Adsorption of Heavy Metals from Landfill Leachate using Fish Scale Biochar

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Abstract

Heavy metal contamination is a serious environmental issue that can affect both humans and animals' health in many ways. The study was to explore the potential of fish scale biochar as an adsorbent for the removal of toxic metals from landfill leachate. The acquired fish scales were properly cleaned with deionised water and allowed to air dry for three days. After that, they were heated to a temperature of 10°C per minute in an inert atmosphere and allowed to sit for 60 minute in a muffle furnace. The initial and final concentrations of heavy metals of landfill leachate was measured using Atomic Absorption Spectrophotometer after treatment with fish scale's biochar at minimum of 0.50 g to a maximum of 2.50 g. The adsorption efficiency of chromium with fish scale biochar ranged 99.71% to 99.84%. The efficiency of cadmium adsorption with fish scale biochar produced about 99.80% to 99.98%. The percentage efficiency of nickel in the landfill leachate ranged from 99.30% to 99.55%. The maximum adsorption capacity (Q_e) for chromium, cadmium, and nickel were 9.52×10^{-6}, -2.80×10^{-5}, and 1.82×10^{-5}, respectively with coefficient of determination (R^2) of 0.7758, 0.1765 and 0.6831, respectively. Fish scale's biochar possesses efficient potentials with its high surface area and porous nature. Further research should be conducted using different time to assess the adsorption efficiency of pollutants.

Keywords: Adsorption efficiency, fish scale biochar, functional groups, landfill leachate, nickel

Introduction

Landfill leachate is a complicated and low-strength effluent that is continuously created as liquids percolate through municipal solid waste landfills (Poblete et al., 2020). Fish scales had chemical functional groups with binding capabilities such as carbonate, phosphate, carboxyl, amide, carbonyl, and hydroxyl (Vieira et al., 2012). Fish scales are typically discarded in landfills due to their low commercial value. The fish processing sector produces around 960 000 t of fish scales each year (Muhammad et al., 2016).

Recently, scientists have looked into using biochar as a cost-efficient and environmentally friendly adsorbent for removing toxic metals from wastewater. A carbon-rich substance called biochar is created when organic waste such as forestry and agricultural waste, is pyrolysed. It is a potent adsorbent for heavy metals in wastewater due to its large surface area and porous structure (Soffian et al., 2022). Global aquaculture is gradually growing in scope, and fish scales are being promoted as a cheap, widely available supply of adsorbent raw material.

Fish-scale biochar has a large specific surface area and a multitude of action sites, it is expected to sequester contaminants from aqueous solutions with predictable results (Xia et al., 2022). Owing to its strong sensitivity to pH and anions, as well as its stable reusability, current literature indicates that fish scale biochar has the potential for practical applications. This study offers not only a guide for choosing biochar, but also a better method for tetracycline hydrochloride breakdown in the environment (He et al., 2023). Using fish scales biochar as an adsorbent to remove toxic metals from landfill leachate has the potential to alleviate the environmental issues related to heavy metal contamination. It is a sustainable and affordable approach. Fish scales are a popular and plentiful byproduct of the fish industry, making them a desirable source of biochar for treatment of wastewater. The main goal of the study was to determine whether fish scale biochar could be used as an adsorbent to remove toxic metals from landfill leachate.

Materials and Methods

Sample collection and processing

The samples were landfill leachate and fish scales. Landfill leachate was collected from Gbalahi (latitude 9.441 and longitude -0. 759), in the Sagnarigu Municipality. Fish scales were purchased at the Tamale Market (latitude 9.4046719 and longitude -0.8474146) in the Tamale Metropolis. The fish scales were placed in a porcelain combustion tank, sealed with an appropriate lid, and heated slowly using a muffle furnace for 60 minute at a temperature of 10°C per minute in an inert atmosphere (100 mL/min of N_2) (Figure 1). After allowing the samples to cool, the char were weighed and stored in a ziplock bag (Figure 2).

