Removal of lead from aqueous solutions and wastewaters using water hyacinth (*Eichhornia crassipes*) roots

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**Abstract**

Dried ground roots of water hyacinth (*Eichhornia crassipes*) were used for removal of Pb(II) from aqueous solution. Batch adsorption experiments were conducted with the dried roots (0.1 g dry weight) using 100 mg/L of Pb(II) aqueous solution adjusted at pH 5.0. Equilibrium was obtained in 90 min with a 92% removal of Pb(II). The effect of contact time, pH, adsorbent dosage, initial metal ion concentration on the adsorption of Pb(II) were also studied. Kinetic studies indicated that the adsorption of Pb(II) followed the pseudo-second-order model with a reaction rate constant (k) of 0.0127 mg/(g.min). Kinetics data conforming to the pseudo-second-order model suggest that chemisorption was the rate-limiting step in the adsorption process. The adsorption data were found to fit best into the Langmuir model (R2 = 0.986). The maximum adsorption capacity was found to be ~50 mg Pb(II) per g of dried roots. To investigate the feasibility of using the water hyacinth roots in a more realistic situation, wastewaters collected from various sources were also tested with the biosorbent. Significant removal of Pb(II) (~88% to ~100%) was observed from the wastewaters at pH 5.0. High adsorption capacity, rapid kinetics, and its low cost make water hyacinth dried roots a good candidate for the removal of Pb(II) from wastewaters.

**Key words:** adsorption, isotherms, low-cost biosorbent, pseudo-second-order kinetic, wastewater, water hyacinth roots

**Highlights**

- Lead could be removed from wastewaters using non-living water hyacinth roots as biosorbent.
- 92% removal of lead from aqueous solution was achieved within 90 min.
- Kinetics indicated that the removal process was controlled by chemisorption.
- Langmuir model conformed to the isotherm data, suggesting a monolayer adsorption.
- The biosorbent removed ~88% to ~100% lead from the real wastewaters.

**INTRODUCTION**

Increasing industrial activities across the globe caused a concomitant increase in the use of heavy metals over the last few decades (Reddy *et al.* 2012). As a result, surface waters all over the world have been heavily contaminated with heavy metals. In Bangladesh, surface waters, especially rivers, have also been contaminated with trace metals due to the indiscriminate disposal of industrial...
effluents. There are over 30,000 factories in and around the capital city of Dhaka (Rampley et al. 2020). These factories are continuously discharging pollutants in the form of organics, heavy metals, pathogens, etc. Bhuiyan et al. (2015) found that chromium, arsenic, lead, and cadmium contents in water and sediment samples of the Buriganga river exceeded critical limits and the permissible limits set by the Bangladesh government. They attributed the elevated concentrations of these metals to industrial activities and urban sewage systems. Rampley et al. (2020) assessed the rivers (Turag, Tongi, Balu, and Buriganga) in and around Dhaka and observed high concentrations of aluminum, cadmium, chromium, iron, zinc, lithium, selenium, and nickel. Heavy metals discharged into aquatic habitats are likely to elevate the level of heavy metal concentrations in microorganisms, flora, and fauna residing in that habitat; these bioaccumulated heavy metals may then come along the food chain (Bhuiyan et al. 2015). Consequently, heavy metal pollution in rivers is a significant threat to aquatic systems and humans as well. There have been increasing ecological and public health concerns associated with these metals. The health risks stem from the potential of heavy metals being accumulated and biomagnified, leading to affecting the neurological system, kidney function, and other organs (Whitehead et al. 2019). These heavy metals are carcinogenic, mutagenic, and often teratogenic (Khli & Hamza-Chaffai 2010). Therefore, it is necessary to treat these metal-contaminated wastewaters before discharge to the environment.

The most applied physical and chemical treatment methods for heavy metal removal are chemical precipitation and subsequent liquid-solid separation by gravity settling; flotation or filtration; sorption (adsorption, ion exchange); membrane processes; electrolytic recovery and liquid-liquid extraction (Aklil et al. 2004). However, some of these methods have significant disadvantages: incomplete removal, high energy requirements, production of toxic sludge or waste products that also require disposal and make them economically unviable for the removal of heavy metals at lower concentrations (Aklil et al. 2004).

