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Evaluation the Biosorption Capacity of Water Hyacinth (*Eichhornia crassipes*) Root for Some Heavy Metals

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Abstract

Heavy metals especially lead (Pb), cadmium (Cd), chromium (Cr) and copper (Cu) are noxious pollutants with immense health hazards on living organisms, these pollutants enter aquatic environment in Iraq mainly Tigris and Euphrates rivers via waste water came from different anthropological activities, This study investigated capacity of dried and ground root of water hyacinth (*Eichhornia crassipes*) in removing the heavy metals from their aqueous solutions. Effects of initial concentrations of the heavy metals and pH of their aqueous solutions were studied. Results of this study revealed excellent biosorption capacity of water hyacinth root in general, removal of Pb was the highest and Cr was lowest. The results showed that the Pb, Cu and Cr removal increased as their initial concentrations increased, with maximum removal of Pb and Cu was in 1000 ppm 99.66% and 96.63% respectively and 85% was the maximum removal of Cr in 750 ppm, in contrast Cd maximum removal was in 250 ppm and the adsorption decreased as initial concentrations increased. Removal of Pb, Cu and Cr was maximum with pH 4 and 5, while Cd removal was maximum with pH 8. This study paves the way to use water hyacinth in many applications to remove the heavy metals especially in waste water treatment plants.

Keywords: *Eichhornia crassipes* root, Biosorption, Heavy metals, Removal efficiency.

تقييم قابلية جذور زهرة النيل على الامتزاز الحيوي لبعض العناصر الثقيلة

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الخلاصة

تعتبر المعادن الثقيلة وبالاخص الرصاص و الكادميوم والكروم والنحاس من الملوثات الضارة و لها خطورة هائلة على صحة الكائنات الحية، تدخل هذه الملوثات البيئة المائية وبصورة رئيسية نهري دجلة والفرات عن طريق مياه الصرف الصحي القادمة من انشطة الانسان المختلفة. تتحرى هذه الدراسة قابلية جذور زهرة النيل الجففة والمطحونة على ازالة المعادن الثقيلة من محاليلها المائية. تمت دراسة تأثير تراكيز المعادن الثقيلة والاس الهيدروجيني للمحاليل المائية لهذه المعادن. أظهرت نتائج هذه الدراسة بشكل عام قابلية ممتازة لجذور زهرة النيل على الامتزاز الحيوي.، أعلى ازالة كانت للرصاص والاقل للكروم. كما أظهرت النتائج ان ازالة الرصاص والنحاس والكروم ازدادت كلما ازدادت تراكيزها، أقصى ازالة للرصاص والنحاس بتركيز 1000 جزء بالمليون كانت 99,66% و 96,63% على التوالي و 85% كانت أقصى ازالة للكروم بتركيز 750 جزء بالمليون، وعلى العكس من ذلك كانت اقصى ازالة للكادميوم بتركيز 250 جزء بالمليون وقل الامتزاز كلما زاددت التراكيز. أقصى ازالة للرصاص والنحاس والكروم كانت في الاس الهيدروجيني 4 و 5 على التوالي ،

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بينما كانت اقصى ازالة للكادميوم في الاس الهيدروجيني 8. تمهد الدراسة الحالية الطريق لاستخدام زهرة النيل في تطبيقات مختلفة لازالة المعادن الثقيلة وخاصة في محطات معالجة مياه الصرف.

Introduction

In the last four decades in Iraq especially in eighties and nineties various industrial sectors thrived precisely military industrialization corporation (MIC), in addition to many other facilities for instance companies of batteries, electrical cables industry, pesticides, textile dyes, steel, tanning of leathers, medical Industries, transportation and electrical generation stations, this industrial flourishing came along with hazardous byproducts and wastes enriched with alarming high levels of heavy metals such as lead (Pb), Cadmium (Cd), Chromium (Cr), Mercury (Hg), Zinc (Zn) and Copper (Cu).

