Study of Adsorption Performance of Biochar for Heavy Metals Removal

Rehab Hefny[1], M. M. Ibrahim[1] and Dalia Morad[1*]

[1]*Department of Civil Engineering, Shoubra Faculty of Engineering, Benha University, Egypt.*

Authors' contributions

"This work was carried out in collaboration between all authors. Authors RH, MMI and DM designed the study, performed the statistical analysis, wrote the protocol, and wrote the first draft of the manuscript. Author DM managed the analyses of the study and managed the literature searches. All authors read and approved the final manuscript.

Article Information

Original Research Article

ABSTRACT

The main objective of this work is to evaluate the performance of four different types of biochars in removing heavy metals from synthetic solution. Four types of biochars are investigated in this study, namely; jazaurin, ficus, orange, and mango biochars. A pilot plant is set up to investigate the efficiency of these biochars as a filter media for synthetic solution treatment. The removal efficiency of different heavy metals is assessed by a four-column pilot plant under different parameters; mean particle size of biochars, initial metal concentration, hydraulic load, and time. Results indicate that the different types of biochars used in this study show high performance in removing the different types of heavy metals utilized (Copper (Cu), Cadmium (Cd), Lead (Pb), and Zinc(Zn)). The removal efficiencies of these heavy metals are more than 99% for all types of biochar. It is concluded that using biochars as a filter media could be an effective solution for removing heavy metals from industrial wastewater in the environmental conditions of Egypt.

Keywords: Biochar; jazaurin; ficus; filter media; heavy metals; industrial wastewater.

Corresponding author: Email: dalia.morad22@yahoo.com;

1. INTRODUCTION

Industrial wastewater typically contains heavy metals and toxic materials [1]. Thus, discharging industrial wastewater into the environment may result in hazardous impacts on both environment and human health [2]. Heavy metals such as Cadmium (Cd), Copper (Cu), Lead (Pb), and Zinc (Zn) are considered the most harmful elements produced from the chemical-intensive industries. High amounts of heavy metals are gathered in the body of humans from the food chain of the living organisms. If the concentrations of these heavy metals overtake the limited dose, they cause serious diseases for health [3]. For an instance, the toxicity of Cu and Cd affects humans by Alzheimer's [4,5]. Cadmium (Cd) replaces calcium and softens the bones by accumulating in it [6]. Kidney disease is related to poisoning by Lead (Pb). Although Zinc (Zn) is considered as a necessary micronutrient, it can be toxic at high levels and lead to some diseases such as anemia and poor immune function [7,8].

Heavy metals treatment techniques, which are commonly used, including coagulation/flocculation, ion exchange, membrane separation, cavitation, advanced oxidation processes, incineration, and adsorption [9].

Adsorption is regarded to be an effective method with low cost because of its high adsorption capacity of heavy metals and ease of implementation [10]. Many types of cost-effective adsorbents are used and investigated for the removal of inorganic contaminants (heavy metals) from water, for example; biomass, zeolites, mineral, agricultural wastes (wood), polymeric materials, and industrial byproducts [10].

Recently, biochar is found to be a good adsorbent due to its physical and chemical characteristics and its low cost which makes it attractive to be used in adsorption [11,12]. Biochar is produced by incineration of biomass, for an instance; wood, crop residue, and manure in an environment with limited oxygen. It is considered to be a cost-effective adsorbent for the withdrawal of heavy metals from wastewater [13].

According to Amin MT et al. [14] found that biochar of orange peel for copper and cadmium removal from wastewater could be used as adsorbent material. Moreover, Wang X, et al. [11]

investigated that biochar of discarded mushroom stick (DMB) was succeeded for the removal of heavy metals such as lead, copper, cadmium, and nickel. Amin MT et al. [15] used banana peel biochar as adsorption filter media for eliminating lead and copper. Piscitelli L et al. [16] studied different types of biochar, this study indicated that each of volcanic rock VR, peat, and its mixtures with biochar had high efficiency to remove pollutants (heavy metals) from water and biochar was better than conventional materials. Reddy et al. [17] concluded that the removal efficiencies of different heavy metals Cd, Cu, Pb, and Zn were 18, 65, 75, and 24%, respectively after passing through the biochar filter.

In Egypt, there are different types of biochar which are always available at a low cost and can be investigated and applied to remove heavy metals from industrial wastewater. Jazaurin, orange, ficus, and mango biochar may not be used before as a filter media and they are available in abundance in Egypt. Copper, Lead, Cadmium, and Zinc are considered to be the most toxic heavy metals diffusing in industrial wastewater.

This study is designed to evaluate the benefits of using four types of wood biochars namely; casuarina (jazaurin), citrus (orange), ficus benjamina (ficus), and mangifera indica (mango) as a filter media for removing heavy metals from synthetic solution. The behavior of these biochars is investigated under different parameters; particle size of biochar, initial heavy metal concentration, hydraulic load, and effect of time.

2. MATERIALS AND METHODS

A pilot plant was conducted to investigate the efficiency of the four types of biochars as a filter media for industrial wastewater treatment.

2.1 Characterization of Materials

2.1.1 Biochar characteristics

Jazaurin, ficus, orange, and mango biochars were collected from Banha-Qalyubia Governorate-Egypt. Each biochar was crashed and then was sieved through five different sizes of sieves as shown in Fig.1 and Table 1.

2.1.2 Synthetic Solution

A synthetic solution was prepared by adding chemicals containing heavy metals to tap water.

Appropriate calculated amounts of cadmium sulfate LR (for Cadmium), lead sulfate (for lead), cupric chloride (for Copper), and zinc chloride (for Zinc) were weighted and added to adjust the required final concentrations of heavy metals in the synthetic solution.

2.2 Pilot Setup

The pilot consisted of four columns, feeding tanks, two pumps, valves and piping, filtering media (biochar), a scale pipe to identify the water level inside the upper feeding tank, and effluent containers. The first pump was used to pump the synthetic solution to the upper tank. The second pump was put in the second tank to keep the solution in a complete mix phase, so preventing metals from settling at the base of the tank. Experimental columns were conducted as shown in Fig. 2 and were installed at the National Research Center (NRC), Egypt. The four columns were made from PVC tubes (Polly Vinyl Chloride) with 10 cm diameter and 120 cm height. The columns were packed with the four types of biochars with a depth of 20 cm. In the top and the bottom of each column, 2.5 cm of support media of gravel was used. A plastic mesh was inserted between each of the two layers to effectively separate them.

