter is Lemnaceae. The term ‘Duckweed’ associates to this group (Miranda et al., 2000). Duckweed has been diagnosed to remove nutrients and organic matter, suspended solids, various metals (As, Cd, Cr, Cu, Ni, Pb, Fe, Au, and Zn) (Sasmaz and Odel, 2009; Miranda et al., 2000; Kara et al., 2003; Rahman and Hasegawa, 2011; Materazzi et al., 2012; Wang et al., 2012). The water hyacinth (Eichorrnia crassipes), is among the most commonly cited species in purifying polluted waters. The plant is speedy growth and able to accumulate nutrients and metals as well. Furthermore, the plants have tested and potentially remove N, P, As, Cd, Cn, Zn and Pb (Ebel et al., 2007; Mishra and Tripathi, 2008; Mishra et al., 2008; Dixit and Dote, 2009; Mahamadi et al., 2010; Hua et al., 2011; Brooks and Robinson; Rahman and Hasegawa, 2011; Wang et al., 2012). The potential use and capacity of Salvinia natans for the removal of metals such as Cu, As, Hg, Ni, Fe, Pb, Zn and Cr from industrial effluents was studied and tested out (Sen and Bhattacharyya, 1993; Espinoza et al., 2005; Dhir et al., 2013; Lima et al., 2014; Sitarska et al., 2014) The plants are also having a high growth rate and metal tolerance capacity to high concentrations (Dhir et al., 2012; Mandal et al., 2013). The current practices for heavy metal treatment are using reverse-osmosis, ion-exchange, electrodialysis and adsorption. Majorities are consuming high cost, energy demanding and metal specific (Mishra and Tripathi, 2008) which led to environmental degradation (Henry, 2000).

Conventional remediation technologies are based on civil and chemical engineering technologies which includes vastly and diversified of physical, thermal and chemical treatments (Hamlin, 2002). Most of metals and radionuclides could not be eliminated from the environment through chemical and biological transformation. The degree of toxicity can be levelled off by through manipulating their speciation, but not in degradation, they are still perpetual in the environment and can accumulate in soil and aquatic environment (Hamlin, 2002).

Phytoremediation intends to eliminate heavy metals or other contaminants from soils or waters using plant which granting cost efficiency and environmental sustainability. The plant is used as a hyperaccumulator with exceptional metal-accumulating capacity to extract metals from the soil (Zhao et al, 2003; Gratao et. al, 2005). The concept of utilizing plants to immobilize metal and toxic pollutants from polluted environments (soils, waste, water, etc.) is applied nearly about 300 years ago in the treatment of waste water (Gratao et al, 2005, Yusoff, 2012). Nonetheless, an early 1980’s, there is no scientific study and development of suitable plants were taken in the place. Phytoremediation unmasks plant’s unique biological mechanisms for human benefit. Phytoremediation unmasks plant’s unique biological mechanisms for human benefit. According to Hooda (2007), there are four sections of this technology, which associate to toxic metal remediation of soil and water.

A rising degree and seriousness of environmental problems related to water bodies forces an idea of the present study to find more species that capable of cleaning up aquatic environments contaminated with metals. Hence, the aim of the research is to assess the potential and capability of study species which is Riccia fluitans as a potential biosequester agent for polluted aquatic environment. Also, to find out the concentration of Mn, Zn and Pb within the plant in water.

2. Materials And Methods

2.1. Plant Collection

Riccia fluitans is a liverwort of the genus Riccia L. was hand-picked from the canal, located in Taman Tasik Taiping, Perak Darul Ridzuan, Malaysia. The plants were brought back to the laboratory in clean plastic bags for further to study the degree of heavy metal uptake by Riccia fluitans. Plants were carefully washed using tap water and then rinse with distilled water, to remove visible debris (Sadler & Rynja, 1992; O’Halloran et al., 1997). Then, the process of drying the sample was carefully done using filter papers (Qualitative circles 110mm) for 10 minutes each batch. Dry weights of the plants were registered with a digital balance a (sensitivity of 0.01). Later, they were maintained in a container below an ordinary fluorescent bulb.