Experiment

The toxic metal concentrations in the landfill leachate before the experiment were determined. Hundred (100) mL of the leachate was measured into five different conical flasks, followed by addition of different masses of biochar (0.5 g, 1.0 g, 1.5 g, 2.0 g, and 2.5 g) into each of the conical flask, labelled and covered. These conical flasks with the samples were then put into a shaker for 45 mins. Upon removal, the concentrations of nickel (Ni), chromium (Cr) and cadmium (Cd) were

Figure 1 Raw fish scales

Figure 2 Fish scales biochar

determined using PINAAcle 900T Perkin Elmer Graphite Furnace Atomic Absorption Spectrophotometer (GFAAS) to measure their concentrations.

Calculation for adsorption efficiency

The symbol Q_e was used for adsorption capacity of each pollutant (Dada et al., 2012). Therefore, the capture calculation of efficiency can be mathematically expressed as:

$$Q_e = \frac{c_i - c_f}{M} \times V \qquad \text{Equ. (1)}$$

To determine the percentage of adsorption, it is also represented as:

$$Q_e = \frac{(c_i - c_f)v}{M} \times 100 \qquad \text{Equ. (2)}$$

The pollutant's initial concentration (C_i), final concentration (C_f) following adsorption, amount (M) of adsorbent, and volume (V) of the solution and adsorption capacity (Q_e) are all represented by the variables.

Adsorption isotherms

The adsorption isotherm models used were the Langmuir adsorption isotherm model and Freundlich adsorption isotherm model.

Langmuir adsorption isotherm model

Langmuir isotherms describe the adsorption of atoms onto a uniform surface, which could be a solid substance with adsorptive properties similar to crystals (Massoudinejad et al., 2019). This can be mathematically represented as a linear equation. The Langmuir isotherm equation formula (Langmuir, 1918). Is shown below.

$$\frac{C_e}{Q_m} = \frac{1}{K_L Q_{max}} + \frac{C_e}{Q_{max}} \qquad \text{Equ. (3)}$$

Where K_L is the Langmuir constant (L/mg), C_e is the concentration of the adsorbate at equilibrium (mg/g), and Q_{max} (mg/g) is the value of adsorbed molecules on the adsorbent surface at any given moment (Kecili and Hussain, 2018). According to this model, the separation factor is R_L. This helps us determine the key elements of the Langmuir adsorption isotherm model more precisely. It is a dimensionless constant and expressed as:

$$R_L = \frac{1}{1+KlCo} \qquad \text{Equ. (4)}$$

Where K_L is the Langmuir constant (mg/g), and C_o is the adsorbate initial concentration.
When the $R_L > 1$ is considered to be unfavourable, $R_L = 1$ means linear, $R_L = 0$ means is irreversible and finally when $0 < R_L < 1$ means is favourable (Ayawei et al., 2017).

Freundlich adsorption isotherm model

The standard Freundlich adsorption isotherm (Freundlich, 1906). Model is

$$Q_e = K_F C_e^{1/n} \qquad \text{Equ. (5)}$$

Where Q_e is the amount of toxic metal removed at equilibrium, per gram of the adsorbent (mg/g), K_F is the Freundlich isotherm constant (mg/g), C_e is the concentration of adsorbate at equilibrium (mg/L) and finally, 1/n is the adsorption intensity.

Results and Discussion

The adsorption efficiency of fish scale biochar for chromium with initial concentrations of 2.17 mg/L at different dosages of 0.50g, 1.00g, 1.50g and 2.00g ranged from 99.71% to 99.84% (Table 1). Many agricultural raw products have been used in the process of adsorption of some toxic metals from wastewater. Gottipati (2012) looked into a similar work on the adsorption of Cr (VI) ions using Bael fruit shell. According to a report, the efficacy of removing Cr (VI) rose as the dose of adsorbent increased.