The applied biochars were namely; jazaurin, ficus, orange, and mango. The synthetic solution was pumped into the upper feeding tank to make the head constant for all columns. Then, the solution was streamed from the bottom of the feeding tank by gravity. The pilot was operating constantly for eight hours for the first three runs

then it was operating for twelve hours to observe the performance of the biochar throughout twelve hours. The pilot plant was controlled for 6 months from April 2019 to September 2019.

2.3 Experimental Procedure

The process was applied in four runs which were performed to estimate the performance of the four biochars in removing heavy metals. First Run was done with different mean particle sizes. It consists of five stages by using five particle sizes of biochar. The first stage was applied to biochar size 1 (0.985 cm). The second stage was applied to biochar size 2 (0.6 cm). The third stage was applied to biochar size 3 (0.35 cm). The fourth stage was applied to biochar size 4 (0.2 cm). Finally, the fifth stage was applied to biochar size 5 less than 0.1 cm. Every stage took about two days (preparing and operating the pilot).

The second run was done with different initial heavy metals concentrations that were adjusted and then added to the influent synthetic solution. This run consisted of five stages with five different initial concentrations of heavy metals: 50,100, 150, 200, and 250 mg/L. In this run, the most effective size of biochar that was identified from run one was used here.

The third run consisted of five stages with five different hydraulic loads: 2, 4, 6, 8, and 12 L/hr. Optimum size and suitable initial concentrations of heavy metals that were identified from the previous runs were used in this run.

Table 1. Summarized the particle sieve sizes for the tested biochars

Size name	Size 1	Size 2	Size 3	Size 4	Size 5
Mean particle size (cm)	0.985	0.6	0.35	0.2	< 0.1

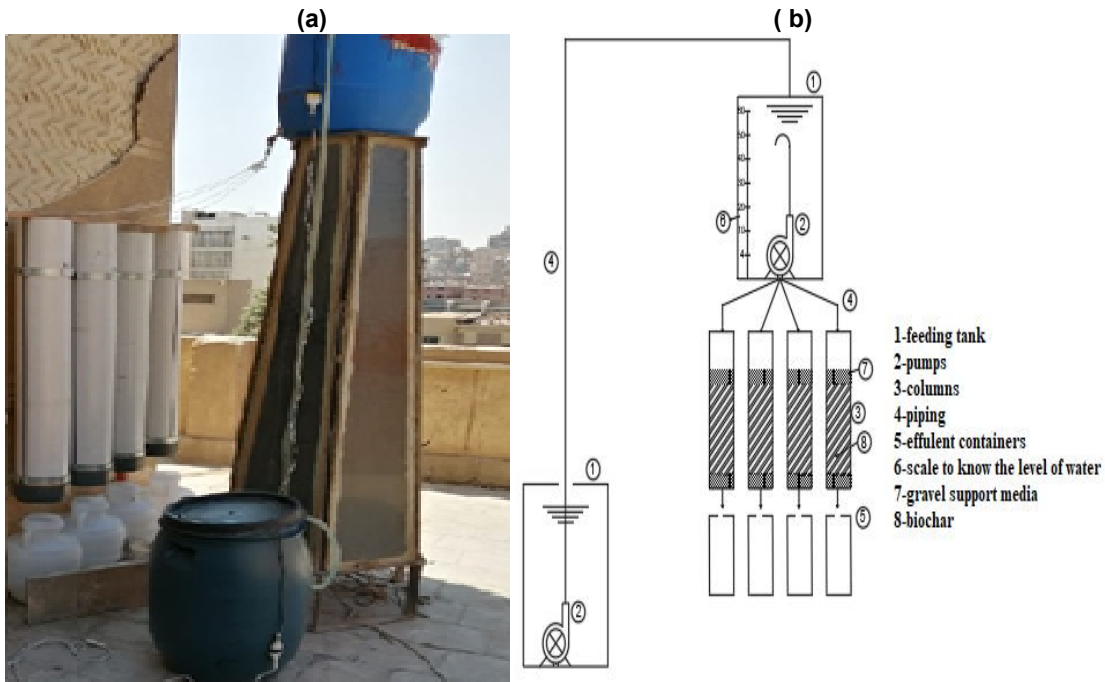Fig. 1. Sizes of studied biochars as a filter media

Fig. 2 (a). Pilot unit, (b). Experimental diagram

The fourth run was done to specify the effect of time on heavy metal adsorption to investigate the performance of each biochar. Then, the breakthrough point was selected. The samples were drawn every hour from the effluent of the four columns throughout 12 hours of operation. Optimum size, suitable initial concentrations of heavy metals, and the best hydraulic load that were obtained from the previous runs were used in this run.

Fig. 3 indicated the approach of the experimental study.
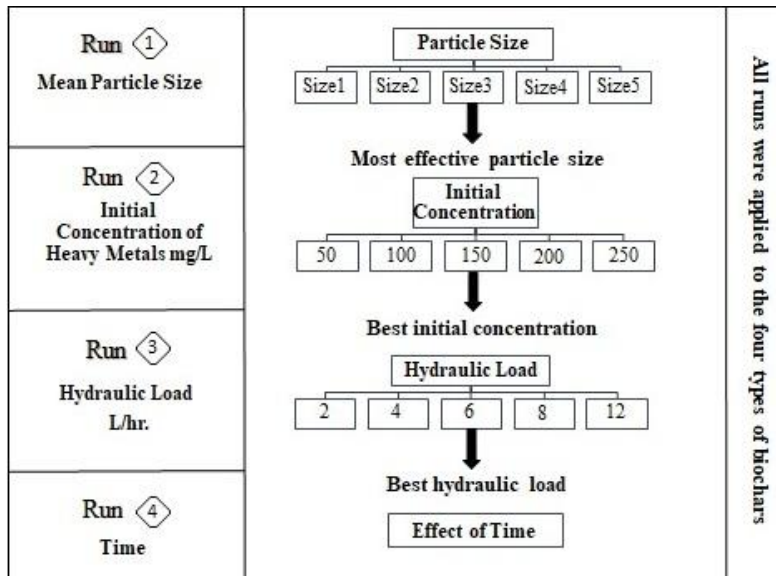
Fig. 3. The approach of the experimental study

