Bio-sorption of Chromium using aquatic plant, *Lepironia articulata*

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Abstract

This work was focused at investigating the improvement of the heavy metal removal process produced by the aquatic plant, *Lepironia articulata* for the treatment of wastewater. The bio-sorption of chromium (Cr) by the aquatic plant, *Lepironia articulata* signifies one of the key alternatives for heavy metal removal. The application of *Lepironia articulate* as bio-absorber of heavy metal hasn't been studied yet. The bio-sorption of chromium (Cr) by the aquatic plant, *Lepironia articulata* near to Taman Anggerik, Kedah, Malaysia, was examined in wastewater contaminated with 4, 8, 12 and 16 mg l^{-1} of Cr. chromium concentrations were analysed in the wastewater regularly and in aquatic plant biomass after the experiments. The results revealed that maintaining pH at 6.1 ± 0.1, temperature at 22 ± 1 ºC and photoperiod at 12 h/j *Lepironia articulata* was capable of accumulating in its biomass 3, 15, 24 and 25 mg g^{-1} DM, for the four preliminary Cr concentrations selected. At the selected Cr concentrations, the heavy metal removal ranged between 62.45–72.84%. The mass balance analysis carried out during the experiment revealed that approximately 40–63% of Cr (based on the preliminary Cr concentrations in wastewater) was eliminated through precipitation process. Thus, bio-sorption of Cr using aquatic plant, *Lepironia articulata* may bring a major point of improvement of the conventional wastewater treatment process.

Keywords: Lepironia articulata, bio-concentration factor, Precipitation, Cr removal.

1. Introduction

Currently, a vast industrial application of chromium is being observed in our civilization (Ponce et al., 2015). Chromium is detected as a severe environmental contaminant for its non-degradablity when discharged to the rivers (Fang et al., 2015). While existing at high levels in water bodies, Cr creates a range of environmental issues, including damage of vegetation, groundwater pollution and metal contamination in the food cycle (Liu et al., 2014). Removal of heavy metals by conventional chemical treatment methods such as precipitation, coagulation–flocculation, adsorption, ionexchange, membrane filtration and other advanced oxidation processes involve huge operational and supervision costs (Lara et al., 2014). Furthermore, these techniques habitually produce by-products that are hazardous to our ecology (Akcil et al., 2015). Therefore, it has become obligatory to recommend a cost-effective green technology to eliminate these heavy metals and improve the effluent standard (González et al., 2014).

There is a substantial prospective for using other techniques that offer usefulness and financial benefits (Siddique et al., 2014). Bio-sorption has currently achieved prominence due to its cost-effectiveness, sustainability and eco-friendliness (Yargıç et al., 2015). This methodology is established on the capability of aquatic plants to absorb and gather metals in their tissues and remove significant extent of these components from wastewater (Hu et al., 2014). The bio-sorption method involves heavy metal uptake by roots and translocation to sprouts and leaves (Gala et al., 2015). Bio-sorption by aquatic plants involves two uptake procedures: absorption which is a preliminary, swift, alterable, metal-gathering system and bio-accumulation, a sluggish, unalterable, ion-sequestration stage (Guo et al., 2014).

Rivers near to Taman Anggerik, Kedah, Malaysia, are highly contaminated with wastewaters carrying Cr because of extensive industrial applications.

Bio-sorption of Cr-contaminated wastewater was studied using the aquatic plant, *Lepironia articulata*. This particular plant was selected as it was easily available, fast-growing, and tolerant to temperature and hassles. This aquatic plant can grow in many water bodies such as ponds, rivers and effluent inlets. Furthermore, a number of earlier works have revealed the capability of different aquatic plants to uptake and eliminate substantial metal contaminants from wastewaters (Deng et al., 2014).

Nevertheless, there is a huge scarcity of data confirming the assessment of contribution of *Lepironia articulata* when cultivated for the elimination of heavy metals. Consequently, this manuscript may help to meet up the increasing demand of the society for heavy metal removal.

