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The adsorption of Cadmium and Lead Ions from aqueous solutions using non living biomass of *Phragmites australis*

Khalid J. Abdallah[*1], Hind Suhail Abdulhay[2]
[1] Department of Biotechniques, Ministry of Science and Technology, Baghdad, Iraq
[2]Department of Biology, College of Science, University of Baghdad, Baghdad, Iraq

Abstract

Adsorption is a simplified new way, easy application , economical and environmentally friendly. In which the use of certain types of plants to remove or reduce toxic heavy metals from water. The current study involved the use of a non-living biomass as a powder for local plant available in the Iraqi environment is *Phragmites australis* .This the study showed the high ability of this plant to remove cadmium and lead ions from the aqueous solutions within variable experimental factors by column bed method which were used to test different sizes of plant powder were (500.1000, 1500 and 2000) µm . These sizes treated with initial concentration of Cd(II), Pb(II) was 25ppm , separately To test the optimum size for maximum adsorption and was 1000 µm . After that were tested different concentrations of Cd, Pb are (25, 50, 75, 100, 125,150,175,200)ppm with powder size of 1000 µm . And the optimum concentration was 100ppm. Different flow rates (0.5, 1, 1.5, 2) ml / min were tested with the powder size at 1000 µm and concentration for each metal was 100ppm and the optimum flow rate was 1 ml / min . All the experiments conducted at constant the mean of pH was 5, 32, temperature 22 ± 2 , contact time ranged (22-40) minutes. Results of statistical analysis showed that the optimum conditions of the maximum adsorption were at 1000 µm of powder size, 100ppm of initial metal concentration, flow rate of 1 ml / min and the high removal rates of cadmium and lead ions by *P. australis* were 95,16 % and 92.76% , respectively .

Keywords: Cadmium and Lead, ***Phragmites australis*** , Adsorption.

امتزاز ايونات الكادميوم والرصاص من المحاليل المائية باستخدام الكتلة الحيوية غير الحية لنبات القصب

خالد جابر عبدالله*[1]، هند سهيل عبدالحي[2]
[1]قسم التقنيات الاحيائية ، وزارة العلوم والتكنولوجيا، بغداد، العراق.
[2] قسم علوم الحيـاة ، كلية العلـوم ، جامعـة بغداد ، بغداد ، العراق.

الخلاصة

الامتزاز الحيوي هو طريقة جديدة مبسطة ، سهلة التطبيق ، اقتصادية وصديقة للبيئة والتي تتضمن استخدام انواع معينة من النباتات لإزالة او خفض المعادن الثقيلة السامة من المياه. تضمنت الدراسة الحالية استخدام الكتلة الحيوية غير الحية كمسحوق لنبات محلي متوفر في البيئة العراقية هو القصب . الدراسة اوضحت القدرة العالية لهذا النبات على ازالة ايونات الكادميوم والرصاص من المحاليل المائية ضمن ظروف تجريبية متغيرة باستخدام طريقة الاعمدة الزجاجية التي استخدمت لاختبار احجام مختلفة من مسحوق النبات

*Email: KhalidJabber1967@yahoo.com

(2000,1500,1000,500) ما يكرومتر . هذه الاحجام عوملت مع الكادميوم والرصاص بتركيز 25 جزء بالمليون كلا على حدة لاختبار الحجم المثالي للامتزاز الاكبر وكان 1000 مايكرومتر. بعد ذلك عوملت تراكيز مختلفة من كل من الكادميوم والرصاص هي(200,175,150,125,100,75,50,25) جزء بالمليون بشكل منفصل مع مسحوق النبات بحجم 1000مايكرومتر. وكان التركيز المثالي لكل عنصر 100جزء بالمليون . اختبرت معدلات جريان مختلفة هي (2,1,5,1,0,5) مل / دقيقة مع مسحوق النبات بحجم 1000مايكرومتر وتركيز الكادميوم والرصاص لكل منهما 100جزء بالمليون وكان معدل الجريان المثالي 1 مل /دقيقة. كل التجارب اجريت بالدالة الحامضية الثابتة بمتوسط 5,32 ، متوسط درجة الحرارة 22 ± 2 ومعدل زمن التماس (22−40) دقيقة . اشارت نتائج التحليل الاحصائي الى ان الظروف المثالية للامتزاز الاكبر كانت 1000مايكرومتر لحجم مسحوق النبات ،التركيز الابتدائي لكل من للكادميوم والرصاص 100 جزء بالمليون ، معدل الجريان 1مل/ دقيقة ومعدلات الازالة العالية للكادميوم والرصاص كانت 95,16 , 92,76 % على التوالي .