3. RESULTS AND DISCUSSION

3.1 Effect of Size

The five sizes of biochars were applied on the four columns with a hydraulic load of 2 L/hr., media depth of 25 cm, and initial heavy metal concentrations of 50 mg/L, as shown in figures from Fig. 4 to Fig. 7. At every stage, five samples were taken. One sample was taken from influent and the other four samples were taken from the effluent of each column. All samples were taken to the laboratory and were analyzed by Inductively coupled plasma atomic emission spectroscopy (ICP-AES). Then, the removal efficiency of the heavy metals; Cu, Cd, Pb, and Zn was calculated by the following equation:

$$\text{Removal efficiency \% = Ci-Cf/ Ci} \qquad (1)$$

Where: Ci; initial heavy metals concentrations of the synthetic solutions, Cf; final heavy metals concentrations after passing through the columns.
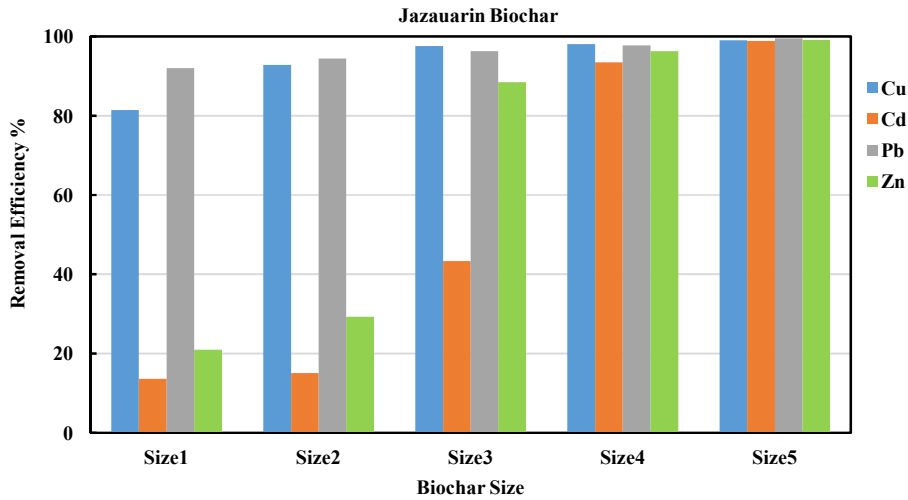

Fig. 4. Removal efficiency of heavy metals of jazaurin biochar under different biochar sizes
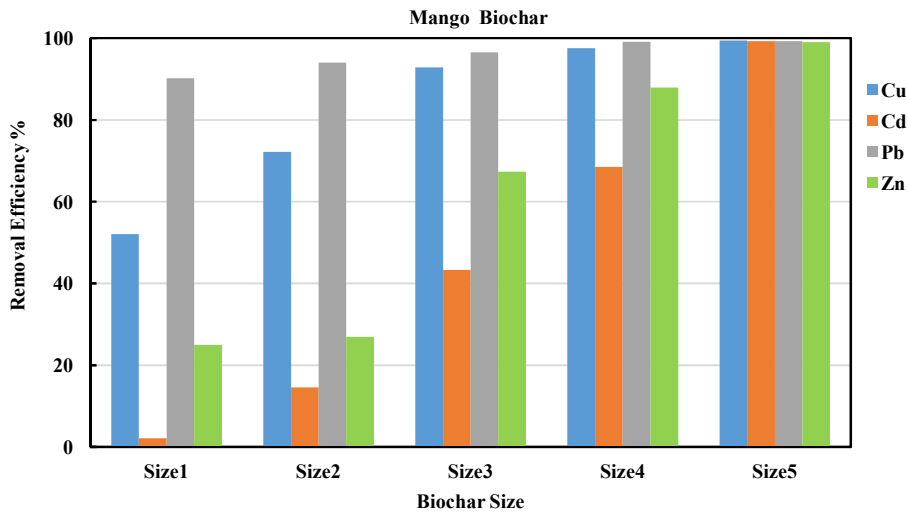

Fig. 5. Removal efficiency of heavy metals of mango biochar under different biochar sizes
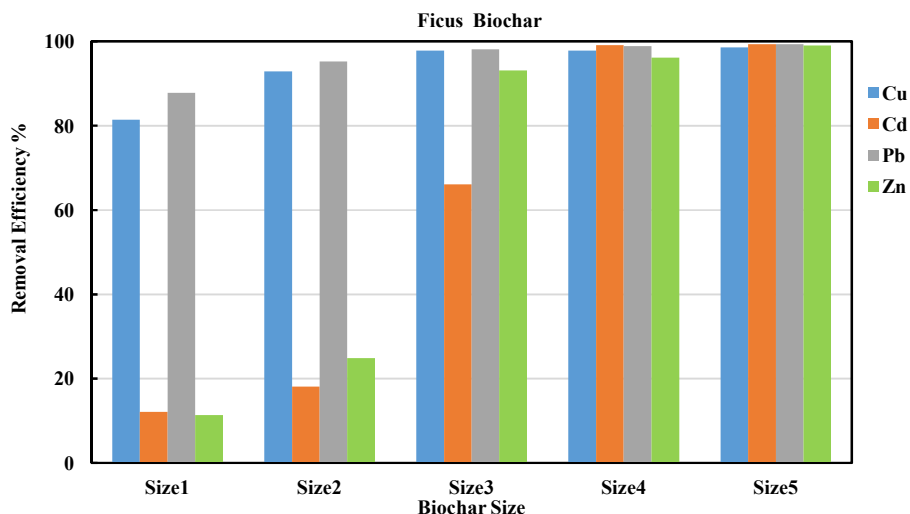
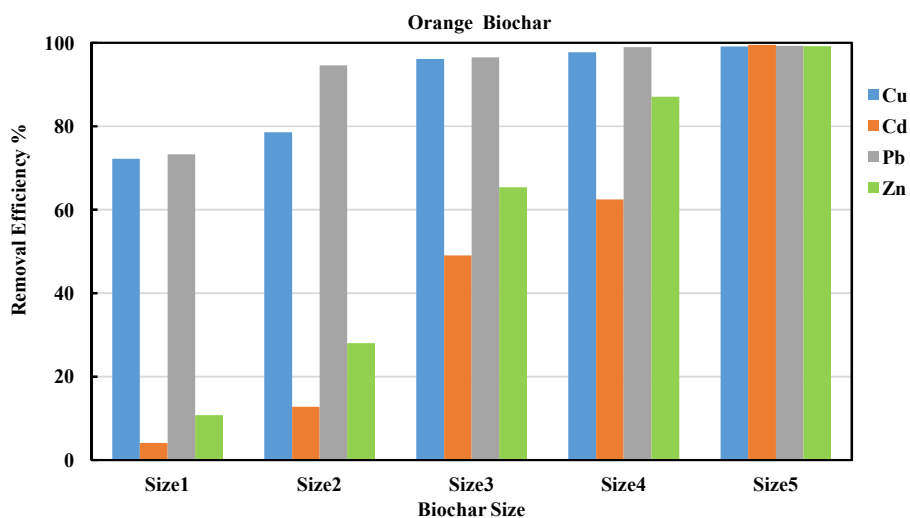**Fig. 6. Removal efficiency of heavy metals of ficus biochar under different biochar sizes**