Therefore, to determine the heavy metal removal efficiency of the aquatic plant, *Lepironia articulate* through the bio-sorption of Cr was the key objective of this present study. Cr removal (%) and quantity of Cr accumulated in plant biomass was measured as a preliminary concentration function under operational conditions. The amount of Chromium precipitated was deducted from the mass balance carried out on the biological process.

2. Materials and Methods

Raw municipal sewage and industrial wastewaters were obtained from four sampling stations (R_1-R_4) along the 12km of Kedah, Malaysia and transported to the laboratory to be used in the experimental purpose. For the minimization of error during the sampling, each sample was obtained separately and used as 4 replicates. *Lepironia articulate* applied in this study was collected from a lake of Gabang, Kuantan, Malaysia. Collected plants were washed softly with distilled water for removing rubbles. Subsequently, plants were planted in 8 plastic containers having wastewater at pH = 6.1 ± 0.1 (Fig. 1). These containers were enclosed with cardboard for preventing algal infection. Oxygen was supplied by an aerator for the growth of the plants. The plants were cultivated at ambient temperature regularly for 12 h daylight. *Lepironia articulate* took 14 days to adapt with the new environment of the wastewater. These ultimate cultures were moved once per week.

2.1. Experimental Setup

Batch tests were carried out in plastic containers having a capacity of 1.5 l under conditions defined for the plants culture (Fig. 1). The temperature and pH were kept fixed at 22 ± 1 ºC and 6.0 ± 0.1. Four wastewater samples having preliminary concentrations of Cr (4, 8, 12 and 16 mg l^{-1}) were chosen to evaluate the ability of *Lepironia articulate* in metal absorption. Approximately 1.5 ± 0.05 g (dry mass) of *Lepironia articulate* were applied to the four wastewater samples having preliminary concentrations of Cr. Batch tests containing controls (without using *Lepironia articulate*) and repetitions of each concentration were carried out in triplicate. Controls were applied in the study to explain the influence of *Lepironia articulate*, in Cr removal from wastewater. Bioassays were carried out after every week of exposure time.

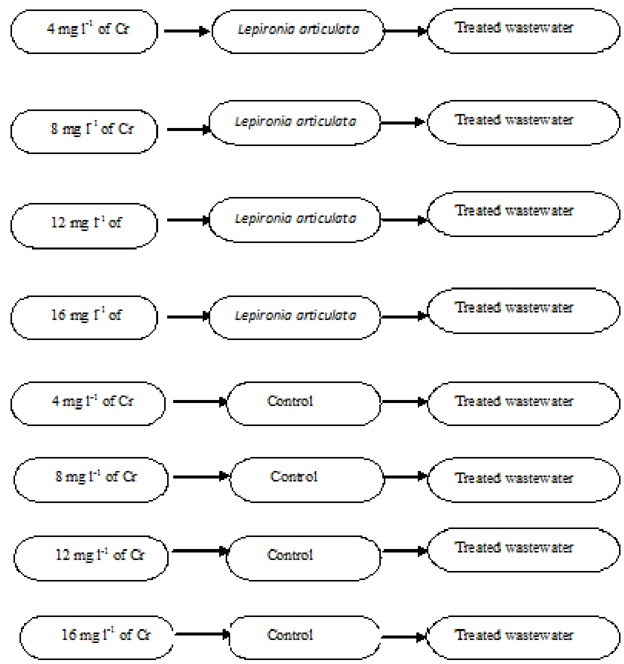

Fig. 1. Experimental set up showing *Lepironia articulate* and control set.

2.2. Methods

The concentrations of heavy metals were analysed through a scheme of sequential extraction according to the procedure of Nguyen and Lee (2014). ICP-OES was applied to analyze the concentration of heavy metals in the extracted liquor during the sequential extraction processes. The heavy metal removal percentage was obtained using the equation:

$$\%\ \text{removal efficiency} = \frac{\text{Ci - Cf}}{\text{Ci}} X100 \qquad (1)$$

Where, C_i and C_f are the initial and final heavy metal concentration.

The bio-concentration factor (BCF) was obtained according to the formula of Rahmani and Sternberg, 1999:

$$\text{BCF} = \frac{\text{Cr in plant biomass}}{\text{Cr in wastewater}} \qquad (2)$$

Where, Cr in plant biomass is in mg kg^{-1} and Cr in wastewater is in mg l^{-1}.