Introduction

It is very hard to find any part of word wide that not contaminated by one way or another due to the civilization and the accelerated various human activities such as industrial, agricultural, medical and even social developments [1]. Environmental contaminants are including wide range of physical, chemical and biological pollutants such as organic compounds and heavy metals [2].

Water contaminated with heavy metals is a crucial problem. Therefore it had received a great attention by using several physio- chemical techniques were applied to remove metal ions from contaminated water such as reverse osmosis, ion exchange, chemical precipitation, activated carbon and electrodialysis. Some of these techniques have several disadvantages such as higher costs, certain difficulties associated with applications and may have unknown impacts on human and environment [3]. Over the past decade there has been increasing interest for the development of plant based remediation technologies which have high efficiency, low cost, low impact, and environmentally friendly, a concept called phytoremediation. It is an integrated multidisciplinary approach to the cleanup of contaminated soils, which combines the disciplines of plant physiology, soil chemistry, and soil microbiology [4]. Phytoremediation can be applied to detoxify areas with trivial pollution of metal, nutrients, organic matter, or contaminants. Adsorption was also found powerful technique for removal of heavy metals. New adsorbents were found successful for removal cadmium and lead and were improved performance of application. Agricultural wastes have been extensively used for treatment wastewater and industrial effluents. Many adsorbents were reported as biosorbents which were obtained from agricultural materials; such as: saw dust, bark, stems, shells, peels, husk, bran. The present study aims to assess the ability *Phragmites australis* for bioremoving cadmium and lead from the aqueous solution in laboratory .

Materials and Methods

Preparation of adsorbent material

Samples of *P. australis* were collected from Al-Shorta district (Karkh) and from Al-Obeidi district(Rusafa). The taxonomic identification of *P. australis* was confirmed by the botanist in plant laboratory/ Biology department/ College of Science/ Baghdad University. The samples of plant were preserved in a plastic bag and transported to laboratory. The samples were washed with distilled water to remove any soil or suspended, dried on sun light for three days with continuous stirring to prevent it from rotting. Furthermore, were dried in oven at a temperature of 80 °C for three days. The dried plant was grounded by electric grinder and screened through different sizes of stainless steel sieves (500, 1000, 1500 and 2000 µm) to get the appropriate particles of plants powder. All samples were stored in a plastic bag till the time of use [5]. 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 pH meter type HANNA.

Testing the efficiency of the adsorbent on the single solution of Cd and Pb:-

A- Preparation standard solution of cadmium and lead

In order to prepare standard solution concentration of 1000 ppm , 2.1 gm of Cd $(NO_3)_2$, Pb $(NO_3)_2$ were dissolved separately in 100 ml of deionized distal water with constant stirring by magnetic stirrer for 30 minutes and then complete the volume to 1000 ml. This solution was sterilized by filtration through 0.45 µm membrane filter, and served as a stock solution for further preparations [6]. Preparation the concentration of heavy metals was done by diluting the stock solution with distilled water to serial dilutions by using the equation: $\mathbf{C_1V_1 = C_2V_2}$ As follow: (25, 50, 75, 100, 1 25,150,175 and 200) ppm of cadmium and lead.

B- Column bed adsorption procedure:

All experiments on *P. australis* powder conducted by laboratory system from packed glass columns, each column contained 5 gm of powder at different sizes of particles were (500,1000,1500 and 2000) µm treated with 50 ml of cadmium and lead solutions separately at different concentrations were (25,50,75,100,125,175 and 200 ppm) . And at different flow rates were (0.5, 1, 1.5 and 2) ml/min, temperature 22±2°C . The total volume of each column was 100 ml , and at the end of each column glass wool was placed to allow the passage of the solutions remaining, which were collect in beakers then were filtered by using Whatman filter paper 0.45 µm , then measure the concentrations of Cd and Pb remaining in solutions by flame atomic absorption spectrophotometer [7].

