The Ability of *L. Articulata* to Remove Polycyclic Aromatic Hydrocarbons (PAHs) from Diesel Contaminated Water in Horizontal Pilot Constructed Wetlands (HCWs) Reactors

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ABSTRACT

This studyproceeds to determine the performance of *Lepironia articulate* (*L. articulata*) in removing PAHs from wastewater on the larger scale of horizontal pilot constructed wetlands (HCWs) in batch operating mode. HCWs dimensions are (1.8 L × 0.9 W × 0.9 H) meters and they operated with constant aeration rate (1 L/min). They were planted with the plant (*L. articulate*) and the water contaminated by diesel at different concentrations of 0 (control), 0.5, 1.25 and 2% (V_{diesel}/V_{water}). The sampling performed on days 0, 7, 15, 20, 40, and 70 and (PAHs) concentrations measured in water to determine PAHs removal by *L. articulate* occurring in phytoremediation. The PAHs concentration in the synthetic waste-water contaminated with diesel was determined through a liquid–liquid extraction method using a gas chromatography (GC-FID). HCWs were affected using *L. articulate* and the percentage removal of PAHs from contaminated water was 98.62%, 98.6% and 96.3% for 0.5%, 1.25% and 2% diesel concentrations, respectively. The biomass parameters of stem height and root length were measured to assess the effect of diesel-contaminated water on *L. articulate* growth and the result suggested that *L. articulata* was able to grow in all diesel-contaminated water concentrations (0.5, 1.25 and 2%). Also, ttemperature, T (˚C), pH, and total suspended solid (TSS) were measured. The percentage of TSS removal from contaminated water with all the concentration was ranged from 90 to 96%.

Keywords: Phytoremediation, HCWs, *L. articulate*, polycyclic aromatic hydrocarbon (PAH), water treatment.

1. Introduction

CW is a shallow basin filled with some sort of substrate, usually soil or gravel, and planted with vegetation tolerant of saturated conditions. The plant that used in this study is *L. articulate*. This plant grows in many regions of the world beside water bodies such as India, China, Southeast Asia and others. *L. articulate* is a genus of the sedge family, known as the grey sedge. Water is introduced at one end and flows over the surface or through the substrate, being discharged at the other end through a weir or other structure which controls the depth of the water in the wetland. Constructed wetlands are engineered systems, designed and constructed to utilize the natural functions of wetland vegetation, soils and their microbial populations, and to treat contaminants in surface water, groundwater, or waste streams [1]. The use of CWs can be assessed in two ways. First, a CW may be used primarily to maximize pollutant removal; its secondary benefits include the preservation and restoration of the natural balance between surface waters and groundwaters, increase of wildlife habitats, and rise in property values [2]. CWs can be used for the treatment of all kinds of wastewaters [3] such as storm water runoff-airport [4]; metal ore mine drainage [5], refinery process water [6], food industry wastewater [7] and fish farm wastewater [8]. Also, Akinbile et al. 2016 treated domestic wastewaters in FSFCWs by using *Azollapinnata* [9]. Gomes et al. 2014 used *Typhadomingensis* in SSFCWs to treat water contaminated with mercury. They found that the system's constant speed to remove mercury was 7 times higher than the control line [10]. Also, In 2016 Warężak et al, was determined the accumulation of PAHs in *Glyceria maxima* taken from wetland wastewater treatment plant vertical flow CW in technical conditions. They found 16 PAHs according to US EPA list were accumulated inside the parts of *Glyceriamaxima* [11].

The technology has increased in popularity in the past few years in countries such as the United States, New Zealand and Australia [12]. In European countries, these constructed wetland treatment systems are usually used to provide secondary treatment of domestic sewage for rural populations. These systems have been seen as an economically attractive, energy-efficient way of providing high standards of wastewater treatment. It is necessary, however, to research the natural reduction of petroleum wastes, especially hydrocarbons in wastewater, to improve this technology. Wetlands have been used to treat petroleum industrial discharges and remediate the soil polluted by crude oils [13].