The adsorption process is one of the most popular and attractive options for the removal of heavy metal ions and other contaminants because of its simplicity, convenience, and high removal efficiency (Afkhami et al. 2007; Hossain et al. 2018). In common sorption processes, activated carbon and synthetic resins are usually used to gain high removal efficiency. However, due to their high production cost, these two sorbents have not gained widespread use and popularity (Zheng et al. 2009). Given this, considerable attention has been focused on the development of adsorbents from various types of biomaterials for the removal of metals from water and wastewater in recent times (Lim et al. 2008a; Gorme et al. 2010; Siboni et al. 2011). Using locally available low-cost biosorbents such as aquatic plants, clay materials, coconut shells, sawdust, chitosan, eggshell, agricultural wastes, etc. may be an alternative wastewater treatment technology because they are inexpensive and environmentally friendly (Munagapati et al. 2010; Sarkar et al. 2017). Low-cost organic biomass contains cellulose, lignin, hemicellulose, extractives, lipids, proteins, simple sugars, starch, etc. which have a variety of functional groups that facilitate complexation and sequestration of heavy metals (Hashem et al. 2005, 2007).

Water hyacinth (Eichhornia crassipes) (Family: Pontederiaceae) is one such promising aquatic plant owing to its superior tolerance to a contaminated environment, rapid growth (Zhang et al. 2014) and high economic value with diverse potential applications (Rezania et al. 2015). Water hyacinth grows profusely in the tropical and subtropical regions (Penfound & Earle 1948) as well as in Bangladesh. Due to its superior bioaccumulation abilities compared to most other aquatic macrophytes (Malik 2007), water hyacinth has gained widespread interest in environmental phytoremediation applications (Rezania et al. 2015). Water hyacinth was successfully used for the removal of Cd and Zn (Hasan et al. 2007). Water hyacinth has also been used as a biosorbent, where dried biomass was used for the removal of heavy metals. Sarkar et al. (2017) used dried shoot powder of water hyacinth for the removal of chromium and copper from standard solutions and tannery effluents and the removal efficacy was found to be high. However, bioaccumulation is
a biochemical process ($E_a \approx 63$ kJ/mol) and energy intensive, whereas biosorption is a physicochemical process ($E_a \approx 21$ kJ/mol) and energy-saving (Kadukova & Vircikova 2005). Moreover, compared to living systems, non-living dried biomass presents advantages such as ease of conservation and ease of transport and handling. Keeping all these in mind, we selected water hyacinth to study the heavy metal removal efficiency of its non-living dried roots. We selected lead as a contaminant because it is one of the heavy metals present in elevated concentrations in many rivers in Bangladesh; for example, the Buriganga (Bhuiyan et al. 2015), the Korotoa (Islam et al. 2015b), the P-aira (Islam et al. 2015a), and the Bangshi (Rahman et al. 2014). Therefore, the present research was aimed at investigating the adsorption potential of dried water hyacinth roots for the removal of lead (Pb(II)) from its aqueous solution under various experimental conditions.

**MATERIALS AND METHODS**

**Materials**

Lead nitrate (Pb(NO₃)₂), cadmium chloride (CdCl₂·2.5H₂O), 80% acetic acid (CH₃COOH), nitric acid (HNO₃), sodium hydroxide (NaOH), hydrochloric acid (HCl), 72% sulfuric acid (H₂SO₄) used in this study were of American Chemical Society (ACS) grade. The standard solutions were prepared by dissolving the required amount of salts in ultrapure water. All glassware was dipped in 10% HNO₃ and washed with ultrapure water at least three times before use.

**Preparation of adsorbent**

Freshwater hyacinth plants were collected from a relatively less polluted area of the Monairkandi branch of river Meghna, Bangladesh. Water samples were also collected from the same spot. The collected plants and water samples were brought to the laboratory. The roots were immediately separated from the plant and washed with copious amounts of tap water. The roots were then washed five times with ultrapure water. The cleaned roots were cut into 1–2 mm segments and then dried at 70 °C until constant weight. After drying, the roots were ground and sieved through a 0.25 mm sieve. The prepared adsorbent was stored in a reagent bottle for future use.

**Characterization of dried water hyacinth roots (DWHR)**

The prepared adsorbent was analyzed for organic matter, mineral matter, cellulose, and lignin content. The adsorbent was also analyzed for lead (Pb), cadmium (Cd), chromium (Cr), and nickel (Ni) contents following standard methods. Lead, Cd, Cr, and Ni contents of the water samples collected from the site of water hyacinth sample collection were also determined. Fourier Transform Infrared (FT-IR) spectroscopy was used to observe and characterize the functional groups present in the roots. Fresh dried roots and spent (after Pb(II) sorption) roots were dried overnight in a vacuum drying oven (Lambtech) and analyzed with Attenuated Total Reflectance (ATR) method with a Perkin Elmer FT-IR/NIR Spectrometer Frontier model.