Fig. 7. Removal efficiency of heavy metals of orange biochar under different biochar sizes

The highest removal efficiencies of heavy metals by the four biochar types were achieved at size5 as resulted in 18]. It recorded the highest removal efficiency of heavy metals (Cu, Cd, Pb, and Zn) with comparing to the other sizes. For instance, at jazaurin biochar, the Cd removal for the first column which contained size 1 was 13.63%, then it enhanced gradually to 98.9% at size 5. On the other hand, the removal of Zn enhanced from 21% at size 1 to 99.17% at size 5. The removal efficiencies of Cu and Pb were at excellent values for all biochar sizes. The smaller the biochar size was, the greater adsorption of heavy metals happened. Because the surface

area of biochar was enlarged with fine particles, the heavy metals were removed by the surface mechanism. It was observed that these results were higher than heavy metals removal efficiency by Ashoori et al. [19]. All types of biochar achieved comparable values of heavy metal removal efficiency.

3.2 Effect of Initial Heavy Metals Concentrations

Five stages with five different initial concentrations of heavy metals: 50, 100, 150, 200, and 250 mg/L were applied. The most

effective biochar size used was less than 0.1 cm. The heavy metals concentrations of the synthetic solution before and after passing through the columns of the pilot plant were determined. Figures from Fig. 8 to Fig. 11 presented the results of the removal efficiencies of the five applied initial heavy metals concentrations of each biochar.

As illustrated in figures from Fig. 8 to Fig. 11, increasing the initial concentration of heavy metals reduced the efficiency of heavy metals removal at the same biochar. As an example, at

jazaurin biochar, the removal efficiency was decreased from 99 % to 40.96% for Cu, from 98.9% to 29.9% for Cd, from 99.6% to 39.23% for Pb, and from 99.17% to 29.8% for Zn. The best initial concentration of heavy metals was 50 mg/L.

It was observed that as the initial concentration of heavy metals increased, the removal efficiency of heavy metals decreased significantly. This reduction in removal efficiency because all active sites of sorption on the surface of biochar were saturated with heavy metals [20].
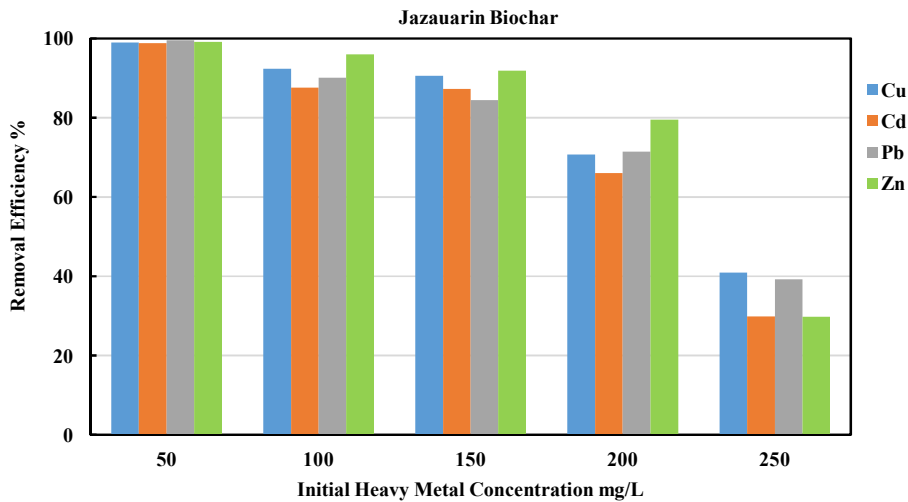

Fig. 8. Removal efficiency of heavy metals at different initial heavy metal concentrations for jazaurin biochar
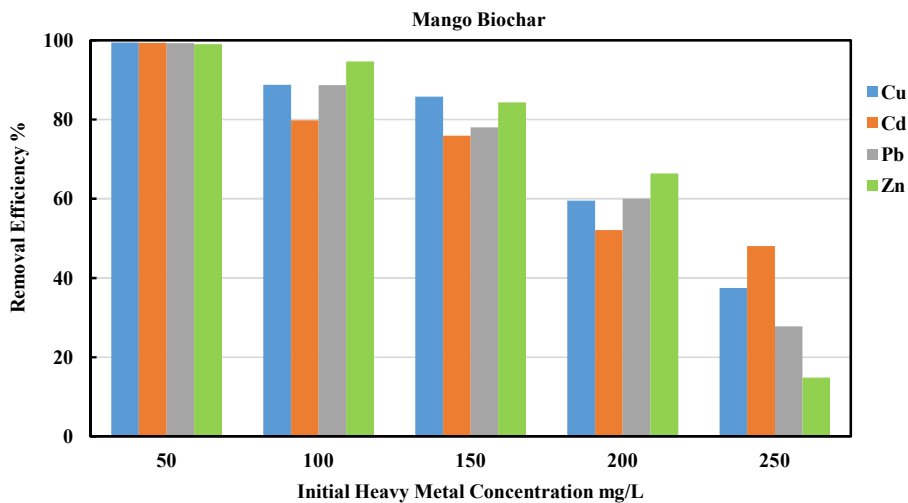

