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The Adsorption of Some Trace Heavy Metals from Aqueous Solution Using Non Living Biomass of Sub Merged Aquatic Plant *Ceratophyllum demersum*

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Abstract

Heavy metals contamination in aquatic ecosystems is considered one of the most important threats of aquatic life. Submerge aquatic plants *Ceratophyllum demersum* in its non living form used for the removal of trace elements. This article studied the ability of the fine powder of *C.demersum* for the removal of some heavy metals (HM) like copper, cadmium, lead and chrome from aqueous solution with in variable experimental factors. The study occupy two treatments the first included different hydrogen ions pH within a range of 4, 5,6and 8 with a constant HM concentration (1000 ppm).While the second treatment represented by using variable HM concentrations within a range of (250,500,750and 1000 ppm) with a constant pH=7.In both treatments the amount of dried plant was 1g.According to analysis of variance the data obtained from this study revealed that removal efficiency of lead Pb reached to 99.9% where as the lower removal percentage % was for chrome Cr about 80%. Also the results indicated that *C.demersum* had high capabilities to remove trace elements, therefore it can be used for refining the waste water.

Keywords: Heavy metals, *Ceratophyllum demersum*, Adsorption.

امتزاز بعض العناصر الثقيلة من المحاليل المائية بأستخدام الكتلة غير الحية لنبات الشمبلان المائي

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الخلاصة

يعد التلوث بالمعادن الثقيله في النظم البيئية المائية واحدة من اهم الملوثات التي تهدد الحياه المائية. وقد أستخدم النبات المائي الشمبلان (الخويصة) *Ceratophyllum demersum* في حالته غير الحية من اجل ازالة هذه المعادن النزرة . ان هذا البحث يدرس قابليه مسحوق نبات الشمبلان *C. demersum* في ازالة بعض هذه المعادن الثقيله مثل النحاس والكادميوم والرصاص والكروم من محاليلهاالمائية ضمن عوامل مختبريه متغايره . احتوت الدراسة على نوعين من المعاملات الاولى تضمنت قيم مختلفة للاس الهيدروجيني ضمن المدى 4و5و6و8 مع تركيز ثابت للعناصر الثقيلة 1000جزء بالمليون . بينما تمثلت المعاملة الثانية بأستخدام تراكيز مختلفة من العناصر الثقيلة ضمن المدى (250و500و750و1000) جزء بالمليون مع ثبات تركيز الاس الهيدروجيني (pH) عند الرقم 7. في كلتا المعاملتين كانت كمية النبات المجفف هي واحد غرام.اعتمادا على التحليل التبايني فأن النتائج التي أستحصلت من الدراسة كشفت ان قابلية أزالة الرصاص وصلت الى 99.9% بينما كانت أوطى قابليه للازالة المعادن متمثلتا بالكروم والتي وصلت الى 80% . أظهرت النتائج ايضا ان نبات الشمبلان *C. demersum* يمتلك امكانية عالية في ازالة المعادن النزرة ، لذلك من الممكن استخدامه في تنقية او معالجة مياه الفضلات .

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Introduction:

