Comparative study of efficiency biosorbents materials (almond, olive, and eucalyptus leaves) in removing of lead from laboratory aqueous solutions

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Abstract

The almond, olive and eucalyptus leaves were investigated as a low-cost biosorbents in removing lead ions from laboratory aqueous solutions. The adsorption experiments were conducted at different lead concentrations, and different biosorbent masses. The pH was adjusted to approximately 4.0, and contact time was 90 min. The obtained filtrates were analyzed for Pb^{+2} content using a Flame Atomic Absorption Spectroscopy (AAS - 220 FS). The results showed similar behavior in respect of the amount of lead adsorbed (q), which were increased with increasing lead concentrations (from approximately 2.0 – 790.0 mg/g), and it decreased with increasing bioadsorbents masses (from approximately 196.0 – 9.8 mg/g). In contrast, the removal percentage was relatively high and fluctuated between 67.4 – 99.6% for all biosorbents used in this study. The study deduced that the biosorbents exhibited high efficiency and sustainability for removing Pb^{2+} from aqueous solution.

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الملخص

أجريت هذه الدراسة لمقارنة كفاءة أوراق اللوز، والزيتون، والكينا كمواد مازة حيوية رخيصة الثمن في إزالة أيونات الرصاص (Pb^{+2}) من المحاليل المائية القياسية. وقد أجريت تجارب الامتزاز باستخدام تراكيز مختلفة من أيونات الرصاص (Pb^{+2}) وكميات مختلفة من المادة الماز، في حين تم تثبيت قيم pH بحدود 4.0 لفترة زمنية مدتها 90 دقيقة تقريبًا. وبعد حدوث عملية الامتزاز تم تحليل الراشح المتحصل عليه باستخدام مطياف الامتصاص الذري اللهبي (AAS – 220 FS). واظهرت النتائج المتحصل عليها سلوك متشابه بالنسبة لكمية أيونات الرصاص الممتزة (q) للمواد المازة الثلاثة حيث زادت الكمية الممتزة من 2.0 – 790.0 ملجم/جم تقريبًا بزيادة تركيز أيونات الرصاص. وأن الكمية الممتزة من أيونات الرصاص قلت بزيادة كتلة المواد المازة من 9.8 – 196.0 ملجم/جم تقريبًا. وفي المقابل بينت النتائج أن النسبة المئوية لكمية المادة الممتزة كامن مرتفعة وتراوحت ما بين 67.4 – 99.6 % لكل المواد المازة المستخدمة في هذه الدراسة. وخلصت الدراسة إلى أن المواد المازة الحيوية أظهرت سلوك متقارب وكفاءة ومقدرة عالية على إزالة أيونات الرصاص (Pb^{+2}) من المحاليل المائية.

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1. Introduction:

The presence of heavy metals in the environment is of major concern because of their toxicity, bio-accumulating tendency, threat to human life and the environment [1]. It is a well known fact that heavy metals can damage nerves, liver, and bones and could also block functional groups of essential enzymes [2, 3]. Heavy metal contamination exists in aqueous waste streams of many industries such as metal purification, metal finishing, chemical manufacturing, mining operations, smelting, battery manufacturing, and electroplating [4 - 6]. As a result of industrial activities and technological development, the amount of heavy metal ions discharged into streams and rivers by industrial and municipal wastewater have been increasing incessantly [7].

Certain heavy metals such as iron, copper, zinc and manganese are required by humans for normal biological functioning. However, heavy metals such as mercury, lead, cadmium are toxic to organisms. Most of the health disorders are linked with specific tendency of heavy metals to bioaccumulate in living tissues and their disruptive integration into normal biochemical processes [4]. Lead poisoning in human body can cause severe damage to kidney, nervous system, reproductive system, liver, and brain and may result in sickness or death. Severe exposure to lead has been associated with sterility, abortion, still birth and neonatal deaths, anemia, coma, mental retardation, and seizures [8, 9].