Fig. 9. Removal efficiency of heavy metals at different initial heavy metal concentrations for mango biochar
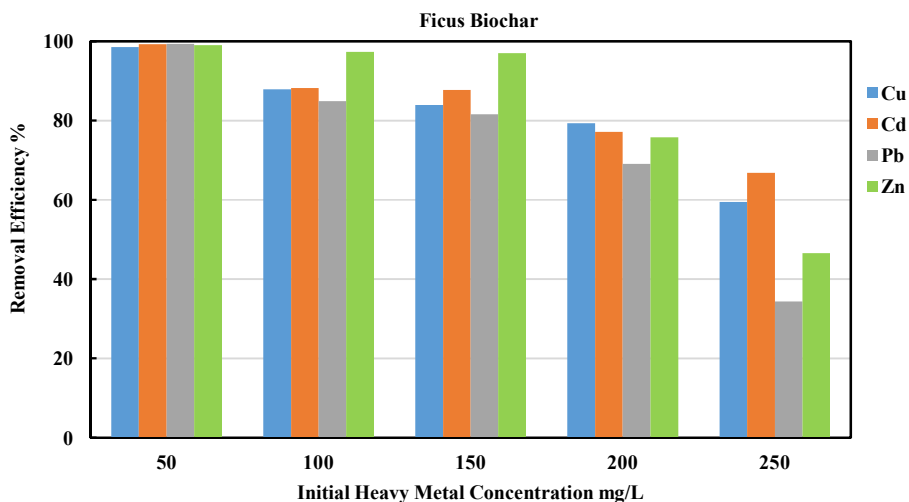
Fig. 10. Removal efficiency of heavy metals at different initial heavy metal concentrations for ficus biochar
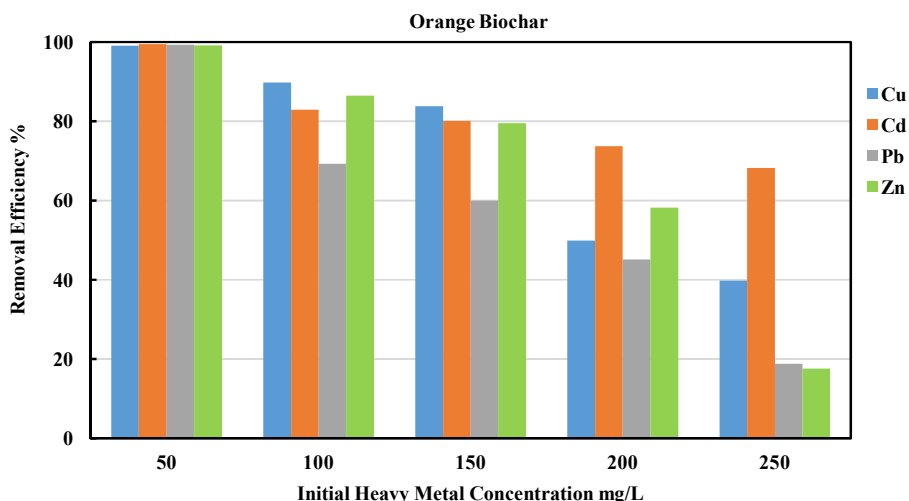

Fig. 11. Removal efficiency of heavy metals at different initial heavy metal concentrations for orange biochar

These results were compared with the results accomplished by [14]. These results, of orange peel biochar, had approximate values of reduction in the removal efficiencies when the initial heavy metal concentrations increased from 50 to 250 mg/L. For an instance, the removal efficiency of copper and cadmium decreased from 99% to 41% and 52%, respectively.

3.3 Effect of Hydraulic Load

The performance of biochar types with the effective size (< 0.1cm) and the suitable initial heavy metal concentration (50 mg/L) was examined under different hydraulic loads. Five different hydraulic loads rate were examined; 2, 4, 6, 8, and 12 L/hr. The removal efficiencies of biochar types at different hydraulic loads were shown in figures from Fig. 12 to Fig. 15.

It was presented that, at the hydraulic load of 2 L/hr., high removal efficiencies of all heavy metals were investigated in the case of all types of biochars > 98 %. Otherwise, at the hydraulic load of 12 L/hr., the removal efficiencies decreased with increasing the hydraulic load.
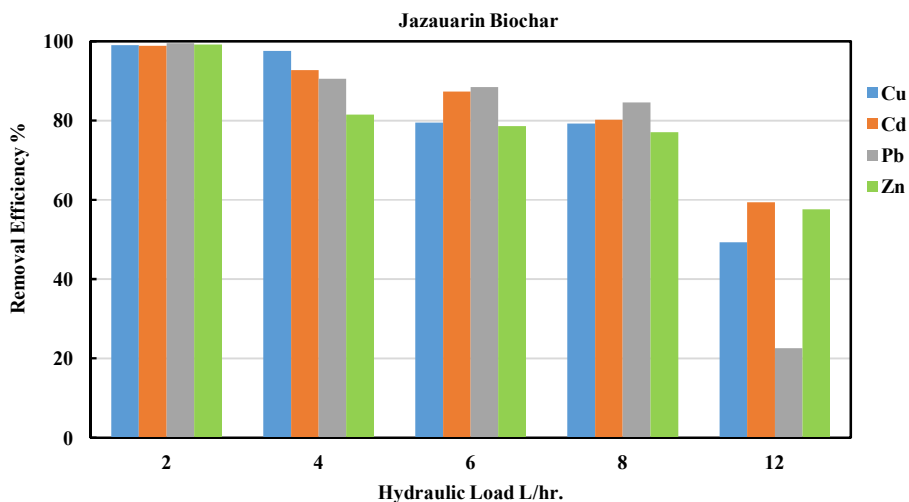
Fig. 12. Removal efficiency of heavy metals of jazaurin biochar at different hydraulic loads
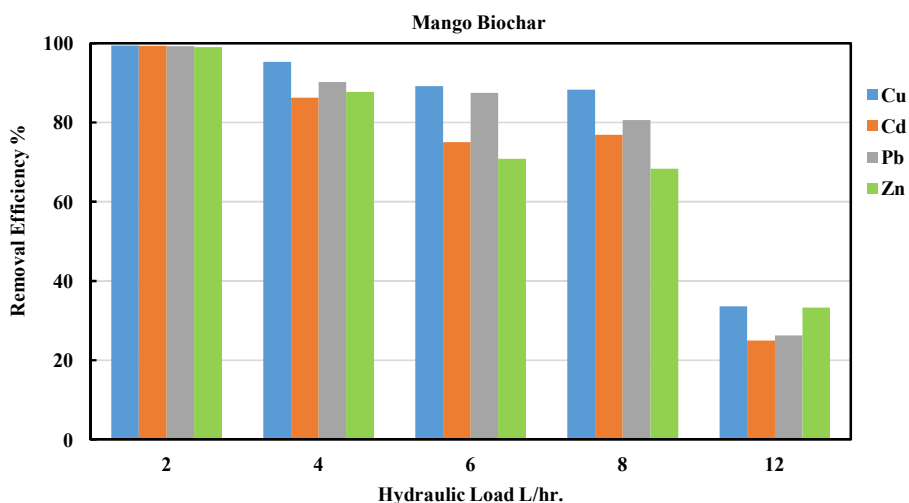

Fig. 13. Removal efficiency of heavy metals of mango biochar at different hydraulic loads

This might be as a result of the decreasing of solid/liquid ratio. When the hydraulic load was increased, the adsorption capacity increased so the removal efficiency of heavy metals decreased. An appropriate reduction of 50–70% in removal efficiency of heavy metals was observed when the hydraulic load was increased from 2 L/hr. to 12 L/hr.

These results were higher than the results accomplished by [19]. For an instance, by using biochar amended woodchip, the removal efficiency for Zn was 50% and all other metals (Cu, Cd, and Pb) had removal efficiency > 80%.

