Biosorption of Cu(II), Pb(II) and Zn(II) Ions from Aqueous Solutions Using Selected Waste Materials: Adsorption and Characterisation Studies

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Abstract

The efficacy of coconut tree sawdust (CTS), eggshell (ES) and sugarcane bagasse (SB) as alternative low-cost biosorbents for the removal of Cu(II), Pb(II) and Zn(II) ions from aqueous solutions was investigated. Batch adsorption studies were carried out to evaluate the effects of solution pH and initial metal concentration on adsorption capacity. The optimum biosorption condition was found at pH 6.0, 0.1 g biomass dosage and at 90 min equilibrium time. The adsorption data were fitted to the Freundlich and Langmuir isotherm models. The adsorption capacity and affinity of CTS, ES and SB were evaluated. The Freundlich constant (n) and separation factor (R_L) values suggest that the metal ions were favourably adsorbed onto biosorbents. The maximum adsorption capacities (Q) estimated from the Langmuir isotherm model for Cu(II), Pb(II) and Zn(II) were 3.89, 25.00 and 23.81 mg/g for CTS, 34.48, 90.90 and 35.71 mg/g for ES, and 3.65, 21.28 and 40.00 mg/g for SB, respectively. The characterisation studies were performed using Scanning Electron Microscope (SEM), Energy Dispersive X-ray Spectrometer (EDX) and Fourier Transform Infrared Spectrometer (FTIR). Interaction with metal ions led to the formation of discrete aggregates on the biosorbents surface. The metal ions bound to the active sites of the biosorbents through either electrostatic attraction or complexation mechanism.

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Keywords

Adsorption; Characterisation; Metal Ions; Coconut Tree Sawdust; Eggshell; Sugarcane Bagasse

1. Introduction

Excessive levels of toxic metals in the water environment have been a worldwide issue for many years [1]. Heavy metals are introduced into water by several industries such as mining, electroplating, petroleum refining and etc. They may pose toxicity to human especially at high concentration [2]-[4]. However, due to their high industrial value their application in industries is irreplaceable. Therefore, it is very important to remove heavy metals from water environment [5] [6].

Various techniques have been applied for the removal of heavy metals from water. This includes membrane filtration, ion exchange and chemical precipitation [7]. These techniques are costly. Adsorption has been proposed as a cost-effective method for water decontamination. Activated carbon is widely used as an adsorbent for water treatment. It is effective to sequester metal ions from water environment. However, activated carbon is expensive [8] [9].

In recent years, a number of alternative adsorbents have been studied for water clean-up. They are inexpensive, efficient and practical to be utilised. Agricultural and industrial wastes, as well as natural minerals are widely used as alternative biosorbents for many years [1] [5]. Agricultural wastes such as tea waste [10] [11], coffee waste [10], watermelon seed hulls [12], kapok fibre [13], lam tree (*Cordia africana*) sawdust [14], *Ricinus communis* [15] and coir fibre [16] have been tested for metal ion adsorption. The application of agricultural wastes as biosorbents for the removal of heavy metals has many advantages such as available in large quantities, renewable in nature, eco-friendly and low-cost [17] [18].

Agricultural waste normally contains a variety of organic compounds (lignin, cellulose and hemicelluloses) and functional groups (hydroxyl, carbonyl and amino). Both organic compounds and functional groups have great affinity for metal ion complexation [11]-[13]. Coconut tree sawdust (CTS) and sugarcane bagasse (SB) are plant-based materials. They may contain a number of organic compounds and functional groups, meanwhile eggshell (ES) consists of carbonate that favours metal ion binding [19].

The aim of this work was to evaluate the potential of CTS, ES and SB as alternative low-cost biosorbents for decontamination of metal ions from aqueous solutions. The adsorption studies were carried out as a function of solution pH and initial metal concentration. The equilibrium data were described by the Freundlich and Langmuir isotherm models. SEM, EDX and FTIR analyses were performed to elucidate the adsorption mechanism(s).

2. Materials and Methods

2.1. Preparation of Biosorbents and Solutions

CTS was supplied by Jati Cemerlang Sawmill, Selangor, meanwhile ES and SB were obtained from My Rasa Restaurant, Selangor. The materials were washed and dried in an oven at 70°C for 7 days. The dried materials were ground using a laboratory mill and sieved through 150 - 250 μm size fraction using an American Society for Testing and Materials (ASTM) standard sieve.

