ORIGINAL PAPER

Mercury removal from aqueous solutions by palm leaves adsorbent

Mitra Mohammadi,[1] Khadije Shamsi,[2] Abdollah Dargahi,*[2] Pegah Sekhavati[3]

1. Department of Environmental Health Engineering, School of Public Health, Kermanshah University of Medical Sciences, Kermanshah, Iran
2. Department of Environmental Health Engineering, School of Public Health, Hamadan University of Medical Sciences, Hamadan, Iran
3. Department of Environmental Health Engineering, School of Public Health, Kurdistan University of Medical Sciences, Kurdistan, Iran

Date of submission: 21 Jun 2017, ***Date of acceptance:*** 31 Jul 2017

ABSTRACT

Mercury is a carcinogenic and teratogenic compound that tends to accumulate in water solutions. In this research, the removal of mercury from an aqueous solution was evaluated by using palm leaves. Experiments were performed to study the adsorption efficiency, the effect of the adsorbent amount, the balance time, the adsorbate concentration, and the pH on mercury removal. The experimental apparatus used was a batch stirred reactor (volume: $1m^3$). The study was conducted under almost isothermal conditions. The test results showed that the optimum adsorbate concentration was 2 g/l, the balance time was three hours, the optimum adsorbent concentration was 15 mg/l, and the pH was 6. The maximum efficiency obtained was 99.24%. The chemical compounds with the highest presence in the palm leaves were LoI (93.76%), and SiO_2 (4.1%), whereas the compound with the lowest presence was Na_2O (0.08%). The mercury removal efficiency increased with an increase in the adsorbent dose and the contact time, and reduced with an increase in the initial mercury concentration. The Freundlich model, using the variables provided in the study, predicted the change in the adsorption kinetics.

Keywords: Palm leaves, Adsorption, Mercury, Isotherm

Introduction

Mercury (Hg^{+2}) is a heavy metal with the atomic number 80. It has a freezing point of –38.83°C and a boiling point of 356.73 °C.[1] Mercury is an important and a useful industrial material, used for conducting numerous experiments, and to manufacture products and instruments. Due to such usage, traces of mercury are found in industrial wastewater.[2] The oil-refining industries, paper and pulp industries, electrical and rubber-processing sectors, nuclear reactors, gold ore sector, and fertilizer industries are the principal sources of mercury that are released in the aquatic environment.[3,4] Mercury enters the food chain, and eventually a large amount of this heavy metal accumulates in human and animal bodies.[5] Mercury can cause chronic and acute poisoning; thus, it is fatal for aquatic animals and dangerous for human health.[6] Hg^{+2} can adversely affect the nerve, brain, and kidneys, and it can cause lung irritation, skin rashes, and vomiting—the list goes on. The lowest limit for any heavy metal (0.001ppm) is prescribed for mercury.[7] Hence, its removal from the vital resources and the environment in general is a prime concern in today's world.[8] Several technologies have been used to remove mercury including ion exchange, adsorption, solvent extraction, reverse osmosis, and membrane processes.[9–11] Adsorption is an appropriate technology for mercury removal,[12] and its efficiency depends upon the characteristics of the contaminant, concentration of the contaminant, temperature, pH, and the dose of adsorbent.[5] Many studies have evaluated the use of naturally available materials—such as

Abdollah Dargahi
a.dargahi29@yahoo.com

Citation: Mohammadi M, Shamsi Kh, Dargahi A, Sekhavati P. Mercury removal from aqueous solutions by palm leaves adsorbent. J Adv Environ Health Res 2017; 5(2): 101-106

walnut shell,[9] fruit shell of *Terminalia catappa*,[13] olive stones,[3] chitosan,[14] palm leaf ash,[15] and agricultural waste[16] as precursors for adsorption. Keeping in mind the necessity of applying an economic and efficient adsorbent, this study aimed to examine palm leaves' efficiency in removing mercury. It also evaluated the importance of isotherm adsorption models for determining adsorbent capacity and optimizing the adsorbent consumption.