As a result of the effect of the previous three parameters, it was indicated that the four types of biochars (jazaurin, mango, ficus, and orange) achieved maximum removal efficiency of these four heavy metals at an optimum mean particle size of less than 0.1 cm, at suitable initial concentrations of 50 mg/L, and at the best hydraulic load of 2 L/hr., as shown in Fig. 16.
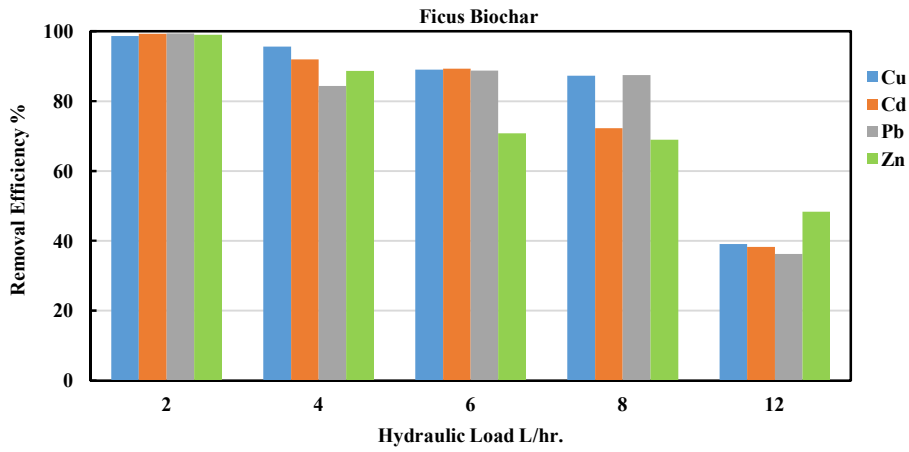
Fig. 14. Removal efficiency of heavy metals of ficus biochar at different hydraulic loads
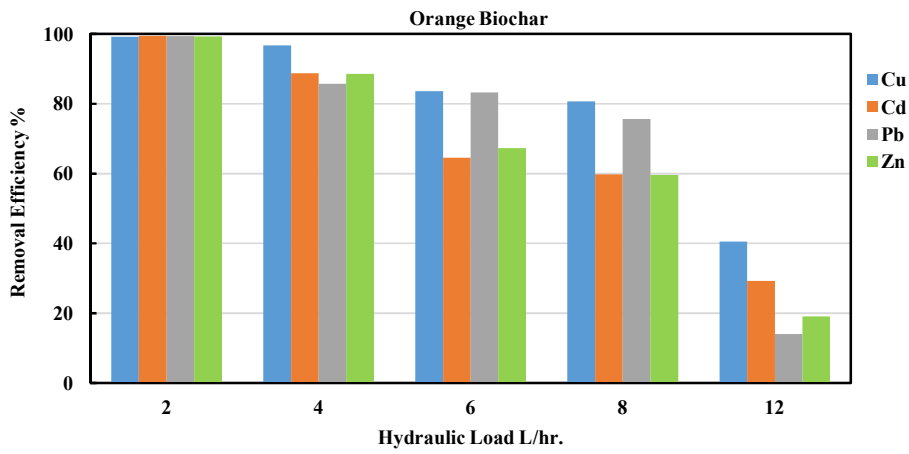

Fig. 15. Removal efficiency of heavy metals of orange biochar at different hydraulic loads
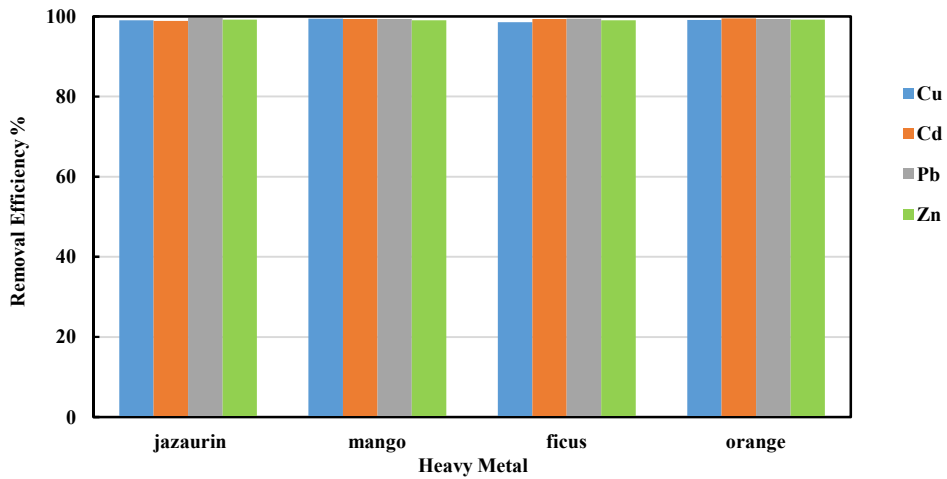

Fig. 16. The removal efficiencies of the four biochars at optimum parameters (mean particle size >0.1 cm, initial heavy metal concentrations 50 mg/L, hydraulic load 2 L/hr.)

3.4 Effect of Time

Samples from the four columns of each biochar type were analyzed around 12 hours to study the effect of time in the removal performance of heavy metals. The breakthrough point of each heavy metal was specified to know the performance of the adsorption of each metal by each biochar type.

The breakthrough point was the point at which the removal efficiency of heavy metals became maximum (approximate 100%) and after it, the removal value was slightly decreased and became constant through one run.

The samples were drawn every hour from the effluent of the four columns throughout 12 hours of operation. Then, these samples were analyzed in the laboratory. Optimum size, suitable initial concentrations of heavy metals, and the best hydraulic load that were got from the previous runs were used here.

At jazaurin biochar, the effluent concentration of Cu was equal to 0 (100 % removal efficiency) after a filtration time of 8 hours. After 8 hours (breakthrough point), Cu concentration started to increase again to the value of 0.133 mg/L until 12 hours. Cadmium, Lead, and Zinc had breakthrough points at 5, 4, 10 hours. Their effluent concentrations stilled equal 0 until 12 hr., as indicated in Fig. 17.

The effluent concentration of Pb was at equilibrium from the fourth hour by mango biochar that was considered to be the maximum removal of it (zero effluent concentration). After 6 hours, Cd concentration was withdrawable totally by mango biochar until the end of the run, as indicated in Fig. 18.

The optimum filtration time (breakthrough point) of Cu, Cd, Pb, and Zn were at 8, 10, 6, 11 hours (100 % removal), respectively, by ficus biochar, as indicated in Fig. 19.