Metal stock solutions (Cu(II), Pb(II) and Zn(II)) of 1000 mg/L were prepared by dissolving an appropriate amount of $Cu(NO_3)_2 \cdot 3H_2O$, $Pb(NO_3)_2$, and $Zn(NO_3)_2$ salts in 0.1 mol/L KNO_3. In this study, 0.1 mol/L KNO_3 was used as an electrolyte to control the ionic strength of metal ions. The stock solutions were diluted to the required concentrations using 0.1 mol/L KNO_3.

2.2. Characterisation Studies

The surface area and pore diameter of the biosorbents were determined using a Quantachrome Autosorb l Micromeritics Surface Analyser. The surface area was measured according to Brunauer-Emmett-Teller (BET) multipoint technique [20], meanwhile the pore diameter was calculated based on Barrett, Joyner and Halenda (BJH) method [21]. The surface area of CTS, ES and SB were 0.4, 6.5 and 2.8 m^2/g, respectively. Meanwhile, the pore

diameter of CTS, ES and SB were 1.9, 11.4 and 7.2 nm, respectively. The surface morphology of the biosorbents was observed using a Hitachi SU 8020 UHR FESEM. The samples were coated with platinum to avoid charging. The elemental composition of the biosorbents was determined by using a Horiba Energy Dispersive X-ray Spectrometer. The functional groups of the biosorbents, as well as binding mechanism(s) were confirmed using a Thermo Nicolet 6700 Fourier Transform Infrared Spectrometer.

2.3. Batch Adsorption Studies

Batch adsorption experiments were carried out by adding 0.1 g of biosorbent to 25 mL of metal ion solution in a conical flask. The mixture was shaken for 90 min at 100 rpm using a protech orbital shaker (model 720). The optimum solution pH was determined in the pH range of 2.0 - 6.0. The solution pH was adjusted using 0.5 mol/L HCl or 0.5 mol/L NaOH. The solution pH before and after interaction with single metal ion was determined using a Thermo Scientific Orion 2-Star pH meter. The effect of initial metal concentration was studied in the range of 10 - 200 mg/L. However, adsorption of Pb(II) by ES was studied in the initial metal concentration ranging from 10 to 500 mg/L. The concentration of metal ion in the supernatant was measured using an AAnalyst 400 Perkin Elmer Atomic Absorption Spectrometer. The amount of metal ion adsorbed onto biosorbent was calculated using Equation (1)

$$q = \frac{(C_o - C_e)V}{w} \tag{1}$$

where q is the amount of metal ion adsorbed, C_o is the initial metal ion concentration, C_e is the equilibrium metal ion concentration, w is the weight of biosorbent, and V is the volume of metal ion solution. Triplicate experiments were carried out for adsorption study.

3. Results and Discussion

3.1. Adsorption Studies

3.1.1. Effect of Solution pH
The pH of the solution significantly affects the amount of metal ion adsorbed onto biosorbents as it influences the properties of the biosorbents, as well as the speciation of metal ions in aqueous solution.

The effect of solution pH on metal ion adsorption is shown in **Figure 1**. From **Figure 1**, an increase in the solution pH from 2.0 to 6.0 has increased the amount of Cu(II), Pb(II) and Zn(II) adsorbed. For example, the amount of Pb(II) adsorbed by CTS, ES and SB increased from 5.37 to 15.07, 16.87 to 24.70, and 5.71 to 13.05 mg/g, respectively. From **Figure 1**, the maximum adsorption of metal ions onto biosorbents was found at pH 6.0. Therefore, pH 6.0 was chosen as the optimum pH for the adsorption system. Many adsorption studies report pH 5.0 - 6.0 as the optimum pH for Cu(II), Pb(II) and Zn(II) adsorption by various biosorbents [22]-[24].

At low pH (2.0 - 3.0), more H_3O^+ ions will be available to compete with Cu(II), Pb(II) and Zn(II) ions for the adsorption sites of the biosorbents. In addition, at low pH most of the functional groups are protonated [25]. This will reduce the number of binding sites available for the adsorption of metal ions. The increase in adsorption capacity at higher pH values can be attributed to the weak inhibitory effect of H_3O^+ ions. The solution pH was kept within the pH range of 2.0 - 6.0 because the precipitation of metal ion was occurred simultaneously at pH values higher than 6.0 [26] [27].

