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REMOVAL OF ORGANIC POLLUTANTS, HEAVY METALS AND TRACE ELEMENTS FROM SEWAGE USING *PHRAGMITES AUSTRALIS* (CAV.) TRIN. EX STEUD.

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Abstract

Potential removal of emerging organic pollutants, heavy metals and trace elements using the reed plant *Phragmites australis* (Cav.) Trin. *ex* Steud was evaluated in the year 2020. HPLC analysis showed that the removal efficiency of pyrene and dibutyl phthalate at the end of four-week experiments were 87.37 ± 4.95% and 83.67 ± 5.62%, respectively. Investigation of heavy metals through ICP-AES showed that the efficiency of heavy metal removal was in order of Ba > Zn > As > Cu > Al > Pb > Cd > Cr > Ag. Trace elements such as P, K and Na were removed as high as 70 % from the sewage. Analysis of *Phragmites* sp., indicated that the removed heavy metals from sewage was mostly found in roots and less translocated to the shoot system. Hence this model study could be extrapolated so that *P. australis* could serve as efficient biomitigator for the removal of emerging organic pollutants, heavy metals, and trace elements.

Introduction

As a result of industrial and agricultural practices for its handling of chemical fertilizers, pesticides, petrochemicals, and wastewater irrigation huge areas of land in the world had been contaminated with organic pollutants and heavy metals. These organic pollutants are highly toxic, carcinogenic, and teratogenic. They persist in water and soil for years and can accumulate in living organisms through the food chain (Sharma *et al.* 2014). Heavy metals, on the other hand, cannot undergo any transformations and can be toxic when prescribed concentration in the environment exceeds. Different heavy metals pose different health effects to the living organisms (Jaishankar *et al.* 2014).

The occurrence of heavy metals and trace elements in the urban sewage is probably due to increased use of electronic devices and metal made utensils in the household appliances. Overuse of these metals and trace elements for years can leach out and eventually ends in the sewage (Chowdury *et al.* 2016, Noreen *et al.* 2017). The serious environmental issue with heavy metals is that they cannot be easily degraded like organic wastes and poses adverse health effects towards living organisms when exceeds critical concentration in the ecosystem. The serious health problems related to exposure towards heavy metals include kidney malfunction, decreased metabolic rates, blood and bone damage and neurological disorders in humans (Praveena and Omar 2017).

Pyrene belonging to the class of high molecular weight polyaromatic compounds occurs in environment due to petrochemical industries or incomplete combustion of organic substances. Apart from the carcinogenicity, the non-carcinogenic effects of pyrene include severe damage to pulmonary, gastrointestinal, renal, and dermal systems (Ravindra *et al.* 2008, Chang *et al.* 2011). Dibutyl phthalate used as a plasticizer renders flexibility to plastics and used as an additive in several cosmetic products. People are primarily exposed to phthalates via ingestion of food and drinks stored in plastic containers and via dermal route by the regular application of cosmetic products

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(Pan *et al.* 2014). USEPA listed phthalates as possible carcinogen from laboratory experiments in 2017. The model pollutants (Pyrene and Dibutyl phthalate) were hydrophobic in nature whose solubility to the water is of low quantities (Ghosh and Mukherji 2016, Benjamin *et al.* 2017).

A few plant species can absorb high levels of pollutants and they are called as hyper accumulators. *P. australis,* a reed plant can grow under extreme conditions (salinity, oxygen, and drought) and had been demonstrated for its capability in removing the pollutants from the environment (Bonanno 2011, Fernandez *et al.* 2017). The root of this plant can grow to extreme lengths allowing the plant to survive in extreme condition. Little information is available regarding the usage of *P. australis* in the removal of organic pollutants and heavy metals from the wastewater in Saudi Arabia (Remesh *et al.* 2019). The present study was aimed to evaluate the potential nature of the reed plant in the removal of pyrene and dibutyl phthalate. Further, Sewage collected from university premises was checked for heavy metals and trace elements removal potential by the reed plant.

Materials and Methods

Dibutyl Phthalate, Pyrene, Ethyl Acetate and Acetonitrile were purchased from Sigma Aldrich USA. All the other chemicals used in the study were of highest purity available and were used in the experiments without any further purification. Milli-Q water was used in the experiments. The study was planned and performed in the laboratory of Center of Excellence in Environmental Studies at King Abdulaziz University, Jeddah, Saudi Arabia. The experiments were carried out in sterile conical flasks in triplicates. The seeds of *P. australis* were collected from the eastern region of Saudi Arabia (Fig. 1). The experiments were conducted once the plant attained considerable growth. Sand was used to grow the plants and later, the organic pollutant was directly added to sand and the experiments were conducted. The concentration of pyrene and dibutyl phthalate used in the experiments was 10 and 25 ppm, respectively. Sacrificial sampling was done once in a week to analyze the residual pollutants and the time span for this experiment was four weeks. The heavy metals and trace elements present in the sewage were analyzed initially and at the end of the experiments (ten weeks study).