Heavy metals are elements having specific gravity that is at least five times the specific gravity of water which is expressed as 1 at 4°C and refers to metallic elements with an atomic weight greater than iron (55.8 g/mol)[1] .These elements introduced to the Tigris and Euphrates rivers through municipal waste water since they had been distributed constantly into different soils by irrigation, therefore drinking water , fruits and vegetables planted in these soils and animals which fed on these plants along with this food chain humans been exposed to constant flow of these heavy metals which have been accumulated resulting in health issues and anxious diseases. Exposure to a high level of the heavy metal caused acute toxicity [2]. Assay of heavy metals in water, plants and soils of different Iraqi provinces achieved by many researchers and the results revealed high levels of different heavy metals in the studied samples. In a study of Al-Hamadani [3] found high Pb concentration in plants collected from Baghdad and other selected areas the highways and cement plants. Also Ameen [4] studied the biological effects of Pb poisoning in Baghdad, and deduced that the children are at great risk than adults due to lower body weight and increasing incidence of cancer and blood poisoning. While AL-Sayegh and Al-Yazichi [5] found out that high concentration of Pb, Cd, Cu and Zn in Mosul city was due to the car exhausts. Chemical precipitation, coagulation, adsorption, ion exchange and membrane filtration are conventional methods used to decrease high concentration of heavy metals in ecosystem especially aquatic environment [6]. In order to decrease the cost and un predicted impacts of using chemicals in the conventional ways promising advance techniques have been developed in adsorption of heavy metals. Biosorption means remove of heavy metals by biological materials. However, biosorption by using algae, fungi, bacteria and plants had been reported as an efficient option with economic viability [7].Water hyacinth *Eichhornia crassipes* this vascular fast growing floating plant commonly found in tropical and subtropical regions of the world with a well-developed fibrous root system and large biomass these anatomical properties possess these plants a great potential in extracting and accumulating heavy metals from water [8]. The present study evaluated the biosorption potentialities of water hyacinth in removing of Pb, Cd, Cr and Cu in a series of concentrations and variable pH conditions for each of these metals.

Materials and Methods

Collection of water hyacinth roots

Eichhornia crassipes (water hyacinth) were collected randomly from the rims of Tigris River, pH and temperature of water recorded. Plants transported to the laboratory where their shoot separated, the roots washed thoroughly with tap water first then distilled water repeatedly and air dried for three days. The entirely dried roots were finely ground without determine diameters of particles, grinding achieved in aid of blender and preserved in a clean glass container in a refrigerator till need [9].

Digestion of roots

Water hyacinth root (adsorbent) digested by using nitric - perchloric acid procedure described by [10] in order to estimate quantity of Pb, Cd, Cr and Cu (adsorbates) already present in the roots. Ten ml of concentrated nitric acid added to 1g from dried roots in a glass container and boiled gently for 30-45 min to oxidize all easy oxidizable materials, after cooling 5 ml of 70% perchloric acid was added to the mixture and boiled till white fume appeared, this mixture cooled and 20 ml of distilled water added and boiled in order to reduce of any remaining fumes. Filtration of the final mixture performed by using Whatman no.42 filter paper and the filtrate was subjected to atomic absorption spectrophotometry.

Preparation of heavy metals stock solutions

Stock solutions of Pb, Cd, Cr and Cu were prepared using a concentration of 2000 ppm concentration by dissolving 3.2g, 5.48 g,11.3g and 7.85g of $PbNo_3$, $CdCl_2$, $K_2Cr_2O_7$ and $CuSo_4$ respectively in 1 liter of Tris base buffer prepared in deionized water.

Batch sorption method

In this procedure 1 g of water hyacinth dried and ground root was mixed with 50 ml from each adsorbate solution at room temperature, the mixture agitated in a shaker apparatus (Lab. Tech.) for 30 min. at 35 °C is the temperature of water at the site where the plant collected, after the shaking period the mixture of adsorbent and adsorbate was left for 24 hr. undisturbed. The next day this mixture was filtered by using Whatman filter paper then centrifuged at 3000 rpm for 10 min. [9, 11]. Heavy metals contents of the filtrate measured by using atomic absorption spectrophotometry (AAS) (ANALY TIK JENA NMVA) in Iraqi center of environmental laboratory in Ministry of environment .

Evaluation biosorption capacity of the adsorbent in variable concentrations of the adsorbate

Series concentrations of (250, 500, 750 and 1000 ppm) from each adsorbate, stock solutions were prepared at room temperature by using the conventional formula of dilution: $C_1 V_1 = C_2V_2$, pH of all these concentrations adjusted at 7 by using pH meter (HANA) and 0.1 N HCl and NaOH, which approach the pH of water where the water hyacinth collected. Then batch method performed to estimate concentrations of adsorbate remains in the solution which reveals biosorption capacity of water hyacinth root (adsorbent).

