IJHS 2016;2(3): 26-30

ijhs.shmu.ac.ir

Original Article

I J H S
International Journal of Health Studies

Sunflower Waste Biomass as a Remarkable Adsorbent for Removal of Heavy Metals from Waste Waters

Shima Mohmmadkhani[1], Jaber Yeganeh[2], Saeid Nazemi[3*]

[1] Health Technology Center, Shahroud University of Medical Sciences, Shahroud, Iran.
[2] School of Nursing and Health, Uremia University of Medical Sciences, Uremia, Iran.
[3] Dept. of Environmental Health Engineering, School of Public Health, Shahroud University of Medical Sciences, Shahroud, Iran.

Received: 17 May 2016
Accepted: 20 June 2016

Abstract

Background: *Today, through various industrial processes, toxic heavy metals are released into aquatic environments that are harmful to the ecosystem. In the present investigation, removal of such contaminants from industrial wastewater is necessary. The purpose was made to extend an ecofriendly technology by using a bio carbon generated from sunflower waste biomass.*

Methods: *The impact of initial pH of solution (2–10), initial heavy metal concentration, and bio carbon dose on the adsorption processes was studied. The residual concentration of samples, Cr(III), Cd(II) and Pb(II) after adding adsorbent and then filteration was determined using atomic absorption spectroscopy.*

Results: *The equilibrium data were found to be well described by the Langmuire model. The Langmuire isotherm feasibility was checked with the dimensionless separation factor (RL).*

Conclusions: *The introduction of a new adsorbent represents a great challenge for both academia and industry, and among all of the methods for removal contamination, we choose adsorption processes. Overall, the work demonstrates the possible use of sunflower waste biomass, as an effective adsorbent for the removal of heavy metals from wastewater.*

Keywords: Adsorbent, Sunflower wasted biomass, Heavy metals.
***Corresponding to:** S Nazemi, **Email:** nazemi@shmu.ac.ir
Please cite this paper as: Mohmmadkhani S, Yeganeh J, Nazemi S. Sunflower wasted biomass as a remarkable adsorbent for removal of heavy metals from waste waters. Int J Health Stud 2016;2 (3):26-30.

Introduction

Heavy metals in wastewater are a significant public and environmental problem. Industries such as tanneries, metal plating facilities, and mining can lead to the contamination of wastewater.[1,2]

Increasing these metals in wastewater can be hazardous for human health, and lead is one of the most harmful elements because of its toxicity and its widespread effects on the environment.[3,4] All Lead compounds are poisonous and can affect the nervous system.[5] Chromium exists in all oxidation states from (III) to (VI). Chromium is corrosive, an irritant, and toxic. The Cr (VI) is a known carcinogen and designated a hazardous pollutant. The maximum allowable limit of total Chromium in drinking water as recommended by the World Health Organization is 0.05 mg/L.[6] Cadmium is another toxic heavy metal of significant environmental and occupational concern, and it has been released to the environment through the combustion of fossil fuels, metal production, application of phosphate fertilizers, electroplating, and the manufacturing of batteries, pigments, and screens.[7,8,9] This heavy metal has resulted in serious contamination of both soil and water. Cadmium has been classified as a human carcinogen and teratogen, impacting lungs, kidneys, liver, and reproductive organs.[6,10] The world Health Organization has set a maximum guideline concentration of 0.003 mg/L for cadmium in drinking water.[11]

The removal of pollutants such as Lead and Cadmium from wastewater has been accomplished through a range of chemical and physical process.[12,13] Traditional methods such as adsorption, precipitation, coagulation, and ion exchange are costly.[14] Among these, biosorption is an interesting technology for the treatment of wastewaters containing heavy metals.[15,16] Today, some natural biowastes have been studied to be used as adsorbents. Some low cost natural materials are as follows: grape baggase,[17] rice husk,[18] saw dust,[19] fly ash,[20] green coconut shell powder,[21] and plant biomass.[22] Plant biomass compositions are very interesting because of biopolymers containing lignocellulos and tannins, which may lead to the binding of metal ions due to the presence of functional groups like hydroxyl, carboxyl, carbonyl, thiol, and amine.[23]