2.3. Statistical Analysis

Standard errors and regression analysis were calculated by the data analysis toolbox in Microsoft Excel, Office 2010. A one-way analysis of variance (ANOVA) was carried out to assess the significant differences in Cr concentrations during this study. Differences were treated to be significant for $p < 0.05$.

3. Results and Discussion

The effect of the plant on Cr removal, Cr absorption in *Lepironia articulate* biomass and the relation of mass balance and Cr precipitation have been explained clearly in this section.

3.1. Performance of plant on Cr removal

Table 1 lists the percentage Cr removal efficiency for four wastewater samples having preliminary concentrations of Cr (4, 8, 12 and 16 mg l^{-1}). Cr removal by *Lepironia articulate* was maximum when Cr level in wastewater was minimum. Particularly, the concrete data showed a higher Cr removal efficiency of 72.84% when preliminary Cr level in the wastewater was about 0.2 mg l^{-1}. However, Cr removal efficiency declined a little when the Cr level was high. Kumari and Tripathi, 2015 applied *Phragmites australis* and *Typha latifolia* for the metal removal from wastewater and observed 68% Cr removal for 14 days.

Table 1 Assessment of Cr removal efficiency obtained from four readings (R_1- R_4)

Cr	R_1	R_2	R_3	R_4
Preliminary concentration (mg l^{-1})	16±0.04	12±0.05	8±0.06	4±0.03
Final concentration (mg l^{-1})	6±0.07	4.26±0.12	2.73±0.05	1.09±0.2
Removal (%)	62.45	64.51	65.85	72.84

To measure the performance of the plant, *Lepironia articulate* in removing and accumulating Cr from the wastewater time dependent experimental procedure was carried out. When wastewater was treated with *Lepironia articulate,* Cr concentrations were found to be decreasing at the end of 12th day and became steady with the exposure time (Figure 2). However, a slight decrease in the Cr concentration was observed for the control treatment.

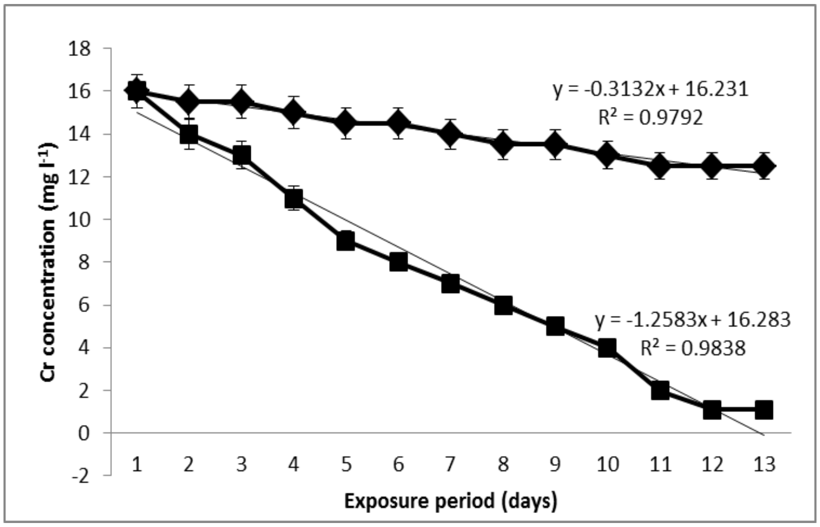

Fig. 2. Chromium concentration removal from wastewater with respect to exposure period, where ■ - with *Lepironia articulate* and ♦ - without *Lepironia articulate*. Vertical bars denote SE, n = 4.

3.2. Cr accumulation in *Lepironia articulate* biomass

The Cr concentrations in *Lepironia articulate* were observed to be increasing with the increase of the preliminary concentrations in wastewater (Figure 3). The Cr concentrations gathered in plant biomass were 5, 15, 26 and 27 mg g^{-1} DM at different Cr concentrations in wastewater. To compute Cr accumulation in *Lepironia articulate* biomass, bio-concentration factor (BCF) was applied in this study. BCF represents an index for the capability of plant biomass to gather metal component corresponding to the component concentration in wastewater (Zayed et al., 1998). The bio-concentration factor value varied from 750 and 1562.5; the maximum value of BCF was reached at 2000 for Cr concentration of 12 mg l^{-1} (Figure 3).