PAHs are widely distributed environmental contaminants that have detrimental biological effects, toxicity, mutagenecity and carcinogenicity and were the first recognised environmental carcinogens [14]. One different feature is that they are highly hydrophobic and, consequently, they cause considerable ecotoxicological concerns [15]. They accumulate in tissues of aquatic organisms and pose health risk to them, and eventually also to humans who consume contaminated seafood [16].

This study evaluated the effect of using *L. articulata* on the removal of PAHs from synthetic wastewater in HCWs. Which, this is the first study used this plant to treat PAHs from wastewater contaminated with different diesel concentration.

2. Materials and Method

In this section, the experimental set-up, the chemicals used and samples analysis are described further.

2.1 Design of Horizontal Pilot Constructed Wetlands (HCWs)

The study was performed in a greenhouse at Universiti Kebangsaan Malaysia (UKM). The pilot constructed wetlands were made from fiberglass, each measuring 1.8 m L × 0.9 m W × 0.9 m H, and 0.5 cm T (Figure 1). The constructed wetland was configured with operation mode (batch). The tank was filled from the bottom to the top sequentially with a layer of medium gravel (Φ 20-50 mm) at 15 cm depth; a layer of fine sand (Φ 0.2-0.5 mm) at 10 cm depth, without supplementation of nutrient or fertilizer and with a layer of fine gravel (Φ 10-20 mm) at 5 cm depth.

An aeration supply at a rate of 1 L/min was provided by an air compressor pump (HP2 Orimas, Malaysia). The selected aeration rate was based on another study which found 1 L/min aeration is a cost-effective operation parameter for hydrocarbon removal in diesel-contaminated water [18]. Aeration in/under substrate beds increases aerobic biodegradation rates [17]. The cross-section of HCWs is depicted in Figures 1.

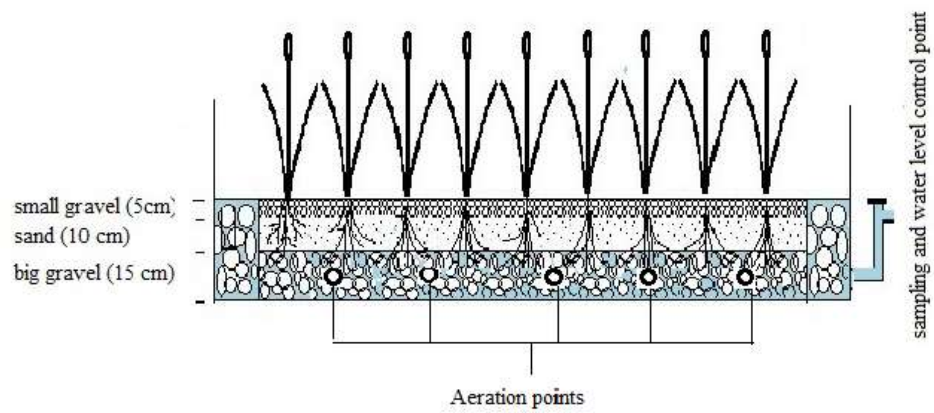


Fig. 1 Cross-section of HCWs

2.2 Selection of Diesel Concentrations for CWs Application

The concentration of diesel was 0 (control), 0.5, 1.25 and 2% depending on preliminary and phytotoxicity test of *L. Articulata*[19]. A preliminary test is physical observation only and it was conducted to estimate the diesel concentration range that plants can survive and tolerate. This estimated diesel concentration range was used in the subsequentphytotoxicity test to further investigate the plant's performance in terms of remediating PAHs from water through the detailed analysis of water, sand and plants besides the effect of PAHs on plant growth.

2.3 Plant Propagation of *L. Articulata*

L. articulata propagation was performed with rhizomes of the plant at the greenhouse in Universiti Kebangsaan Malaysia (UKM). Before the plant being used in the experiment it was germinated for one month with 45-55 cm length were used for each treatment tank. Each pilot CW was planted with 50 plants of *L. articulata* and the capacity of the tank was 100 L. Therefore, 0.5, 1.25 and 2% diesel concentrations were used to evaluate the ability of HCWs to tolerate phytoremediated diesel. The exposure duration was 72 days. Occasionally tap water was added during the prolonged exposure to maintain the level of water in the subsurface flow (SSF) system and also for plant growth.