Evaluation biosorption capacity of the adsorbent in variable pH values with constant concentration of the adsorbate

Solutions of Pb, Cd, Cr and Cu with 1000 ppm were prepared in Tris base buffer which unified pH of all these solutions at 9.3, drops of 0.1 N HCl used to adjust pH condition of each one of these solutions to 2, 4, 5, 6, 7, 8 in aid of pH meter. Then batch method performed in order to estimate uptake capability of the adsorbent in these diverse pH conditions.

Calculation removal percentage of the adsorbates by the adsorbent

The removal percentage of adsorbates (heavy metals) by the adsorbent (water hyacinth root) was calculated by using this equation followed by [12]:

$$\textbf{Removal\%} = \frac{Ci-Cf}{Ci} \times 100\%$$

$\mathbf{C_i}$ and $\mathbf{C_f}$ represent initial and final metal concentrations (mg/L or ppm).

Results and Discussion

Results recorded ultimate adsorption of lead (Pb), cadmium (Cd), chromium (Cr) and copper (Cu) onto finely ground root of water hyacinth (*Eichhornia crassipes*).The aim of this study was get rid of metallic pollutants from waste water before discarding into river by using finely ground root of water hyacinth, the maximum removal from aqueous solutions of these heavy metals was evaluated.. Concentrations of these heavy metals presence in water hyacinth dried root prior experiments were assessed by using atomic absorption spectrophotometry (AAS), results revealed that filtrate from digestion of the dried root possessed 3.1, 2.34, 1.56 and 0.78 ppm of Pb, Cd, Cr and Cu respectively.

Effect of heavy metals concentrations

In order to optimize initial concentrations of heavy metals other parameters were fixed (adsorbent dose 1g., temperature as in study area 30 C, 7.3 was the pH of water at the location at the area where the plant collected, thus, pH of aqueous solutions of the heavy metals was adjusted to 7), in this experiment removing of the heavy metals differed along with their different concentrations (250, 500, 750 and 1000 ppm) as shown in figure-1.

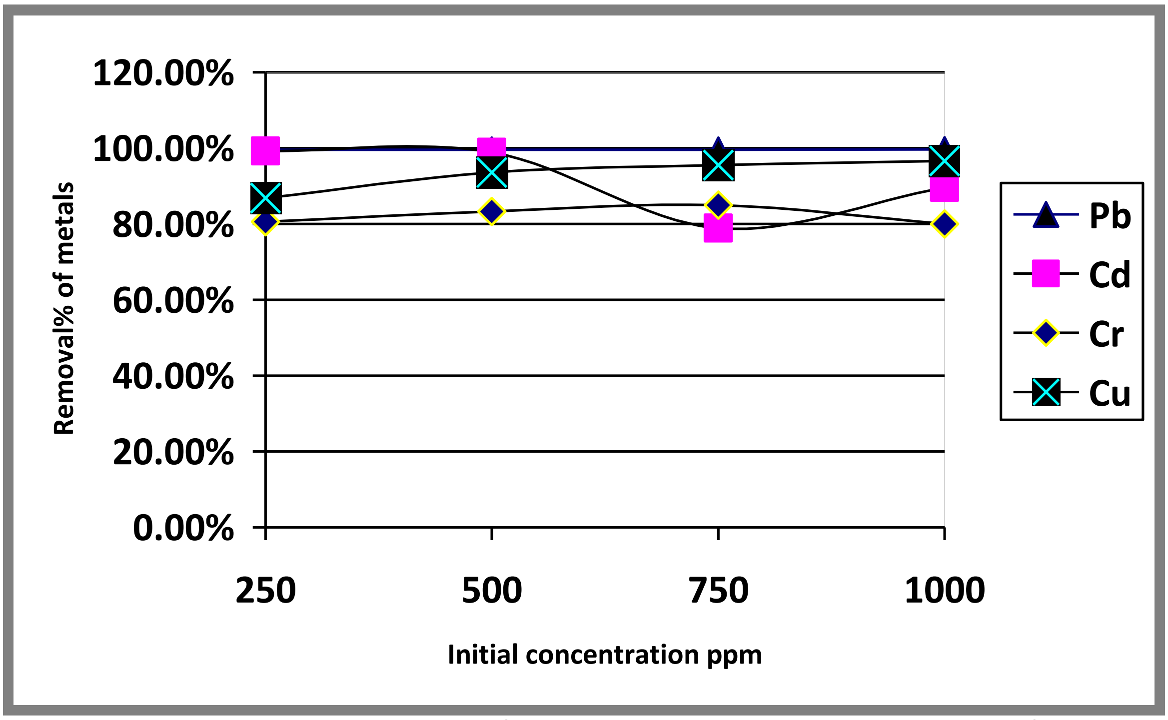

Figure 1- Variations in biosorption capacity of water hyacinth root determines by removal % of (Pb, Cd, Cr and Cu) in different concentrations at pH 7