Several works have reported that aquatic plants were capable in accumulating and removing Cr from wastewater. Kovacik et al. (2015) used *Scenedesmus quadricauda* for Cr removal and observed 200- 500 μg g^{-1} Cr accumulation for the exposure time of 24 hour. Similarly, Tripathi et al. (2015) used *chlorophyll florescence* for the removal of Cr (VI) and attained 1.8 mg g^{-1} DM Cr (VI) accumulation in leaf area after 8 days of exposure time.

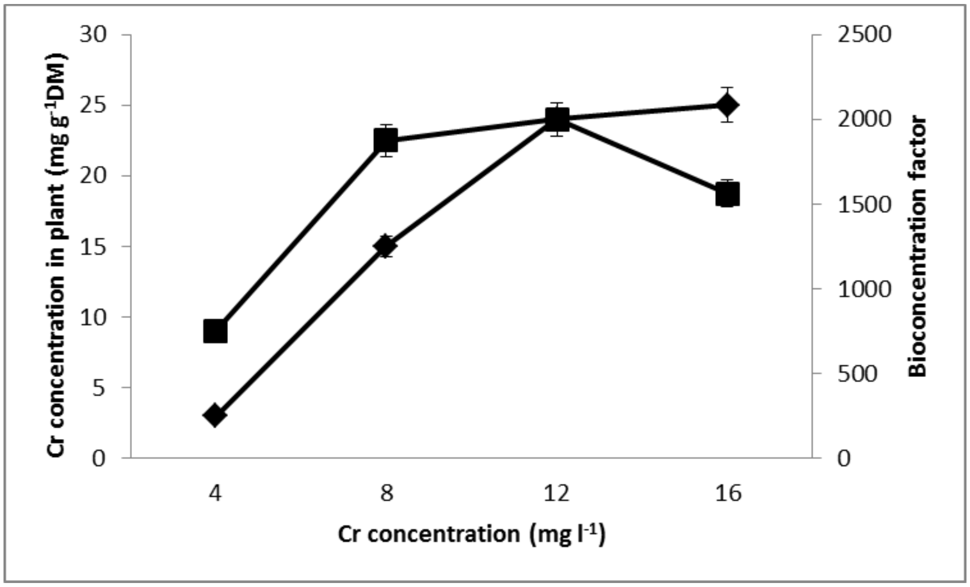

Fig. 3. Influence of Cr concentration in wastewater on the metal accumulation in *Lepironia articulate* tissues and Cr bio-concentration factor, where, ♦ - Cr concentration in plant and ■ - bio-concentration factor. Exposure period was maintained to 13 days. Vertical bars denote SE, n = 4.

While studying Phyto-toxicity and accumulation of Cr in carrot plants Ding et al. (2014) reported that the carrot plants were able to accumulate 0.06 to 2.21 mg kg^{-1} Cr when cultivated in a soil with pH<7.9. An aquatic plant is recognized as a sustainable bio-accumulator which has a bio-concentration factor value above 1000 (Wang et al., 2014). The concrete data revealed that *Lepironia articulate* was a sustainable accumulator of Cr (Figure 3) and might be proficient for Cr removal from wastewater. Nevertheless, this plant might be more efficient than other aquatic plants in metal removal from wastewater.

3.3. Mass balance and Cr precipitation

Figure 4 shows that with respect to the four preliminary concentrations chosen in the present study, the quantity of Cr removal from wastewater was greater than that gathered in plant biomass.