2.4 Sampling and Monitoring of Physicochemical Parameters

The water samples were collected from each pilot on the sampling days (0, 7, 14, 28, 42, and 72) in clean dark glass bottles. For physicochemical analysis of pH and temperature T (℃) were measured with a multi-probe of IQ 150 (IQ Scientific Instruments, Spectrum Technologies, Plainfield, U.S.A). For the analysis of total suspended solids (TSS) in water medium was conducted on each sample day using portable data logging spectrophotometer (HACH, DR/2010, USA).

2.5 Plant Biomass

On each day of sampling, the length and wet weight of plant were measured for roots and shoot. This is done to study the effect of the diesel on the growth of plant.

2.6 Extraction and Analysis of PAHs in Water

The extraction of PAHs from water was done using Dichloromethane (DCM) every sampling day. 100 mL water samples were extracted using liquid-liquid extraction [20] with 30 mL dichloromethane (DCM) using a separatory funnel. The extracts were combined, filtered and dried with anhydrous sodium sulphate. The extracts were then concentrated by rotary evaporation [21] and eventually under a slow stream of dry air [22]. The samples were cleaned up by high-purity glass wool during the extraction of the water samples. All samples were taken in triplicate.

The percentage of PAH removal on each sampling day of water was determined using Equation (1):

$$\text{Removal of PAHs (\%)} = \frac{(\text{PAHs})_0 - (\text{PAHs})_t}{(\text{PAHs})_0} \times 100 \qquad (1)$$

3 Results and Discussion

3.1 Monitoring of the Physicochemical Parameters of Wastewater

Environmental parameters such as temperature, pH, T and TSS concentration were monitored every sampling day.

3.1.1 pH and Temperature

The variation in physicochemical parameters of T and pH during the 72 days of experiment is shown in Table 1. The wastewater temperature generally ranged between 25.2 and 28.1^{o}C in the system. The temperature range was within the optimal temperature required for the biodegradation of hydrocarbons in temperate climates generally ranging from 20 to 30°C [23]. The pH ranged from 7.34 to 7.69. The temperature and pH did not appear to be affected by oil contaminated with different concentrations according to Ji et al. (2007) [13].

Table 1 The variation in T and pH of water during the diesel exposure period (72 days)

parameters	value
T(C^{o})	25.2- 28.07
pH	7.34-7.69

3.1.2 Total Suspended Solids (TSS)

Figure 2 shows the result of TSS analysis on each sampling day. TSS on day zero and seven was high and above standard A but below Standard B [24] and followed a reducing trend during the experimental time. On day zero, TSS was 87.3, 79.7, 74.7 and 82 mg/L for 0, 0.5, 1.25 and 2% diesel concentrations respectively. Then, TSS reduced to 3.7, 3.7, 3.3 and 4 mg/L at the end of the exposure period for the same concentration with a removal percentage of 95 to 96%. The high removal of TSS from the water contaminated with diesel was caused by mechanisms in the pilot tank, caused physically by filtration and sedimentation through layers of gravel and sand, chemically by adsorption and precipitation and biologically by biodegradation and plant assimilation [25].