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

The removal percentage (RE) of heavy metal by adsorbents was calculating by using the following equation [8] $\mathbf{RE\ (\%) = Ci - Cf / Ci \times 100}$

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

D- Statistical analysis

All experiments data were subjected to various statistical tests for the significant differences such as; analysis of variance and least significant differences test (LSD test) [9].

Results and Discussion

Factors affecting biosorption

Particle size of biosorbent

Maximum adsorption of Cd and Pb obtained at size of the powder1000 µm and biosorption of Cd and Pb were decreased when the particle size of powder was increased to 1500 µm and 2000 µm as shown in Table-1 and Figure-1 , because it is the appropriate size, which provides greater surface area and more active sites . And increase of particle size more than appropriate size will not added more active sites because it will be saturated with metal ions and adsorption will be decrease[3].

Table 1 - Mean of Cadmium and Lead ± standard deviation biosorbed at concentration of 25 ppm by different powder sizes of *P. australis* at flow rate of 1ml/min.

Powder size	Mean biosorbed metal (ppm) ± SD	
	Cd	Pb
500 µm	81.16 ± 4.44	79.72 ± 8.12
1000 µm	84.68 ± 5.73	82.68± 4.53
1500 µm	79.92 ± 7.51	77.48 ± 6.19
2000 µm	72.64± 8.62	70.64 ± 7.11

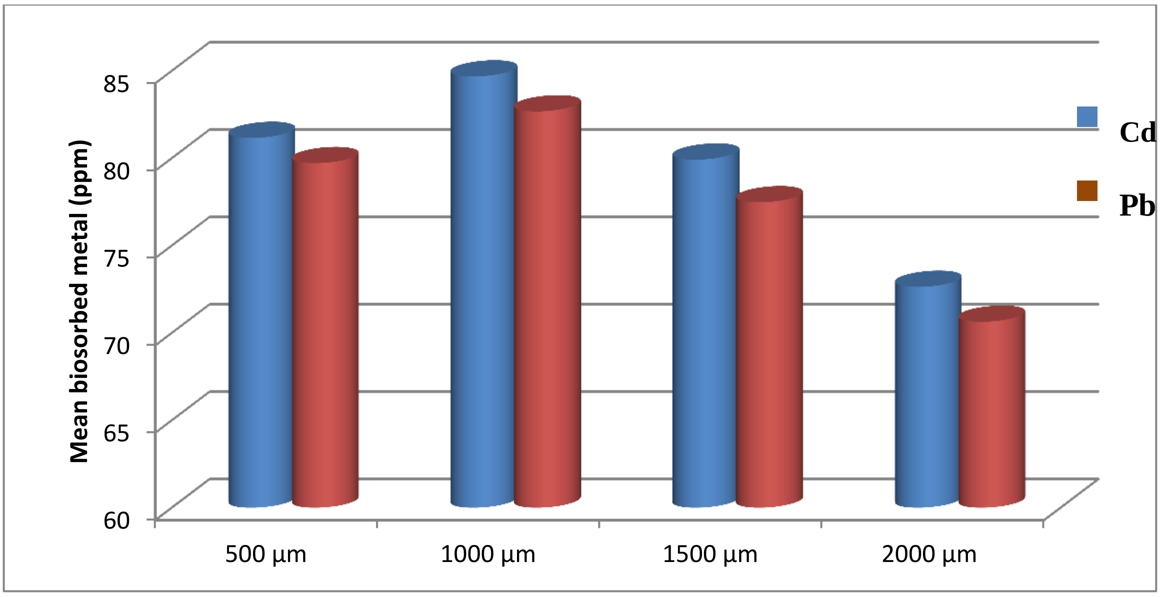

Figure 1 - Mean of Cadmium and Lead biosorbed at concentration of 25 ppm by different powder sizes of *P. australis* at flow rate of 1ml/min.