Most heavy metals are cations, carrying a positive charge, such as lead and cadmium. Soil particles tend to have a variety of charged sites on their surfaces, some of which are positive and some others are negative. The negative charges of these soil particles tend to attract and bind the positively charged metal cations, preventing them from becoming soluble and dissolve in water. The soluble form of metals is more dangerous because it is easily transported, hence more readily available to plants and animals [10].

Many attempts were made to remove a heavy metal from standard and waste water aqueous solution. Activated carbon was used and it displays high adsorption capacity; but the high cost presents a major drawback for practical applications, especially in the field of industrial effluent treatment where activated carbons may play a very useful role. Efforts have been made to develop low cost adsorbents for the removal of heavy metals from aqueous solutions. A number of natural and synthetic adsorbents like agricultural waste's carbon [11 - 13], clay [14], neem leaves [15], cooked tea dust [16], zeolites [17], teak leaves activated carbon [18], cashew nut shell activated carbon [19], fly ash [20] etc have been studied by various researchers for the removal of heavy metals. In this work we will investigate the ability of using almond, olive, and eucalyptus leaves as low cost biosorbents in removing lead from standard aqueous solutions, due to abundant availability of these leaves.

2 – Materials and Methods

2.1 - Standard Solution

The Pb^{+2} standard solution was prepared from Pb $(CH_3COO)_2.3H_2O$ salt without further purification. About 18.31 g of Pb $(CH_3COO)_2$ was weighed and dissolved to obtain standard solution of Pb^{+2} 10000 mg/L, and further working solutions of different concentrations were prepared as and when required.

2.2 - Collection and Preparation the Biosorbents

The biosorbents were collected from private farm in Tarhuna using polyethelene bags and washed with distilled water several times to remove dirt particles and dried for three hours in an oven at 150 ºC and then allowed to cool at room temperature, subsequently they were crushed and then finally sieved into particle size of 0.5 mm. The sieved adsorbents were stored in an air-tight container. No other chemical modification was taken place [21].

2.3 – Analytical Procedure

- Effect of initial lead ion concentration

The experiments were carried out by taking five conical flasks of 150 ml. In each flask, 25 ml of 200, 400, 800, 1600, and 3200 mg/L of Pb^{2+} were mixed with 0.5 g of biosorbents, and 25 ml of buffer solution that has pH = 4.0 to adjust the pH of the experiment's environment to approximately 4.0, and each flask was sealed tightly. The mixtures were shaken on a reciprocating shaker at shaking speed of 155 rpm at room temperature in triplicate. After 90 min, the mixture was filtered through filter paper of ϕ 110 nm (ALTAY). The obtained filtrates were analyzed for Pb^{+2} content using an Flame Atomic Absorption (AAS - 220 FS).

- Effects of biosorbents mass on adsorption of lead ions

Five conical flasks of 150 ml were taken. In each flask, 25 ml of 800 mg/L of Pb^{2+} were mixed with 0.1, 0.5, 1.0, 1.5, and 2.0 g of biosorbents, and with 25 ml of buffer solution that has pH = 4.0 to adjust the pH of the experiments environment to approximately 4.0, and each flask was sealed tightly. The mixtures were shaken on a reciprocating shaker at shaking speed of 155 rpm at room temperature

in triplicate. After 90 min, the mixture was filtered through filter paper of ϕ 110 nm (ALTAY). The obtained filtrates were analyzed for Pb^{+2} content using a Flame Atomic Absorption spectroscopy (AAS - 220 FS).