According to the results one gram of water hyacinth root showed remarkable capacity in adsorption the heavy metals with different concentrations. In general, the highest biosorption of the metals (represented by removal %) was against Pb in concentration 250, 500, 750 and 1000 Ppm , while the lowest biosorption was against Cr in concentrations 250, 500 and 1000 Ppm and against Cd in 750 Ppm, as elaborated in table-1. The variations in removal % of the heavy metals with different concentrations showed no regular trend, removal % of Pb and Cu by the adsorbent increased as the initial concentrations of the metals increased, Padmapriya and Murugesan [13] deduced from resulted data that biosorption of Pb and Cu by water hyacinth increased as their initial concentrations increased, the same pattern could be found in Cr except in 1000 Ppm the adsorption capacity of the adsorbent decreased, the maximum adsorption of Cd was in low initial concentration, and that could be due to all active sites on adsorbent surfaces were occupied by the metal [14].The interaction between the active sites on the powder of water hyacinth root and the metals representing by biosorption could be explained physically in Van der Waals forces between positively charged heavy metals in this study and the negatively charged particles in the adsorbent [15]. Ion exchange could chemically the mechanism responsible for the adsorption. The intrinsic adsorption of the materials is determined by their surface areas which can be observed by the effect of different sizes of adsorbents on adsorption capacity [16]. Matai and Bagchi [17] reported that oxides of Na, K, Mg and Ca presence in the ash of water hyacinth. Mahmood *et al*. [18] figured out from their results that ash of water hyacinth contains oxides of Na, K, Mg and Ca, Fe, Al and Si which are basic amphoteric, these oxides interact with water produce insoluble hydroxides resulting in elevation of pH of the ash, due to low Ksp (constant for solubility product) the hydroxides of: Pb^{2+}, Cd^{2+}, Cr^{2+} and Cu^{2+} precipitate, precipitation and co-precipitation cause adsorption of these metals onto water hyacinth. The deionized water used in the batch sorption method may remove soluble ions and create unoccupied sites for attachment by the heavy metals [19].Table-1 shows the ultimate biosorption capacity of heavy metals. The adsorption of Ni, Zn, Pb, Cd, Cr, and Cu founf by Mahmood *et al*. [18] using water hyacinth ash increased as the initial concentrations of these metals increased, the maximum biosorption was in highest concentration 30 µg/ml (30 ppm).

Table 1- Variations in removal % of heavy metals (Pb, Cd, Cr and Cu) in different concentrations by water hyacinth root.

Initial concentration of metals in Ppm	Lead(Pb)		Cadmium(Cd)		Chromium(Cr)		Copper(Cu)	
	Final Concentration in ppm after adsorption (F.C.)	Removal of metals in % (R %)	F.C.	R %	F.C.	R %	F.C.	R %
250	1.1	99.56	2	99.2	48.5	80.6	32.9	86.84
500	2.12	99.57	5.5	98.9	83.5	83.3	32	93.6
750	3.21	99.58	78.9	78.9	150	85	33.4	95.55
1000	3.4	99.66	103.4	89.66	200	80	33.2	96.63

Mohammed *et al*.[20] Found the effects of some factors on biosorption of Pb by water hyacinth leaves, the maximum biosrption of Pb with 1000 Ppm initial concentration was 58%, while this study achieved 99.66% removing of Pb at the same concentration. This study could be applicable, perforate bags with small porosity which prevent ground water hyacinth root from diffusing outward; these bags could disperse on contaminated water bodies to adsorb heavy metals. Another application could make benefit from water hyacinth powder as stationary phase resemble to resins in bio separation techniques to purify water from heavy metals by designing purifying water systems.