**Metal solutions**

A standard 1,000 mg/L stock solution of Pb(II) was prepared. The synthetic solutions required in the sorption experiments were prepared from the standard solution through dilution. Deionized water was used in all cases.
Batch sorption experiments

In order to study the effect of contact time, pH, sorbent dosage, and metal concentration on Pb(II) sorption by DWHR, adsorption experiments were carried out at room temperature \((25 \pm 2 \, ^\circ C)\) using a rotatory shaker at 150 rpm. After agitation, the synthetic solutions were filtered through a Whatman filter paper No. 40 \((8 \, \mu m\) particle retention). The filtration was done to separate the dried root biomass from the synthetic solution. The dried roots were activated in deionized water for 2 h before every sorption experiments. Three replicates of the control and treatment were run during the sorption experiment with aqueous Pb(II) solutions.

Effect of contact time

The effect of contact time was studied conducting batch experiments with an initial Pb(II) concentration of 100 mg/L, pH \(5.0 \pm 0.05\), 0.1 g sorbent dosage, and at different times \((5, 10, 15, 20, 30, 60, 90, 120, \text{ and } 240 \, \text{min})\). The pH was kept at 5.0 based on some previous studies.

Effect of sorbent dosage

Batch experiments were carried out with different dosages of DWHR \((0.025, 0.05, 0.1, 0.2, \text{ and } 0.25 \, \text{g/50 mL})\) to determine the optimum dosage for metal removal. In this experiment, the initial metal concentration was kept constant at 100 mg/L, the pH was kept at \(5.0 \pm 0.05\), and the equilibrium time was kept at 90 min. The equilibrium time was set based on the contact time study.

Effect of pH

Pb(II) uptake onto DWHR as a function of pH was studied varying the metal solution pH from 1.5 to 6.0. The pH was adjusted using diluted NaOH and HCl. The synthetic solutions of 100 mg/L Pb(II) were agitated with 0.1 g/50 mL of sorbent dosage for 90 min of equilibrium time.

Effect of metal concentration and isotherm study

To understand the isotherm behavior of DWHR during Pb(II) removal, experiments were conducted at pH \(5.0 \pm 0.05\) with 0.1 g/50 mL sorbent dosage, 90 min of equilibrium time, and varying metal concentrations of Pb(II) \((50\text{–}300 \, \text{mg/L})\).

Removal study with real wastewaters

In order to study the efficacy of DWHR in removing Pb (II) from wastewaters, wastewaters were collected from various sources. A variety of industries were selected for the removal studies, including battery, dyeing, and ship-breaking industries. All of them were known to contain a high amount of Pb(II) in their wastewaters. The lead-acid battery industry was located in Kamrangirchar, the automobile battery industry in Mirzapur, the dyeing industries in Tejgaon and Sreepur, and the ship-breaking industry in Jahanabad. Removal studies were first carried out with DWHR and the raw wastewaters. The concentration of Pb(II) was determined before and after the removal studies. The pH of the wastewaters was then adjusted at 5.0 and the removal studies were done again. The Pb(II) concentrations were again determined in the pH-adjusted wastewaters. The two sets of data were then analyzed. All the studies were done in triplicate.
Calculation of results

The results obtained from the sorption experiments were at first evaluated by Dixon's Test (at 5% level) to identify and reject if there were any outliers. The results of the concentration of three replicates of the control and the residual concentration of metals in the three replicates of the treated solution or wastewaters were then averaged and the mean results were then used to determine the percentage of metal removal and the amount of metal ions adsorbed on the adsorbent by the following formula:

\[
\text{Removal (\%)} = \frac{C_0 - C_f}{C_0} \times 100
\]

where, \(C_0\) is the initial metal concentration and \(C_f\) is the residual metal concentration after treatment, and

\[
q_{eq} = \frac{(C_0 - C_f)V}{m}
\]

where, \(q_{eq}\) is the amount of metal ions (unit mass, mg) adsorbed per gram of dried roots, \(V\) is the volume of metal solution in liters and \(m\) is the dry mass of water hyacinth roots in grams.

Statistical analysis

All the calculations were performed using Microsoft Excel (version 2020). One-way analysis of variance (ANOVA) followed by Tukey's Post-hoc test was carried out by Minitab statistical software (version 19). The data were checked for normality and homoscedasticity before the parametric test (one-way ANOVA). Statistical significance was determined based on whether \(p\) values were <0.05 or not.