2.4 - Pb^{+2} Adsorption Capacity

The concentration of Pb^{+2} adsorbed onto the surface of biosorbents used in this study was calculated by the following equation:

$$q_{(mg/g)} = \frac{(C_o - C_f) \times V_{(L)})}{w_{(g)}}$$

Where, q is the amount of Pb^{+2} adsorbed on used biosorbents (mg/g), C_o is the initial Pb^{+2} concentration in the solution before adsorption (mg/L), C_f is the final concentration of Pb^{+2} in the solution after adsorption (mg/L), V is the volume of the Pb^{+2} solution (L) and w is the weight of the bisorbent. Adsorption system was quantified by calculating the adsorption percentage (E%) as defined by the following equation:

$$(E\%) = \frac{(C_o - C_f)}{C_o} \times 100$$

3 - Results and Discussion

3.1 – Effect initial lead ion concentration on lead adsorption

The obtained results in the Table 1, and in Fig. 3.1showed effects of variation in lead ion concentrations on the amount of lead adsorbed on almond, olive, and eucalyptus leaves. Also, they showed the lead removal percentage (Pb%).

It can be observed that the three bioadsorbents materials showed similar abilities of adsorbing lead ions on their

surfaces. Fig. 3.1a illustrates that the amount of lead ions adsorbed (q) was low at lower lead ions concentrations (about 2.0 mg/g at 100 ppm). The adsorbed amount of lead ions then increased with increasing the initial lead concentration up to maximum value (about 796.3 mg/g at 1600 ppm).

These observations are in agreement with the literatures for removing Cu^{2+} and Pb^{2+} using oil palm shell [22], and for removing Cd^{2+} using seaweed *H.valentiae* [23]. These studies have found that the amount of ions adsorbed per unit adsorbent weight increase as the lead ion increases. They attributed these observations into the fact that, at higher initial concentration a driving force was created to overcome mass transfer resistance that enabled the adsorbate ions to move sufficiently close to the sorbent to be adsorbed onto its binding sites. The sorbents used in this study displayed powerful ability in removing lead ions from aqueous solutions in compared with oil palm shell. As the amount of lead ions adsorbed on eucalyptus leaves reached 17.8 mg/g at 200 ppm, whereas it does not exceed 2.0 mg/g on oil palm shell at the same concentration.

In contrast, lead removal percentage (removal efficiency) (Fig. 3.1b) did not exhibit regular trend with increasing lead ion concentrations, with exception of eucalyptus leaves. This may due to low biosorbents amount (0.5 g) relative to initial lead ion concentration, which fluctuated between 100 – 1600 ppm, or due to appearance small particles of biosorbents in filtrated solutions after experiment (despite were filtered twice), which may lead to varying in Pb^{2+} concentrations from solution to another.

Table 1: Effect of initial lead ions concentration on the adsorption of lead on 0.5 g of biosorbents (pH = 4.0 and contact time of 90 min).

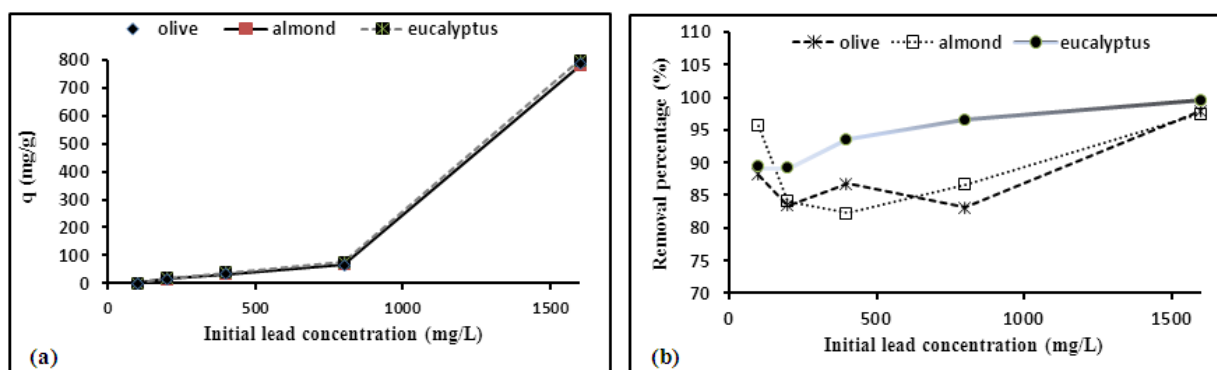| Pb^{2+} conc. mg/L	almond leaves		olive leaves		eucalyptus leaves	
	q (mg/g)	Removal (%)	q (mg/g)	Removal (%)	q (mg/g)	Removal (%)
100.0	1.9	95.7	1.8	88.2	1.8	89.5
200.0	16.8	84.1	16.7	83.4	17.8	89.2
400.0	32.9	82.3	34.7	86.8	37.4	93.6
800.0	69.3	86.6	66.5	83.1	77.3	96.6
1600.0	780.0	97.5	783.5	97.9	796.3	99.5