Effect of pH on removal of heavy metals

In order to optimize pH of heavy metals aqueous solutions, the other parameters were fixed (adsorbent dose 1g., temperature as in study area 30° C, concentration of heavy metals 1000mg/l or 1000Ppm), pH of the prepared aqueous solutions were varied 4,5,6,7 and 8.Water hyacinth root showed spectacular adsorption capacity especially at pH 4 and 5 against Pb, Cu and Cr then slightly decreased as pH increased as shown in table-2 and figures-2 and -3. At acidic pH the adsorbent surface will converted to carboxylate and phenolate which give active sites on adsorbents surfaces, at alkaline medium hydrogen ions removed by hydroxide ions, therefore adsorption decreases [21]. The biosorption of heavy metals increase as the initial concentrations of biosorbent increase due to increase in diffusion coefficient lead to increase in mass transfer coefficient of heavy metals, at low concentration removal % of chromium was low due to decrease mass transfer coefficient of chromium with the increase of initial concentrations, the mass transfer driving force of the metal ion species between the aqueous solution and biosorbent increased, resulted in increase in chromium biosorption [22]. However, removal of Cd increased as pH increased and the highest removal of Cd was at pH 8 as shown in table-2 and figure-2, the same deduction was obtained from the results of [23], alkalinity is useful to eliminate Cd^{2+} .The pH8 may be a combination of both adsorption and precipitation on the surface of the coagulants, at pH>8, the fraction of Cd(OH)+ , $Cd(OH)_2$ in the solution, increase with increase of pH, this also enhanced the cadmium removal [23]. A related explanation by [24] at a higher H+ concentration, the adsorbents surface becomes more positively charged such that the attraction between adsorbents and metal cations is reduced. In contrast, as the pH increases, more negatively charged surface becomes available thus facilitating greater metals removal.

Table 2- Variations in removal % of 1000 ppm heavy metals (Pb, Cd, Cr and Cu) by water hyacinth root in different pH values.

pH value of metal solution (1000 Ppm)	Lead(Pb)		Cadmium(Cd)		Chromium(Cr)		Copper(Cu)	
	Concentration in ppm after adsorption (C.)	Removal of metals in % (R %)	F.C.	R %	F.C.	R %	F.C.	R %
4	2.37	99.75	88.55	91.15	180	82	32.5	96.75
5	1.68	99.85	100.8	89.92	172	82.8	33.8	96.62
6	26.25	97.38	86.75	91.33	184	81.6	34	96.6
7	3.4	99.66	103.4	89.66	200	80	34.2	96.7
8	2.8	99.72	63.8	93.62	186	81.4	34	96.6

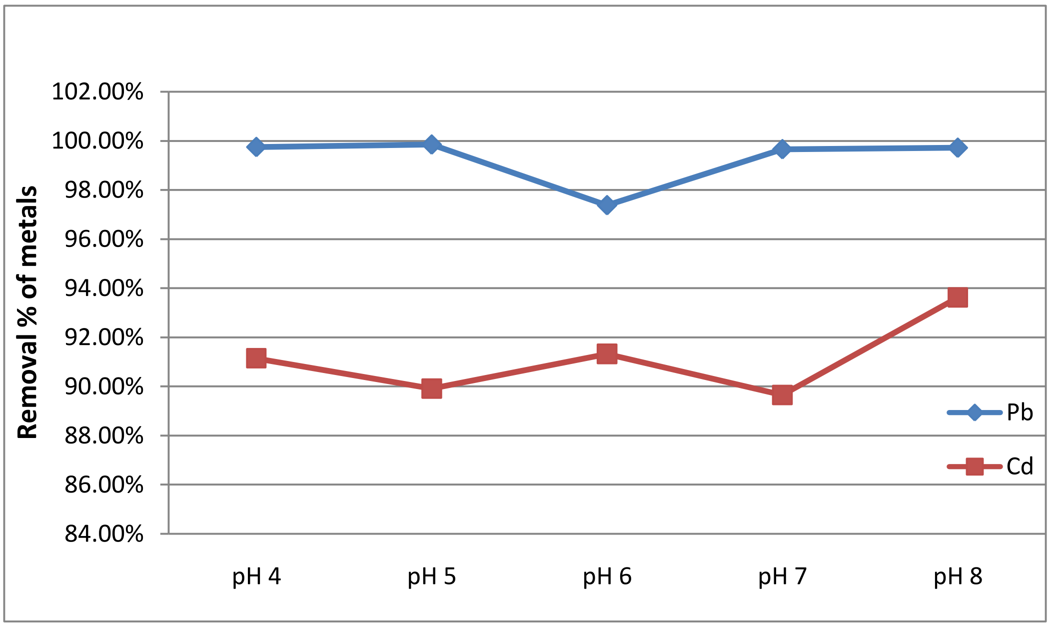

Figure 2- Effect of pH on removal % of 1000 ppm lead and cadmium by water hyacinth root.