RESULTS AND DISCUSSION

The ash or mineral matter content of the water hyacinth root biomass was found to be 19.0%, which was almost identical (18.43%) to the findings of Mukaratirwa-Muchanyereyi et al. (2016). A number of other researchers also reported a more or less similar amount of mineral matter in water hyacinth roots; for example, 17% (Kouraim et al. 2014), 20.2%, and 16.29% (Poddar et al. 1991). The organic matter of the roots was found to be 81.0%, which was similar to the finding (81.57%) of Mukaratirwa-Muchanyereyi et al. (2016). The lignin and cellulose contents of the root biomass were 22.44% and 15.59%, respectively. Kouraim et al. (2014) found the lignin and cellulose contents of water hyacinth to be 15 and 28%, respectively. Ahn et al. (2012) reported the lignin content of water hyacinth roots varying from 3 to 28%. In a study with land plants, Bhattacharya & Kumar (2010) obtained cellulose content between 30 and 50%, and lignin content between 15 and 30%. Total nitrogen (N) content in the root biomass was found to be 0.86%, which is lower than the content found by Kouraim et al. (2014) and Ngah & Hanafiah (2008); their analyzed N contents were 2.0% and 1.2%, respectively. Therefore, the background concentrations obtained for water hyacinth in this study are in agreement with the previous findings of other researchers.

Generally, heavy metal contents in aquatic plants are higher than in the water bodies where the plants are growing (Abdel-Sabour et al. 1996). In the present study, Pb and Ni contents were below the detection limits (BDL) of the instrument (Table S1, Supplementary Material). However, Pb and Ni concentrations were 2.60 mg/kg and 3.90 mg/kg in the dried water hyacinth roots, respectively. Abdel-Sabour et al. (1996) worked with water hyacinth and reported that although the heavy metal content in the water of river Nile was below 0.012 mg/L, the roots of water hyacinth grown in that
water contained 25.1 mg/kg Pb, 1.0 mg/kg Cd, 3.2 mg/kg Cr, and 2.4 mg/kg Ni. In a recent work by Shafy et al. (2016), the Pb content of the roots of water hyacinth grown in the Nile river was found to vary from 54.8 mg/kg to 123.3 mg/kg across the year.

Characterization of water hyacinth roots

The FT-IR spectrum of DWHR revealed the presence of many functional groups, indicating the complex nature of the molecular structure of roots of water hyacinth. Figure 1 shows the peaks observed in the FT-IR spectra of freshwater hyacinth root biomass. The band at 3,340 cm\(^{-1}\) is attributed to O-H stretch vibration (Parikh 1974; Sundari & Ramesh 2012). The band at 2,924.17 cm\(^{-1}\) is attributed to C-H stretch vibration for alkanes (Liu et al. 2006). The band at 2,297.45 cm\(^{-1}\) was probably due to non-conjugated C= N stretching vibration (Parikh 1974). The peak at 1,628.41 cm\(^{-1}\) is assigned to the C=O stretch vibration of carboxylate (Liu et al. 2006; Southichak et al. 2006). Sundari & Ramesh (2012) reported a similar peak on water hyacinth nanofibers. The bands at 1,419 cm\(^{-1}\) and 1,321.6 cm\(^{-1}\) are attributed to C-H bending vibrations or C-H deformation (Pandey & Pitman 2003; Osman et al. 2010). The strongest peak in DWHR was observed at 1,004.62 cm\(^{-1}\), which is assigned to C-O stretches. The presence of C-O stretch indicates the presence of alcoholic hydroxyl groups (Lim et al. 2008b), especially that of primary alcohols. This hydroxyl group of primary alcohols can be found in coumaryl alcohols, which is one of the building units of lignin (Tan 2010). Thus, the strongest peak at 1,004.62 cm\(^{-1}\) confirms the lignin structure of water hyacinth roots (Neto et al. 1995). Besides, the peaks at 797.05 and 687.94 cm\(^{-1}\) are attributed to -CH= CH-(cis) bonds (Smith 2016). Thus, the most intense bands in the FT-IR of freshwater hyacinth root biomass are 1,004.62, 1,628.41 and 3,340 cm\(^{-1}\), attributed to C-O stretches typical of lignin, C= O stretch vibration of carboxylate and O-H stretches typical of cellulose, respectively (Cordeiro et al. 2011).

![Figure 1](http://example.com/figure1.png)

**Figure 1** | FT-IR graph for fresh dried water hyacinth roots (DWHR).

The FT-IR study demonstrates the fact that the water hyacinth root biomass is mainly lignocellulosic in composition. The FT-IR spectrum also shows that pure water hyacinth root biomass contained a greater percentage of lignin than cellulose, which can be substantiated by the results of cellulose and lignin content analysis.