Fig. 3.1: Effect initial lead ion concentration on the amount of lead adsorbed (a); and on the removal percentage of lead (b).

3.2 – Effect of biosorbents mass on adsorption of lead ions

The obtained results in the Table 3.2 and in Fig. 3.2 showed effects of variation in sorbents masses on the amount of lead adsorbed on almond, olive, and eucalyptus leaves. Also, they showed the lead removal percentage (Pb%).

Again, the sorbents showed similarity in adsorbing lead ions on their surfaces. At constant concentration of lead ions (400 ppm), the amount of lead ions adsorbed decreases with increasing sorbents mass. It was observed that, the amount adsorbed on eucalyptus leaves, for example, decreased from 196 mg/g to approximately 10 mg/g as sorbent mass increased from 0.1 – 2.0 g. These results are in agreement with previous studies, which conducted using different biosorbent masses such as seaweed *H.valentiae* [23], and *Parthenium* (*P. hysterophorus* L.) weed [24]. This was attributed to that lowering lead ions to binding sites ratio at high mass of sorbent ($\frac{\text{lead ions}}{\text{binding sites}}$), where the ions are distributed onto larger amount of biomass binding sites [22, 25 and 26].

Table 2: Effect of biosorbents mass on adsorption of lead at constant lead ion concentration of 400 mg/L (pH = 4 and contact time of 90 min).

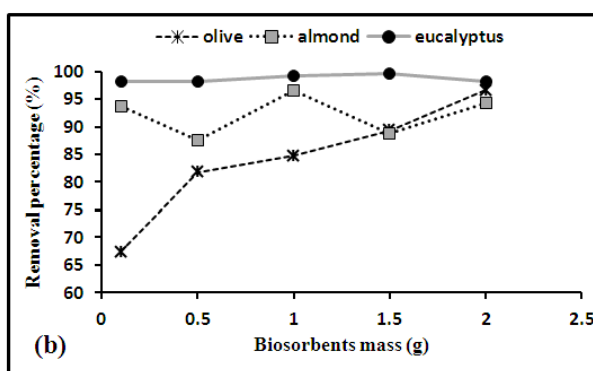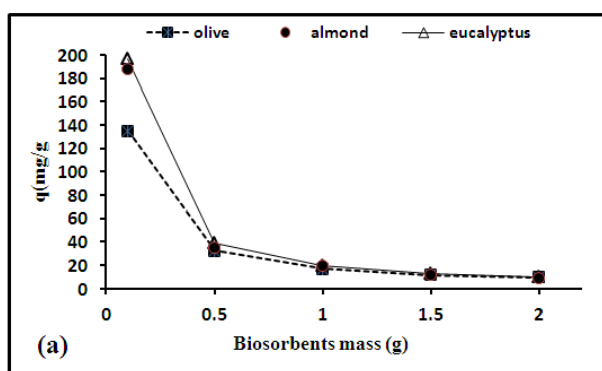| Biosorbent mass (g)	almond leaves		olive leaves		eucalyptus leaves	
	q (mg/g)	Removal (%)	q (mg/g)	Removal (%)	q (mg/g)	Removal (%)
0.10	187.5	93.8	134.9	67.4	196.3	98.1
0.50	35	87.5	32.7	81.8	39.3	98.2
1.00	19.3	96.6	16.9	8.84	19.8	99.3
1.50	11.8	88.7	11.9	89.4	13.2	99.6
2.00	9.4	94.3	9.6	96.6	9.8	98.1

Fig. 3.2: Effect of biosorbents mass the adsorbed amount of lead (a); and on the removal percentage of lead (b).

