



## Removal of Some Traces Heavy Metals from Aqueous Solutions by Water Hyacinth Leaves Powder

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### Abstract

The pollution of aquatic ecosystems with toxic heavy metals is representing a major environmental issue, as a result of releasing these metals to ecological ambient without treatment, leading to their persistence and non-biodegradation in the environment. Various traditional methods are utilized as an attempt to remove heavy metals from waste water but still without making any actual progress. This study hypothesizes that *Eichhornia crassipes* (water hyacinth) dried leaves powder is potential in removing some of these heavy metals (HM), including lead, copper, cadmium and chrome from aqueous solutions via biosorption influenced by some variable experimental factors. This aim was approached by using two different experimental conditions: (i) investigating the effect of different pH values, ranged between 4-8 with a constant (HM) concentration (1000 ppm), (ii) using variable (HM) concentrations with a range (250, 500, 750 and 1000 ppm) in which constant pH value equal to 7 was maintained. Additionally, the amount of leaves powder used throughout the study was 1g. The data obtained from this study revealed that higher removal efficiency was observed with lead (Pb) which reached to 99.9%, whereas the lowest was with chrome (Cr) which its removal was up to 80% in both experimental conditions. These results suggest that *E.crassipes* in its non-living form is efficient in the treatment of waste water and other industrial effluents containing trace elements.

**Keywords:** Heavy metals, *Eichhornia crassipes*, Biosorption

### ازالة بعض العناصر الثقيلة من المحاليل المائية بواسطة مسحوق اوراق نبات زهرة النيل المائي

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### الخلاصة

ان تلوث الانظمة المائية بالمعادن الثقيلة يعد من المشاكل البيئية الرئيسية، لكونها تطلق الى المحيط البيئي بدون معالجه مما يتسبب ببقائها وثباتيتها و هي غير قابله للتحلل الحياتي. عدد من الطرق التقليديه استخدمت لازالة المعادن الثقيلة لكن اي منها لم تعطي نتائج مقبولة او واعدته. هذه الدراسه تكشف القدره الحيويه على الامتزاز لمسحوق اوراق نبات زهرة النيل المجفف في ازالة بعض العناصر الثقيله مثل الرصاص و النحاس و الكاديوم و الكروم من محاليلها المائية ضمن عوامل مختبريه متغايره. احتوت الدراسه على نوعين من المعاملات: الاولى تضمنت مديات مختلفه من الالاس الهيدروجيني و هي 4 و 5 و 6 و 8 مع تركيز ثابت للمعادن 1000 جزء بالمليون، بينما تمثلت الثانيه باستخدام تراكيز متغايره للعناصر الثقيله ضمن المدى (250 و 500 و 750 و 1000) جزء بالمليون مع ثبات التركيز الهيدروجيني عند الرقم 7. في جميع

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التجارب كانت كمية مسحوق الاوراق واحد غرام. ان النتائج المستحصلة من البحث كشفت الكفاءة العاليه للازالة الرصاص و التي وصلت الى 99.9% بينما كانت الاوطى لمعدن الكروم و التي وصلت 80% في كلتا المعاملتين. لقد اكدت هذه النتائج قابلية النباتات المائية كزهرة النيل بشكلها غير الحي في معالجة مياه الفضلات وغيرها من الدفقات الصناعيه الحاويه على معادن نزره.