Factors like over population, industrialization, rapid urbanization, over use of pesticides, detergents and agricultural chemicals, liquid and solid waste products and discharge of municipal wastes are contributing in heavy metal pollution of normal water resources [1]. The increased loading of heavy metals in the aquatic ecosystem causes an imbalance state of habitat conditions that threats the native biota(living organisms) growing under such abnormal conditions, as a result accumulation of high concentration of metals such as Cd, Cu, Cr, Pb, Co, Hg, Ni, and Zn have been recorded as heavy metals that posses the ability to assimilate and transferred within food chains by processes of bioaccumulation and biomagnifications [2].Copper and Cadmium can become a sanitary and ecological which threat drinking water resources even at very low concentrations especially for local people since they utilized this water for daily requirements [3]. Similar reports by various authors had indicated that lead has toxic effects on biological system and that Chromium, anon essential micronutrient is considered as the most toxic heavy metal because of its mobility and long residence in surface and ground water [4].Some fresh water macrophytes including *Ceratophyllum demersum* has been investigated for its removal of heavy metals [5].*C. demesum* belongs to the family Ceratophylaceae, its common name is (coontail or hornwort) [6]. It is submerged free floating rootless, perennial aquatic macrophytes, which grows in stagnant water and is worldwide in distribution [7]. Many adsorbent were reported as bioabsorbents which are obtained from agricultural materials such as stem [8], leaves [9] and shells [10]. A rang of methods have been applicated for heavy metals removal and the most important one is adsorption [11]. Other methods were used like the reverse osmosis, ion exchange, electro dialysis etc [4]. The disadvantages of these methods in comparison with adsorption are expensive, limited application and sensitive for operating and conditions [12]. It has been long known that aquatic plant, both living and dead is heavy metals accumulators and therefore the use of aquatic plants for the removal of heavy metals from waste water gained a high interest [13]. Therefore biosorption is an alternative method that can be appropriate for treating effluents with low metal concentrations and can also be used to remove other contaminants such as dyes and organic compounds [3]. The main purpose of this study is to investigate the adsorption of heavy metals such as copper, cadmium, lead and chrome by using non living biomass of *C. demersum* and study the ability of this plant to remove them from aqueous solutions beside the influence of some factors on the removing of these metals such adsorbent dose and hydrogen ion pH.

Materials and Methods:

1-Preparation of adsorbent material:

Aquatic macrophyte *Ceratophylum demersum* (horn wort) plant was collected from the bank of Tigris River in Al-Jadyria campus in August 2014. Healthy green plants were selected to assess removal capacities of heavy metals. The plants were transported to laboratory immediately by using plastic pools, and then identified in the herbarium of college of science in the university of Baghdad according to [14].Samples were thoroughly washed by tap water and then with distilled water to remove any soil/sediment particles attached to the plant surface. The plant (shoot apex) was dried for three days away from sun light. The dried biomass was ground with mechanical grinder, after being ground grinded, the very small particles (powder) of plant was put in an air container for further use [12].In addition some properties of water collecting area were measured including: the water temperature by using thermometer (0-100) ºC and hydrogen ion concentration pH by using HANNA after calibration with buffer solution (pH=7) before using.

2-Instrumentations:

All the following instruments were used to obtain adsorption experimental results which include:

- **a.** Shaker incubator was: Lab Tech R.
- **b.** pH meter : professional Bench top pH meter .
- **c.** Center fuge: Jouan C4i.
- **d.** Sensitive balance: Kern ABS.
- **e.** Atomic absorption spectrophotometer (AAS) used was: Analy Tikjena Nmvaa Atomic absorption Spectrophotometer.

3-Digestion of plant:

In order to estimate the quantity of Cu,Cd,Pb and Cr (adsorbates) already present in the plant *C.demersum* shoot apex (stem and leaves) digested by using nitric- perchloric acid procedure describe by[15].Ten ml of concentrated nitric acid added to 1 g from dried plant in a glass container boiled gently for 30-45 min to oxidize all easy oxidizable materials, after cooling 5 ml of 70% perochloric acid was added to mixture and boiled till white fume appeared ,this mixture cooled and 20 ml distilled water added and boiled in order to reduce of any remaining fumes. The final mixture was filtered by using Whatman no.42 filter paper and the filtrate was subjected to atomic absorption spectrophotometer to estimate the percentage of heavy metals.

4-Testing the ability of *C.demersum* powder in the removal of heavy metal in aquatic solutions:

A- Preparation of stock solutions for sorption experiments:

Stock solutions of Pb, Cd, Cr and Cu were prepared with 2000 ppm concentration by dissolving 3.2 g, 5.48 g, 11.3 g, and 7.85 g of the following heavy metal salts which include Pb (NO3)2, CdCl2, K2Cr2O7 and CuSO4 respectively in one liter of tris base buffer which prepared in deionized water, the solutions were prepared using a standard flask, the range of concentrations used were prepared by serial dilution of stock solution with deionized water [16].