The efficiency of fish scale biochar adsorption of cadmium at a concentration of 0.32 mg/L with different dosages of 0.5, 1.0, 1.5 and 2.0 g ranges from 99.97% to 99.98% in an ascending order (Table 1). The fish scale biochar showed stronger affinity for cadmium than for the other metals. The amount of dosage can affect adsorption (Table 1). This is comparable to the study conducted in the period of green chemistry by Abbey et al. (2023) on the elimination of hazardous metals from the aqueous phase using biochar made from cocoa pod husk.

The efficiency of fish scale biochar adsorption of nickel at a concentration of 0.67 mg/L with different dosages of (0.5, 1.0, 1.5 and 2.0 g) ranges from 99.30% to 99.55% in an ascending order (Table 1). The percentage efficiency of nickel in the landfill leachate with concentration of 0.67 mg/l ranged from 99.30% to 99.55% (Table 1).

coefficients of determination (R^2) for chromium, cadmium and nickel were 0.7758, 0.1765 and 0.6831 respectively (Figures 1, 2, and 3). Chromium had maximum adsorption capacity of 9.52×10^{-6} mg/g, KL of -3.02×10^{-3} and R^2 of 0.7758. Cadmium had Q_{max} of -2.80×10^{-5} and R^2 of 0.1765 as compared to a higher Q_{max} and R^2 reported by (Ding et al., 2016). Nickel had a maximum adsorption of 1.82×10^{-5} mg/g as compared to 13.53 mg/g reported by Kristianto et al. (2019) and KL of -2.87×10^{-3} which is much less as compared to a K_L 0.6

TABLE 1

Adsorption percentage of heavy metals

Pollutant	Dosage	Initial Concentration (mg/L)	Final Concentration (mg/L)	Percentage (%)
Chromium	0.50	2.17	0.0063	99.71
	1.00	2.17	0.0058	99.73
	1.50	2.17	0.0049	99.77
	2.00	2.17	0.004	99.82
	2.50	2.17	0.0035	99.84
Cadmium	0.50	0.32	0.000087	99.97
	1.00	0.32	0.00008	99.98
	1.50	0.32	0.000074	99.98
	2.00	0.32	0.00007	99.98
	2.50	0.32	0.00063	99.8
Nickle	0.50	0.67	0.0047	99.3
	1.00	0.67	0.0044	99.34
	1.50	0.67	0.004	99.4
	2.00	0.67	0.0038	99.43
	2.50	0.67	0.003	99.55

Langmuir isotherm

Langmuir isotherm was used in the experimental process to describe how the adsorption capacity of the fish scale biochar for the Cr, Cd and Ni in the landfill leachate. Q_{max} (mg/g) is the maximum adsorption capacity for the heavy metals, where chromium was 9.52×10^{-6} mg/g, cadmium was -2.80×10^{-5}mg/g and nickel was 1.82×10^{-5} mg/g (Table 2). R_L for chromium was 17.25, cadmium was 17.28 and nickel was 17.25 (Table 2). The Langmuir report by Kristianto et al. (2019). Additionally, the adsorption of hazardous or heavy metals with a finite number of identical sites was done using the Langmuir isotherm. The Langmuir constant represents the relationship between the absorbates and the absorbent (Al-Ghouti and Da'ana, 2020). The greater the contact between the adsorbent and the adsorbate, the larger the amount of the constant; conversely, the weaker the interaction, the lower the value (Tran et al., 2019).

