Original Research Article

Study of Adsorption Performance of Biochar for Heavy Metals Removal

ABSTRACT

The main objective of this work was to evaluate the performance of four different types of biochars in removing heavy metals from industrial wastewater. Four types of biochars were investigated in this study, namely; jazaurin, ficus, orange, and mango biochars. A pilot plant was set up to investigate the efficiency of these biochars as a filter media for industrial wastewater treatment. The removal efficiency of different heavy metals was assessed by a four-column pilot plant under different parameters; mean particle size of biochars, initial metal concentration, hydraulic load, and time. Results indicated that the different types of biochars used in this study showed high performance in removing the different types of heavy metals utilized (Copper (Cu), Cadmium (Cd), Lead (Pb), and Zinc(Zn)). It was 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.

1. INTRODUCTION

Industrial wastewater typically contained heavy metals and toxic materials (Bali1 et al., 2019). Thus, discharging industrial wastewater into the environment may result in hazardous impacts on both environment and human health (Göde et al., 2017). Heavy metals such as Cadmium (Cd), Copper (Cu), Lead (Pb), and Zinc (Zn)were considered the most harmful compounds produced from the chemical-intensive industries. High amounts of heavy metals were gathered in the body of humans from the food chain of the living organisms. If the concentrations of these heavy metals overtook the limited dose, they caused serious diseases for health (M.A. Barakat, 2011). Heavy metals treatment techniques, which were commonly used, including coagulation/flocculation, ion exchange, membrane separation, cavitation, advanced oxidation processes, incineration, and adsorption (Ranade et al. 2014).

Adsorption was regarded to be an effective method with low cost because of its high adsorption capacity of heavy metals and ease of implementation (Mireles et al., 2019). Many types of cost-effective adsorbents were 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 (Mireles et al., 2019).

Recently, biochar was found to be a good adsorbent due to its physical and chemical characteristics and its low cost which made it attractive to be used in adsorption (Wang et al., 2019). Biochar was produced by incineration of biomass, for an instance; wood, crop residue, and manure in an environment with limited oxygen. It was considered to be a cost-effective adsorbent for the withdrawal of heavy metals from wastewater (Ahmad et al., 2014).

(Amin et al., 2019) found that biochar of orange peel for copper and cadmium removal from wastewater could be used as adsorbent material. Moreover, (Wang et al., 2019) investigated that biochar of discarded mushroom stick (DMB) was succeeded for the removal of heavy metals such as lead, copper, cadmium, and nickel. (Amin et al., 2018) used banana peel biochar as adsorption filter media for eliminating lead and copper. (Piscitelli et al., 2018) 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., 2014) 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 were different types of biochar which were always available at a low cost and could be investigated and applied to remove heavy metals from industrial wastewater. Jazaurin, orange, ficus, and mango biochar might not be used before as a filter media and they were available in abundance in Egypt. Copper, Lead, Cadmium, and Zinc were considered to be the most toxic heavy metals diffusing in industrial wastewater.

This study was designed to evaluate the benefits of using four types of biochars namely; jazaurin, orange, ficus, and mango as a filter media for removing heavy metals from synthetic solution.

The behavior of these biochars was investigated under different parameters; particle size of biochar, initial heavy metal concentration, hydraulic load, and effect of time.

2. MATERIAL 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 Figure.1 and Table 1.

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

Figure 1 Sizes of studied biochars as a filter media

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, a feeding tank, two pumps, valves and piping, filtering media (biochar), a scale pipe to identify the water level inside the upper feeding tank, and effluent containers. Experimental columns were conducted as shown in figure 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. The pilot plant was controlled for 6 months from April 2019 to September 2019.