3.1.2. Effect of Initial Metal Concentration
The effects of initial metal concentration on the adsorption of Cu(II), Pb(II) and Zn(II) ions onto biosorbents are shown in **Figure 2**. From **Figure 2**, the amount of metal ion adsorbed by CTS, ES and SB increased with increasing initial metal concentration. For example, the amount of Cu(II), Pb(II) and Zn(II) adsorbed onto ES increased from 2.33 to 30.66 mg/g, 2.42 to 83.35 mg/g, and 2.02 to 24.07 mg/g, respectively. A significant amount of metal ions adsorbed at high initial metal concentration can be related to two main factors, namely high probability of collision between metal ions with the biosorbent surface and high rate of metal ions diffusion onto biosorbent surface. As discussed by Wang *et al.* [28], high initial metal concentration accelerates the driving force and reduces the mass transfer resistance.
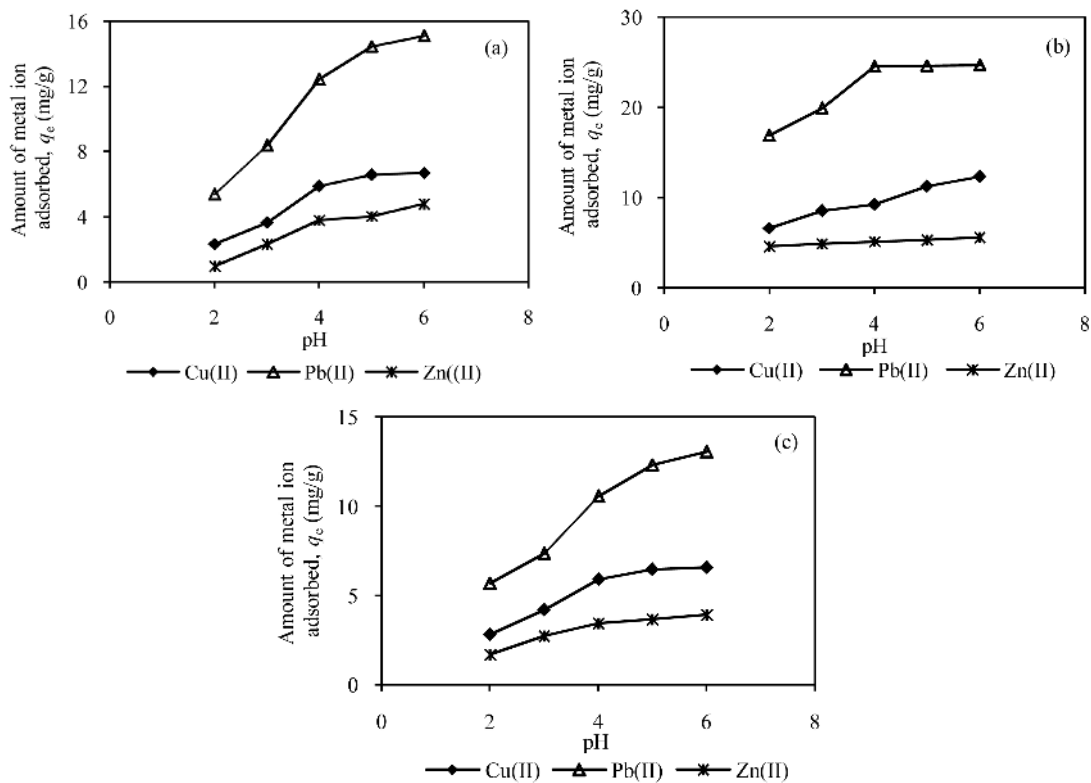
Figure 1. Effect of solution pH on adsorption by (a) CTS, (b) ES and (c) SB.
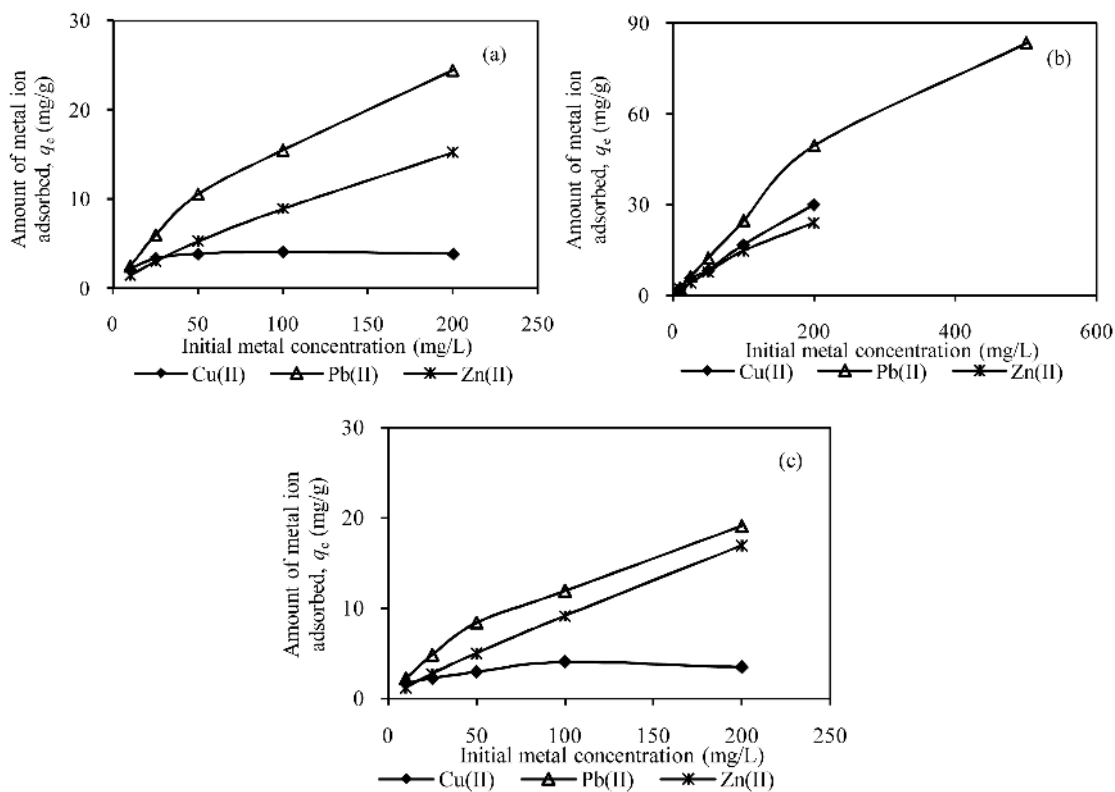