TABLE 2

Data modelling of Langmuir adsorption isotherm

	Langmuir				Freundlich			
Ions	Qmax (mg/g)	KL (l/mg)	R_L	R^2	$^1/n$	N	K_F (mg/g)	R^2
Chromium	9.52×10^{-6}	-0.00302	17.25	0.7758	2.43	0.41	7.26	0.8909
Cadmium	-2.80×10^{-5}	-0.00102	17.28	0.1765	-0.34	-2.95	1.15	0.2518
Nickle	1.82×10^{-5}	-0.00287	17.25	0.6831	3.26	0.31	3.56×10^{9}	0.7864

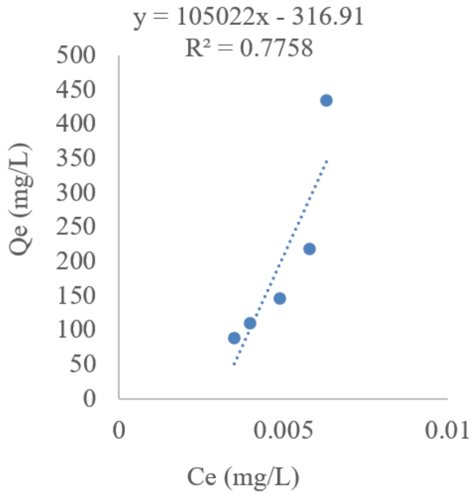

Fig. 1 Langmuir isotherm for chromium

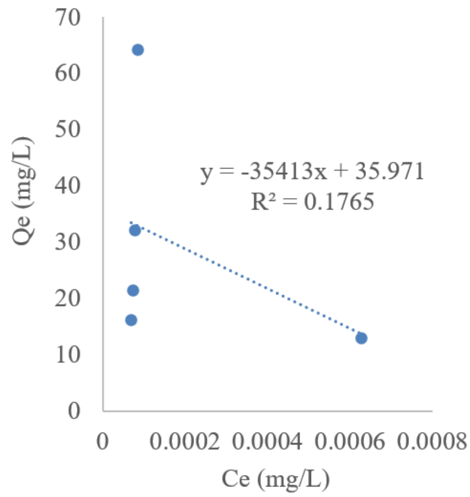

Fig. 2 Langmuir isotherm for cadmium

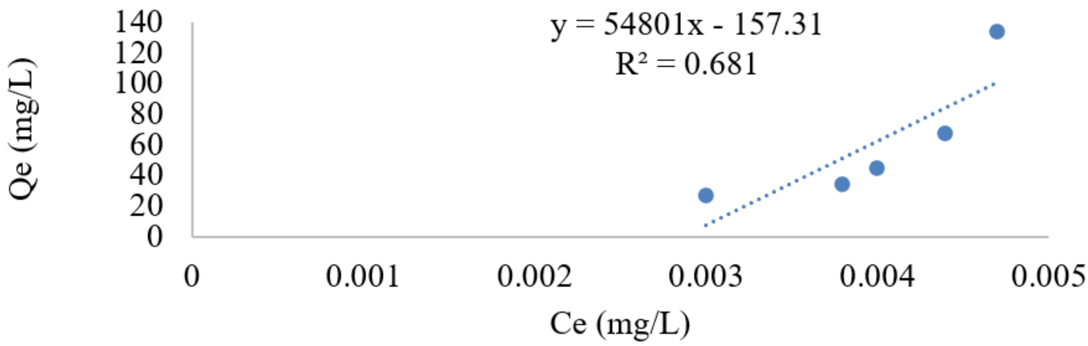

Fig. 3 Langmuir isotherm for nickel

Freundlich adsorption isotherm was employed to estimate the fitness of chromium, cadmium and nickel unto the surface of fish scale biochar adsorbent and the adsorption of toxic metals. The $^1/n$ values obtained from the experiment for chromium, cadmium, nickel were 2.43, -0.34, and 3.26, respectively, and those for the KF (mg/g) for chromium, cadmium and nickel were 7.26, 1.15, and 3.56 x 10^9, respectively (Table 2). The Freundlich adsorption isotherm coefficients of determination (R^2) values for chromium, cadmium and nickel were 0.8909, 0.2518 and 0.7864, respectively (Figures 4, 5 and 6).