Studies show that several biological types of adsorbent have been investigated for sorption of different heavy metals from effluents. In this study we strive to use sunflower waste biomass as efficient adsorbents. Sunflower is one of the significant oil producing resources, and after extraction of oil, massive quantities of sunflower head and stalks are produced that are burnt in farms that are just causing environmental pollution.[24] Also sunflower waste biomass contains functional groups like hydroxyl, carboxyl, and carbonyl as indicated by FT-IR analysis reported elsewhere.[25] The adsorbents have a good capacity for adsorption of heavy metal ions like Cr (VI) and Cd (II), etc., from aqueous solutions.[26,27] Recently, scientists have used various substances as adsorbents; for example, Zhen Zhu and Wei Li used Zinc oxide-functionalized MCM-41 (ZM) as an adsorbent for the removal of Pb+2 from an aqueous solution, and the results indicate that the ZM has potential as a promising application in the field of water pollutant treatment because ZM can be used consecutively.[28] Some scientists used activated carbon as adsorbent for the removal of heavy metal ions and dyes, but it cost is more for them rather than using biosorbents as adsorbents. Also the aim of this study is to characterize the effect of pH, metal ion concentrations and adsorbent dosages on the adsorption of metal ions by sunflower waste biomass. Then adsorbent isotherms such as the Langmuire, Freandlich, and Temkin models were studied for the experimental data.

Materials and Methods

A stock solution (1000 mg/L) of Pb (II), Cd (II), and Cr (III) ions was prepared by dissolving analytical grade substances of $Pb(NO_3)_2$, Cd $(NO_3)_2$, and $CrCl_3.6H_2O$.

In order to prevent the formation of metal hydroxide and to return the metal ion to the dissolved state, the stock solution was acidified to the desired pH, and the desired pH values of the solutions were adjusted using 0.1 N HCl and 0.1 N NaOH. All chemicals and reagents were analytical grade.

The sunflower head and stems were collected directly from the agricultural farms. They were ground into fine powder and were mixed and concentrated with H_2SO_4 in the ratio of 2:1 (H_2SO_4: sunflower, v/w) and carbonized at 150°C in a hot air oven for 24 h. The charred material was repeatedly washed with deionized water until excess acid was removed and finally soaked in 2% Na_2HCO_3 (w/v) overnight to remove any residual acid from the material. The adsorbent was washed again with deionized water several times and dried in a hot air oven at 150°C for 8 h as reported by Jain et al.[25]

Batch adsorption studies were conducted by placing a certain amount of bio sorbent in contact with solutions. All adsorption experiments were performed at room temperature. To study the influence of parameters on the aqueous solutions, mixtures in a screw-top flasks were agitated on a rotating shaker at 150 rpm for a period of 180 min, which caused mixtures to definitely reach equilibrium. Then after filtration through Whatman filter paper, the filtrate was collected, and analyzed for unabsorbed metal ions using an atomic absorbance spectrophotometer with an air- acetylene flame.

The adsorbed amount of Pb (II), Cd (II), and Cr (III) and Cr (VI) ions onto the adsorbent were calculated by the following equations:[29,30]

$$(1) \qquad q_t = \frac{(C_0 - C_t)}{M} V$$

$$(2) \qquad q_e = \frac{(C_0 - C_e)}{M} V$$

where C0 is the initial concentration (mg/L), Ct is the amount of concentration (mg/l) at any time t and C_e is the amount of concentration (mg/L) in equilibrium, V is solution volume (L); and M is MnO_2/MWCNT nanocomposite mass (g). As a specific amount of solution with a certain concentration.

Results

As we know, the pH of solution influences the distribution of active sites on the surface of an adsorbent, thus in this study, the pH of solution was varied in the range of 2–10, and the results showed that among these, the pH values of 3, 10, and 7 for Chromium, Cadmium, and Lead, respectively, had a higher removal percentage compared to other pH values.

