SYNTHESIS OF BIOCHAR FROM AGRICULTURAL WASTE AND APPLIED IN REMEDIATION OF Pb^{+2} IONS REMOVAL FROM WASTEWATER

*Halah M. Qasim¹

Lubna A. Alzubaidi²

Zaidun N. Abudi²

- 1) Department Environmental Engineering, Mustansiriyah University , Baghdad, Iraq
2) Assist prof, Mustansiriyah University, Baghdad, Iraq

Abstract: The aim of this paper is to synthesis an adsorbent Biochar (BC) from agricultural waste collected from tree pruning waste in college of engineering/ Mustansiriyah University. Biochar (BC) was prepared from pyrolysis and tested to remove heavy metal Pb (II) from its aqueous solution. Initial metal ion concentration in the range (10 to 150mg/L), pH of solution in the range (1-7), adsorbent dose range (0.01-0.3 g) and contact time varying from (10 to 150) min, were studied. The experimental adsorption isotherms were fitted with the Langmuir and Freundlich models. Langmuir with high correlation coefficient ($R^2 = 0.9935$) found to be more represented to the experiments. The results showed that the highest Pb(II) removal efficiency was (100%) at optimization condition pH 6, at room temperature for 150 min, 0.3 g adsorbent dose and 100 mg/L metal ion concentration. Maximum adsorption capacity was 76.34 mg /g.

Keywords: Adsorption, Pb (II), Biochar, Agricultural waste, Isotherm.

1. Introduction

Pollution with heavy metals represents a global issue currently according to its wide uses and non-biodegradability naturally. In addition, heavy metals have high toxicity and bioaccumulation capability in human body and food chain[1, 2]. Heavy metals have a serious danger on both aquatic and overland lives [3].

The latest maximum allowable levels of pollutants (MCLs) were issued by the Environmental Protection Agency (EPA). This is known of the order that Lead metal ion belongs to the highest toxic heavy metal ions. One of the most important remediation strategies is to minimize the bio availability of these metals and thus minimize their toxicity and accumulation in plants and animals [4].

Iraqi aquatic environment is severely polluted with heavy metals [5, 6]. Conventional treatment methods for heavy metals pollution are divided into three categories, physical, chemical and biological methods [7]. Many approaches have now been applied to eliminate heavy metals ions from wastewater, such as ion exchange, electro coagulation, electro dialysis, membrane isolation, reverse osmosis, packed bed filtration, solvent extraction of solvents and adsorption. [8,9]. The various technologies used to remove toxic metal ions from wastewater adsorption mechanism has received considerable attention due to its performance , availability , low

*Corresponding Author: eng.hala33.m@gmail.com

operating costs, versatility and flexibility to design and application [10,11,12].

Nevertheless, many of the commercial sorbents currently applied have been provided at a great cost. Therefore, relatively cheap and environment friendly adsorbents are needed urgently [13]. Bio charcoal is a black, carbon-rich and porous substance obtained by heating any biomass at extreme temperatures ($> 250\text{ }^{\circ}\text{C}$) under insufficient oxygen conditions, this method known as pyrolysis. [14, 15]. Many of studies have been performed in recent years to examine the use of biochar for the removal of pollutants from aqueous solutions. Biochar has a great potential to effectively tackle water pollutants, provided the wide availability of feedstock, low cost and favorable physical / chemical surface characteristics. [15]. Biochar products are typically extracted from forestry, agricultural, and industrial waste. Additionally, waste materials used as biochar production not only address the waste disposal problem but also improving plant management and protect the environment [16].

Biochar tends to be a new low-cost and efficient adsorbent potential relative to activated carbon (AC). The production of activated carbon requires higher temperatures and an additional activation process. Comparatively, biochar production is cheaper with lower energy requirements. [17-21]. In addition, turning invasive plants into bio charcoal will enhance invasive plant management and protect the ecosystem. [22]. The conversion of biomass into biochar as a sorbent is thus a 'win-win' approach, both to improve waste management and to protect the environment. [17, 18].

A variety of research studies on the removal of heavy metals by biochar in aqueous solutions.