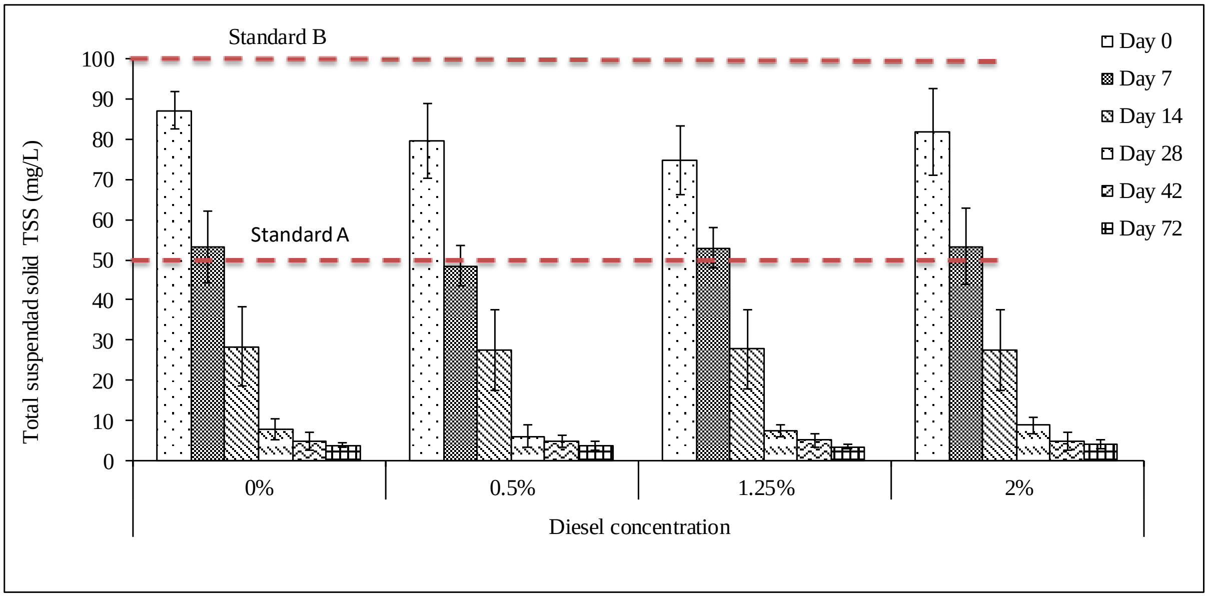
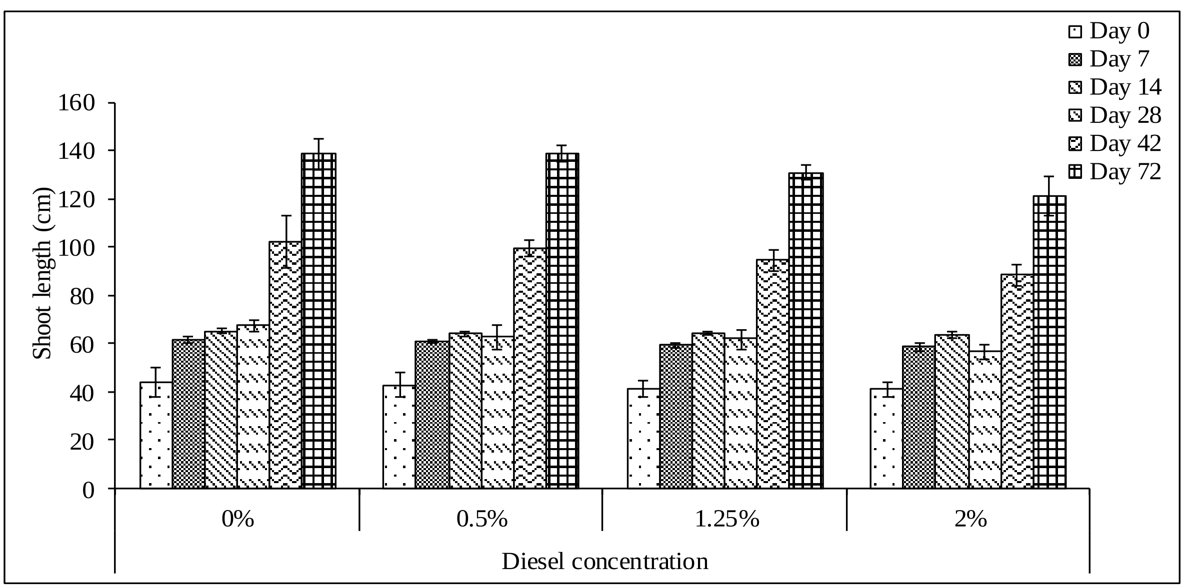


Fig. 2.Effluent concentrations of TSS for treatment systems at different dieselconcentrations.