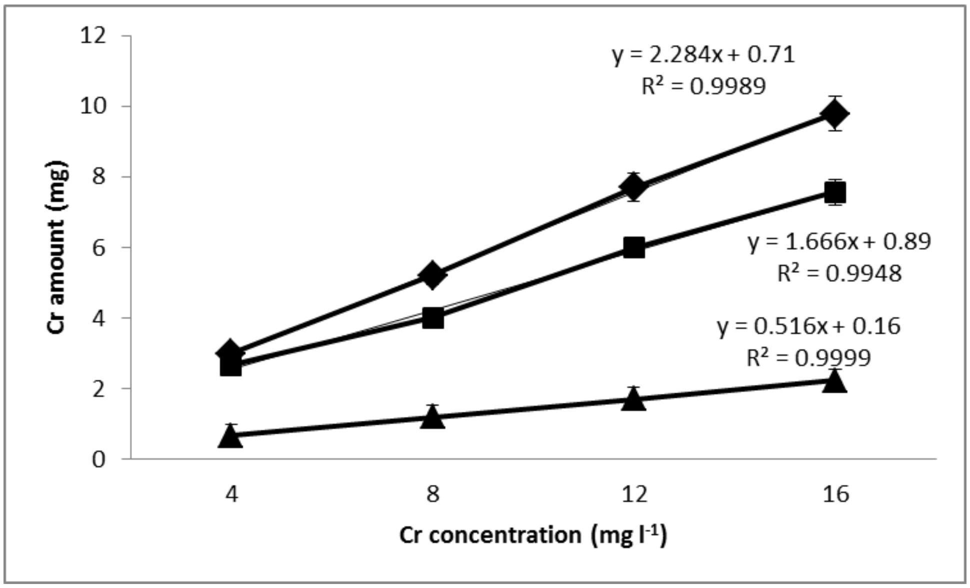

Fig. 4. Linear correlation between amount of Cr removed, accumulated and precipitated and Cr concentration in wastewater.

Uysal et al. (2013) used a pilot plant with uninterrupted flow for the elimination of Cr ion from wastewater by *Lemna minor L.* and observed that the Cr removal was more than that absorbed by the plant. The portion of Cr precipitated was deducted from mass balance calculation carried out on the biological system following the formula given below:

$$\text{Initial concentration of Cr in wastewater} = \text{Residual Cr in wastewater + Accumulation of Cr in plant + Precipitated Cr} \quad (3)$$

The outcomes of the mass balance calculation were revealed in Figure 5. By the application of *Lepironia articulate*, Cr was eliminated from wastewater through precipitation. Precipitation contributed a key part in Cr removal when the preliminary concentration of Cr was 4 mg l^{-1}; about 63% of Cr was precipitated while 5% was accumulated in *Lepironia articulate* biomass. For the rest of the preliminary concentrations ranging from 8 to 16 mg l^{-1}, 40% to 50% of Cr was removed from wastewater through precipitation.

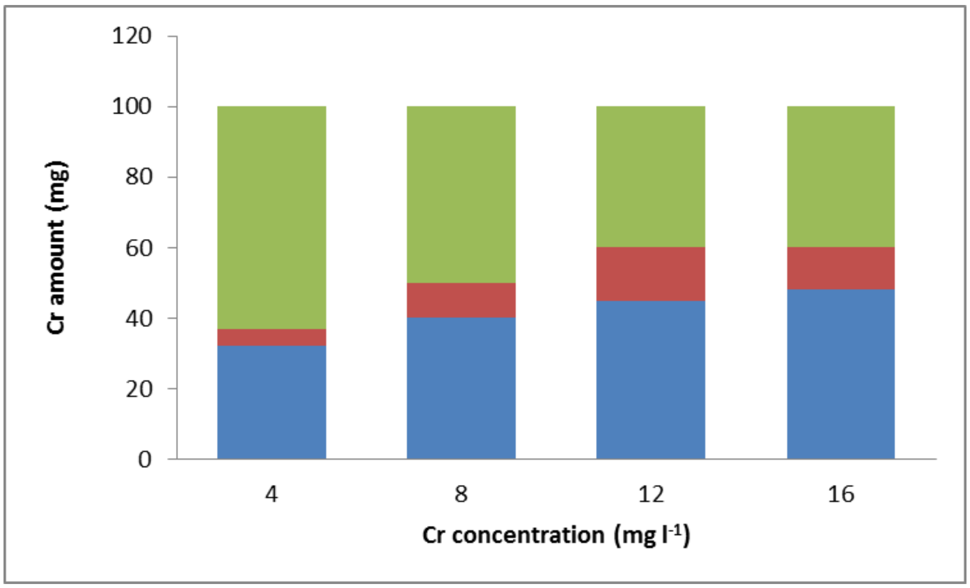

Fig. 5. Mass balance analysis for Cr- *Lepironia articulate*.