At orange biochar, the withdrawal of Cd an Pb was after 5 hr. and 1 hr., respectively, which were lower than Cu and Zn removal time (5 hr. and 8 hr.), as indicated in Fig. 20.

The heavy metals adsorption was very rapid and was observed during the first hours of filtration due to the more active sites at the biochar surface. In this experiment, the highest heavy metals removal efficiency might be referred to the types of biochar media used in addition to the biochar characteristics as investigated by El Hanandeh et al. [21].

These results were higher than the results accomplished by Adil et al. [22]. The maximum removal of cadmium, copper, lead, and zinc was at 2, 3, 4, and 4 hr. by biochar of paper mulberry. In our study, the removal efficiency was reached to more than 99 % from the first hour. These values of effluent concentration of these four heavy metals were suitable to discharge this water to fresh water according to the allowable standards, as shown in Table 2.
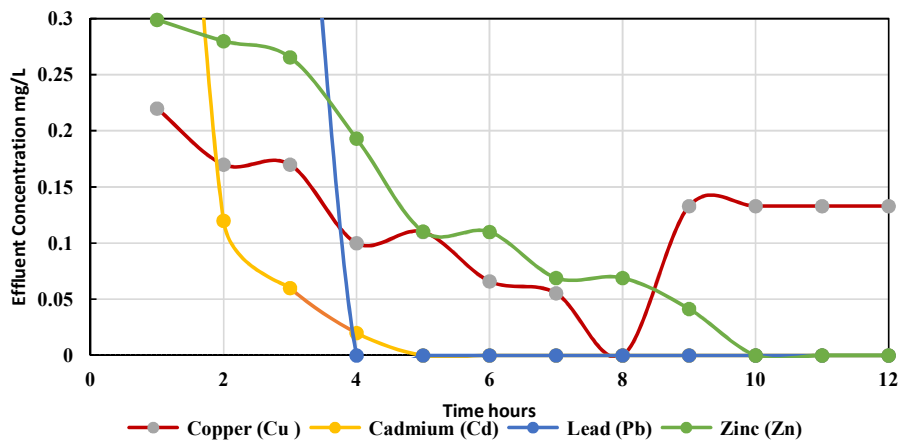

Fig. 17. Effluent concentrations of the four heavy metals by jazaurin biochar throughout 12 hours
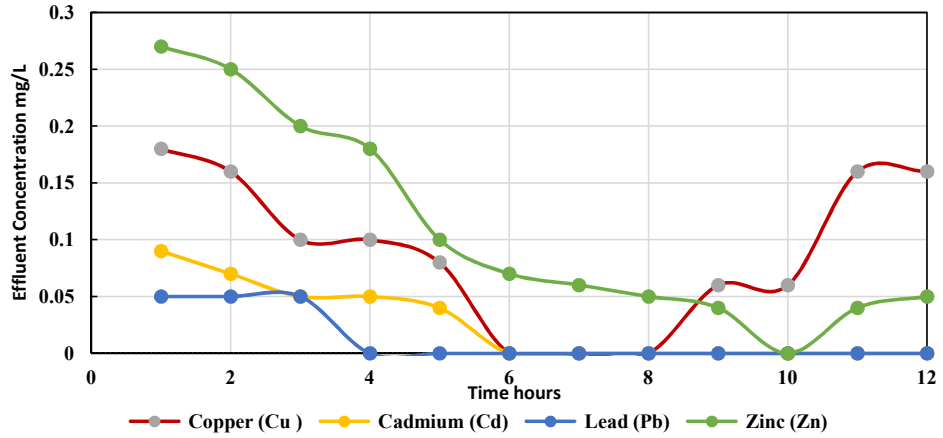
Fig. 18. Effluent concentrations of the four heavy metals by mango biochar throughout 12 hours
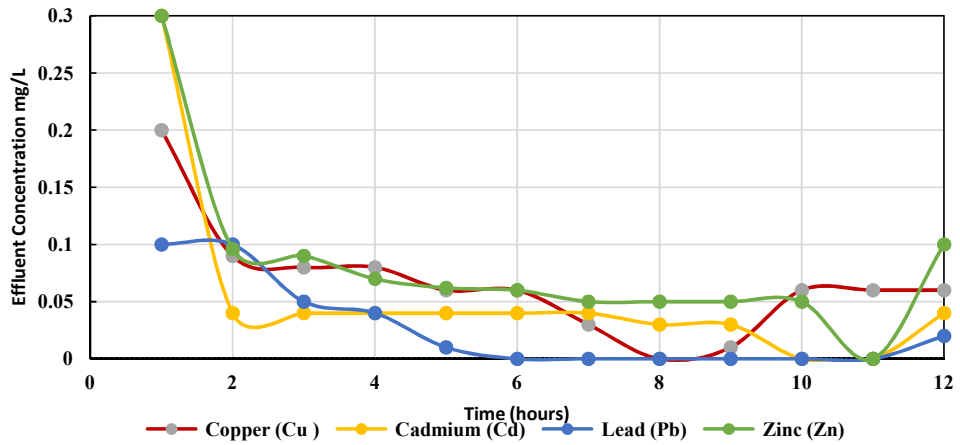

Fig. 19. Effluent concentrations of the four heavy metals by ficus biochar throughout 12 hours
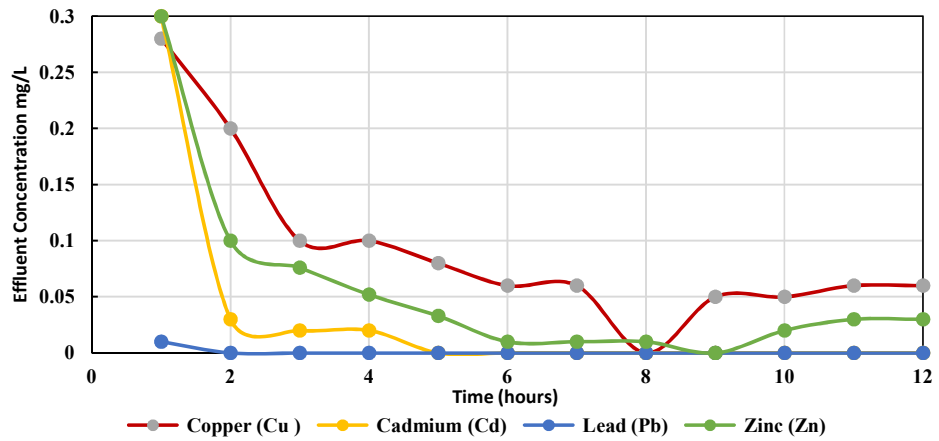