## Introduction

Multiple factors contribute to heavy metals pollution. Different human activities, including rapid industrialization, urbanization, mining and agriculture, lead to an elevation in the emission of toxic heavy metals which might damage or alter both natural and manmade ecosystems [1]. Among these hazardous heavy metals Cd, Cr, Pb, Ni, Hg, Cu, Co, and Zn. Metals are mobilized, carried in to the food web, then increased in concentration at every level within food chain and are passed on to the next higher level in phenomenon called bio-magnification [2]. The aquatic ecosystems are more susceptible towards the harmful effects of heavy metals in which the aquatic organisms are in a close and prolonged exposure with soluble metals [3]. The non-biodegradability of these ions is the most important feature that distinguishes them from other pollutants [4]. Recent studies already proved the ability of these metals in their binding to different protein molecules, preventing the replication of DNA, as a result causing defects in cell division [3]. One of the commonest ions identified in industrial effluents is copper [5]. Even in low concentrations, copper is considered toxic to organisms while the extreme consumption of it will lead to numerous human health hazards such as anemia and lung cancer [6]. The fair concentration of copper in drinking water must not exceed 1.3 ppm as recommended by US-EPA and WHO organization [7]. On the other hand cadmium is non-essential for living organisms, but it has a negative effect on environment especially plants [8]. Different reports had indicated that lead can cause adverse impacts on human health and environment which might include severe damage to the kidney, nervous and reproductive system and liver [9]. Simultaneously, chromium has received a wide spread attention because of its use in various industrial applications [10]. However, permissible limit of it is 0.1mg/L and 0.05 mg/L for industrial effluents and potable water respectively according to US-EPA [11]. Its nocuous influence represented by its high mobility in soil and aquatic systems, as well as its capability of being adsorbed by skin, therefore it is regarded as carcinogenic and mutagenic in nature [12]. Some fresh water macrophytes, including *Eichhornia crassipes*, has been found in large amounts around the irrigation canals and fresh water bodies throughout the year in tropical and sub tropical countries [13]. *E. crassipes* (water hyacinth), belonging to family Pontederiaceae, is a wild ferns and sub merged aquatic plant floating on the water surface forming dense mats [14]. These criteria belong to its rapid growth from daughter plants by means of runners or stolon (aerial stem forming many roots) then produces a large amount of seed which persist in the environment up to thirty years [14]. A range of methods have been applied for heavy metals removal and the most important one is adsorption [15]. Biosorption can be regarded as an alternative to conventional or traditional methods; it is based on passive uptake of toxicants by using dead (inactive biological materials) derived from biological sources [16]. This process is occurred as non-directed physicochemical interaction between metals (sorbate) (solvent) and sorbent or biosorbent (solid phase) which has a higher affinity in being attached and bound with different mechanisms until equilibrium is established between them [17]. Different methods have been already applied like chemical precipitation, ion exchange and reverse osmosis [9]. The disadvantages of these methods in comparison with adsorption not limited in low cost but also including the generation of secondary products which might be challenging to get rid of, as well as its inefficiently in removing heavy metals lower than 100mg/L [18]. Therefore, biosorption is representing an alternative method that can be appropriate for treating effluents that contain heavy metals low concentrations and can also be used to remove other contaminants such as dyes and organic compounds [19].

The main purpose of this study aims to investigate the capability of dried biomass of *E. crassipes* in the removal of heavy metals such as Cd, Cr, Cu and Pb from aqueous solutions beside the influence of some factors like adsorbent dose and hydrogen ion pH.

## Materials and Methods

### 1. Sampling and preparation of biomass

The living biomass of *E.crassipes* (water hyacinth) plant was harvested from large floating masses in Tigris River at Al-Jadyria campus in August 2014. The plants were transported to the laboratory directly, by using plastic pools, and identified in the herbarium of college of science / Baghdad University according to [14]. Collected samples were washed several times by tap water and then with distilled water to remove any adhering particles. From the washed biomass, leaves were taken and dried three days in shade. The dried biomass was grounded, using mechanical grinder. After being ground grinded, the very small particles (powder) of plant were put in container and used for metal biosorption [16]. In addition, several physicochemical properties of water from samples collecting area were measured like: water temperature by using thermometer (0-100) ° C and hydrogen ion concentration pH by using HANNA after calibration with buffer solution (pH=7) before using.

### 2. Digestion of plant

In order to estimate the quantity of Cu, Cd, Pb and Cr (adsorbate) already present in *E.crassipes*, leaves were digested by using nitric - peroxychloric acid procedure describe previously by AOAC [20]. Briefly, 10 ml of concentrated nitric acid was added to 1g from dried plant in a glass container and boiled gently for 30-45 min to oxidize all easy oxidizable materials. After cooling, 5 ml of 70% peroxychloric acid was added to the mixture and boiled again till white fume appeared. Thereafter, this mixture cooled and 20 ml distilled water added and boiled in order to reduce of any remaining fumes. Finally, the resultant mixture was filtered by using Whatman no.42 filter paper and the filtrate was subjected to atomic absorption spectrophotometer (AAS) (Analytik Jena Nymva) to estimate the percentage of heavy metals.

### 3. Testing the ability of *E.crassipes* powder in the removal of heavy metals in aquatic solutions:

#### A. preparation of stock solutions for sorption experiments:

Stock solution of Pb, Cd, Cr and Cu were prepared with 2000 ppm concentration by dissolving 3.2 g, 5.48g, 11.3g and 7.85g of the following heavy metal salts respectively which include Pb (NO<sub>3</sub>)<sub>2</sub>, CdCl<sub>2</sub>, K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> and CuSO<sub>4</sub> respectively in one liter of tris base buffer which is prepared in deionized water. These solutions were prepared using a standard flask, the range of concentrations used were prepared by serial dilution of stock solution with deionized water [21].