B-Batch sorption experiments:

The all experiments were carried out with plant *C. demersum* in 200 ml flasks containing 1 g of plant powder mixed with 50 ml from each adsorbate solution at room temperature. The mixture agitated in shaker apparatus for 30 min and it's adjusted at 35 ºC similar of water temperature where the plant was collected. After each adsorption run the mixture (adsorbent and adsorbate) was left for 24 hr. undisturbed. The mixtures were filtered next day by using Whatman filter paper , then these samples were centrifuged (3000,10 min) for sold -liquid separation and the heavy metals concentration in solution was analyzed by atomic absorption spectrophotometer [17].

C-Effect of metal concentration:

In order to evaluate the biosorption capacity of adsorbent in different concentrations of the adsorbate, the following concentrations were prepared from the stock solution of each adsobate (heavy metals) (HM) which include (1000, 750, 500, 250ppm) by using conventional formula of dilution: C1V1= C2V2. During all these four concentrations the pH value adjusted at 7 which approach the pH of water where the plant was collected. Then batch method which described before to estimate concentrations of adsorbate remains in the solution which reveals biosorption capacity of horn wort shoot apex (adsorbent).

D-Effect of pH:

In order to evaluate the biosorption capacity 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 which unified pH of all these solutions at 9.3, drops of 0.1 N HNO3 used to adjust pH condition of each one of these solution to 4, 5, 6 and8 in aid of pH meter, then the same batch method performed to estimate uptake capability of adsorbent in these diverse pH conditions.

E-Calculation of removal percentage of the adsorbates by adsorbent:

The removal percentage (RE) of adsorbates (heavy metal) by adsorbent horn wort shoot apex was calculating by using the following equation [18], Removal efficiency (RE):

$$Removal\ (\%) = \frac{(Ci - Cf)}{ci} * 100$$

Where Ci and Cf are the initial and final concentrations respectively and its unit is (mg/L or ppm).

F-Statistical analysis:

To calculate significant differences, analysis of variance (one way - ANOVA P≤ 0.05) was used to indicate the significant differences between the removal percentage by using (Microsoft excel Windows ® 2007).

Result and Discussion:

Aquatic plants play a major role in nutrient and heavy metal recycling in many aquatic ecosystems, heavy metals and other contaminants can be removed by aquatic plants and one of these important plants is *C.demersum* which is commonly observed in water bodies throughout the word, it's used in water quality studies to monitor heavy metals and other pollutants present in sediment and water and its accumulate pollutants at a higher level than their surrounding [19]. For this reason *C.demersum* (shoot apex) is used to determine the ability of this plant for removing some heavy metals from aqueous solution. In this study the plants were collected during August 2014 at summer because of the peak of growth of plant in this season, this may be attributed to the environmental conditions that are more appropriate in this season while the environmental conditions are not suitable to the growth of macrophytes at winter [20]. As mention before, the concentrations of Cu, Cd, Pb and Cr were measured in digested plant by using the method explained previously to know the actual concentrations of these heavy metals in *C.demersum* in its natural state; table-1 shows the actual concentrations obtained from the experiment.

Table 1- The values of heavy metals concentration in digested horn wort and water collecting area.

	Cd ppm	Cr ppm	Cu ppm	Pb ppm
water sample	0.003	0.008	0.03	0.05
Ceratophyllum demersum	0.007	1	1.5	7

The result which was obtained above give a confirmation of the suitability of using this plant and this agrees with results found previously by [3] this can be explained that unrooted submerged vegetations such as *C.demersum* require nutrient up take from the water. Therefore the concentration of heavy metals in plant is more than in water. Table-2 shows the percentage of heavy metals removed by horn wort or coontail in different hydrogen ion values (pH) with 1 g adsorbent and constant concentrations of adsorbate (HM).