Fig. 20. Effluent concentrations of the four heavy metals by orange biochar throughout 12 hours

Table 2. Summary the standards and specifications of allowable discharged treated industrial effluent to fresh water [23]

Parameter	Standards & specifications mg/L
Copper	Not to exceed 1
Zinc	Not to exceed 1
Cadmium	Not to exceed 0.01
Lead	Not to exceed 0.05

4. CONCLUSION

- The use of biochars types (jazaurin, ficus, orange, and mango) as a filter media had a promising performance for industrial wastewater treatment.
- The four biochars types had the optimum performance on the adsorption of heavy metals with comparable to other studies that used different biochars.
- The most effective mean particle size of biochar was of less than 0.1 cm compared with other investigated sizes of 0.985, 0.6, 0.35, and 0.2 cm.
- The best initial concentrations were from 50 mg/L to 150 mg/L.
- The optimum hydraulic load was 2 L/hr. compared with other applied hydraulic loads of 4, 6, 8, 12 L/hr.
- The four heavy metals were adsorbed from the first hour of filtration.
- The maximum removal efficiencies of Cu, Cd, Pb, and Zn were more than 99% for all biochar types at the optimum parameters.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

REFERENCES

1. Bali M, Tlili H. Removal of heavy metals from wastewater using infiltration-percolation process and adsorption on activated carbon. International Journal of Environmental Science and Technology. 2019;16(1):249-258.
2. Göde C, Yola ML, Yılmaz A, Atar N, Wang S. A novel electrochemical sensor based on calixarene functionalized reduced graphene oxide: Application to simultaneous determination of Fe (III), Cd (II) and Pb (II) ions. Journal of Colloid and Interface Science. 2017;508:525-531.
3. Barakat MA. New trends in removing heavy metals from industrial wastewater. Arabian Journal of Chemistry. 2011;4:361–377.
4. Wang LK, Chen JP, Hung Y, Shammas NK. Heavy Metals in the Environment. CRC Press; 2009.
5. Nzediegwu C, Prasher S., Elsayed E, Dhiman J, Mawof A, Patel R. Effect of biochar on heavy metal accumulation in potatoes from wastewater irrigation. Journal of Environmental Management. 2019;232:153-164.
6. Wang CH, Bhattacharyya MH. Effect of cadmium on bone calcium and 45Ca in nonpregnant mice on a calcium-deficient diet: Evidence of direct effect of cadmium on bone. Toxicology and Applied Pharmacology. 1993;120(2):228-239.
7. Lichtfouse E, Hamelin M, Navarrete M, Debaeke P. Sustainable agriculture. Springer; 2009.
8. Fosmire GJ. Zinc toxicity. Am. J. Clin. Nutr. 1990;51:225–227.
9. Ranade VV, Bhandari VM. Industrial wastewater treatment, recycling and reuse. Butterworth-Heinemann; 2014.
10. Mireles S, Parsons J, Trad T, Cheng CL, Kang J. Lead removal from aqueous solutions using biochars derived from corn stover, orange peel, and pistachio shell. International Journal of Environmental Science and Technology. 2019;16(10): 5817-5826.
11. Wang X, Li X, Liu G, He Y, Chen C, Liu X, Zhao Y. Mixed heavy metal removal from wastewater by using discarded mushroom-stick biochar: Adsorption properties and mechanisms. Environmental Science: Processes & Impacts. 2019;21(3):584-592.
12. Wang H, Gao B, Wang S, Fang J, Xue Y, Yang K. Removal of Pb (II), Cu (II), and Cd (II) from aqueous solutions by biochar derived from KMnO4 treated hickory wood. Bioresource Technology. 2015;197:356-362.
13. Ahmad M, Rajapaksh, AU, Lim JE, Zhang M, Bolan N, Mohan, D, Ok YS. Biochar as a sorbent for contaminant management in soil and water: A review. Chemosphere. 2014;99:19-33.
14. Amin MT, Alazba AA, Shafiq M. Application of the biochar derived from orange peel for effective biosorption of copper and cadmium in batch studies: isotherm models and kinetic studies. Arabian Journal of Geosciences. 2019; 12(2):46.

15. Amin MT, Alazba AA, Shafiq M. Removal of copper and lead using banana biochar in batch adsorption systems: Isotherms and kinetic studies. Arabian Journal for Science and Engineering. 2018;43(11): 5711-5722..

16. Piscitelli L, Rivier PA, Mondelli D, Miano T, Joner EJ. Assessment of addition of biochar to filtering mixtures for potential water pollutant removal. Environmental Science and Pollution Research. 2018; 25(3):2167-2174.

17. Reddy KR, Xie T, Dastgheibi S. Evaluation of biochar as a potential filter media for the removal of mixed contaminants from urban storm water runoff. Journal of Environmental Engineering. 2014;140(12): 04014043.

18. Frišták V, Pipíška M, Lesný J, Soja G, Friesl-Hanl W, Packová A. Utilization of biochar sorbents for Cd 2+, Zn 2+, and Cu 2+ ions separation from aqueous solutions: comparative study. Environmental monitoring and Assessment. 2015;187(1): 4093.

19. Ashoori N, Teixido M, Spahr S, LeFevre GH, Sedlak DL, Luthy RG. Evaluation of pilot-scale biochar-amended woodchip bioreactors to remove nitrate, metals, and trace organic contaminants from urban stormwater runoff. Water Research. 2019; 154:1-11.

20. Komkiene J, Baltrenaite E. Biochar as adsorbent for removal of heavy metal ions [Cadmium (II), Copper (II), Lead (II), Zinc (II)] from aqueous phase. International Journal of Environmental Science and Technology. 2016;13(2):471-482.

21. El Hanandeh A, Gharaibeh M, Albalasmeh AA. Phosphorus removal efficiency from wastewater under different loading conditions using sand biofilters augmented with biochar. International Journal of Environmental Science and Technology. 2018;15(5):927-934.

22. Adil S, Mashiatullah A, Asma M, Abid J, Ghaffar, A. Heavy metal removal efficiency of paper mulberry biochar and commercially available silica powder from simulated industrial wastewater. Iranica Journal of Energy and Environment. 2014; 5(4):446-452.

23. RNPDP. Environmental Pollutions and Legislative Regulations: Law 48/1982 and Decree 8/1983. Aug. 1995, River Nile Protection and Development Project NWRCMPWWR-CIDA. Project No. 344/17564, Candian Exceuting Agency; 1995.

Peer-review history:
The peer review history for this paper can be accessed here:
http://www.sdiarticle4.com/review-history/64422