Initial concentration of the metal

In the current study according to statistical analysis biosorption capacity of the biomass increased with increasing initial concentration of the Cd, Pb ions till up to optimum concentration 100ppm , which has got the highest removal of Cd , Pb ions was 95.16 , 92.76 % . The percentages removal of the Cd , Pb ions decreased gradually markedly with an increase in the initial concentration of the metal ions from 125 to 200 ppm as shown in Table-2 and Figure-2. This might be due to the rapid saturation of all metal binding active sites of the biosorbent at a certain high concentration of the metal ions [10].

Table 2 - Mean of cadmium and lead ± standard deviation biosorbed at different metal concentrations by using 1000 µm of powder of *P. australis* at flow rate of 1ml/min.

Concentrations (ppm)	Mean biosorbed metal (ppm) ± SD	
	Cd	Pb
25	84.04 ± 9.13	79.96 ± 9.14
50	86.38 ± 6.92	81.86 ± 7.39
75	90.36 ± 6.56	86.65 ± 7.55
100	95.16 ± 4.18	92.76 ± 3.75
125	89.41 ± 5.28	85.98 ± 8.32
150	88.33 ± 4.24	79.32 ± 5.57
175	77.87 ± 8.82	74.76 ± 6.19
200	72.78 ± 9.24	67.23 ± 4.61

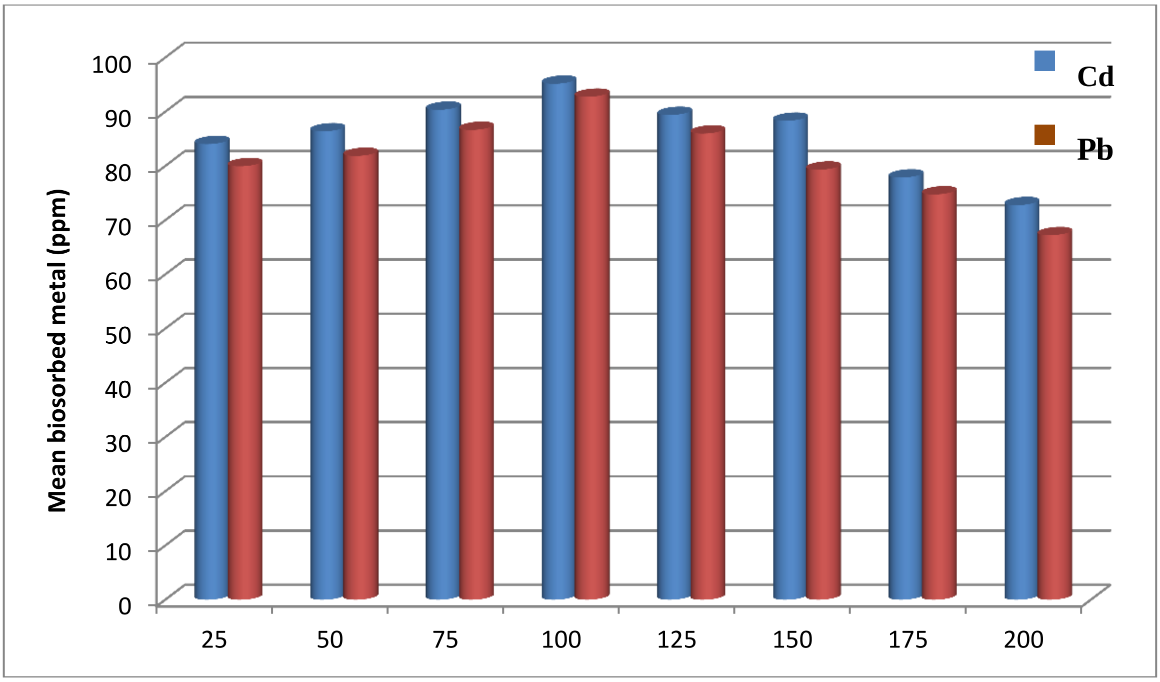

Figure 2 - Mean of Cadmium and Lead biosorbed at different concentrations by using 1000 µm of powder size of *P. australis* at flow rate of 1ml/min.