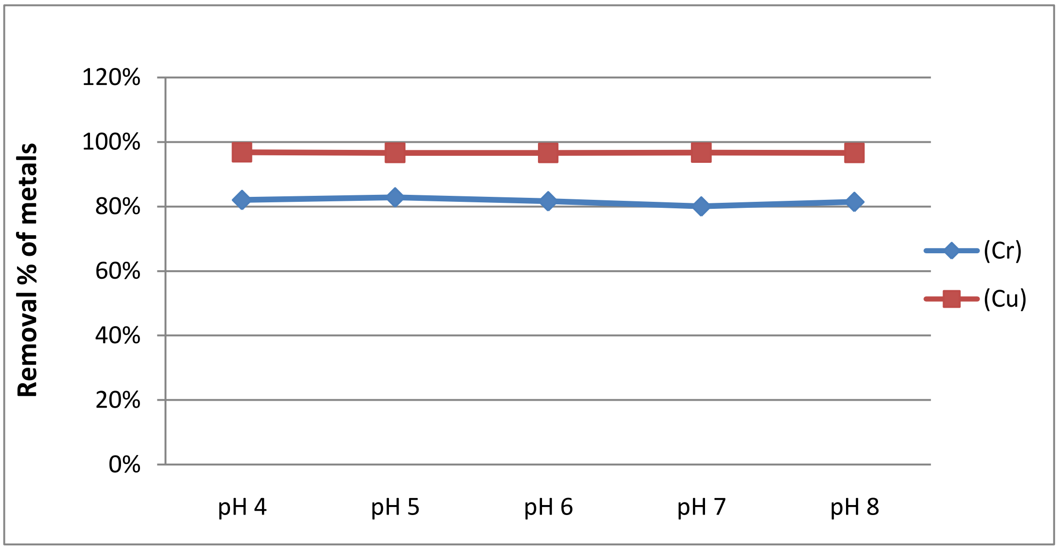

Figure 3- Effect of pH on removal % of 1000 ppm chromium and copper by water hyacinth root

Conclusion

Water hyacinth root showed excellent biosorption for the studied heavy metals which may be offers a new highly efficiency and not chemical techniques to remove these pollutants in addition to reduce cost. Results referred that Pb was the highest removed heavy metal while Cr was the lowest. Adsorption of Pb, Cu and Cr increased as their initial concentrations increased, Cd adsorption data were the opposite. Maximum adsorption of Pb, Cu and Cr was in acidic pH, in contrary Cd maximum adsorption was in basic pH.

References

1. Kabata, A., and Pendias, H. **2001**. *Trace Elements in Soils and Plants.* 3rd edition, CRC press, Washington, D.C., pp.: 550.
2. Komatina, M. **2004**.*Medical Geology, Effects of Geological Environmental on Human Health-Development in Earth and Environment Sciences-2.* Oxford, UK, pp.: 482.
3. Al-Hamadani, R. **1987** .Industrial Pollution by Heavy Metals on Soil and Plant" M.Sc. Thesis, College of Medicine. University of Baghdad (Arabic), Baghdad, Iraq, pp: 100-111.
4. Ameen, N. H. **2009**. Biological effects of lead poisoning in Baghdad city. *Iraqi Journal of Biotechnology*, 8(1):242-251.

5. AL-Sayegh, A., and Al-Yazichi, K. **2001**. Car exhausts pollution in Mosul city. *Rafidain Journal of Science*, College of Science, University of Mosul, (in Arabic), 12(2):122-123.

6. Steinhauser, M.B.G. **2008**. Adsorption of ions onto high silica volcanic glass, *Applied Radiation and Isotopes*.66(1).

7. Malakootian, M. Almasi A.and. Hossaini, H. **2009**. Pb and Co removal from paint industries effluent using wood ash. *International Journal of Environmental Science and Technology*, 5: 217-222.