Cao et al. in (2009) prepared biochar from Dairy manure at pyrolytic temperature (200°C) to adsorb heavy metal Pb(II) and organic pollutant Atrazine and compare it with AC. "The biochar was 6 times more effective in Pb sorption than AC" [17]. Liu and Zhang in (2009) prepared biochar from Rice husk at pyrolytic temperature (300°C) to remove Lead from water [23]. Tong et al. in (2011) prepared biochars from three crop straws at ($400\text{ }^{\circ}\text{C}$) and investigated Cu (II) adsorption under acidic conditions [24]. Mohan et al. (2007) The adsorption of toxic water materials with rapid pyrolysis biochar generated from oak bark, pine bark, oak wood and pine wood in an auger-fed reactor at 400 and $450\text{ }^{\circ}\text{C}$ was tested and concluded that the maximum adsorption for these samples occurred over a pH range of 3-4 for arsenic (As) and between 4 and 5 for Pb and Cd. In the same research, ion exchange was found to be the dominant mode by which biochars adsorbed toxic metal ions [25].

This study aims to prepare highly effective biochar from agricultural waste and investigate the adsorption properties of heavy metal Pb^{+2} . The adsorption equilibrium isotherm models related to the process were also performed.

2. Materials and Methods

2.1. Materials

To prepare (1000 mg/L) stock solution of Pb (II) 1.6 g of nitrate salt was taken and dissolved into Deionized water. Test solutions pH were adjusted using 0.1 M NaOH, 0.1 M HCl. All chemicals were purchased from chemical bureaus in Iraq.

2.2. Synthesis of Biochar

Leaves were collected from tree pruning waste in college of engineering, then washed thoroughly with tap water to remove dirt then washed with distilled water. After that the leaves were oven

dry at 105 °C for 18 hours then grinded and sieved to 150 µm particle size, placing the powder in thick Aluminum foil then in an iron box then set it down in the Electrical furnace (Carbolite CWF1200/ UK) for pyrolysis at 360 °C for 1 h.

2.3. Batch Adsorption Experiments

The batch experiments were conducted by batch mode adsorption unit using (150) mL Erlenmeyer flasks. 0.1g of the adsorbent and 50mL of the Pb (II) prepared solutions were mixed together and shaken in the shaker. In order to determine the effect of physicochemical parameters such as pH, initial metal ion concentration of the solution, adsorbent dose, and contact time. Experiments were conducted at room-temperature (20±5 °C). To adjust pH of solutions 0.1 M NaOH or 0.1 M HCL was added.

By Contacting with adsorbents, the pH of each solution was found to be in the range of 1–7, and then the prepared solution was agitated by shaker at agitating speed of 200 rpm and for 150 min. After agitating the mixtures were filtered through filter papers and by using Atomic Absorption spectrophotometer (A-shimadzu aa-7000f /japan) final concentrations of metal ion have been obtained. The percentages of metal ion removal or the quantity of metal ion adsorbed have been computed by the following equations:

$$R\% = \frac{C_o - C_e}{C_o} * 100 \quad (1)$$

$$q_e = \frac{V}{m} (C_o - C_e) \quad (2)$$

Where C_o and C_e (mg/L) are the initial and final liquid phase concentrations of the ions respectively. The metal uptake at the equilibrium

q_e in (mg/g), V is the volume of the solution (in L), and m is the amount of sorbent used in gram.

3. Results and Discussion

3.1. Effect of pH

The effect of the pH on the removal of Pb (II) ions from aqueous solutions using biochar powder has been studied with a range of (1-7) using 0.1 M NaOH, 0.1 M HCl for pH adjustment. (Fig. 1) shows that the relationship between the pH of the solution and the ratio of removal is a direct relationship up to the value of pH = 6, after which the rate of removal increases sharply until it reaches the maximum value. The reason of decreasing lead adsorption efficiency at low values of pH may be due to the competition of positive hydrogen ions of metal ions on the adsorption sites, which increases with the decrease in the value of the acid function. However, at the higher value of the pH, the positive hydrogen ions will decrease due to the increase in the concentration of negative hydroxide ions, which will reduce competition. Thus, the adsorption of lead ions will increase, the concentration in the solution decreases and the removal rate increases. The acid function is one of the most important factors to be studied and verified in any adsorption process to know the ideal value that separates adsorption from precipitation. Therefore, the sharp and rapid rise in the removal rate at pH values greater than 6 can be attributed to the precipitation state that occurs, which reduces the concentration of Pb^{+2} ions in the solution, but precipitates at the bottom of the beaker, thus decreasing the removal rate. Accordingly, the optimum pH for Pb^{+2} adsorption is 6.