Fig. 1. *Phragmites australis* collection from the eastern region of Saudi Arabia.

Residual Pyrene and Dibutyl Phthalate were extracted using solvent extraction method (APHA 2005). Pyrene was eluted on a C18 column (Pinnacle II C18 5µm, 250x4.6mm, Restek, USA) and detected at a wavelength of 254 nm with acetonitrile as mobile phase at a flow rate of 1 ml/min. Dibutyl Phthalate was eluted on a C18 column (Pinnacle II C18 5µm, 250x4.6mm, Restek, USA) and detected at a wavelength of 254 nm with a mixture of Methanol and Milli-Q water (60 : 40) as mobile phase at a flow rate of 1ml/min.

In the present study, Sewage was obtained from the Wastewater Treatment Plant within the University premises of Jeddah, and initial concentration of heavy metals and trace elements were calculated. Following this, the sewage was added to pots grown with *P. australis.* The outlet samples were collected at the end of ten weeks experiment. The outlet sample is analyzed for the heavy metals and trace elements. At the end of ten-week experiments, the treated sewage was transferred to clean glass containers and acidified to pH 2 using few drops of concentrated sulphuric acid. Roots and shoots of the reed plant were dried and crushed using a pestle mortar. The crushed roots and shoots were then digested with aqua regia mixture for 1 hr at 100°C in a hot plate. After digestion, the contents were filtered using a Whatman filter paper and the filtrate was used in the further analysis. The samples were analyzed in ICP-AES (Shimadzu, Japan) for the presence of heavy metals and trace elements.

Results and Discussion

The pyrene removal efficiency of the plants through the roots after the first week of the experiment was 16.44 ± 2.35 %. The slow removal of pyrene during the first week may be attributed to hydrophobic nature of the pollutant which results in slow release of the compound. During the progression of study, the removal of pyrene by the plant was gradually increased. At the end of 2^{nd} and 3^{rd} week, the removal efficiency of pyrene was around 41.65 ± 2.49 % and 68.47 ± 3.78 %, respectively (Fig. 2). The removal efficiency of pyrene at the end of the study was determined to be 87.37 ± 4.95%. However, in the control flasks, 8.64 ± 2.14% of pyrene was found to be removed. The slight increase in the removal of pyrene in the control flasks as compared with its initially added concentration might be due to photolysis or volatile nature of the compound (Sivaraman *et al.* 2010).