Table 2- The removal percentage of constant HM concentration by using 1g of *C.demersum* and variable pH values

	Cf	Cd (removal %)	Cf	Cu (removal %)	Cf	Pb (removal %)	Cf	Cr (removal %)
pH 4	79.6	92	34.4	96.5	5	99.5	160	84
pH 5	81	92	31.5	96.8	3.12	99.6	200	80
pH 6	85	91.5	33.7	96.6	16.8	98.3	200	80
pH 8	30.1	97	32.2	96.8	5.22	99.4	190	81

Cf final concentration

According to statistical analysis, significant differences are scored between the columns (Removal percentage %). The table above elucidates that lead (Pb) has the higher removal percentage which reached to 99.6% at 5 pH than in the case of chrome (Cr) which had lowest records (80% at 5 and 6 pH respectively). The pH of aqueous solution plays an important role in adsorption capacity, experimental study by Pourkhabbaz *et.al*. (2011) showed that the accumulation of Pb in shoots (leaves and stems) of submerged aquatic plants was the result of adsorption from water, while the accumulation Cu and Cd was mainly due to adsorption by root and trans location within the plant to the shoot, because shoot apex powder was used in the study therefore the high adsorption of lead was occurred [19].

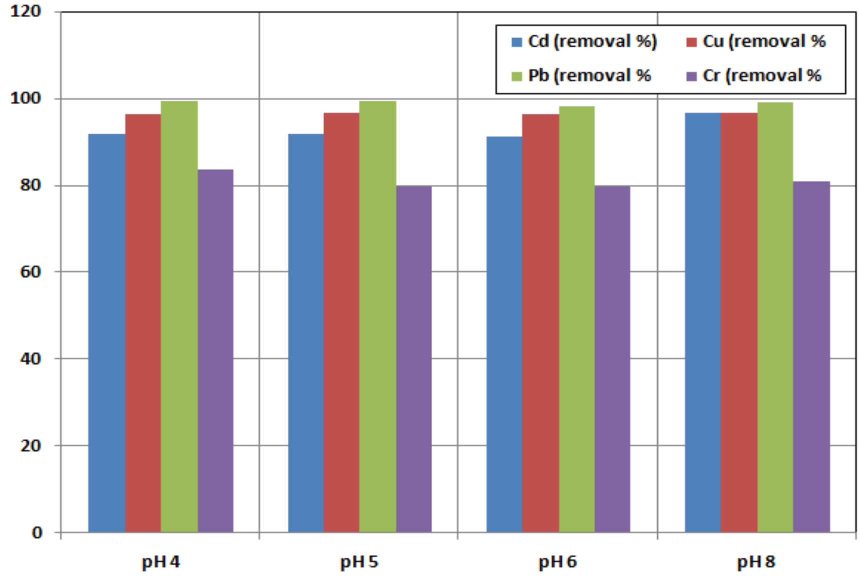

Figure 1- Effect of variable pH values on the removal of heavy metals by *C.demersum* (adsorbent dosage: 1g, HM: 1000ppm, pH range 4, 5,6and8)

According to experimental results, the maximum percent (%) for Cr removal was obtained at pH 4; figure-1 shows the change of percent removal of chromium with pH, it can be observed from the figure that chromium removal (%) decreased with increasing pH value in range of (5-8). As mentioned before lead has highest removal efficiency it means that *C.demersum* has most capability adsorption for Pb as compared with other kinds of trace elements [3].Aquatic plants are showing greater potential in ameliorating the metal load of waste water by active up take surface adsorption [21].In general the range of pH used in this experiment is suitable for heavy metal removal similar results have been reported by [22] that the sorption was a function of pH and was greatest at a pH value which was slightly more acidic than the pH at which there was bulk precipitation of metal hydroxide. Also the removal % of Cr decrease with an increasing in hydrogen ion, the explanation of this fact that at acidic pH the adsorbent surface will be converted to carboxylate and phenolate which give a site on the surface of adsorbent , at alkaline medium hydrogen ions removed hydroxide ions and therefore adsorption decrease [23]. 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 by using 1g *C.demersum* and constant hydrogen ion pH