In respect of effects of biosorbents mass on the removal percentage of lead ions (%), the biosorbent materials used in this study exhibited slight variations. The removal percentage of lead ions on olive leaves increased as the sorbent mass increase, it is fluctuated between 67.4% for 0.1 g of olive leaves mass to 96.6% for 2.0 g of olive leaves mass. This is in agreement with previous literatures [22, 25 and 26]. This was attributed

to the availability of more empty binding sites in large masses in compared with lower masses, which has less binding sites to adsorb the same amount of lead ions. On the other hand, the eucalyptus leaves showed elevated lead ions removal percentage. It was approximately 98.0%, but it does not influence by biosorbent mass. Finally, the lead ions removal percentage on almond leaves was also high, and also does not influence by biosorbent mass. This may be because of the adsorptive nature of these biosorbents.

4- Conclusion

In general, it can be concluded that the almond, olive, and eucalyptus leaves showed high efficiency for removing lead ions on their surfaces in compared with other biosorbents materials such as seaweed *H.valentiae*, *Parthenium* (*P. hysterophorus* L.) weed, Rice husks, maize cobs and sawdust.

5 - References

[1] - J. C. Igwe, A. A. Abia, "A bioseparation process for removing heavy metals from waste water using biosorbents", *African Journal of Biotechnology*, Vol. 5 (12), pp. 1167-1179, (2006).

[2] – S. Chaudhari, V Tare, "Removal and Recovery of Heavy Metals from Simulated Wastewater Using Insoluble Starch Xanthate Process", Practice Periodical of Hazardous, Toxic, and Radioactive Waste Management, © ASCE, pp.170-180, (2008).

[3] – V. Geetha, R. K. Singh and V. Sahu, "A comparative study on the removal of heavy metals by adsorption using fly ash and sludge: A review". *International Journal of Application or Innovation in Engineering & Management* (IJAIEM), Volume 2, Issue 7, July (2013).

[4] - G. Issabayeva, M. K. Aroua, N. M. Sulaiman, "Study on palm shell activated carbon adsorption capacity to remove copper ions from aqueous solution". *Desalination*, 262, 94-98 (2010).

[5] - S. Liang, X. Guo, N. Feng, Q. Tian, "Application of orange peel xanthate for the adsorption of Pb^{2+} from aqueous solutions". *Journal of Hazardous Materials,* 170, 425-429 (2009).

[6] - S. Lu, S. W. Gibb, "Copper removal form wastewater using spent-grain as biosorbent". *Bioresource Techonology*, 99, 1509-1517 (2007).

[7] - H. Serencam, A. Gundogdu, Y. Uygur, B. Kemar, V. N. Bulut, C. Duran, M. Soylek, and M. Tufekci,. "Removal of cadmium from aqueous solution by Nordmann fir (Abies nordmanniana (Stev.) Spach. Subsp. Nordmanniana) leaves". *Bioresource Technology*, 99, 1992-2000 (2007).

[8] – K. Zhang, W. H. Cheung, M. Valix. "Roles of physical and chemical properties of activated carbon in the adsorption of lead ions". *Chemosphere* 60:1129–1140 (2005).

[9] – D. B. Botkin, E. A. Keller. "Environmental science: earth as a living planet", 3rd edn. Wiley, New York, pp 286 (2000).

[10] - S. S. Ahluwalia and D. Goyal. (2005). Microbial and plant derived biomass for removal of heavy metals from wastewater. *Bioresource Technology*, 98, 2243-2257.