2.2. Heavy Metals Preparation

About 1.0 g (fresh weight) of Riccia fluitans was floated in 40mL of metal salts (pH 4.5-5.0) in a sterile container (60mL/48mm) in a laboratory conditions. The initial concentrations for individual experiments were varied from 1.0, 2.0 and 5.0 mg/L and controlled of each metal prepared by using

$MnSO_4H_2O$, $ZnSO_47H_2O$ and Pb $(NO_3)_2$. Each treatment was prepared in ten replicates; a total of 33 containers was involved in this experiment (including control for each concentration). Control treatment (metal without plants) was needed to correlate the results and to confirm the effect of metal ions on Riccia fluitans growth. The concentrations of heavy metals in water samples were determined using MERCK standard to provide calibration and quality assurance for each analytical batch. From each tube, samples were measured and collected weekly, and the study was conducted for 4 weeks. All the prepared treatment was maintained at 25ºC during the 30 days of Zn, Pb and Mn exposure.

2.3. Heavy Metals Removal

Removal was determined by quantifying the concentration of metal left in the medium after immersion of plants. The plants were taken out from the treatment metal, meanwhile the treatment metal itself was filtered using filter papers (Qualitative circles 110mm). Concentration of heavy metals was determined by DR5000 using reagents by MERCK following each of the elements.

2.4. Statistical Analysis

Analysis of variance (ANOVA) was calculated to test the validity of the data and the significance of the variation in the data of three heavy metals studied Fe, Mn and Cu in different concentration for Riccia fluitans at different period of time (week 1 - week 4).

3. Results And Discussion

Analysis of variance showed significant difference ($p>0.001$) between heavy metals uptake, concentration ranges (1.0 mgl^{-1}, 2.0 mgl^{-1} and 5.0 mgl^{-1}) and period of time (week 1 until week 4). Based on the results obtained (Figure 1), heavy metals sequestration rate by Riccia fluitans were observed on reduction of concentration of Fe, Mn and Cu in water samples. In this study, the capability of R. fluitans to remediate was higher by increasing period of time (week 4) at different concentration ranges except for 1 mgl^{-1}, of Mn and Cu and this is in agreement with Mishra et al. (2008) and Dhir and Srivastava (2011). In contrast, the emergent aquatic plant species are usually sequestered lower amounts of metals than submerged aquatic species (Kamal et al., 2004). Species such as Centella asiatiaca and E. crassipes had a maximum removal of Cu in solution about 99.6% (Mokhtar et al., 2011). In another study, Lemna minor showed a resistant to environmental toxicity and rapidly with growing. (Wang, 1990; Miranda et al., 2000).

On the other hand, the removal efficiencies were increased from 1.0 mgl^{-1} up to 5.0 mgl^{-1} for all heavy metals studied however certain heavy metals were fluctuated (Figure 1). Both Fe and Mn were decreased at 2 mgl^{-1}, surprisingly were increased at 5 mgl^{-1} except for Cu. As for example in this study showed for Mn at 1 mgl^{-1} were 0.69 mgl^{-1} at week 1, increasing up to 0.19 mgl^{-1} respectively. Cu is an essential micronutrients for plant metabolism, however the excessive can effect on physiological and biochemical processes (Lia and Xiong, 2004; Mazen, 2004). At high concentration of Cu, L. gibba growth was inhibited due to toxicity (Khellaf and Zerdaoui, 2010). In contrast, Hydrilla vercillata, Elodea Canadensis and Salvinia natans showed toxicity to Cu and Ni also after 5 days (Begum and HariKrisna, 2010). The experimental plants showed good performance in removing the metal even they were able to remove <50 % of metals solution.

4. Conclusion

In conclusion, Riccia fluitans was tested for concurrent removal of three heavy metals Fe, Mn and Cu. The aquatic plants proved as effective in remediate and sequester of these heavy metals at three concentration ranges (1.0 mgl^{-1}, 2.0 mgl^{-1} and 5.0 mgl^{-1}). The high correlation between period of time and types of heavy metals with different concentration indicates that this plant can be effective used for removal of heavy metals from solution of different heavy metals.