Contact time (Flow rate time)

Effect of the contact time between the adsorbent and adsorbate on the removal of the Cd , Pb ions was determined by time periods of flow rate and it was calculated when the first drop of the solution spilled through (1-2) min from the column until the last drop of it and was ranged between 22-40min , as showed in Table-3 and Figure-3 . The fast removal of Cd , Pb and most adsorption occurred in the beginning may be due to a larger adsorbent surface area being available for the adsorption of the metal as well as a large number of available adsorptive sites [11]. The adsorption kinetics changed rapidly along with the contact time, after that they decreased. This was probably caused by the decrease in the concentration gradient between the initial concentration and the equilibrium concentration of the solution with the progress of the adsorption process and adsorption of most the metal ions onto the adsorbent surface in the equilibrium time [12, 13].

Table 3- Mean of cadmium and lead ± standard deviation biosorbed at concentration of 100 ppm by using 1000 µm powder of *P. australis* at different flow rates.

Flow rate ml/min	Mean biosorbed metal (ppm) ± SD	
	Cd	Pb
0.5	94.32 ± 5.18	93.48 ± 3.11
1	95.54± 2.32	92.87 ± 4.23
1.5	89.30 ± 5.12	88.80± 6.44
2	83.47 ± 7.16	81.96 ± 5.32

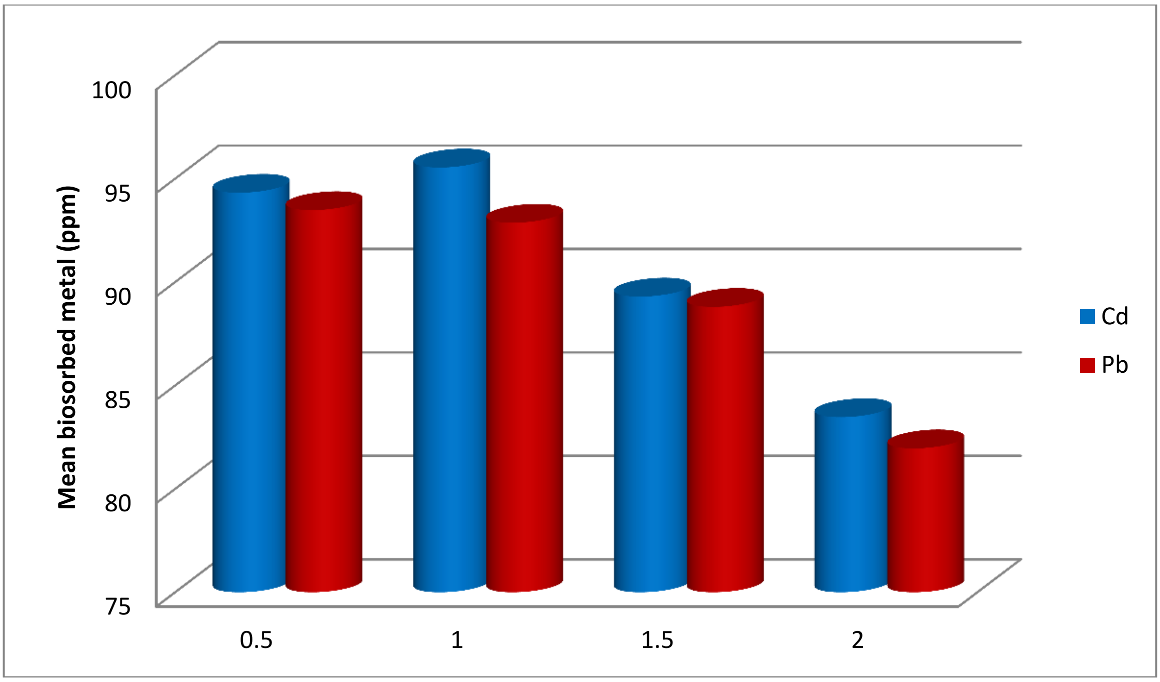

Figure 3 - Mean of Cadmium and Lead biosorbed at concentration of 100 ppm by using 1000 µm powder size of *P. australis* at different flow rates.