#### B. Batch sorption experiments

All experiments were conducted with *E.crassipes* in a 200ml flask at room temperature by shaking 1g of plant powder mixed with 50 ml from each adsorbate solution. The mixture agitated by shaker apparatus (shaker incubator: Lab Tec R.) for 30 min and adjusted at 35°C similarly to water temperature from where plant samples were collected. After each adsorption run, the mixture (adsorbent and adsorbate) was left for 24hr. undisturbed. Mixtures were filtered next day using Whatman filter paper, then these samples were centrifuged (using centrifuge: Joun C4i) at 3000 for 10min, the heavy metals concentration in solution was analyzed by atomic adsorption spectrophotometer [22].

#### C. Influence of metal concentration:

In order to analyze the adsorption potential of adsorbent in different concentration of the adsorbate, the following concentrations were prepared from the stock solution of each adsorbate (heavy metals) (HM) which include (250,500,750,1000 ppm) by using conventional formula of dilution: C<sub>1</sub>V<sub>1</sub>=C<sub>2</sub>V<sub>2</sub>. Throughout all experiments of these four concentrations, the pH value was adjusted at 7 which match the pH of water from which the plant was collected. Then batch method described previously to approximate concentration of adsorbate remaining in the solution could reveal biosorption capacity of water hyacinth leaves.

#### D. Influence of pH

In order to analyze the adsorption potential of adsorbent in variable pH values with constant concentration of adsorbate, therefore solutions with 1000 ppm for each heavy metal were prepared by using tris base buffer with unified pH of all these solutions at 9.3, drops of 0.1N HNO<sub>3</sub> used to adjust pH condition of each one of these solution to 4,5,6 and 8 in aid of pH meter (Professional Bench top pH meter), then the same batch method performed to estimate up take capability of adsorbent in these diverse pH conditions.

### E. Calculation of removal percentage of the adsorbate by adsorbent

The removal efficiency (RE) of adsorbate (heavy metal) by adsorbent water hyacinth leaves was calculated by using the following equation [23]:

$$\text{Removal (\%)} = \frac{(C_i - C_f)}{C_i} * 100$$

$C_i$  and  $C_f$  are the initial and final concentration respectively and measured by mg/L or ppm.

### Result and Discussion

Aquatic plants play a major role in monitoring or minimizing of contaminants including heavy metals in aquatic ecosystem. Many studies reported the importance of different water plants in their acting as biosorbent. For instance, Abdel wahab *et al.* [24] has demonstrated that external and intra particle diffusion of  $\text{Cr}^{+6}$  ions on the surfaces of Guava seeds are both involve in sorption process. The medicinal herb *Foeniculum vulgari* was used by Rao *et al.* [25] in removing  $\text{Cd}^{+2}$  ions from waste water. The results obtained by Olivera *et al.* [26] revealed the efficiency of *Sargassum* as a biosorbent for Sm III and Pr III in solutions. However there are certain disadvantages of using living plants for biosorbent purposes; such as its necessary to constructed artificial ponds near the intended point as well as the phytotoxic effect of these ions which might result in inhibiting chlorophyll synthesis and necrosis [16]. In contrast, moving and handling dead biomass is more advantageous compared to living form [13]. Moreover, researches have been done extensively on roots of these plants while little is known about its leaves [5]. For this reason *E.crassipes* leaves are used to determine the ability of this plant for removing some metals. As mentioned previously, the concentrations of Cu, Cd, Cr and Pb were measured in digested plant leaves by methods described above in order to determine the actual concentrations of these heavy metals in water hyacinth leaves in its natural state. Table-1 shows these results obtained from experiment.

**Table 1**-Levels of heavy metals in digested plant and water collecting area

	<b>Cd ppm</b>	<b>Cr ppm</b>	<b>Cu ppm</b>	<b>Pb ppm</b>
<b>water sample</b>	0.003	0.008	0.03	0.05
<i>Eichhornia crassipes</i>	0.01	1.5	2	10

According to the above results, this plant has the ability to accumulate these ions and these findings agree with what was already found and that the amounts of heavy metals (HM) in are due to absorption during the life time of the plant [26]. Komy *et al.* [5] revealed that cell wall made of functional groups consisting of proteins, carbohydrates and lipids which act as binding sites for these interactions. Therefore, the concentration of heavy metals in plant is accumulative.

Table-2 shows the percentage of heavy metals removed by water hyacinth in different hydrogen ions values (pH) with 1g adsorbent and constant concentrations of adsorbate (HM).