The concentration of metal ions was found by varying the concentration of metal ions in the range of 10–70 mg/L, with a 10 mg/L variation, and optimized metal ios concentrations as 30, 60, 60 mg/L for Cr, Cd, and Pb, respectively, show a higher percentage of removal as compared with other concentrations.

The effect of adsorbent dose was evaluated using various quantities of adsorbent ranging 0.1–0.5 g, with the variation of 0.1 g, The adsorbent dose of 0.5, 0.5, and 0.1 g gives more of a removal of Cr, Cd, and Pb, respectively, as compared with other adsorbent dosages.

The isotherm equations were used to help predict the distribution of atoms or molecules between the liquid phase and solid phase at an equilibrium state. In this study, the experimental adsorption isotherm data were calculated by three importantly used models such as the Langmuir, Freundlich, and Temkin isotherm models. The parameters obtained from these models provided essential evidence for the prediction of the mode of the sorption mechanism and the effect of the affinity between the adsorbent and adsorb ate molecules.

The linearized form of Langmuir adsorption isotherm equation is as follow:

$$(3) \qquad \frac{1}{q_e} = \left(\frac{1}{K_L q_m}\right)\frac{1}{C_e} + \frac{1}{q_m} \quad \text{OR} \quad \frac{C_e}{q_e} = \frac{1}{q_m K_L} + \frac{C_e}{q_m}$$

The linearized form of Freundlich adsorption isotherm equation:

$$(4) \qquad \mathrm{Ln}q_e = \left(\frac{1}{n}\right)\mathrm{Ln}C_e + \mathrm{Ln}K_F$$

The linearized form of Temin adsorption isotherm equation:

$$(5) \qquad q_e = B_l \mathrm{Ln}C_e + B_l \mathrm{Ln}K_T$$

where C_e (mg/L) is the equilibrium concentration of Cr, Cd, and Pb ions, and q_e (mg/L) is the amount of heavy metals adsorbed at equilibrium; q_m (mg/g) is the maximum adsorption at monolayer and K_L (L/mg) is the Langmuir constant, including the affinity of binding sites. $K_F[(mg/g)(L/mg)_{1/n}]$ and n are Freundlich constants indicating adsorption capacity and intensity, respectively.

K_T (L/g) and B_1 are the Temkin constants (K_T is the equilibrium binding constant and B_1 is related to the heat of adsorption). The amounts of Langmuir, Freundlich, and Temkin parameters were calculated from the slope and intercept of linear plots of $1/q_e$ versus $1/C_e$, Ln q_e versus Ln C_e and q_e versus Ln C_e, respectively.[31,32,33] Also, the essential characteristics of the Langmuire isotherm can be express by the dimensionless constant called equilibrium parameter R_L, defined by.[34]

$$(6) \qquad R_L = \frac{1}{1 + bC_0}$$

Further we display the adsorption isotherms plots (Figure. 1-3) where C_0 is the initial concentration of metal ion (mg/L). The R_L value indicates the mode of sorption of the isotherm process, whether the process is unfavorable ($R_L > 1$), or Linear ($R_L=1$), or favorable ($0<R_L<1$), or irreversible ($R_L=0$). Also, constant factor models and correlation coefficients (R^2) from linear models were fitted by the experimental results of adsorption processes by using Excel software and comparisons with each other. All investigated parameters were shown on table 1- 6.