(a) **(b)**

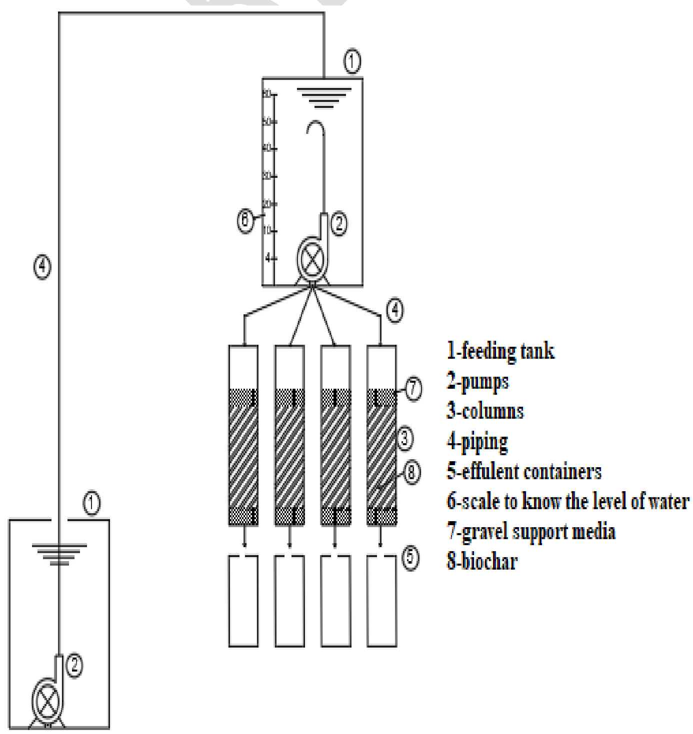

Figure 2 (a): Pilot Unit, (b): Experimental Diagram

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.

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.

Figure 3 indicated the approach of the experimental study.

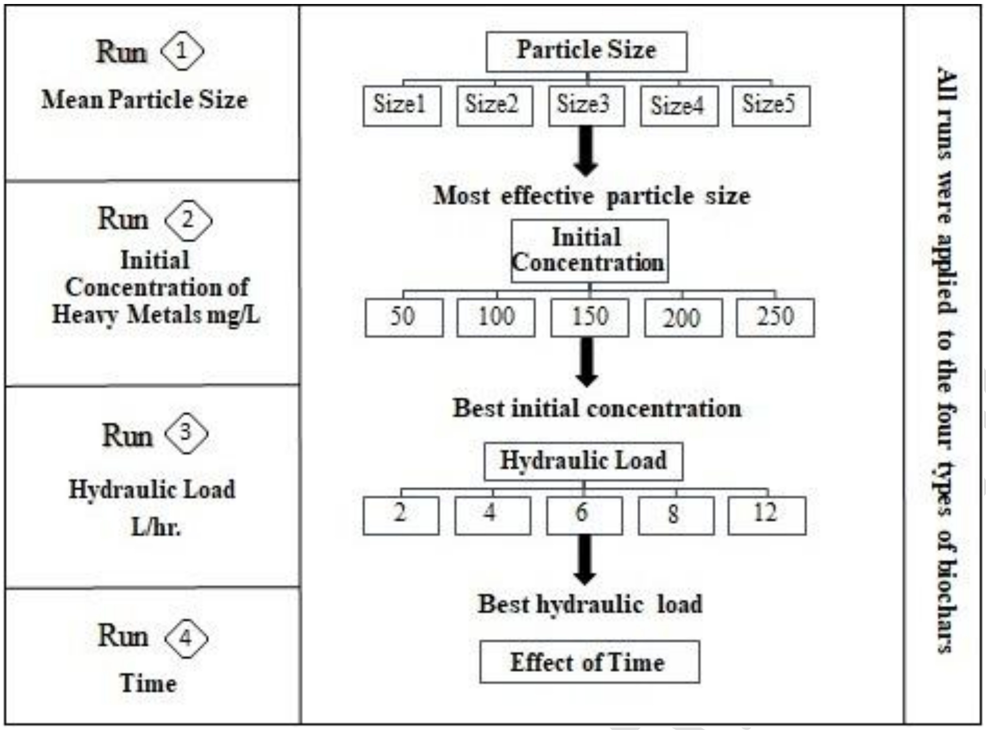

Figure 3 The approach of the experimental study

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 25cm, and initial heavy metal concentrations of 50 mg/L, as shown in Table 2. 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:

Removal efficiency %= $\frac{Ci-Cf}{Ci} * 100$ Equation (1)

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

Table 2 Summarized the removal efficiencies of heavy metals by biochars types at different particle sizes of biochars

Particle Size	Removal Efficiency, %															
	Jazaurin Biochar				Mango Biochar				Ficus Biochar				Orange Biochar			
	Cu	Cd	Pb	Zn	Cu	Cd	Pb	Zn	Cu	Cd	Pb	Zn	Cu	Cd	Pb	Zn
Size1	81.46	13.63	92.07	21	52.04	2.16	90.2	25	81.46	12.12	87.8	11.4	72.19	4.11	73.28	10.8
Size2	92.85	15.09	94.44	29.31	72.19	14.62	94.07	26.91	92.85	18.1	95.2	24.89	78.57	12.8	94.62	28
Size3	97.55	43.39	96.31	88.44	92.85	43.3	96.56	67.32	97.82	66.03	98.13	93.1	96.15	49.05	96.56	65.35
Size4	98.12	93.5	97.8	96.29	97.5	68.5	99.1	87.93	97.83	99.1	98.9	96.14	97.8	62.5	99.03	87.06
Size5	99	98.9	99.6	99.17	99.4	99.3	99.29	99.03	98.6	99.3	99.41	99	99.13	99.5	99.3	99.2

The higher removal efficiencies of heavy metals by the four biochar types were achieved at size5, as shown in Table 1. 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., 2019). 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. Table 3 presented the results of the removal efficiencies of the five applied initial heavy metals concentrations of each biochar.

Table 3 Summarized the removal efficiencies of heavy metals by biochars types at different initial concentrations of heavy metals

Initial Concentr-ation mg/L	Removal Efficiency, %															
	Jazaurin Biochar				Mango Biochar				Ficus Biochar				Orange Biochar			
	Cu	Cd	Pb	Zn	Cu	Cd	Pb	Zn	Cu	Cd	Pb	Zn	Cu	Cd	Pb	Zn
50	99	98.9	99.6	99.17	99.4	99.3	99.29	99.03	98.6	99.3	99.41	99	99.13	99.5	99.3	99.2
100	92.4	87.6	90.11	96.02	88.8	79.8	88.67	94.7	87.93	88.22	85	97.39	89.8	82.9	69.33	86.5
150	90.6	87.3	84.44	91.88	85.8	75.89	78.02	84.37	84	87.77	81.6	97.04	83.8	80.08	60	79.53
200	70.76	66.04	71.5	79.6	59.6	52.09	60	66.39	79.3	77.22	69.05	75.81	49.9	73.68	45.1	58.25
250	40.96	29.9	39.23	29.8	37.53	48.1	27.76	14.83	59.5	66.84	34.38	46.59	39.8	68.25	18.84	17.58

As illustrated in Table 3, 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.

When the initial heavy metal concentrations increased from 50 mg/L to 250 mg/L, the removal efficiency decreased. Moreover, the rate of sorption increased at higher initial heavy metals concentration, so the uptake of heavy metals at initial heavy metal concentrations of 250 mg/L was slow.

This reduction in removal efficiency because all active sites of sorption on the surface of ficus biochar were saturated with heavy metals.

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 Table 4.

Table 4 Summarized the removal efficiencies of heavy metals by biochars types at different hydraulic loads.