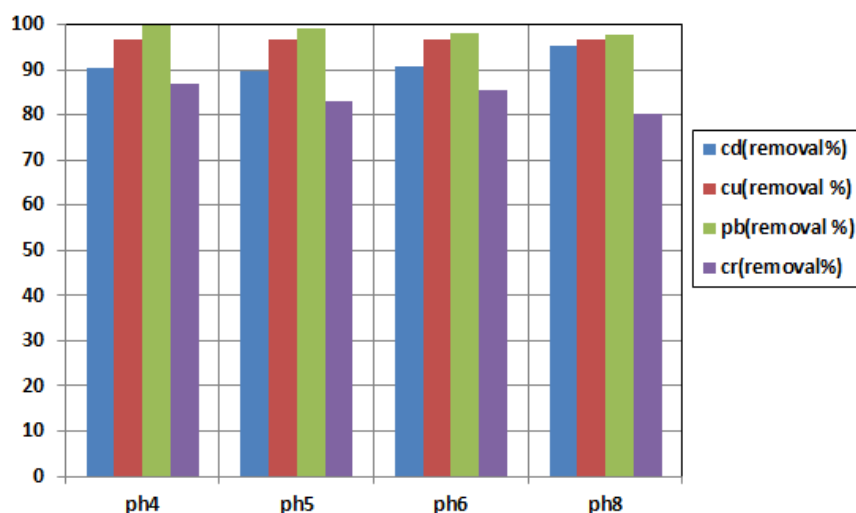
**Table2** - Removal percentage of constant HM concentration (ppm) by using 1g of *E.crassipes* and variable pH value

	<b>*Cf</b>	<b>Cd (removal %)</b>	<b>Cf</b>	<b>Cu (removal %)</b>	<b>Cf</b>	<b>Pb (removal %)</b>	<b>Cf</b>	<b>Cr (removal %)</b>
<b>ph4</b>	95.9	90.4	33.3	96.6	0.94	99.9	130	87
<b>ph5</b>	103.7	89.6	33.8	96.6	6.9	99.3	168	83.2
<b>ph6</b>	93.4	90.6	33.1	96.7	19.7	98	146	85.4
<b>ph8</b>	46.2	95.3	33.4	96.7	20.6	97.9	198	80.2

\*Cf final concentration

These results demonstrate that hydrogen ion concentration (pH) influences the adsorption process. Anzeze *et al.* [9] found that pH is one of the important factors that affect the solubility of metal ions through altering the positive sites occupied by protons on the adsorbent surface with negative charge

when elevated from 2 to a higher value than 7; therefore more binding sites are available for positive ions. This fact proved by Komy *et al.*[5] when they gained typical adsorption of  $\text{Cu}^{+2}$  with pH increased up to 4.5 and proved that its uptake does not depend only on surface charge but on process include (ionization /deprotonization) of the acidic sites. For this reason Cu, Cd and Pb ions in the experiment have a highest rate at pH8 and 4 respectively and in consequence the retention of metal ions in these conditions is determined both by biosorption and precipitation.



**Figure 1**-Effect of variable pH values on the removal of heavy metals by *E.crassipes* (adsorbent Biomass: 1g, HM: 1000 ppm, pH range 4, 5,6and 8)

According to experimental results, the maximum percent (%) for Cr removal was obtained at pH 4; Figure-1 shows the changes in the percent of chromium removal with pH. It can be observed from the figure that chromium removal (%) is decreased by increasing pH values (5-8). Similarly, this was found by Arungandhi *et al.* [3] when they succeeded in increasing adsorption rate up to 81.21% for chromium with pH fluctuated between (2-4) and decreased to 53.41 % at pH7.

The explanation of these findings might be that at acidic media (pH=2-4) the predominant species of chromium will be  $\text{Cr}_2\text{O}_7^{-2}$ ,  $\text{HCrO}_4^-$ ,  $\text{Cr}_3\text{O}_{10}^{-2}$  and  $\text{Cr}_4\text{O}_{13}^{-2}$  and the surface of adsorbent is positively charged which leads to an electrostatic attraction between them [27]. Therefore the removal efficiency of chromium decreases with increasing the pH.