Materials and Methods

In the present study, the effects of pH (4, 6, and 8), contact time (zero, three, six, and nine hours), adsorbent concentration (15, 30, 45, and 90 mg/l), and adsorbate dose (1.5, 2, 2.5, and 3 g) on mercury removal were examined. The pH was regulated using 1N nitric acid and sodium hydroxide solution. To obtain a proper mixture of the adsorbent and mercury, an orbital mixer with an intensity of 300 rpm maintained at 25 °C was used.[17] For separating the adsorbent particles from the aqueous solution, the samples were filtered with the help of a 0.2-micron fiberglass filter. Atomic adsorption spectroscopy (Perkin Elmer 4100) was done for mercury residue measurement and the mercury efficiency removal was evaluated. All the chemical substances and reagents used in this study have a purity of 99.99% and were purchased from Merck Co., Germany. In order to prepare the adsorbent, the palm leaves were washed and dried. They were then crushed and screened with the help of 30 mesh sieves with a pore size of 0.5 mm. The leaves were further dried by the dry Heat at a temperature of 100 °C until it reached a constant weight. The mercury stock solution (1,000 mg/l) was prepared by dissolving mercury in double-distilled water and then various concentrations were prepared (15, 30, 45, and 90 mg/l). The Langmuir isotherm is valid for the single-layer surface adsorption. In this model, it was assumed that the surface adsorption energy was constant and the material, which adsorbed in the surface adsorption, had no migration.[18] The equation is as follows:

$$\frac{C_e}{q_e} = \frac{1}{K_l\, q_{max}} + \frac{C_e}{q_{max}} \qquad (1)$$

The Langmuir isotherm is presented as a separation factor in Equation 2:

$$R_l = \frac{1}{1 + K_l\, C_0} \qquad (2)$$

The Freundlich isotherm described the multi-layer adsorption based on the interaction between the surface adsorbent molecules. With the increase in surface coverage, the surface adsorption energy had decreased exponentially.[19] This equation is represented as Equations 3 and 4:

$$q_e = K(C_e)^{1/n} \qquad (3)$$

$$Ln\, q_e = Ln\, K_f + \frac{1}{n}\, Ln\, C_e \qquad (4)$$

The surface area of the palm leaves was measured by a surface analyzer (Quantachrome Autosorb-1 analyzer) using the BET method.

Results and Discussion

As mentioned earlier, the aim of the present study was to determine the efficiency of palm tree leaves in removing mercury from aqueous solutions. The use of this adsorbent for mercury removal was very effective and its application in mercury removal was approved. The characteristics of palm leaves are shown in Table 1.

Table 1. Chemical compounds in palm leave (%) by HPLC

Chemical compounds	level	Chemical compounds	level
SiO_2	4.1	SO_3	0.1
Al_2O_3	0.31	Na_2O	0.08
Fe_2O_3	0.16	MgO	0.4
K_2O	0.71	P_2O_5	0.28
LoI	93.76	SO_3	0.1

Effect of Adsorbent Concentration

As shown in Fig. 1, by increasing the palm leaves' adsorbent dosage from 1.5-3 mg/l, one can increase the removal efficiency from 72.6% to 85.2%. Adsorbent dose is a key parameter controlling the accessibility to and the availability of the adsorption sites. Increasing the adsorbent dose results in increasing removal efficiency.[20] In the present study, while increasing the adsorbent dose from 1.5 g to 3 g, there was a 13% increase in the removal efficiency. This phenomenon could be attributed to the fact that increasing the adsorbent dose resulted in an increasing surface area, which in turn gave rise to a greater removal efficiency.[21]

The initial rapid and high adsorption rate was possibly due to the presence of voids on the adsorbent surface. By increasing the exposure time, these locations were gradually filled in with mercury, thereby increasing the rate of mercury removal.[22] Nad Ali et al. achieved similar results in mercury removal with the help of palm tree leaf.[23] Asar et al. studied the adsorption of heavy metals using the wastes of the boron enrichment process and found similar results.[25] Ding et al., Kuar et al., and Ornek et al. obtained similar results.[17, 24, 26] The absorption process depends on the charge and the mobility of the ions present in the solution. Cations and anions were absorbed by the counter ions present on the surface and the micropores of the adsorbent.