Effect of pH

Heavy metal sorption on the surface of biosorbent is a pH dependent process, which affects the functional groups of biosorbent and the metal ions chemistry in solution [14]. As a result, pH affects the availability of metal ions in solution and metal binding sites on biosorbent surfaces. Adsorption increased with increase in pH until it reached a maximum at optimum value of pH, and at lower pH adsorption decrease .This may be due to the fact that the active adsorption sites remain protonated at low pH , and become less available for metal ion adsorption , due to competition between H ions and metal ions. And with the increase in pH to the optimum value occur deprotonation and replaced by metal ions on the active sites[15]. In the current stud the high removal rates of Cd and Pb were due to Important advantages of *P.*australis as following :

1. This was probably due to chemical and texture of surface for *P.australis* made it more compact (having more binding sites , more numbers and or types of functional groups) which enabled all the binding sites/organic ligands free for metal ions, and thus enhanced metal adsorption efficiency [16].
2. The effect of surface porosity of powder of *P.australis* on adsorption efficiency ,as mentioned [17] that the adsorption process for porous solids can be separated in three stages : Mass transfer, sorption of ions on to sites, intra particular diffusion .
3. The surface structure and nature of texture *P. australis* tissues may be highly porous and heterogeneous (micro, meso, macro porous) are suitable for the diffusion of metal ions intra particles [18] .
4. The higher tolerance of *P. australis* for various harsh environmental conditions such as temperature, water lack , salinity, the growth in contaminated environment at high levels of pollutants near sewage discharges plants and existence of the plant along the year.These advantages of *P. australis* due to the influence of genotype and ecotype in the adaptation process .

Removal rates of Cd were higher than the removal of Pb by *P. australis* separately due to properties of cadmium as following :

1. Metal removal is increased as the ionic radii of metal cations affect the ion exchange and adsorption process reported that differential absorption of metal ions may be related to the difference in their ionic radii. The larger the ionic radius, its tendency to hydrolyze is the lesser leading to increased adsorption and vice versa [19, 20] .

2. The differences in affinities of the various metal ions for biomass may be attributed to differences in the electrode potentials for metals, the greater the electrode potential , its affinity is greater for biomass [21] .
3. The high removal of Cd ions may be attributed to its higher affinity and ability to form stronger complexes with organic ligands / binding sites on the biomass more than Pb ions, according to [22].
4. The complex interactions of several factors such as ionic charge, ionic radius and electrode potential will account for the differences in the metal removal capacity of the biomass. As a result, ordering of the metal ions adsorption based on a single factor is very difficult [23].

The following table shows the differences between Cd and Pb as mentioned above :

Table 4- shows Ionic charge, ionic radii and electrode potentials of Pb and Cd.

Metal	Ionic charge	Ionic radii (A˚)	Electrode potential (V)
Pb	+2	1.32	0.12
Cd	+2	1.58	0.40

References

1- Abed Al-Razzaq, H. T. **2011.** Effect of domestic wastewater from pumping station of Al-Kadimiya on ecological properties of Tigris River. M.Sc. Thesis. Collage of Science, University of Baghdad. 123 pp.

2- Hei-Ti**,** H**. 2013.** *Plant Pathogens (Viruses): Biological Control*. The online platform for Taylor & Franccis Group content. **2**, pp:935-947.

3- Dhabab, J.M.; Hussien, K.A. and Nasser, T**. 2012**. Removal of cadmium ions from industrial waste water using Iraqi *Ceratophyllum demersum***.** *Al-Mustansiriyah J. Sci***. 23 (8):71-84.**

4- Cunningham, S. D. and Ow, D. W**. 1996**. Promises and Prospects of Phytoremediation. *J. plant physiol*. **110**(3): 715-719.

5- Al-Hashimi, A. M and Jabir, A. B**. 2008.** Biosorption of dissolved Pb (II) in dilute aqueous solutions by using agro-waste products. *Journal of Engineering***. 14**: 2257-2273.

6- APHA (American Public Health Association). **1998.** *Standard methods for the examination of water and waste water*, 20th Ed. Amr. Public Health Ass. Washington, DC.

7- Uysal,Y., Aktas , D.and Yardimciel, D. **2013**. Removal of Cr (IV) ions from waste water by waste plane tree (*Platanus orientalis L.)* leaves. *Journal of Selcuk University Natural***,** 312-323.