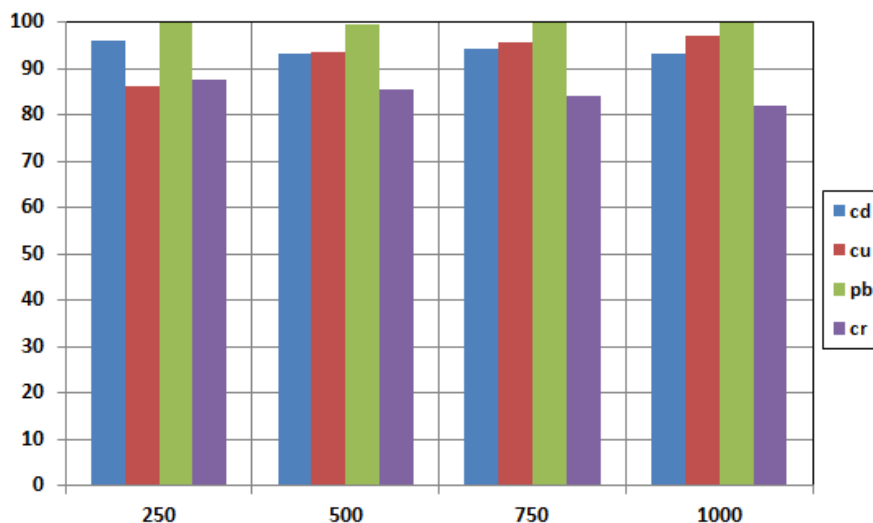
In this study, lead has the highest removal percentage (99.9%), as reported previously, this may be due to binding sites for (Pb) might not be the same for other ions and its larger atomic weight lead to more paramagnetic and electronegative compared to other metal ions [28]. Zhang *et al.* [29] demonstrated that the hydrolysis constant of lead (Pb) is much greater ( $\log k \text{ Pb} = -7.71$ ), implying that the ionic properties could make it more favorable to sorption sites.

Table-3 shows the percentage of heavy metals removal with variant concentrations, constant hydrogen ion and 1g adsorbent.

**Table 3**-The removal percentage of variable HM concentration (ppm) by using 1g *E.crassipes* and constant hydrogen ion pH.

Cd			Cu			Pb			Cr		
Ci	Cf	removal %	Ci	Cf	removal %	Ci	Cf	removal %	Ci	Cf	removal %
250	9.9	96	250	34.2	86.3	250	0.8	99.7	250	31	87.6
500	34	93.2	500	32.8	93.4	500	1.94	99.6	500	73	85.4
750	42.3	94.4	750	30.9	95.8	750	0.71	99.9	750	120	84
1000	68.7	93.1	1000	30.9	97	1000	0.31	99.9	1000	180	82

The effect of heavy metal on the adsorption of *E.crassipes* was investigated and is elucidated in Figure-2. Heavy metal concentrations were tried in range of 250,500,750 and 1000 ppm and with constant pH value at (7).



**Figure 2-** Effect of concentration on the removal of heavy metal by *E.crassipes* (adsorbent dosage: 1g, HM: 250, 500, 750 and 1000 ppm, pH=7).

Results exhibited in Table-3 revealed that the higher removal percentage was observed for Pb, reaching to 99.9 % whereas the lowest was observed for Cr 82%.

This agrees with the fact that heavy metals are positively charged, and that adsorbents have oxide receptacle sites which are basic or amphoteric when reacting with water producing hydroxide responsible for the negative charge and showing high adsorption capacity between them [17]. This fact exhibited extensively by Komy *et al.* [5], they revealed that biomass of *E.crassipes* possesses active components of protein, carbohydrate as well as elemental analysis which constructed their tissues which are filled with functional groups like (-COOH, -NH<sub>2</sub>, -NH-, -OH, C=O and PO<sub>4</sub><sup>3-</sup>) that are responsible for great physical contact between biomass surface and metal ions solution and the entrapment of these ions inside particles pores. The same approach was obtained by [30] and [31] when the adsorption capacity of Cu and Cr was studied respectively, suggesting that (-OH) and (-C=O) groups are the main constituents in *E.crassipes* samples around the world, acting as chelating factors in plant material. As observed in Table-3, the removal percentage altered depending on the initial concentration of metals ions despite the constant concentration of adsorbent biomass (1g) in all experiments. This attributed to the fact found previously [16], that beside the role of adverse charged between biomass and (HM) ions, adsorption capacity depending on two forces: diffusion and mass transfer coefficient; at low concentration level of (HM) ions, the removal percentage is decreased due to a lack in sufficient adsorbent sites and vice versa; an increase in initial concentrations leads increasing the mass transfer force which driving more ions towards binding sites. Moreover Anzeze *et al.* [9] observed the effect of temperature on adsorption process and indicated that adsorption (%) increases with an increase in temperature up to 40 °C due to either creation of some new sorption sites on adsorbent surface or an increase in the intra particle diffusion rate of sorbate, so that suitable temperature was used in this study 35 °C and great biosorption would be observed in all experimental stapes.

In conclusion. *E.crassipes* in its non-living form is efficient in the removal of heavy metals ions and attributed to dissolve this ecological hazard.

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