[11] – S. D. Bansal, V. K. Garg. "A comparative study for the removal of hexavalent chromium from aqueous solutions by agriculture wastes carbons". *Journal of Hazardous Materials*, 17, pp. 83-92, (2009).

[12] - R. Ayyappan, A. C. Sphia, K. Swaminathan, S. Sandhya. "Removal of Pb(II) from aqueous solutions using carbon derived from agricultural wastes", *Process Biochemistry*, 40, pp. 1293-1299, (2005).

[13] - E. Demirbas, M. Kobya, E. Senturk, T. Ozkan. "Adsorption kinetics for the removal of chromium (VI) from aqueous solutions on the activated carbons prepared from agricultural wastes", Water SA, Vol.30 No.4, pp. 533-539, (2004).

[14] - P. Saha, S. Datta, S. K. Sanya. "Application of Natural Clayey Soil as adsorbent for the Removal of Copper from Wastewater". *Journal of Environmental Engineering* © asce / December, pp. 1409-1417, (2010).

[15] – S. Gupta, B. V. Babu. "Adsorption of Cr(VI) by a low cost adsorbent prepared from neem leaves", Proceedings of National conference on environmental Conservation (NCEC-2006), pp.175-180, (2006).

[16] - S. Dhanakumar, S. G. Solaraj, R. Mohanraj, S. Pattabhi. "Removal of Cr (VI) from aqueous solution by adsorption using cooked tea dust, Indian Journal of Science and Technology", Vol.1 No.2, pp. 1-6, (2007).

[17] - E. Erdem, N. Karapinar, R. Donat. "The removal of heavy metal cations by natural zeolites", *Journal of Colloid and Interface Science*, 280, pp. 309–314, (2004).

[18] – A. A. Jafa, S. Balasubramanian, "Adsorption of Pb(II) ions on teak leaves activated carbon- a kinetic and equilibrium study", *Der Chemica Sinica*, 1 (2), pp.35-43, (2010, www.pelagiaresearchlibrary.com

[19] – S. Tangjuank, N. Insuk, J. Tontrakoon, V. udeye. " Adsorption of Lead(II) and cadmium (II) ions from aqueous solutions by adsorption on activated carbon prepared from cashew nut shells", *world Academy of Science, Engineering and Technology*, 52 , pp. 110-116, (2009).

[20] I. J. Alinnor. "Adsorption of heavy metal ions from aqueous solution by fly ash", *Fuel* 86, pp. 853–857, (2007).

[21] – H. A. Zahir, S. K. M. Mohamed. "Removal of heavy metals from wastewater using low cost adsorbents". *Archives of Applied Science Research,* **6,** 52-54, (2014).

[22] – H. L. H. Chong, P. S. Chia, M. N. Ahmad. "The adsorption of heavy metal by Bornean oil palm shell and its potential application as constructed wetland media". *Bioresour Technol* 2013;130:181.6.

[23] – A. Rathinam, B. Maharshi, S. K. Janardhanan, R. R. Jonnalagadda, B. U. Nair. "Biosorption of cadmium metal ion from simulated wastewaters using Hypnea valentiae biomass: a kinetic and thermodynamic study". *Bioresour Technol* 2010;101:1466.70.

[24] – V. Venugopal, K. Mohanty. "Biosorptive uptake of Cr(VI) from aqueous solutions by Parthenium hysterophorus weed: Equilibrium, kinetics and thermodynamic studies". *Chem Eng J* 2011;174:151.8.

[25] – N. T. Abdel-Ghani and G. A. El-Chaghaby. "Biosorption for metal ions removal from aqueous solutions: A review of recent studies". *International Journal of Latest Research in Science and Technology*, 3, 1: 24 – 42, (2014).

[26] – D. Kumar, J. P. Gaur. "Metal biosorption by two cyanobacterial mats in relation to pH, biomass concentration, pretreatment and reuse". *Bioresour Technol* 2011;102:2529.35.