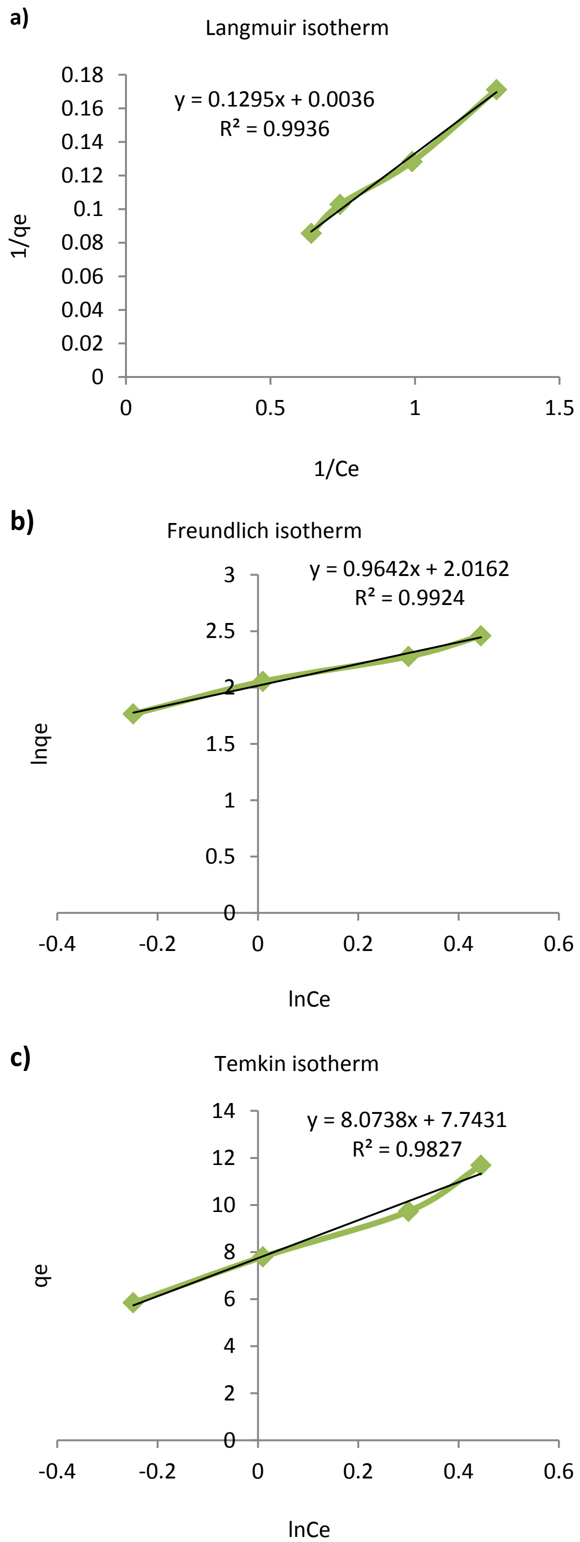

Figure 1. Plots of linearized Langmuir (a), Freundlich (b), and Temin (c) adsorption isotherms for Cr ions