Hydraulic Load L/hr.	Removal Efficiency, %															
	Jazaurin Biochar				Mango Biochar				Ficus Biochar				Orange Biochar			
	Cu	Cd	Pb	Zn	Cu	Cd	Pb	Zn	Cu	Cd	Pb	Zn	Cu	Cd	Pb	Zn
2	99	98.9	99.6	99.17	99.4	99.3	99.29	99.03	98.6	99.3	99.41	99	99.13	99.5	99.3	99.2
4	97.58	92.7	90.6	81.52	95.29	86.28	90.2	87.73	95.6	92	84.4	88.68	96.7	88.71	85.7	88.5
6	79.5	87.3	88.5	78.66	89.2	75.06	87.5	70.81	89.05	89.3	88.75	70.83	83.57	64.5	83.28	67.33
8	79.25	80.22	84.6	77.02	88.3	76.94	80.6	68.33	87.3	72.22	87.5	68.9	80.7	59.8	75.57	59.6
12	49.3	59.41	22.59	57.7	33.6	25	26.29	33.3	39.1	38.2	36.29	48.3	40.56	29.29	14.07	19.05

Table 4 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.

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.

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 Figure 4

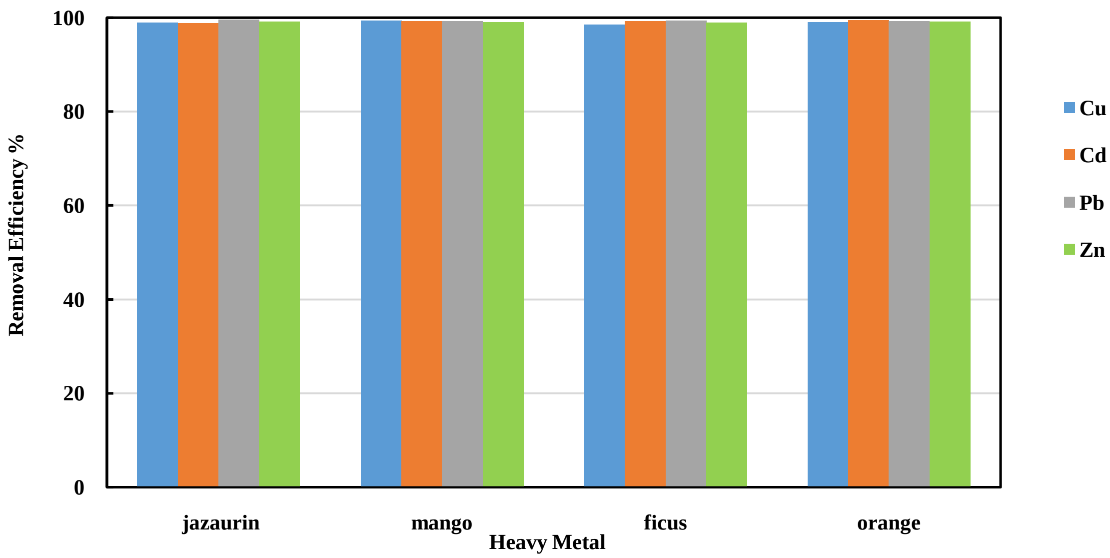

Figure 4 The removal efficiencies of the four biochars at optimum parameters (mean particle size <0.1 cm, initial heavy metal concentrations 50 mg/L, hydraulic load 2 L/hr.)

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 Table 5.

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 higher heavy metals removal efficiency might be referred to the types of biochar media used in addition to the biochar characteristics as investigated.

Table 5 Summarized the effluent of heavy metals concentrations by jazaurin biochars through 12 hours

Jazaurin Biochar												
Heavy metal	Time (hour) / Effluent concentration mg/L											
	1	2	3	4	5	6	7	8	9	10	11	12
Copper (Cu)	0.22	0.17	0.17	0.1	0.11	0.066	0.055	0	0.133	0.133	0.133	0.133
Cadmium(Cd)	0.9	0.12	0.06	0.02	0	0	0	0	0	0	0	0
Lead (Pb)	0.9	0.833	0.6	0	0	0	0	0	0	0	0	0
Zinc (Zn)	0.299	0.28	0.2656	0.1932	0.1104	0.11	0.069	0.069	0.0414	0	0	0

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 6.

Table 6 summarized the standards and specifications of allowable discharged treated industrial effluent to fresh water (RNPDP 1995).

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.

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