Table 2. Constant of synthetic cadmium adsorption model by adsorbent

Freundlich adsorption isotherm	Langmuir adsorption isotherm
n= 1.89 g/lit	q_{max}= 0. 29 mg/g
K_f =0.0029 mg/g	K_L=0.069 l/mg
R^2 = 0.997	R^2 = 0.987
-	R_L= 0.6

Effect of Contact Time

As Fig. 2 showed, the adsorption rate is high during the initial contact time. However, after three hours, the mercury adsorption reduces due to the desorption that has occurred during that time. In the present study, increased adsorption was achieved by increasing the contact time. This is consistent with the results found by Madrakian et al.[27] Possibly, this increase in adsorption could be due to increasing incidents of mercury molecules with palm leaf surface.[28] By increasing the time, due to the increasing repellence power among the mercury molecules, occupying the residual site would be very difficult. In the sorption mechanism, mercury ion is removed by ion exchange and physico-chemical sorption.[28] Ion mobility and the interaction rates among the counter-charged ions and the absorbent surface are important issues in aqueous solutions.[29]

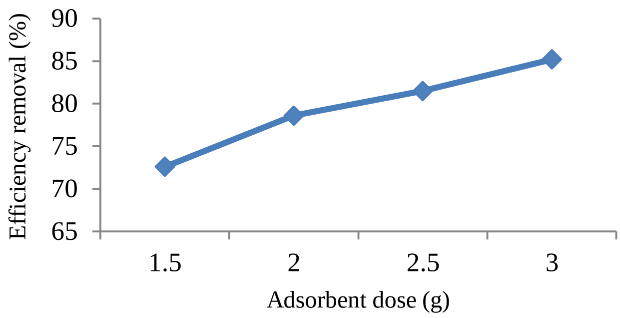

Fig. 1. The removal efficiency based on the various adsorbent concentrations

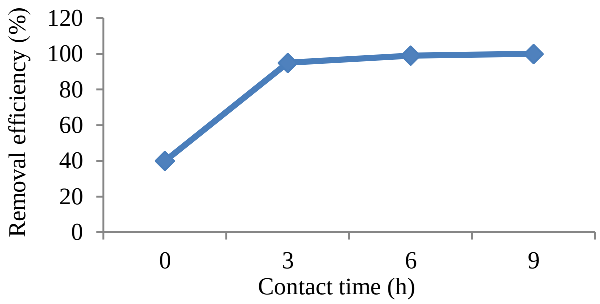

Fig. 2. The removal efficiency in different contact time

Effect of Mercury Concentrations

The results showed that the mercury adsorption percentage had reduced as the concentration increased, and the removal percentage was reduced from 78.97% to 49.41% (Fig. 3). Adsorption efficiency was decreased by increasing the adsorbate concentration.[30] In lower concentrations of mercury, sufficient active sites are available. Therefore, it was observed that the absorption rate was independent from the metal concentration. But in higher concentrations, the metal ion numbers are more than in active absorption sites. Thus, the removal percentage of metal ions depends on the initial concentration of mercury and decreases by increasing the initial mercury concentration.[31] By increasing the initial concentration, the weight of the amount absorbed increased. Since the ratio of absorbent to solution is constant in high concentrations, due to the saturation of the exchangeable sites by the absorbate, the efficiency of absorption is decreased. In most cases, mercury adsorption occurs at two to four hours of equilibrium time. When a layer is formed on the active sites of the adsorbent, the adsorption rate decreases.[32]

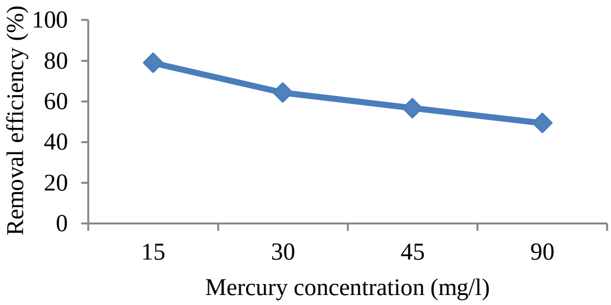

Fig. 3. Removal efficiency in various Mercury concentrations (the optimum adsorbent amount of 3 gr and balance time of 3 hours)