8- Argum, M.E., Dursun, S., Ozdemir, C. and Karatas, M. **2007.** Heavy metal adsorption by modified Oak saw dust : thermodynamics and kinetics. *J. Hazard. Mat*., **141**:77-85.

9- Gomez, K. A. and Gomez, A. A.1984. *Statistical procedures for agricultural research*. 2nd edition, A Wiley interscience puplication, John Wiley & Sons. New Yourk. U.S.A

10- Meitei, M. D and Prasad, M. N. V**. 2014.** Adsorption of Cu (II), Mn (II) and Zn (II) by *Spirodela polyrhiza* (L.) Schleiden: equilibrium, kinetic and thermodynamic studies**.** *J. Ecological Engineering***. 71**: 308–317.

11- Goher, E.M.; Abdel-Satar , M.A.; Ali ,H.M. and Hussian , M.A**. 2016** . Biosorption of some toxic metals from aqueous solution using non-living algal cells of *Chlorella vulgaris*. *J. Eelem*. **21**(3): 703-714

12- Li C. **2008.** Batch and bench-scale fixed-bed column evaluations of heavy metal removals from aqueous solutions and synthetic landfill leachate using low-cost natural adsorbents. M.Sc. Thesis in Engineering University Kingston , Ontario, Canada , 1-332.

13- Li C. and Champagne, P. **2009.** Fixed-bed column study for the removal of cadmium (II) and nickel (II) ions from aqueous solutions using peat and mollusk shells. *J. Hazard. Mater***. 171**(1-3): 872-878.

14- Shafique, U. A. Ijaz, M. Salman *et al*., **2012.** Removal of arsenic from water using pine leaves. *Journal of the Taiwan Institute Chemical Engineers*.. **43**(2): 256–263.

15- Dubey, A., Mishra, A. and Singhal, S. **2014.** Application of dried plant biomass as novel low-cost adsorbent for removal of cadmium from aqueous solution. *Int. J. Environ. Sci. Technol*, **11:** 1043–1050.

16- Verma, V. K., Gupta, R.K. and Rai, J.P.N**. 2005.** Biosorption of Pb and Zn from pulp and paper industry effluent by water hyacinth (*Eichhornia crassipes*). *J. Sci. Ind. Res*. **64:** 778–781.

17- Tan, G. and Xiao, D**. 2009.** Adsorption of cadmium ion from aqueous solution by ground wheat stems. *J. Hazard Mater***, 164**: 1359-1363.
18- Mishra, V., Balomajumder, C. and Agarwal, V. K. **2010.** Biosorption of Zn (II) onto the surface of non-living biomasses: A comparative study of adsorbent particle size and removal capacity of three different biomasses. clean water, air and soil Pollution.. *J. En.Che*., **211**(1): 489-500.
19- Baig, T. H, Garcia, A. E, Tiemann, K.J and Gardea, J. L.**1999**. Adsorption of heavy metal ions by the biomass of *Solanum elaeagnifolium* TorresdeyDepartment of Chemistry and Environmental Sciences and Engineering, University of Texas . Proceedings of the Conference on Hazardous Waste Research. 131-142. p 135
20- Ashraf, M.A., Wajid, A., Mahmood, K, Maah, J. M, and Yousoff, I. **2011.** Removal of heavy metals from aqueous solution by using mango biomass. *African Journal of Biotechnology*, **10**(11): 2163-2177.
21- Mattuschka , B. and Straube , G**. 1993.** Biosorption of metals by waste biomass**.** *J. Chem. Technol. Biotechnol***. 58**: 57-63**.**
22- Chubar, N., Carvalha, J. R., and Correia, N.J.M. **2004.** Cork biomass as biosorbent for Cu (II), Zn(II) and Ni(II). Colloids Surf., *Phycochem. Eng. Aspects***. 230**: 57–65.
23- Sekhar, K. C.; Kamala, C. T.; Chary, N. S. and Anjaneyulu, Y**. 2003.** Removal of heavy metals using a plant biomass with reference to environmental control. *Int. J. Miner. Process*. **68**: 37-45.