**Sorption experiment**

**Effect of contact time**

Batch studies were conducted to see the effect of contact time on the sorption of Pb(II) onto the roots of water hyacinth. It was revealed that the sorption was rapid for the first 60 min and equilibrium was
reached within 90 min (Figure 2). This was probably due to most of the cations being removed by the sorbent within the first 60 min of contact time. After very rapid adsorption, the rate of sorption slowed down. The driving force for sorption; that is, the concentration difference between the bulk solution and the solid-liquid interface, was initially higher, which resulted in a faster sorption rate initially. After the initial period, a decrease in the sorption rate was probably owing to the slower diffusion of solute into the interior of the sorbent (Zhu et al. 2008).

**Effect of pH**

The effect of pH on metal sorption was studied by many researchers, and their findings indicated that the pH values of the solution could significantly influence biosorption (Bayramoğlu & Arca 2009; Ozdemir et al. 2009). The pH level affects the network of negative charges on the surface of the biosorbent, as well as the physico-chemistry and hydrolysis of the metal (Reddy et al. 2012). Therefore, in the present study, batch studies were performed at varying pH values (1.5, 3.0, 4.5, 5.0, 5.5, and 6.0) to find the optimum pH for maximum Pb(II) removal. At pH 6.0, there was a tinge of cloudiness in the solution indicating the onset of precipitation. Therefore, the pH study was performed within that scale.

The removal of Pb was observed to increase with increasing pH (from 1.5 to 5.0) (Figure 3). It was also seen that at highly acidic conditions (pH 1.5), the amount of metal removal was small (10.60% removal). This was due to the presence of a higher concentration of H⁺ ions in the solution, which
competed with metal ions for the adsorption sites of the biosorbent (Shin et al. 2007). A sharp increase in metal ion binding was observed from pH 3.0 to 5.0. The highest removal (93.75%) was seen at pH 5.0. A decreased biosorption was observed at pH 5.5 and then the biosorption slightly increased at pH 6.0. It was already mentioned that at pH 6.0 there was a shade of cloudiness in the solution. Precipitation might have occurred at pH 6.0 that resulted in higher biosorption at pH 6.0 compared to pH 5.5. Thus, it can be suggested that relatively lower adsorption at lower pH values and above the optimum value (pH 5.0) was due to heavy protonation of the negatively charged binding sites and formation of metal hydroxides, respectively (Yan & Viraraghavan 2003).

Effect of sorbent dosage

The results showed that with an increase of DWHR dosage from 0.025 to 0.1 g, the Pb(II) removal increased from 37% to almost 93% (Figure 4). Even though 100% removal was achieved by 0.25 g dosage of roots, 0.1 g dosage was considered as the optimum dose given the fact that lower dosage will cost less capital and resource. Several researchers reported similar results, stating that the increase in sorbent amount causes a subsequent increase in adsorption sites that results in the increase in adsorption capacity (Parvathi et al. 2007; Saraswat & Rai 2010). Thus, the increment in the adsorption efficiency occurs until saturation with an increase in sorbent dosage.

![Figure 4](http://iwaponline.com/wpt/article-pdf/16/2/404/873957/wpt0160404.pdf)

**Figure 4** | Effect of sorbent dosage on Pb(II) removal by DWHR at 25 ± 2 °C. Initial concentration = 100 mg/L, pH = 5.0, and equilibrium time = 90 min. Differences were determined by one-way ANOVA followed by Tukey’s pairwise comparison (p < 0.05). Different letters above the bar indicate the significance of differences between different adsorbent dosages.

Effect of metal concentration

It was observed that at the lowest concentration, the removal was the highest and the removal percentage decreased with the increase in metal concentration (Figure 5). At 50 mg/L of initial concentration of Pb(II), the removal percentage was ~98%. On the other hand, the lowest percentage was observed at 300 mg/L (44%). Erdem et al. (2004) and Xiaofu et al. (2008) also reported that the adsorption efficiency of sorbents decreased with increasing initial metal concentration. El-Ashtoukhy et al. (2008) explained that at low concentrations, metals are adsorbed by specific sites. With increasing metal concentrations, the specific sites are saturated followed by the occupation of the exchange sites, which results in less adsorption efficiency.
Adsorption kinetics

In order to evaluate the kinetic rate, the rate-controlling steps, and the adsorption mechanism of Pb(II) ions onto DWHR, the contact time (kinetic study) data were interpreted by the pseudo-first and pseudo-second-order models. The models were fit with the optimized values derived from the sorption study. The optimum conditions taken for the models are as follows: initial concentration = 100 mg/L, pH = 5.0, sorbent dosage = 0.1 g, and equilibrium time = 90 min. A conformation between experimental and calculated models are expressed in terms of the coefficient of variation (R² values are shown in Table 1). The relatively higher R² values are regarded to be the more applicable model to the adsorption of Pb(II).