Effect of pH

The results showed that with an increase in the pH, the removal efficiency increased too, reaching its maximum level of pH=6 (Fig. 4). For mercury, the maximum uptakes were found on the palm leaf surface at solution pH near the adsorbate's point of zero charge (pH_{pzc}). The pH_{pzc} in this study was 5.6. One of the other important parameters affecting the adsorption process was the adsorbent pH value. The adsorption process is very sensitive to solution pH. Ionic activity has a prominent role in metal adsorption. Studies show that the optimum pH range for mercury removal is between 5 and 6.[22] The pH had an important contribution in the total process. However, the adsorption capacity that resulted from the pH greatly influenced the adsorbent surface charge, ionization level of materials in solution, dissociation of the functional groups in active sites, and the solution chemistry. Therefore, the pH had a great impact on the removal of organic and inorganic materials from the aqueous solutions. In acidic pHs, removal efficiency was high due to the protonation of active sites and an increasing charge density on the adsorbent surface (phenolic, carboxylic, and hydroxyl).[33] In fact, the reason for decreasing efficiency by increasing the pH value was the ionization of the adsorbent and absorbate. This also caused the creation of repellence power and decreased removal efficiency.[34] Ruiz studied mercury removal and found that by increasing the pH up to 6, the increasing rate of the mercury removal continued. However, increasing the pH above 6

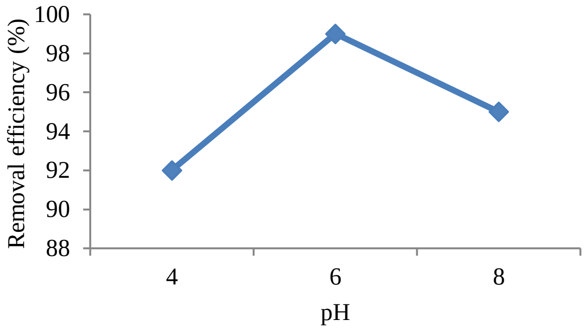

Fig. 4. The removal efficiency based on the pH (the optimum adsorbent level 3 gr and balance time of 3h and optimum adsorbate concentration of 15 mg/l)

decreased this rate. Our results are consistent with the results found by Ruiz.[35]

Evaluating Isotherm Adsorption

Based on the results displayed in Table 1, the R_L level in Langmuir model was in the range of 0–1, which showed that the adsorption process was desirable on the adsorbent. The amount in the Freundlich isotherm of 1-10 also represented that the adsorption process was desirable. Evaluation of the linear isotherm and the R^2 correlation coefficient showed a good adaption of experimental results with the Freundlich and Langmuir models. The absorption rate depends on kinetics, and the Longmuir and Freundlich absorption equilibrium. The absorption isotherms were discontinuous for these studies.[36] The absorption isotherms are equations for explaining the equilibrium state of the absorbent among the solid and fluid phases. In the present study, experimental data was evaluated using the Freundlich and Longmuir absorption isotherms. According to the results of the isotherm equations, the mercury absorption isotherm on the palm leaf followed the Freundlich and Longmuir isotherms. Arumugam et al. studied nickel absorption using synthesized SBA-15 and sugarcane leaf ash. Likewise, Aranda Garcia et al. studied nickel absorption using chestnut fruit bark and found that absorption had more agreement with the Freundlich isotherm, which is consistent with our results.[37] Meanwhile, Malarvizhi found more agreement with the absorption data of the Longmuir isotherm. This is in contrast with the results found in the present study.[38] The findings of the present study showed that by increasing the absorbent dose and the contact time, removal efficiency increased, while there was an inverse relationship between absorbent concentration and absorbent efficiency. The absorption isotherm followed the Freundlich model.

The BET analysis presented no significant changes on the surface of the palm leaves after mercury adsorption. Hence, we suggest that the surface area contributed less to the mercury adsorption.

Conclusion

To sum up, the present study showed that the palm leaf—being small in size, having a great cross-section and great reactivity for mercury heavy metal removal from aqueous solutions—could be effective for mercury removal. Although the present study was conducted on a pilot and laboratory scale, and has an industrial application, it requires more comprehensive studies in the semi-industrial and higher scales.

Acknowledgement

The authors gratefully acknowledge the Research Council of Kermanshah University of Medical Sciences (Grant Number: 95656) for its financial support.