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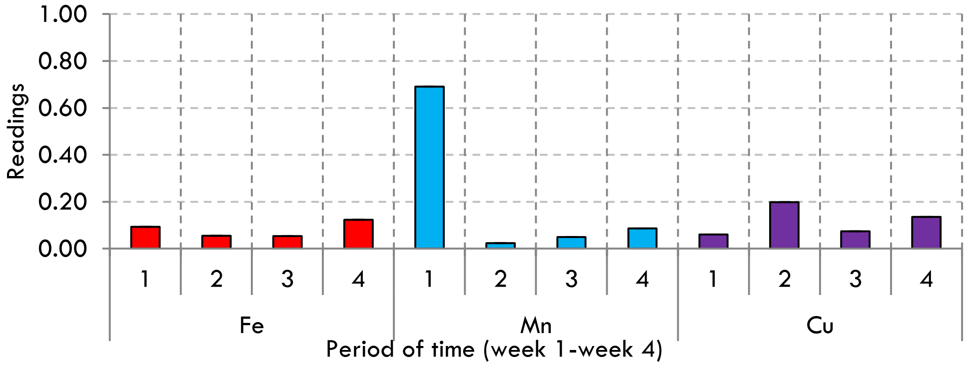
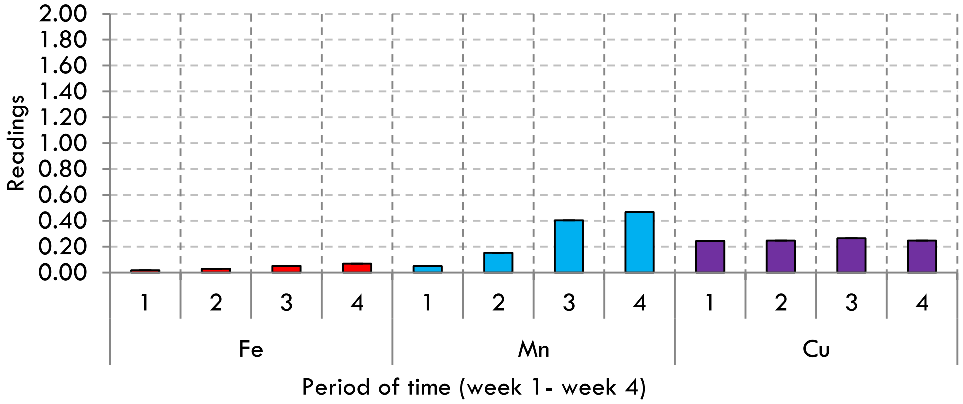
A.



B.



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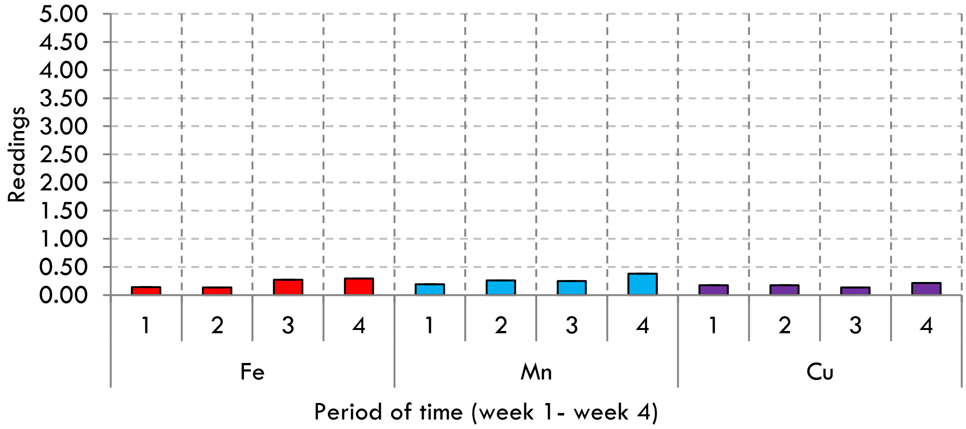

Figure-1. Assessment of Fe, Mn and Cu sequestration rate by *Riccia fluitans* for 1.0 mgl^{-1}, 2.0 mgl^{-1} and 5.0 mgl^{-1} at different incubation period at week 1, week 2, week 3 and week 4
A. Fe, Mn and Cu sequestration rate for 1.0 mgl^{-1} at week 1 until 4
B. Fe, Mn and Cu sequestration rate for 2.0 mgl^{-1} at week 1 until 4
C. Fe, Mn and Cu sequestration rate for 5.0 mgl^{-1} at week 1 until 4

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