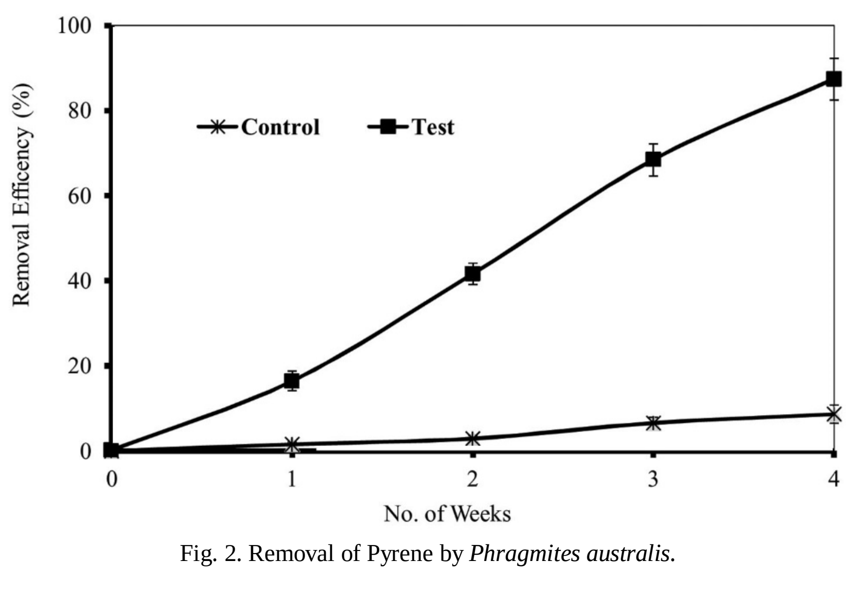

Fig. 2. Removal of Pyrene by *Phragmites australis.*

Dibutyl Phthalate (DBP) is an emerging contaminant and had been studied for its removal efficiency by *P. australis*. The removal efficiency of DBP by the roots of the plant at the end of the first week was 28.46 ± 3.45%. At the end of 2^{nd} and 3^{rd} week, the removal efficiency of DBP was found to be 55.77 ± 4.11% and 76.39 ± 6.42%, respectively (Fig. 3). The gradual decrease of DBP during the study is due to the lipophilic nature of the compound. The removal efficiency of DBP in the test flasks at the end of the four weeks study was found to be 83.67 ± 5.62%. Control flasks experience little loss of DBP which was due to the volatile nature of the compound (Sivaraman *et al.* 2010). The removal of DBP in the control flasks at the end of the study was found to be 8.84 ± 2.19%.

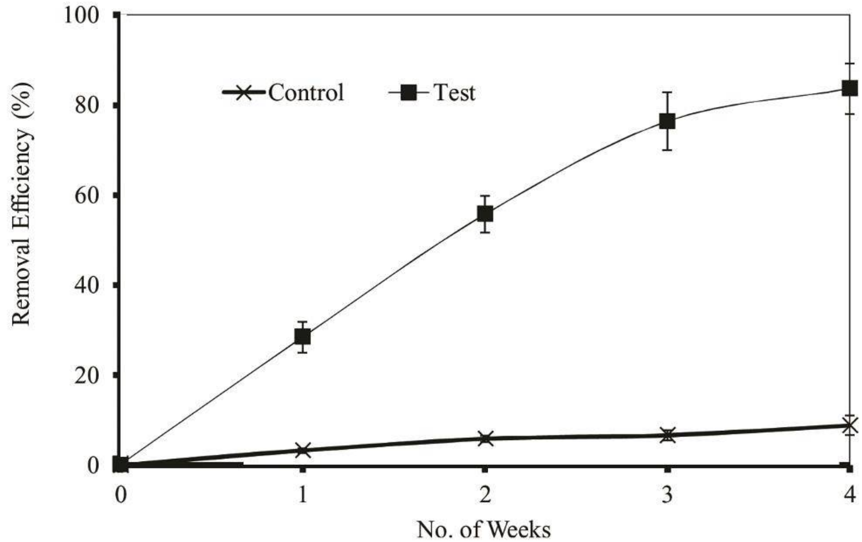

Fig 3. Removal of Dibutyl Phthalate by *Phragmites australis*.

The removal efficiency of heavy metals was in the order of Ba > Zn > As > Cu > Al > Pb > Cd > Cr > Ag (Fig. 4). The reed plant greatly removed the heavy metal barium from the sewage which accounts for 84.19 ± 6.15% while the least removed from the sewage was silver which account to 21.34 ± 1.39%. The presence of mixture of heavy metals greatly influenced the difference in the removal efficiency.

Analysis for heavy metals in the root and shoot system of the plant indicates the accumulation of heavy metals from the wastewater. Most of the metals accumulated in the roots and mobilization of metals did not occur for some heavy metals from the root system to the shoot system (Table 1). The proportion of heavy metals accumulated in the roots was higher than that of the shoots. Zinc from the wastewater absorbed onto the roots whose concentration increased by six folds and mobilized to the shoot system. The concentration of zinc mobilized to the shoot system increased by two folds at the end of the study.

Chromium present in the wastewater absorbed onto roots and its concentration increased to twelve folds at the end of the study. Chromium was also found to be translocated to shoots whose concentration in the shoots increased by three folds. The concentration of copper found in the roots was found to be increased by eleven folds. The concentration of barium increased by three folds in the root system. There was no significant translocation of copper and barium to the shoot system. Lead accumulated in the roots by seven folds and translocated to shoot system whose concentration in the shoots was increased by three folds. Arsenic from the wastewater accumulated in the roots by the four-fold but no translocation was found in the shoots. The concentration of cadmium increased by three folds in the root system and two-fold increase was found in the shoot system. Silver was found below detection limits both in the root and shoot system.