Cd			Cu			Pb			Cr		
Ci	**Cf**	**Removal %**	**Ci**	**Cf**	**Removal %**	**Ci**	**Cf**	**Removal %**	**Ci**	**Cf**	**Removal %**
250	3.5	98.6	250	30.9	87.6	250	3.51	98.5	250	43.5	82.6
500	47.4	90.5	500	29.9	94	500	3.94	99.9	500	81	83.8
750	5.8	99.2	750	31.3	95.8	750	1.2	99.8	750	151	79.8
1000	92.7	90.7	1000	33.1	96.7	1000	0.43	99.9	1000	212	82

Ci Initial concentration, Cf Final concentration

The effect of heavy metal concentration on the adsorption of *C.demersum* was investigated and is depicted in figure-2. Heavy metal concentrations were tried in range of 250,500,750 and 1000 ppm for these experiments. In all experiments the pH value maintained at (7).

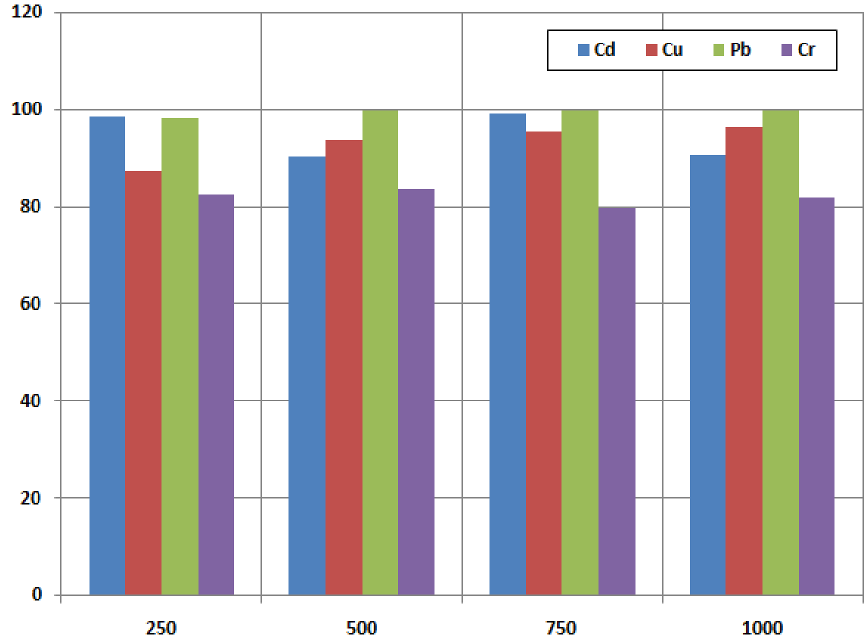

Figure 2- Effect of concentration on the removal of heavy metal by *C.demersum* (adsorbent dosage: 1g, HM: 250,500,750 and 1000 ppm, pH=7)

The statistical analysis shows there are significant differences are scored between initial concentration and removal percentage for each heavy metal (table3). The results that are exhibited in table-3 revealed that the higher removal percentage was observed for Pb which reached to 99.9% where as the lowest was observed for Cr which reached to 79.8%.This agree with the fact obtained in previous study in which the average removal efficiency of Pb was almost 100% after treatment by *C.demersum* , so that batch adsorption studies showed that this plant would adsorb zinc ,lead and copper [3].Tan *et.al.*(2009) found that the adsorption process for porous solids can be separated in three stages : Mass transfer, sorption of ions on to sites, intra particular diffusion.

For this reason very small particles of dried plant was used to gain a highly removal of heavy metals (adsorbate) as observed in tables-1 and -2. The same thing was found by Dhabab *et.al.* (2012) who mentioned that increase of surface area accompanied with decrease particle size, but the increase of particle size will not added more active sites because a metal ion will be saturated and adsorption will be decrease. In addition, the capability of *C.demersum* shoot apex powder for removal of Pb, Cu and Cd were more than Cr .From this study we concluded that *C.demersum* in its non living form could contribute to dissolve problem of heavy metals pollution.

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