References

1. Campanella L, Cardarelli E, Ferri T, Petronio B. Mercury removal from petrochemical wastes. Water Res 1986; 20(1): 63-65.
2. Aydın YA, Aksoy ND. Adsorption of chromium on chitosan: Optimization, kinetics and thermodynamics. Chem. Eng. J 2009; 151(1): 188-194.
3. Wahby A, Abdelouahab-Reddam Z, El Mail R, et al. Mercury removal from aqueous solution by adsorption on activated carbons prepared from olive stones. Adsorption .2011; 17(3): 603-609.
4. Almasi A, Dargahi A, Amrane A, Fazlzadeh M, Mahmoudi M, Hashemian A. Effect of the retention time and the phenol concentration the stabilization pond efficiency in the treatment of oil refinery wastewater. Fresenius environmental bulletin 2014; 23(10a): 2541-2548.
5. Almasi A, Mohammadi M, Atafar Z, Azizi A, Amirian F, Dargahi A. Study the Efficiency of Processed Walnut Bark Powder for Methylene Blue Color Removal from Aqueous Solutions. Der Pharma Chemica 2016, 8(13): 253-257.
6. Shafeeq A, Muhammad A, Sarfraz W, Toqeer A, Rashid S, Rafiq M. Mercury removal techniques for industrial waste water. World Acad. Sci. Eng. Technol 2012; 6: 12-26.
7. Bessbousse H, Rhlalou T, Verchère J-F, Lebrun L. Mercury removal from wastewater using a poly (vinylalcohol)/poly (vinylimidazole) complexing membrane. Chem.Eng. J 2010; 164(1): 37-48.
8. Dargahi A, Gholestanifar H, Darvishi P, Karami A, Hasan SH, Poormohammadi A, et al. An investigation and comparison of removing heavy metals (lead and chromium) from aqueous solutions using magnesium oxide nanoparticles. Pol. J. Environ. Stud 2016; 25(2): 557-562.
9. Zabihi M, Asl AH, Ahmadpour A. Studies on adsorption of mercury from aqueous solution on activated carbons prepared from walnut shell. J. hazard. mater 2010; 174(1): 251-256.
10. Miretzky P, Cirelli AF. Hg (II) removal from water by chitosan and chitosan derivatives: a review. J. hazard. mater 2009; 167(1): 10-23.
11. Mohsen-Nia M, Montazeri P, Modarress H. Removal of Cu 2+ and Ni 2+ from wastewater with a chelating agent and reverse osmosis processes. Desalination 2007; 217(1): 276-281.
12. Godini H, Dargahi A, Mohammadi M, Ahagh MH, Mohammadi S, Jalilian Z. Application of Response Surface Methodology for Optimization of Ammonia Nitrogen Removal from Aqueous Solutions Using Powdered Activated Carbon. Research Journal of Environmental Sciences 2017; 11 (1): 36-47.
13. Inbaraj BS, Sulochana N. Mercury adsorption on a carbon sorbent derived from fruit shell of Terminalia catappa. J. hazard. mater 2006; 133(1): 283-290.
14. Shafaei A, Ashtiani FZ, Kaghazchi T. Equilibrium studies of the sorption of Hg (II) ions onto chitosan. Chem. Engin. J 2007; 133(1): 311-316.
15. Ghorbani F, Sanati A, Younesi H, Ghoreyshi A. The potential of date-palm leaf ash as low-cost adsorbent for the removal of Pb (II) ion from aqueous solution. Int. J. Eng. Trans. Appl 2012; 25(4): 269.