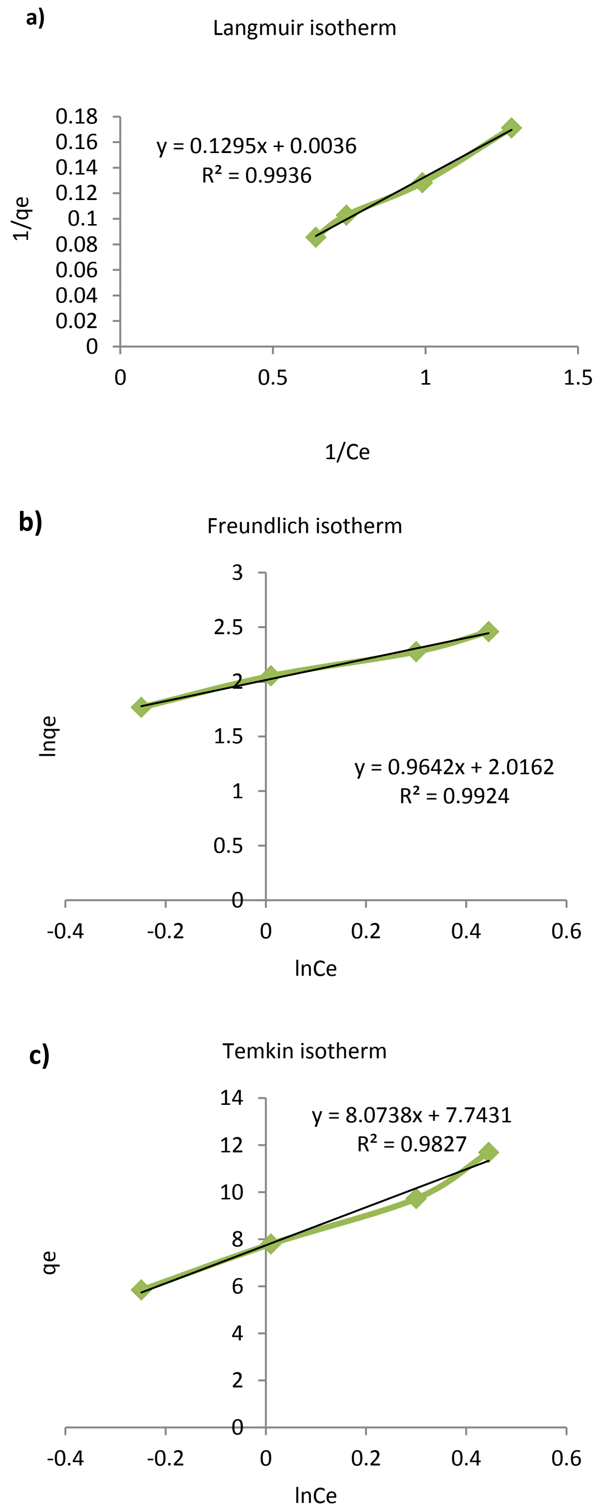

Figure 2. Plots of linearized Langmuir (a), Freundlich (b), and Temin (c) adsorption isotherms for Cd ions