For cadmium, the Freundlich isotherm value was 3.56×10^9. Cadmium's $^1/n$ value was 3.26, which was greater than 1 and indicated that the adsorption was advantageous with the heterogeneous surface. According to a related study by Abbey et al. (2023), the value of cadmium's $^1/n$ was 1.6. In this study, the N value for cadmium was -2.95, and the R^2 value was 0.2518, although Abbey et al. (2023) reported a cadmium value of 0.12. The Freundlich isotherm model (Figures 4, 5 and 6) provides the greatest fit for the experiment in terms of cadmium adsorption. According to Ayawei et al. (2017), the Freundlich isotherm provides an equation that allows the exponential distribution of active sites and their energies on heterogeneous adsorbent surfaces. The K_F is a Freundlich constant that shows adsorption capacity of an adsorbent. Chromium had a K_F of 7.26. This shows that the adsorption is co-operative since $^1/n$ greater than 1 (Ayawei et al., 2017). Co-operative adsorption is an

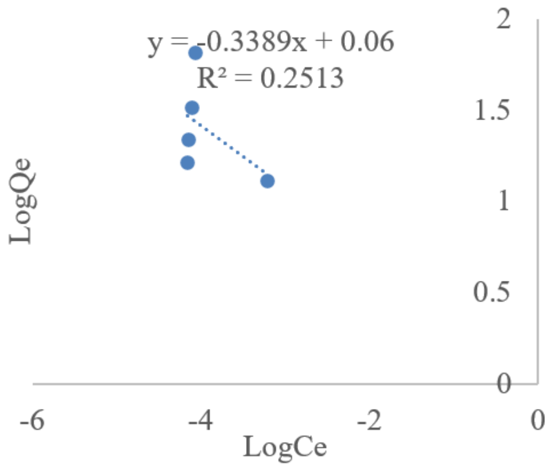

Fig. 4 Freundlich isotherm for chromium

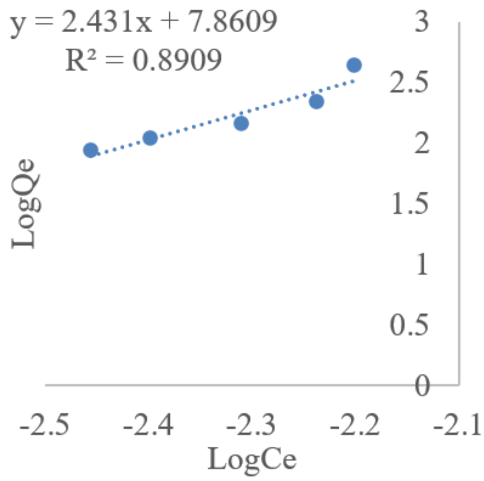

Fig. 5 Freundlich isotherm for cadmium

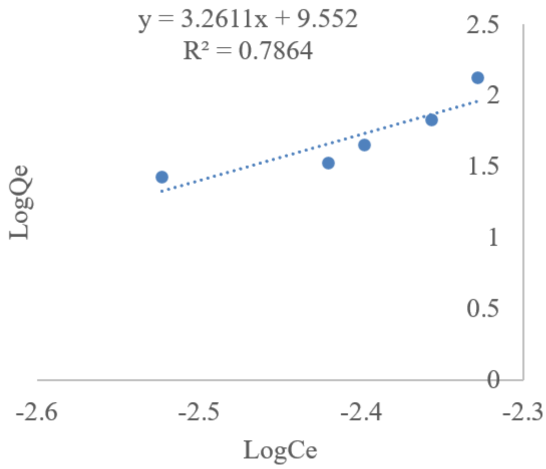

Fig. 6 Freundlich isotherm for nickel

adsorption in which deposited adsorbate (fish scale biochar) influences the adsorption of "new" adsorbate molecules (metals). Which is low as compared to 82.25 of a report by (Obiad et al., 2020) and the 1/n recorded for chromium 2.43 which is greater than that of 1.226 reported by (Obiad et al., 2020).