Figure1. Effect of pH on removal efficiency.

3.2. Effect of Pb^{+2} Concentration

Effect of various concentrations on Pb^{+2} adsorption has been investigated in the range (10-150mg/L) at 20 ± 5 °C. In (Fig. 2) it was obvious that the Pb^{+2} adsorption capacity of BC increased with an increase in equilibrium concentration.

As the Pb^{+2} initial concentration increases from 10 to 150 mg/L efficiency removal declines from 58.3% to 18%. Initial abrupt decrease in Pb^{+2} concentration is presumably up to the presence of a large number of the sorption sites on BC surface and the deterioration of the obtainable sorption sites, this has led to the slow reduction of Lead concentration [26]. 100 mg/L was taken as an optimum concentration because the BC is saturated with metal ions.

Figure2. Effect of initial concentration on removal efficiency.

3.3. Effect of adsorbent dosage

Fig. 3 Illustrates that the adsorption of metal ions increased from 14.51 to 100% for Pb^{+2} , as BC dose increased from 0.01 to 0.3 gram. This is because more adsorption sites are available at higher dose of adsorbent, due to increased surface area, resulting in higher Pb^{+2} removal [27]. The optimum amount of biochar is 0.3 g.

Figure 3. Effect of Dose on Lead removal efficiency.

3.4. Effect of contact time

Influence of contact time on adsorption of Pb^{+2} on BC has been investigated in the range of (10-150 minutes) for optimum concentration of 100 mg/L of Pb^{+2} metal ions (Fig. 4). The highest rate of metal ions removal from the solution occurred within 150 minutes of contact time. Therefore, the optimum contact time for adsorption of Pb^{+2} was considered to be 150 min.

Figure 4. Effect of contact time on Lead removal efficiency.

4. Adsorption isotherm

4.1. Langmuir isotherm

This model was tested by plotting C_e/q_e versus C_e , as shown in (Fig.5). Langmuir constants (K_L , q_m) were found by applying the following equation:

$$\frac{C_e}{q_e} = \frac{1}{q_m K_L} + \frac{C_e}{q_m} \quad (3)$$

4.2. Freundlich isotherm

This model was tested by plotting $\log q_e$ versus $\log C_e$ as shown in (Fig.6). Freundlich constants (K_F , n) were found by applying the following equation:

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \quad (4)$$

Langmuir isotherm model assumes monolayer sorption which consistent with chemical adsorption, while Freundlich isotherm model assumes multilayer sorption which consistent with physical sorption.

The results show that the experimental equilibrium data of the adsorption isotherms (Table 1) were suited to both the Freundlich and Langmuir isotherm equations, but Langmuir isotherm model provide better satisfactory than Freundlich isotherm model.

Figure 5. Langmuir adsorption isotherm model.

Figure 6. Freundlich adsorption isotherm model.

Table 1. Coefficients of isotherm that applied for Pb^{+2} removal by BC.

Adsorbent	Langmuir isotherm			Freundlich isotherm		
	K_L	q_m	R^2	K_F	n	R^2
Biochar	30.18	76.34	0.9935	18.56	3.03	0.9212

5. Surface characterization of biochar

The biochar sample was characterized for its surface area (BET). The surface area was found 369.55 m^2/g . Furthermore, Fourier transform infrared (FT-IR) spectroscopy (Fig.7) was made to identify functional groups and their changes before and after adsorption process. These tests were made for the sample of best removal

Figure 7. FT-IR test for (a) Biochar before adsorption (b) Biochar after adsorption.