16. Garg U, Kaur M, Jawa G, Sud D, Garg V. Removal of cadmium (II) from aqueous solutions by adsorption on agricultural waste biomass. J. hazar. mater 2008; 154(1): 1149-1157.
17. Kaur R, Singh J, Khare R, Cameotra SS, Ali A. Batch sorption dynamics, kinetics and equilibrium studies of Cr (VI), Ni (II) and Cu (II)
18. from aqueous phase using agricultural residues. Applied Water Science 2013; 3(1): 207-218.
19. Das G, Pradhan N, Madhu G, Preetham H. Removal of cadmium from aqueous streams by Zeolite synthesized from fly ash. JMES 2013; 4(3): 410-419.
20. Seyd Mohammadi A, Asgari G, Dargahi A, Mobarakian SA. Equilibrium and synthetic equations for index removal of methylene blue using activated carbon from oak fruit bark. J. Mazandaran Uni Med Sci 2015; 24 (121): 172-187.
21. Li Y, Wang J-d, Wang X-j, Wang J-f. Adsorption–desorption of Cd (II) and Pb (II) on Ca-montmorillonite. Ind. Eng. Chem. Res 2012; 51(18): 6520-6528.
22. Mohan D, Sarswat A, Ok YS, Pittman CU. Organic and inorganic contaminants removal from water with biochar, a renewable, low cost and sustainable adsorbent–a critical review. Bioresour. Technol 2014; 160: 191-202.
23. Naiya TK, Bhattacharya AK, Das SK. Adsorption of Cd (II) and Pb (II) from aqueous solutions on activated alumina. Adv. Colloid Interface Sci. 2009; 333(1): 14-26.
24. Alavi SN, Pariz Z, Dargahi A, Mohamadi M. Evaluation the palm leaves efficiency as a natural adsorbent for removing cadmium from aqueous solution: isotherm adsorption study. IJ PT 2016; 8(2): 13919-13929.
25. Ding Y, Jing D, Gong H, Zhou L, Yang X. Biosorption of aquatic cadmium (II) by unmodified rice straw. Bioresour. Technol 2012; 114: 20-25.
26. Atar N, Olgun A, Wang S. Adsorption of cadmium (II) and zinc (II) on boron enrichment process waste in aqueous solutions: batch and fixed-bed system studies. Chem, Eng. J 2012; 192: 1-7.
27. Örnek A, Özacar M, Şengil İA. Adsorption of lead onto formaldehyde or sulphuric acid treated acorn waste: equilibrium and kinetic studies. Biochem. Eng. J 2007; 37(2): 192-200.
28. Madrakian T, Afkhami A, Ahmadi M, Bagheri H. Removal of some cationic dyes from aqueous solutions using magnetic-modified multi-walled carbon nanotubes. J.hazar. mater 2011; 196: 109-114.
29. Saadatjou N, Rasoulifard M, Heidari A. Removal of Basic Red 46 using low-cost adsorbent of hardened paste of portland cement from contaminated water. J Color Sci Tech 2009; 2(4): 221-226.
30. Godini H, Dargahi A, Mohammadi M, Shams Khorramabadi GH, Azizi A, Tabandeh L, Jalilian Z. Efficiency of Powdery Activated carbon in Ammonia-Nitrogen Removal from Aqueous Environments (Response Surface Methodology). Arch Hyg Sci 2017; 6(2): 111-120
31. Agarwal H, Sharma D, Sindhu SK, Tyagi S, Ikram S. Removal of mercury from wastewater use of green adsorbents–a review. Electron. J. Environ. Agric. Food Chem. 2010; 9(9): 1551-1558.
32. Li X-m, Zheng W, Wang D-b, et al. Removal of Pb (II) from aqueous solutions by adsorption onto modified areca waste: Kinetic and thermodynamic studies. Desalination 2010; 258(1): 148-153.
33. Ngah WW, Hanafiah MAKM. Removal of heavy metal ions from wastewater by chemically modified plant wastes as adsorbents: a review. Bioresour. Technol 2008; 99(10): 3935-3948.
34. Gerente C, Lee V, Cloirec PL, McKay G. Application of chitosan for the removal of metals from wastewaters by adsorption—mechanisms and models review. Crit. Rev. Env. Sci. Technol 2007; 37(1): 41-127.
35. He J, Lu Y, Luo G. Ca (II) imprinted chitosan microspheres: an effective and green adsorbent for the removal of Cu (II), Cd (II) and Pb (II) from aqueous solutions. Chem. Eng.J 2014; 244: 202-208.
36. Green-Ruiz C. Mercury (II) removal from aqueous solutions by nonviable Bacillus sp. from a tropical estuary. Bioresour.Technol 2006; 97(15): 1907-1911.
37. Aranda-García E, Cristiani-Urbina M, Pineda-Camacho G, Cristiani-Urbina E. Nickel (II) biosorption by acorn shell of Quercus crassipes humb. & bonpl. J. Biotechnol 2010; 150: 233.
38. Ossman ME, Mansour MS. Removal of Cd (II) ion from wastewater by adsorption onto treated old newspaper: kinetic modeling and isotherm studies. IJIC. 2013; 4(1): 13.
39. Malarvizhi T, Santhi T. Removal of Ni (II) ions from aqueous solution onto lignite fired fly ash. Res. J. Chem. Environ 2013; 17(3): 10-18.