Fourier Transform Infrared Spectroscopy (FTIR) of the fish scale biochar

The FTIR Spectrum of Fish Scale Biochar is shown in Figure 7 and summarised in Table 3. The bands around 3383.33 cm^{-1} were attributed to N-H groups and hydroxyl groups (3200 - 3400 cm^{-1}). This study lends support from Yuan et al. (2011) which reported that at lower temperature (300 and 500 ◦C) the number of bounds were representative of functional groups present in biochar. The bond in the region 1015.40 cm^{-1} was due to C-F, C-O and SiO_2 stretching vibration where the bands around 872.53 cm^{-1} were due to C-C groups. The bands in 600.99 cm-1 depicted the presence of C-Cl whilst those in 555.72 cm^{-1} band showed the presence of C-Br of a functional group of alkyl halide. The presence of bands around 450 cm^{-1}, 800 cm^{-1}, and 1040 - 1100 cm^{-1} reflected the nature of the feedstock used in the biochar production which can also be assigned to SiO_2. In plant physiology, silica is the most important component for plant phytoliths because it prevents the plant's carbon from being degraded (Parr, 2006). Guo and Chen (2014) predicted a novel silicon-carbon architecture that might offer an evaluation viewpoint for biochar stability.

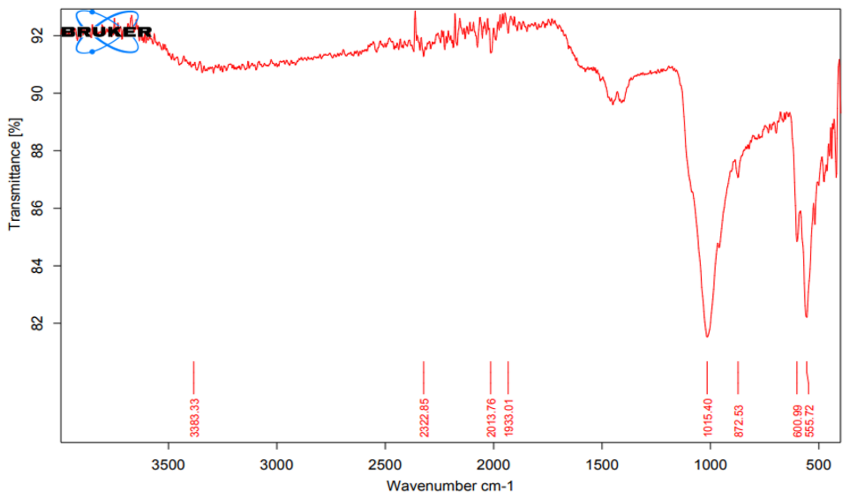

Fig. 7 A spectrum showing the transmittance (%) against the wavelength (cm^{-1})

TABLE 3

The wavelengths, transmittance with their corresponding functional group and bond

Wavelength (1/cm)	Transmittance	Bond type	Functional group
3383.33	0.9096	N-H, OH	Amide
2322.85	0.9128		
2013.76	0.9140		
1933.01	0.9209		Aromatic ring
1015.40	0.8152	C-F, C-O	Ester, alkylhalide
872.53	0.8707	C-C	Alkane
600.99	0.8484	C-Cl	Alkylhalide
555.72	0.8222	C-Br	Alkylhalide

Conclusion

The use of fish scale biochar as an adsorbent to remove efficiently the three toxic metals has proven to be very efficient. Fish scale is a raw material obtained from agricultural waste that is cost effective and friendly to the environment which was used in the production of the biochar. The biochar has a very strong affinity for chromium, cadmium and nickel for the adsorption of toxic metals from landfill leachate. It has highly significant adsorption percentages for a number of toxic metals detected in leachate. The temperature, dosage of adsorbent, contact and rotary time and pH of the landfill leachate have an impact on the adsorption capacity. Langmuir isotherm favors the adsorption of chromium but Freundlich isotherm model favors the cadmium.

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Conflict of Interest

The authors have no conflict of interest regarding this research article.

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