Table 1 | Parameters constants of pseudo-first-order and pseudo-second-order kinetic models for Pb(II) sorption by DWHR, at 25 ± 2 °C (initial concentration = 100 mg/L, pH = 5.0, sorbent dosage = 0.1 g, and equilibrium time = 90 min)

| Metal ion | Experimental qe,exp (mg/g) | Pseudo-first-order model qe,cal (mg/g) | k1 (min⁻¹) | R² | Pseudo-second-order model qe,cal (mg/g) | k2 g/(mg.min) | R² |
|-----------|---------------------------|--------------------------------------|------------|----|--------------------------------------|---------------|----|
| Pb(II)    | 39.74                     | 5.71                                 | 0.0304     | 0.8475 | 40.82                                | 0.0127        | 0.9999 |

Pseudo-first-order kinetic model

The pseudo-first-order kinetic model was proposed by Lagergren (1898), which was the earliest model describing the adsorption rate related to adsorption capacity. The integral form of the model was generally expressed as follows:

\[ \log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \]

where, \( q_e \) (mg/g) is the amount adsorbed at equilibrium time, \( q_t \) (mg/g) is the amount adsorbed at time (t) and \( k_1 \) (min⁻¹) is the adsorption rate constant.
If the pseudo-first-order kinetics is applicable, a linear relationship is obtained. The rate of variation is proportional to the first power of concentration if it is of strict surface adsorption. The relation between the initial solute concentration and adsorption rate will not be linear when pore diffusion limits the adsorption process. In the kinetic study, the first-order equation of Lagergren did not apply well during the entire contact time and was only applicable to the initial 60 min of the adsorption process. The plotting of $\log(q_e - q_t)$ versus time deviated considerably from the theoretical data after a short period (<20 min). The slope and intercept of the curve were used to determine the first-order constant $k_1$, capacity $q_e$, and the corresponding linear regression correlation coefficient, $R^2$ value (Table 1, Figure S1, Supplementary Material).

The pseudo-first-order model failed to provide a realistic estimate of $q_e$ (mg/g) of adsorbed Pb(II) as the experimental value of $q_e$ (39.7 mg/g) was far higher than the fitted value (5.71 mg/g) as shown in Table 1. This underestimation of the amount of binding sites is probably because $q_e$ was determined from the y-intercept ($t = 0$). The intercept is strongly affected by the short-term Pb(II) uptake, which is usually lower than the equilibrium uptake. This is a disadvantage of using the linearized first-order model. Therefore, the adsorption of analyte ions onto DWHR was not considered as being a first-order reaction even though the correlation coefficient $R^2$ is relatively high (0.8475).

**Pseudo-second-order kinetic model**

The pseudo-second-order model was developed based on the assumption that the rate-limiting step may be chemisorption promoted by either valence forces, through the exchange of electrons between the parties involved, or covalent forces, through the sharing of electrons between the biosorbent and sorbate (Ho & McKay 1999). The sorption rate is proportional to the square of the number of unoccupied sites. Vadivelan & Kumar (2005) reported that most of the adsorption system followed a pseudo-second-order kinetic model which can be linearly be expressed as,

$$
\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t
$$

where, $k_2$ (g/(mg.min)) is the rate constant of adsorption. A plot of $t/q_t$ versus $t$ should give a linear relationship for the applicability of the second-order kinetic. The rate constant ($k_2$) and adsorption at equilibrium ($q_e$) can be obtained from the intercept and slope, respectively. The initial adsorption rate, $h_0$ (mg/(g.min)) is defined by,

$$
h_0 = k_2 q_e^2
$$

The parameter constants (Table 1, Figure S1) derived from the pseudo-second-order kinetic model indicate that the data fitted more into the pseudo-second-order model. The pseudo-second-order model provided a very close estimate of $q_e$ (mg/g) of adsorbed Pb(II). Therefore, chemisorption most probably played the predominant role for the Pb(II) removal capacity of the dried water hyacinth roots.

**Isotherm studies**

Langmuir and Freundlich adsorption isotherms were tested for the adsorption data obtained by conducting an isotherm study with DWHR (0.1 g dry weight) with varying concentrations of Pb(II) solutions (50–300 mg/L).
The Langmuir model assumes that there is no interaction between the adsorbate molecules and the adsorption is localized in a monolayer (Langmuir 1918).

\[ q_e = \frac{q_m b C_e}{1 + b C_e} \]

where \( C_e \) (mg/L) is the equilibrium concentration of the remaining ions in the solution; \( q_e \) (mg/g) is the amount of ions adsorbed per mass unit of adsorbent at equilibrium; \( q_m \) (mg/g) is the amount of ions at complete monolayer which is also called the sorption maximum, and \( b \) (L/mg) is the Langmuir constant related to the affinity of binding sites which is a measure of the energy of adsorption. The Langmuir equation can be described by the linearized form:

\[ \frac{1}{q_e} = \frac{1}{q_mB} \times \frac{1}{C_e} + \frac{1}{q_m} \]