8. Weiliao, S. and Chang, W.L. **2004**. Heavy metals phytoremediation by water hyacinth at contracted wetlands in Taiwan, *Journal of Aquatic Plant Management*. 42: 60-68.

9. Shawky, S., Geleel, M.A. and Aly, A.**2005**. Sorption of uranium by non-living water hyacinth roots. *Journal Of Radioanalytical and Nuclear Chemistry* .365:81-84.

10. AOAC.**1990**. *AOAC official methods of analysis*. 15th edition. *Association of Official Analytical Chemists*, Arlington, Virginia, pp.:84–85.

11. Rauf, N., Ikram, M. and Tahir, S.S. **1999**. Adsorption studies of Cu (II) from aqueous/acidic solution onto bentonite. *Adsorption Science and Technology*. 17: 431-440.

12. Argun, M. E., Dursun, S., Ozdemir, C. and Karatas, M. **2007**. Heavy metal adsorption by modified oak sawdust: Thermodynamics and kinetics. *Journal of Hazardous Materials*, 141: 77-85.

13. Padmapriya , G. and Murugesan, A.G. **2012**. Phytoremediation of various heavy metals (Cu, Pb and Hg) from aqueous solution using water hyacinth and its toxicity on plants. *International Journal of Environmental Biology*, 2(3): 97-103.

14. Zouboulis,A.I., Lazaridis N.K.and Matis, K.A.**2002**. Removal of toxic metal ions from aqueous systems by biosorption floatation. *Journal of Chemical Technology and Biotechnology*, 77:958-964.

15. Alluri, H.K.,.Ronda, S.R, Setalluri, V.S. Singh, J., Suryanarayana ,B. and Venkateshwar, P. **2007**. Review. Biosorption: An eco-friendly alternative for heavy metals removal. *AfricanJournal of Biotechnology*. 6(25), 2924-2931.

16. Igwe, J.C. and Abia, A.A. **2003**. Maize cob and husk as adsorbents for removal of cadmium, lead and zinc ions from waste water, *The Physical Scientist*, 2: 210-215.

17. Matai, S. and Bagchi , D.K. **1980**. Water hyacinth: A plant with prolific bioproductivity and photosynthesis. In: Gnanam, A. Krishnaswamy, S. and Kham, J.S. (eds.). *Proc. Internat. Symp. On Biol.Applications of Solar Energy*. *In a HandBook of Energy Crops*.MacMillan Co. of India, Madras, India, 113-144.

18. Mahmood, T., Malik, S.A. and Hussain , S.T. **2010**. Biosorption and Recovery Of Heavy Metals From Aqueous Solutions By *Eichhornia crassipes* (Water Hyacinth) Ash. *BioResources*, 5(2): 1244-1256.

19. Zhang, Y., Fan, C., Meng, Q., Diao, Z., Dong, L., Peng, X., Ma, S. and Zhou, Q.**2009**. Biosorption of Pb^{2+} by Saccharomyces cervisiae in static and dynamic adsorption tests. *Bulletin of Environmental Contamination and Toxicology*.83: 708-712.

20. Mohammed, A. K., Ali, S. A., Najem, A. M. and Ghaima, K. K.**2013**. Effect of Some Factors on Biosorption of Lead by Dried Leaves of Water Hyacinth (*Eichhornia Crassipes*). *International Journal of Pure and Applied Sciences and Technology*, 17(2):72-78.

21. Dhahab, J.M., Hussien, K.A. and Nasser, T. **2012**. Removal of Cadimium ions from industrial wastewater using Iraqi *Ceratophyllum demersum.Al-Mustansiriyah Journal of Science*. 23(8).

22. Salinas, E., Orellano, M. E. D., Rezza, I., Martinez, L., Marchesvky, E., and Tosetti, M. S. D. **2000**. Removal of cadmium and lead from dilute aqueous solutions by Rhodotorula rubra. *Bioresource Technology*. 72: 107-112.

23. Xu, Y, Yang, L. and Yang, J.**2010**. Removal of cadmium (II) from aqueous solutions by two kinds of manganese coagulants. *International Journal of Engineering Science and Technology*. 2(7):1-8.

24. Najua, D.T., Luqman, C.A., Zawani, Z.and Suraya, A.R.**2008**. Adsorption of copper from aqueous solution by Elais Guineensis kernel activated carbon, *Journal of Engineering Science and Technology*, 3: 180-189.