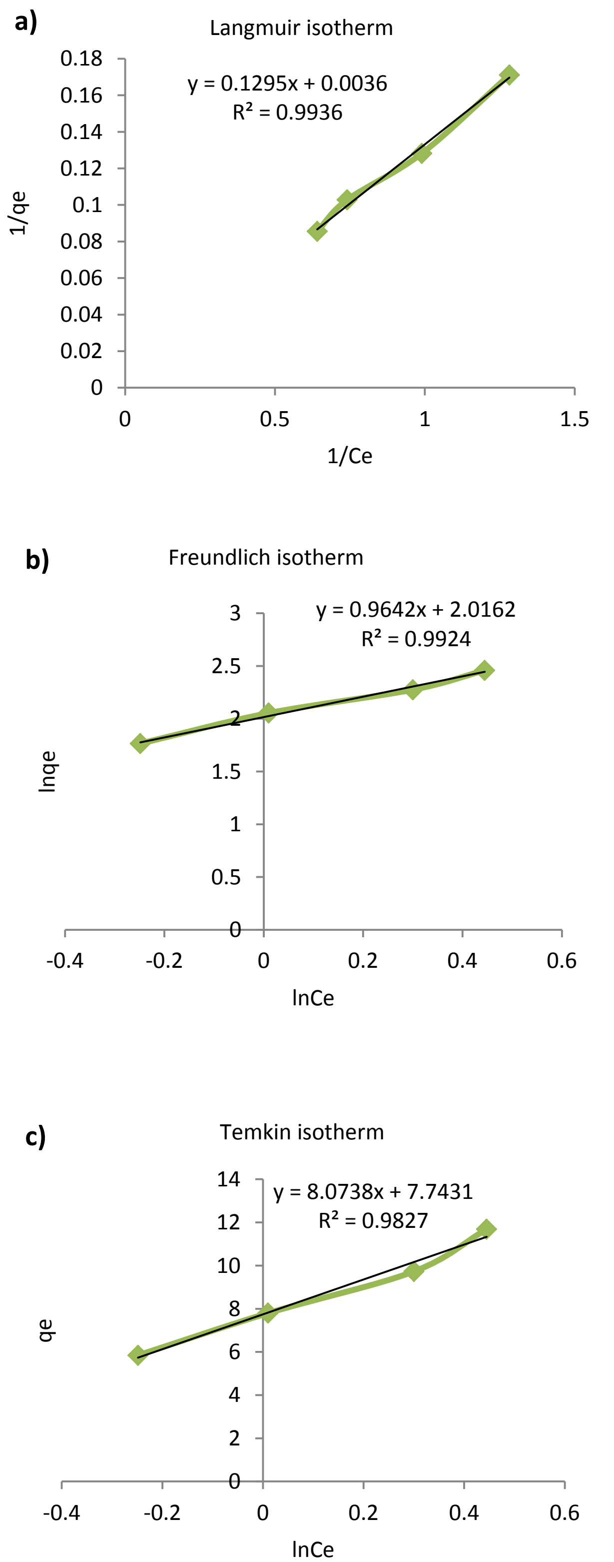

Figure 3. Plots of linearized Langmuir (a), Freundlich (b), and Temin (c) adsorption isotherms for Pb ions

Table 1. Amount of C0, Ce, qe, RL and removal percentage of Cr

Initial concentration (mg/L)	Concentration at equilibrium (mg/L)	Uptake amount at equilibrium (mg/g)	R_L	Removal percent
30	1.5	5.7	0.02	95
40	4.9	7.02	0.01	87.75
50	11.2	7.76	0.01	77.6
60	21	7.8	0.01	65

Table 2. Isotherm parameters for the adsorption of Cr ions onto adsorbent

Q_M (MG/G)	k ($L^{1/n}.mg^{(n-1)/n}.g^{-1}$)
8.05	5.56
b (L/mg)	N
1.602	8.071

Table 3. Amount of C0, Ce, qe, RL and removal percent of Cd+2

Initial concentration (mg/L)	Concentration at equilibrium (mg/L)	Uptake amount at equilibrium (mg/g)	R_L	Removal percent
30	0.78	5.844	0.54	97.4
40	1.01	7.798	0.47	97.475
50	1.35	9.73	0.41	97.3
60	1.56	11.688	0.37	97.4

Table 4. Isotherm parameters for the adsorption of Cd+2 onto adsorbent

q_m (mg/g)	k ($L^{1/n}.mg^{(n-1)/n}.g^{-1}$)
277.7	7.509
b (L/mg)	N
0.027	1.037

Table 5. Amount of C0, Ce, qe, RL and removal percent of Pb+2

Initial concentration (mg/L)	Concentration at equilibrium (mg/L)	Uptake amount at equilibrium (mg/g)	R_L	Removal percent
30	3.9	5.22	0.319	87
40	5.3	6.94	0.260	86.7
50	7.6	8.48	0.219	84.8
60	10	10	0.190	83.3

Table 6. Isotherm parameters for the adsorption of Pb+2 onto adsorbent

q_m (mg/g)	k ($L^{1/n}.mg^{(n-1)/n}.g^{-1}$)
24.44	2.1511
b (L/mg)	N
0.07	1.481920569

Discussion

The aim of this study was to reveal the potential of sunflower waste biomass as an effective adsorbent for the removal of heavy metals. Though the activated carbon was prepared from waste biomass the results indicate that sunflower waste biomass has enough efficacy for removing heavy metals. The data from the batch of bio sorption studies provided essential information in terms of optimum pH, bio carbon dose for the removal of ions from wastewater. The bio sorption process is significantly controlled by the pH of the solution. The low cost of this compound may offer unique advantages for its use in water treatment. The value of r^2 for the Langmuire isotherm for all systems shows much more compatibility. In this study, the dimensionless separation factors were lying in the range of $0 < R_L < 1$, this shows that the isotherm process was feasible. Thus, the above findings encourage us to explore the sunflower waste biomass surface further for the removal of various pollutants based on their physicochemical diversities, and works are in progress.

Acknowledgement

This study was supported by shahroud University of Medical Sciences (grant No: 9139).

Conflict of Interest

The authors declare that they have no conflict of interests.