The Langmuir constants \( b \) and \( q_m \) are calculated from the slope \( (1/q_mB) \) and intercept \( (1/q_m) \) of the plots of \( 1/q_e \) (Y-axis) and \( 1/C_e \) (X-axis). The separation factor, \( R_L \), is used to predict the affinity between adsorbate and adsorbent. \( R_L \) can be derived from the following equation.

\[ R_L = \frac{1}{1 + bC_0} \]

The \( R_L \) value indicates the shape of the isotherm. \( R_L \) values between 0 and 1 indicate favorable adsorption (McKay et al. 1982). \( R_L \) value being equal to 0, 1 and >1 indicates irreversible, linear, and unfavorable adsorption, respectively.

The Freundlich isotherm model is an empirical relationship describing the adsorption of solutes from a liquid to a solid surface, and the model assumes that in the adsorption process different sites with different adsorption energies are involved (Freundlich 1906). The Freundlich isotherm can be applied for non-ideal sorption on heterogeneous surfaces and multilayer sorption. It also assumes that the adsorbent has a different affinity for adsorption. The Freundlich equation is expressed as:

\[ q_e = K_F C_e^{1/n} \]

where \( K_F \) and \( n \) are Freundlich constants indicating adsorption capacity and intensity or the favorability of the sorption process, respectively. When the \( 1/n \) values are small, it implies that the adsorption occurs in a fairly wide concentration range. Adsorption is favorable for values \( 0.1 < 1/n < 1.0 \) (Kadirvelu & Namasivayam 2000). Values of \( 1/n \) being less than unity are an indication that significant adsorption takes place at low concentrations but the increase in the amount adsorbed becomes less significant at higher concentrations (Baquero et al. 2003; Moreno-Piraján & Giraldo 2010). To determine the constants \( K_F \) and \( n \), the Freundlich equation can be described by the linearized form:

\[ \log q_e = \log K_F + \frac{1}{n} \log C_e \]

Values of \( K_F \) and \( n \) are calculated from the intercept and slope of the linear plots of \( \log q_e \) vs. \( \log C_e \). Adsorption data fitted better into the Langmuir (\( R^2 = 0.986 \)) than the Freundlich (\( R^2 = 0.908 \)) isotherm (Table 2, Figure S2). The fact that the Langmuir isotherm most closely represented the experimental data could be interpreted as an indication of homogenous adsorption, leading to a monolayer binding. From the Langmuir isotherm model, the maximum sorption capacity was found to be 49.75 mg Pb/g (dry weight). The \( R_L \) values for Pb(II) ranged from 0.0038 to 0.02 (for 50–300 mg/L), indicating favorable adsorption process (Table 2). The magnitude of \( K_F \) and \( n \) from
the Freundlich isotherm shows that it is possible for easy separation of heavy metal ions from aqueous solution and high adsorption capacity. Also, the higher the $K_F$ value is, the greater the adsorption intensity.

**FT-IR characterization of spent DWHR**

FT-IR characterization of the functional groups was done on spent or used DWHR to confirm the adsorption mechanism and to determine the functional groups involved in the binding of Pb(II) ions onto the biosorbent. The infrared spectra of the biosorbent laden with Pb(II) (Figure 6) contained band of O-H stretch vibration, but the peaks shifted to a higher wave number at 3,611.04 cm$^{-1}$ and 3,346.40 cm$^{-1}$ respectively. The band at 2,924.17 cm$^{-1}$, C-H vibration, is also present in the spent biosorbent, but with a slight shift to a lower wave number to 2,919 cm$^{-1}$. The band at 2,297.45 cm$^{-1}$, attributed to non-conjugated C = N stretching vibration, was present only in the fresh DWHR but was absent in spent DWHR. The band at 1,628.41 cm$^{-1}$, assigned to C = O stretch vibration of carboxylate, was also present in spent DWHR but with a shift in lower wave number to 1,618.41 cm$^{-1}$. In the case of the band at 1,321.6 cm$^{-1}$, assigned to C-H bending, the peak shifted downwards to lower energy at 1,379 cm$^{-1}$ in spent DWHR. A new band at 1,237.45 cm$^{-1}$ was observed in Pb(II) laden DWHR, which can be assigned to carboxylate (Reddy et al. 2010). The strongest peak observed at the 1,004.62 cm$^{-1}$, attributed to the C-O stretch bond, was found to shift downward to lower energy at 1,027.69 cm$^{-1}$ indicating the involvement of the C-O functional group in the metal binding. When the FT-IR spectra were compared between fresh and spent DWHR (Figures 1 and 6), it can be seen that the Pb sorption occurred more at C-O and O-H functional groups, which are among the most intense bands present in the fresh DWHR. The shifts in the bands indicate that there were binding