6. Conclusions

Biochar synthesized from agricultural waste used as low cost adsorbent was successful for Pb^{+2} removal. Application of Biochar was found to be a best material regarding cost-effective and environmental concerns. The results gained from this study were extremely well described by the theoretical Langmuir isotherm. Best removal efficiency was 100% at the conditions (pH 6, concentration 100 mg/L, dose 0.3g, contact time 150 min).

Acknowledgements

The authors would like to thank Mustansiriyah University/college of engineering Baghdad-Iraq for its support in the present work and the Laboratory staff in the College of Engineering for their support and help through the period of the experiments.

Conflict of interest

There are no conflicts to declare.

Abbreviations

BC	Biochar
AC	Activated carbon
Pb(II)	Divalent lead
MCLs	maximum allowable contaminant levels
EPA	Environmental Protection Agency
m	Mass of adsorbent
C ₀	Initial metal concentration
C _e	Final metal concentration
R ²	correlation coefficients
KL	Langmuir constant
KF	Freundlich constant
n	Freundlich constant
q _e	Amount of metal ion adsorbed
q _m	Maximum adsorption capacity
V	Volume of the solution
BET	Brunauer–Emmett–Teller
FTIR	Fourier transform infrared

7. References

- He, J., & Chen, J. P. (2014). *A comprehensive review on biosorption of heavy metals by algal biomass : materials, performances, chemistry and modelling simulation tools*. Bioresource technology, 160, 67-78.
- Ayangbenro, A. S., & Babalola, O. O. (2017). *A New Strategy for Heavy Metal Polluted Environments: A Review of Microbial Biosorbents*. International Journal of Environmental Research and Public Health, 14, 94.
- Zeng, X., Guo, X., Su, G., Danquah, M. K., Zhang, S., Lu, Y., Lin, L. (2015). *Bioprocess considerations for microalgal-based wastewater treatment and biomass production*. Renewable and Sustainable Energy Reviews, 42, 1385–1392.
- Ahmad, M., Rajapaksha, A.U., Lim, J.E., Zhang, M., Bolan, N., Mohan, D., Vithanage M., Lee S.S., Ok Y.S. (2014). *Biochar as a sorbent for contaminant management in soil and water: a review*. Chemosphere 99, 19–33.
- Al-Haidarey MJS, Hassan FM, Al-Kubaisey ARA, Douabul AAZ (2010). *The geoaccumulation index of some heavy metals in Al- Hawizeh Marsh, Iraq*. E-J Chem, 7(S1):S157–S162.
- Al-Obaidy AHMJ, Al-Janabi ZZ, Al-Mashhady AAM (2016) *Distribution of some heavy metals in sediments and water in Tigris river*. J Global Ecology Environ, 4(3):140–146.
- Cheng, S. Y., Show, P., Lau, F., Chang, J., & Ling, T. C. (2019). *New Prospects for Modified Algae in Heavy Metal Adsorption*. Trends in Biotechnology, 1–14.
- Parmar, M., Thakur, L.S., (2013). *Heavy metal Cu, Ni and Zn: toxicity, health hazards and their removal techniques by low cost adsorbents: a short overview*. Int. J. Plant Anim. Environ. Sci. 3, 2231–4490.
- Gunatilake, S., (2015). *Methods of removing heavy metals from industrial wastewater*. Methods 1.
- Fu, F.; Wang, Q. (2011). *Removal of heavy metal ions from wastewaters: A review*. J. Environ. Manage, 92, 407.
- Murugesan, A.; Ravikumar, L.; SathyaSelvaBala, V.; Senthil Kumar, P.; Vidhyadevi, T.; Dinesh Kirupha, S.; Kalaivani, S. S.; Krithiga, S.; Sivanesan, S. (2011). *Removal of Pb (II), Cu (II) and Cd (II) ions from aqueous solution using polyazomethineamides: Equilibrium and kinetic approach*. Desalination. 271, 199.