3.2. Biomass of *L. articulata*

Biomass parameters of stem height and root length were measured to assess the effect of diesel-contaminated water on *L. articulate* growthin every sampling day. On day zero, the length of the upper plant was 43.7, 42.6, 41.3 and 58.3 cm then increased to 138.3, 138.7, 130.7 and 121.3 cm at day 72 with diesel concentrations of 0, 0.5, 1.25 and 2%, respectively (Figure 3).



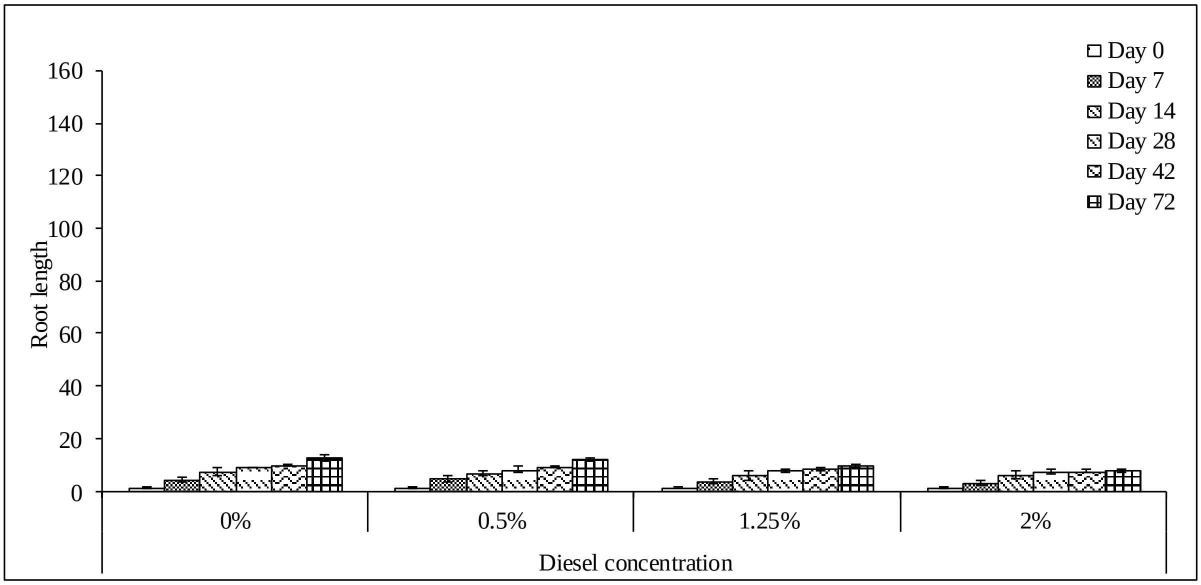


Fig. 3.Growth response parameters of *L. articulata*: shoot and root length. Bars indicate the standard error of the three replicates (n = 3).

At the same time, the result indicates that the growth of plants depends on the diesel concentration. The greater the diesel concentration, the more plant growth decreases. Also, the plant growth without diesel was higher than with diesel. This trend is similar in root length as well. The root length was 12.5, 11.9, 9.4 and 7.8 cm for diesel concentrations of 0, 0.5, 1.25 and 2%, respectively at the end of the exposure period as shown in Figure 3.

6.3.4 PAHs Removal from Water in Constructed Wetlands

PAHs removal in the water during pilot-scale operation is showed in Figure 4. PAHs removalwas recorded from the extraction of synthetic wastewater of different diesel concentrations (0, 0.5, 1.25 and 2%) during the 72 day treatment period. In each CW 100 L of contaminated water with different concentrations of diesel was treated during 72 days. PAHs concentration in the water decreased in all diesel concentrations (0.5, 1.25 and 2%) until the last day of the exposure, with removal rate faster at lower diesel concentrations. At the end of the exposure (72 days), the removal percentage was at its best and PAHs concentration reduced to 0.41, 0.57 and 1.21 mg/L at diesel concentrations of 0.5, 1.25 and 2% with removal percentages of 96.5, 97.8 and 98.0 %, respectively. The contaminants were degraded inside the plant or outside the plant by enzymes [26].Kavamura and Esposito (2010) showed that organic compounds were degraded or mineralized by specific enzyme activity or rendered non-toxic via enzymatic modification [27].