**Table 2 | Isotherm parameter constants for Pb(II) sorption onto roots of water hyacinth**

| Metal ion | $R^2$ | $q_m$ (mg/g) | $b$ (L/mg) | $R_L$ | $R^2$ | $K_F$ (mg/g)(L/mg)$^{1/n}$ | $n$ |
|-----------|-------|--------------|------------|-------|-------|-----------------------------|-----|
| Pb(II)    | 0.987 | 49.75        | 0.8627     | 0.0038-0.02 | 0.909 | 23.52                      | 5.63 |

![Figure 6](http://iwaponline.com/wpt/article-pdf/16/2/404/873957/wpt0160404.pdf)
processes taking place on the surface of the biosorbent, and the greater the shift, the stronger the bond between the biosorbent and the adsorbed metal (Karnib et al. 2014).

Removal study with real wastewaters

Removal study with real wastewaters was carried out with or without pH adjustment (Figure 7 and Table S2). The pH adjustment was done to simulate the batch experiment where the highest amount of Pb(II) was removed. The results of the removal of Pb(II) by DWHR from both raw and pH adjusted wastewaters (WW) are presented in Figure 7. The biosorbent worked efficiently in four of the wastewaters, removing 75–97% Pb(II). However, the DWHR biosorbent failed to remove a significant amount of Pb from the wastewaters of the automobile battery industry. When pH was adjusted to 5.0, the removal of Pb drastically increased from ∼21% to ∼93% in the automobile battery industry’s wastewater. This increase in removal was in line with the removal of Pb found in the sorption experiment with aqueous solutions at the same pH. Other industrial wastewaters also showed an increase in Pb removal due to pH adjustment.

Possible implementation of the technology

Water hyacinth is a nuisance in tropical and subtropical countries, including Bangladesh. It suffocates aquatic life by preventing the diffusion of oxygen. It blocks waterways and thereby obstructs navigation. It affects tourism by reducing the aesthetic values of water bodies. To deal with water hyacinth, herbicides have previously been employed. However, using herbicides creates additional environmental problems. Moreover, the ultimate disposal of expired water hyacinth is a substantial problem, which renders countries incurring a huge loss. Therefore, the use of water hyacinth for the treatment of wastewater is an attractive option. In the present study, the maximum adsorption capacity was found to be 49.75 mg of Pb per gram of dried water hyacinth root biomass. In the wastewater, the adsorption capacity may be reduced by the interference from other heavy metals. Assuming that the Pb sorption will be reduced by half, the amount of root biomass required can be calculated for a wastewater having a concentration of 10 mg Pb/L. Using the figure of 25 mg of Pb per gram of dried root biomass and the Pb concentration of 10 mg/L, 400 g of dried water hyacinth root biomass would be required to remove 10 g of Pb from 1,000 L of water. Therefore, if a wastewater treatment plant

![Figure 7](http://iwaponline.com/wpt/article-pdf/16/2/404/873957/wpt0160404.pdf)
generates 10,000 L of Pb-laden wastewater per day, 4,000 g or 4 kg of dried water hyacinth biomass would be needed per day. However, a detailed cost-benefit analysis needs to be done to see the feasibility of using dried water hyacinth root in a wastewater treatment plant. Even though the water hyacinth biomass is not expensive, the costs involving water hyacinth transportation, handling and regeneration will need to be determined before the biosorbent could be employed in a real wastewater treatment plant.

CONCLUSIONS

The aim of the present study was to find a cheaper and locally available alternative to expensive sorbents for the removal of heavy metals (e.g. Pb) from wastewaters. In Bangladesh, there is a general reluctance on the part of the industrialists to operate effluent treatment plants that require expensive chemicals. To address that problem, a cheaper alternative was sought in this study. Non-living dried water hyacinth root was tested for its efficacy as a biosorbent and it was found to be an effective sorbent for removal of Pb(II) from aqueous solution. The removal kinetics was found to be fast which enhances its applicability as a biosorbent. The Freundlich isotherm indicates that chemical sorption was responsible for Pb(II) removal by water hyacinth roots. The biosorbent also exhibited very promising Pb(II) removal in pH-adjusted wastewaters. A scale-up calculation was also done to determine the quantity of biosorbent required for Pb(II) removal from wastewater. The findings of this research have considerable implications for the possible future application of this biosorbent in wastewater treatment plants.

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DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

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