12. Sirianuntapiboon, S.; Hongrisuwan, T. (2007). *Removal of Zn²⁺ and Cu²⁺ by a sequencing batch reactor (SBR)*. Bioresour. Technol. 98, 808.
13. Wang, Y. & Liu, R. (2018). *H₂O₂ treatment enhanced the heavy metals removal by manure biochar in aqueous solutions*. Science of the Total Environment 628–629, 1139–1148.
14. Tan, X., Liu, Y., Zeng, G., Wang, X., Hu, X., Gu, Y., Yang, Z., (2015). *Application of biochar for the removal of pollutants from aqueous solutions*. Chemosphere. 125, 70–85.
15. Xiao, X., Chen, Z., Chen, B., (2016). *H/C atomic ratio as a smart linkage between pyrolytic temperatures, aromatic clusters and sorption properties of biochars derived from diverse precursory materials*. Sci. Rep. 6, 22644.
16. Malik, D. S., Jain, C. K., Yadav, A. K. & Banerjee, S. (2017). *Role of Plant-Based Biochar in Pollutant Removal: An Overview*. Advanced Materials for Wastewater Treatment (John Wiley & Sons, Inc.).ch9. 313–330.
17. Cao, X., Ma, L., Gao, B., Harris, W., (2009). *Dairy-manure derived biochar effectively sorbs lead and atrazine*. Environ. Sci. Technol. 43, 3285–3291.
18. Zheng, W., Guo, M., Chow, T., Bennett, D.N., Rajagopalan, N., (2010). *Sorption properties of greenwaste biochar for two triazine pesticides*. J. Hazard. Mater. 181, 121–126.
19. Karakoyun, N., Kubilay, S., Aktas, N., Turhan, O., Kasimoglu, M., Yilmaz, S., Sahiner, N., (2011). *Hydrogel-biochar composites for effective organic contaminant removal from aqueous media*. Desalination 280, 319–325.
20. Ahmad, M., Lee, S.S., Dou, X., Mohan, D., Sung, J.K., Yang, J.E., Ok, Y.S., (2012). *Effects of pyrolysis temperature on soybean Stover and peanut shell-derived biochar properties and TCE adsorption in water*. Bioresour. Technol. 118, 536–544.
21. Lu, H., Zhang, W., Yang, Y., Huang, X., Wang, S., Qiu, R., (2012). *Relative distribution of Pb²⁺ sorption mechanisms by sludge-derived biochar*. Water Res. 46, 854–862.
22. Dong, X., Ma, L.Q., Zhu, Y., Li, Y., Gu, B., (2013). *Mechanistic investigation of mercury sorption by Brazilian pepper biochars of different pyrolytic temperatures based on X-ray photoelectron spectroscopy and flow calorimetry*. Environ. Sci. Technol. 47, 12156–12164.
23. Liu, Z., Zhang, F.S., (2009). *Removal of lead from water using biochars prepared from hydrothermal liquefaction of biomass*. J. Hazard. Mater. 167, 933–939.
24. Tong, X.J., Li, J.Y., Yuan, J.H., Xu, R.K., (2011). *Adsorption of Cu (II) by biochars generated from three crop straws*. Chem. Eng. J. 172, 828–834.
25. Mohan, D., Pittman, C.U., Bricka, M., Smith, F., Yancey, B., Mohammad, J., Steele, P.H., Alexandre-Franco, M.F., Gómez-Serrano, V., Gong, H., (2007). *Sorption of arsenic, cadmium, and lead by chars produced from*

- fast pyrolysis of wood and bark during bio-oil production*. J. Colloid Interface Sci. 310, 57-73.
26. Chen, Y., Wang, F., Duan, L., Yang, H., Gao, J., (2016). *Tetracycline adsorption onto rice Husk ash, an agricultural waste: its kinetic and thermodynamic studies*. J. Mol. Liq. 222, 487-494.
27. Gupta, N., Kushwaha, A. K. & Chattopadhyaya, M. C. (2011). *Adsorptive removal of Pb^{2+} , Co^{2+} and Ni^{2+} by hydroxyapatite/chitosan composite from aqueous solution*. Journal of the Taiwan Institute of Chemical Engineers 43,125-131.