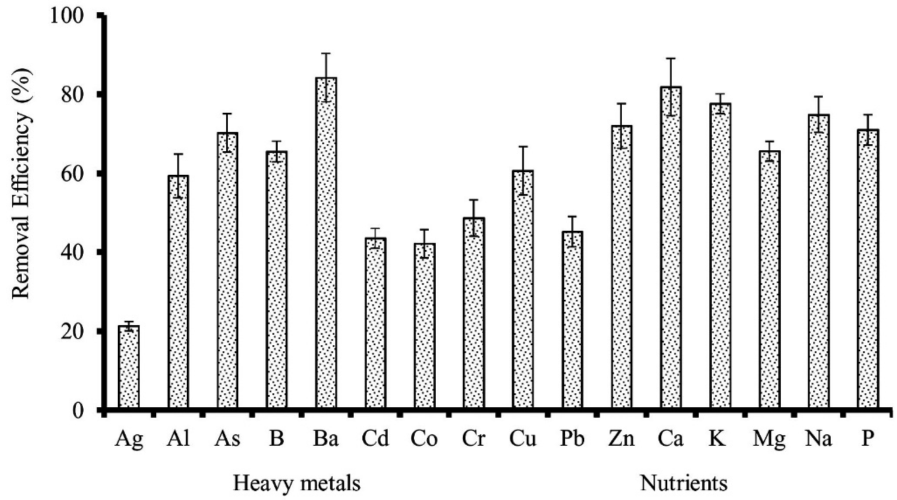

Fig. 4. Removal of Heavy metals and trace elements by *Phragmites australis.*

Table 1. Heavy metals in *P. australis* at the end of experiments.

Heavy metal	Roots (mg/Kg)	Shoots (mg/Kg)
Zn	1.6458 ± 0.0941	0.5516 ± 0.0453
Cr	1.8936 ± 0.1361	0.4734 ± 0.0812
Cu	2.6741 ± 0.837	BDL
Ba	0.9486 ± 0.0136	BDL
Pb	0.9744 ± 0.0751	0.4176 ± 0.0195
As	0.3936 ± 0.0091	BDL
Cd	0.2853 ± 0.0139	0.1902 ± 0.0492
Ag	BDL	BDL

The success of biological treatment method is greatly influenced by using the indigenous biological agents in the process (Megharaj *et al.* 2011). In the present study, an attempt was made to remove the toxic pollutants and heavy metals from the wastewater with the help of the reed plant *P. australis,* obtained from the Eastern province of Saudi Arabia. *P. australis* removed these organic compounds at a removal efficacy of 87.37 ± 4.95% and 83.67 ± 5.62%, respectively. Washing the roots with ethyl acetate followed by analysis using HPLC indicates that these model pollutants were adsorbed onto the surface of the roots. The concentration of pyrene and dibutyl phthalate analyzed in the roots was found to be 8.12 and 17.83 ppm, respectively. The mobility and bioavailability of the pollutants in the contaminated environment are mostly controlled by their adsorbent (Turpeinen *et al.* 2000, Olaniran *et al.* 2013). Roots of *P. australis* acted as a suitable adsorbent for the removal of pyrene and dibutyl phthalate.

Sewage obtained from the treatment plant of the University premises contained a mixture of heavy metals at varying concentrations which were used as such in the experiments. The degree of heavy metal removal was also varied, with barium was removed at higher rates and silver was found to be least. On an average 50% of heavy metals and trace elements present in the wastewater were removed by the reed plant at the end of ten weeks study. Heavy metal removal by the reed plant might be due to the excretion of phytosiderophores that forms a complex with free heavy metal ions (Tsednee *et al.* 2012).

Heavy metals and trace elements were removed in this study by many different processes including plant uptake and accumulation. It was found during the study that the heavy metal uptake by the roots and translocated to the shoots for certain metals. Increasing the time span of the study might result in larger translocations of heavy metals from the roots to the shoot system. Harvesting the shoot system time to time might be a viable option to remove accumulated heavy metals and elements for the long-term usage of the treatment technology. High-sorption performance under low concentration condition of organic pollutants and heavy metals present in the wastewater were attributed for the biosorbent made of reed biomass. *P. australis,* the reed biomass is abundant in nature and can grow under the extreme conditions. With the aim of sustainable growth, this feature can be utilized for the reuse of biomass of *P. australis* as biosorbent for the removal of organic pollutants and heavy metals present in the wastewater.

The reed plant efficiently removed the toxic organic pollutants in the laboratory scale study. Use of *P. australis* greatly removed the heavy metals and trace elements from the sewage and its removal efficiency depend upon the mixture of metals present in the sewage. From the present study, it may be concluded that reed plant, *P. australis* serve as the versatile agent to remove the toxic organic pollutants, heavy metals, and excess trace elements from the contaminated environments.

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