The Statistical analysis revealed significant differences ($p < 0.05$) between removal, accumulation and precipitation and Cr concentration in wastewater. The change of removal, accumulation and precipitation (mg) with respect to the preliminary Cr concentrations showed linearity (Figure 4). The regression coefficient values ranged from 0.994 to 0.999.

3.4. SEM study

Figure 6 demonstrates the surface features of heavy metals sorption at a magnification of 1000 and 5000. The substance has a porous texture with an enormous, reachable surface area that supports metal absorption. The surface of the biomass and pores are representing the absorption of heavy metals.

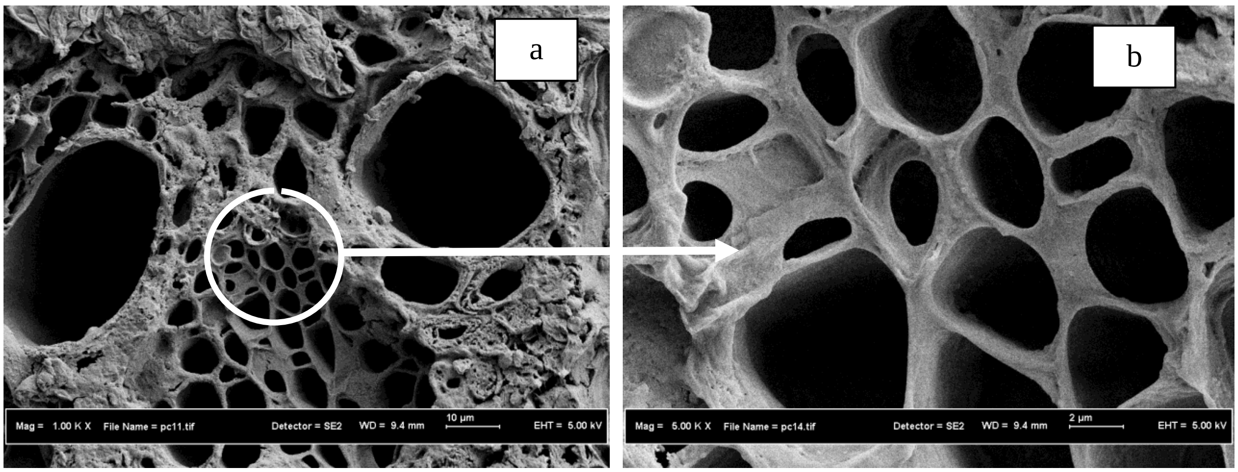

Fig. 6. SEM of (a, b) heavy metals loaded dried ***(****Lepironia articulata****)*** biomass ×1000 and 5000.

4. Conclusions

Contamination of toxic and hazardous metals in wastewater is a severe environmental issue that may be resolved by bio-sorption. For this work, heavy metal removal by the bio-sorption of *Lepironia articulate* from Cr contaminated wastewater was examined. The bio-sorption of Cr by the aquatic plant, *Lepironia articulate* in wastewater turned out to be successful. The present study offers a highly efficient novel alternative to the wastewater treatment. The importance of introducing novel technology for heavy metal removal from wastewater has extensively been acknowledged in environmental science. For the selected Cr concentrations, the heavy metal removal ranged between 62.45–72.84%. *Lepironia articulate* biomass was able to accumulate Cr up to 27 mg g^{-1} DM. The mass balance analysis carried out during the experiment revealed that approximately 40–63% of Cr (based on the preliminary Cr concentrations in wastewater) was eliminated through precipitation process. High removal and Cr-accumulation ability of *Lepironia articulate* establish it as a sustainable option for bio-sorption process. The traditional treatment methods generate hazardous sludge which is the main limitation with them. Finally, the industrial application of this green technology may make the heavy metal removal process more cost effective.

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