References

1. Brinza L, Nygard CA, Dring J, Gavrilescu M, Benning LG. Cadmium tolerance and adsorption by the marin brown alga fucus vesiclosus from the Irish sea and the Botnian sea. Bioresource Technology 2009;100:1727-33. doi:10.1016/j.biortech.2008.09.041

2. Baysal Z, Cinar E, Bulut Y, Alkan H, Dogru M. Equilibrium and thermodynamic studies on biosorption of Pb(II) onto candida albicans biomass, J Hazard Mater 2009;161:62-7. doi:10.1016/j.jhazmat.2008.02.122

3. Abdel-Halim SH, Shehata AM, El-Shahat MF. Removal of lead ions fom industrial waste water by different types of natural materials. Water Res 2003;37:1678-83. doi:10.1016/S0043-1354(02)00554-7

4. Edmond KM, Zandoh C, Quigley MA, Amenga-Etego S, Owusu-Agyei S, Kirkwood BR. Delayed breastfeeding initiation increases risk of neonatal mortality. Pediatrics 2006;117:e380-6. doi:10.1542/peds.2005-1496

5. Zhang K, Cheung WH, Valix M. Roles of physical and chemical properties of activated carbon in the adsorption of lead ions. Chemosphere 2005;60:1129-40. doi:10.1016/j.chemosphere.2004.12.059

6. Federal-Provincial-Territorial Committee on Drinking Water Microbiological quality of drinking water: heterotrophic Plate Count 2005.

7. Sharma YC. Thermodynamics of removal of cadmium by adsorption on an indigenous clay. Chem Eng. J 2008;145;64-68. doi:10.1016/j.cej.2008.03.006

8. Alloway BJ, Steinnes E. Anthropogenic additions of cadmium to soils. in: M. J. McLaughlin, B.R. Singh (Eds.). Cadmium in soils and plants. Netherlands: Springer; 1999. p. 97-124.

9. Pérez-Marín AB, Zapata VM, Ortuño JF, Aguilar M, Sáez J, Lloréns M. Removal of cadmium from aqueous solutions by adsorption onto orange waste. J Hazard Mater 2007;139;122-31. doi:10.1016/j.jhazmat.2006.06.008

10. Mahalik MP, Hitner HW, Prozialeck WC. Teratogenic effects and distribution of cadmium (Cd+2) administerted via osmotic minipumps to gravid Cf-1 mice. Toxicol Lett 1995;76:195-202. doi:10.1016/0378-4274(95)80003-V

11. World Health Organization. Guidelines for Drinking Water Quality. Geneva:ISBN;2006. 515 p.

12. Mousavi HZ, Hosseynifar A, Jahed V, Dehghani SAM. Removal of lead from aqueous solution using waste tire rubber ash as an adsorbent. Brazilian Journal of Chemical Engineering 2010;27:79-87. doi:10.1590/S0104-66322010000100007

13. Chojnacka K. Biosorption of Cr(III) ions by eggshells. Journal of Hazardous Materials 2005;121;167-73. doi:10.1016/j.jhazmat.2005.02.004

14. Ali I1, Gupta VK. Advances in water treatment by adsorption technology. Nat Protoc 2006;1:2661-7. doi:10.1038/nprot.2006.370

15. Mohammadkhani Sh, Gholami MR, Aghaei M, Thermodynamic study of Cr+3 ions removal by "MnO2/MWCNT" nanocomposite. Oriental Journal of Chemistry 2015;31:1429-36. doi:10.13005/ojc/310321

16. Nazemi S. Concentration of heavy metal in edible vegetables widely consumed in Shahroud, the north east of Iran. J. Appl. Environ. Biol. Sci 2012;2:386-91.