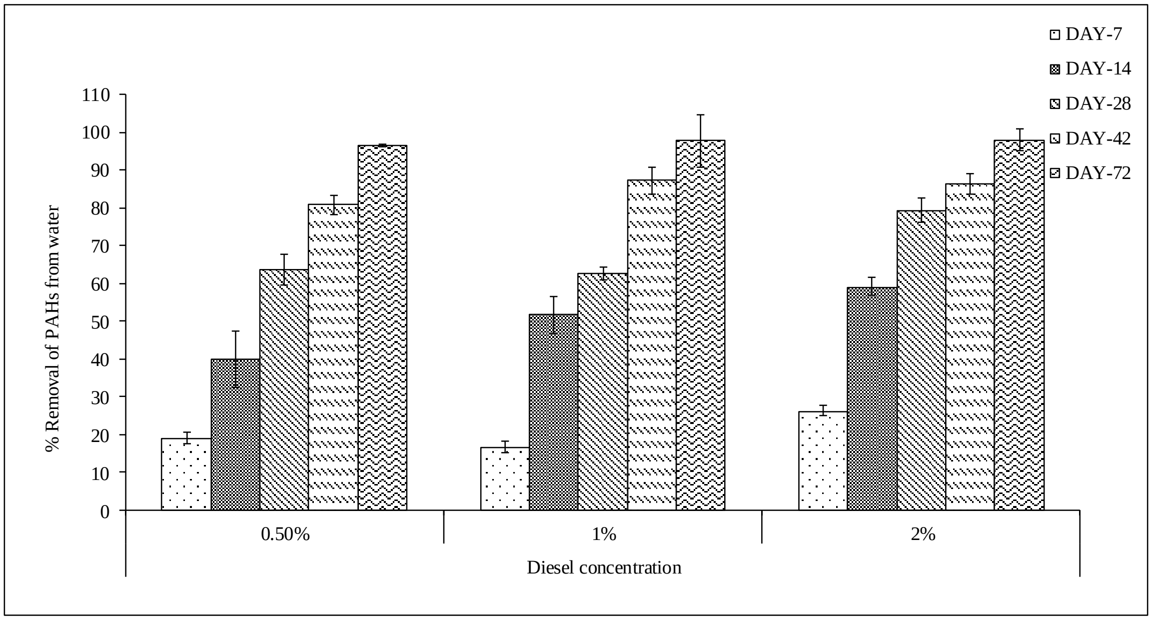


Fig. 4. Percentage of PAHs removal from the water by *L. articulata*during 72 days of diesel exposure. Bars indicate the standard error of the three replicates (n = 3).

7. Conclusion

The plant growth in CWs suggested that *L. articulata* was able to grow in all diesel-contaminated water concentrations (0.5, 1.25 and 2%). On day 72, the length of the upper plant was 138.3, 138.7, 130.7 and 121.3 cm with diesel concentrations of 0, 0.5, 1.25 and 2%, respectively. TSS was generally changed with the time in all concentrations, showing marked decreases. The high removal efficiency of total suspended solids was in all concentration at the end of the exposure period with a removal percentage of 95 to 96%.

For different diesel concentrations, the greater PAHs removal efficiency from water in CWRwas in the end of exposure.CWR had a greater efficiency and performance in the removal of diesel concentrations until 2%. It was 96.5, 97.8 and 98.0 % for 0.5, 1.25 and 2% diesel concentrations, respectively. Phytoremediation in pilotscale CWs may be utilized in situ as treatment systems to polish organics and suspended solids removal in industrial wastewater.

8. Acknowledgements

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