17. Farinella NV, Matos GD, Lehmann EL, Arruda MA. Grape baggase as an alternative natural adsorbent of cadmium and Lead for effluent treatment. J Hazard Mater 2008;154:1007-12. doi:10.1016/j.jhazmat.2007.11.005

18. Zulkali MMD, Ahmad AL, Norulakmal NH. Oryza Sativa L. husk as heavy metal adsorbent: optimization with Lead as model solution. Bioresource Technology 2006;97:21-5. doi:10.1016/j.biortech.2005.02.007

19. Yu B, Zhang Y, Shukla A, Shukla SS, Dorris KL. The Removal of heavy metals from aqueous solution by sawdust adsorption- Removal of Lead and comparison of it's adsorption with Copper. J Hazard Mater 2001;84:83-94. doi:10.1016/S0304-3894(01)00198-4

20. Cho H, Oh D, Kim K. A Study on Removal characteristics of heavy metals from aqueous solution by fly ash. Journal of Hazardous Materials 2005;127:187-195. doi:10.1016/j.jhazmat.2005.07.019

21. Pino GH, Souza de Mesquita LM, Torem ML, Pinto GAS. Biosorption of cadmium by green coconut shell powder. Minerals Engineering 2006;19:380-7. doi:10.1016/j.mineng.2005.12.003

22. Chandra Sekhar K, Kamala CT, Chary NS, Anjaneyulu Y. Removal of heavy metal using a plant biomass with reference to environmental control. International Journal of Mineral Processing 2003;68:37-45. doi:10.1016/S0301-7516(02)00047-9

23. Witek-Krowiak A Analysis of temperature-dependent adsorption of Cu+2 ions on sunflower hulls: kinetics, equilibrium and mechanism of the process. Chem Eng J 2012;192:13-20. doi:10.1016/j.cej.2012.03.075

24. Sharma SK., Karla KL, Grewal HS. Fermentation of enzymatically saccharified sunflower stalks for ethanol production and its scale up. Bioresource Tech 2002;85:31-33. doi:10.1016/S0960-8524(02)00076-7

25. Jain M, Garg VK, Kadirvelu K. Adsorption of hexavalent chromium from aqueous medium onto carbonaceous adsorbents prepared from waste biomass. J Environ Manage 2010;91:949-57. doi:10.1016/j.jenvman.2009.12.002

26. Jain M, Garg VK, Kadirvelu K Equilibrium and Kinetic studies for sequestration of Cr(VI) from simulated wastewater using sunflower waste biomass. J Hazard mater 2009;171:328-34. doi:10.1016/j.jhazmat.2009.06.007

27. Jain M, Garg VK, Kadirvelu K Cadmium (II) sorption and desorption in a fixed bed column using sunflower waste carbon calsiom-alginate beads. Biosorption Technol 2013;129:242-8. doi:10.1016/j.biortech.2012.11.036

28. Zhu, Z. and Li, W. Efficient adsorption and desorption of Pb2+ from aqueous solution. Journal of Environmental Chemical Engineering 2013;1:838-43.doi:10.1016/j.jece.2013.07.022

29. El-Sheikh AH, Sweileh JA, Al-Degs YS. Effect of dimensions of multi-walled carbon nanotubes on its enrichment efficiency of metal ions from environmental waters. Anal Chim Acta 2007;604:119-26. doi:10.1016/j.aca.2007.10.009

30. Hu J, Shao D, Chen C, Sheng G, Ren X, Wang X. Removal of 1-naphthylamine from aqueous solution by multiwall carbon nanotubes/iron oxides/cyclodextrin composite. J Hazard Mater 2011;185:463-71. doi:10.1016/j.jhazmat.2010.09.055

31. Langmuir I. The constitution and fundamental properties of solids and liquids part I. solids. Jornal of the American Chemical Society 1916;38:2221-2295. doi:10.1021/ja02268a002

32. H. M. F. Freundlich, "Uber die adsorption in losungen," Zeitschrift fur Physikalische Chemie-Leipzig 1906;57:385–470,

33. Temkin M., Pyzhev V. Kinetics of Ammonia Synthesis on Promoted Iron Catalysts. Acta Physicochimica URSS 1940;12:217-222.

34. Amin NK, Removal of reactive dye from aqueous solutions by adsorption onto activated carbons prepared from sugarcan baggase Pith. Desalination 2008;223:152-61. doi:10.1016/j.desal.2007.01.203