Figure 2. Effect of initial metal concentration on adsorption by (a) CTS, (b) ES and (c) SB.

In the case of Cu(II) adsorption by CTS and SB, there was no great difference in adsorption capacity at initial metal concentration of 50 - 200 mg/L for CTS and 100 - 200 mg/L for SB. This scenario can be explained by the fact that the active sites of both biosorbents reached saturation point at around 3.00 - 4.00 mg/g of Cu(II). Therefore, the increment in adsorption capacity after this point is negligible.

The removal percentage of metal ions decreased with an increase in initial metal concentration. The ratio of metal ions to active sites is low at low initial metal concentration. In contrast, this ratio is relatively high at high initial metal concentration. In other words, the number of metal ions was much higher than the number of active sites available for adsorption. Therefore, the adsorption efficiency was rather low at low initial metal concentration. For example, the removal percentage of Cu(II), Pb(II) and Zn(II) by ES decreased from 84.58 to 7.73%, 99.47 to 49.19%, and 57.89 to 30.97%, respectively.

3.1.3. Isotherm Models

Adsorption isotherm models have been used to describe the distribution of metal ions between the solid phase (adsorbent) and liquid phase (solution) when equilibrium was reached. The Freundlich and Langmuir isotherm models have been widely used to describe the interaction between metal ions in solution and adsorbents.

Freundlich isotherm model is an empirical equation based on adsorption on a multilayer heterogeneous surface. The linear form of the Freundlich equation is expressed as Equation (2) [29]

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \tag{2}$$

where C_e is the equilibrium concentration of metal ion (mg/L), q_e the amount of metal ion adsorbed per unit weight of adsorbed at equilibrium (mg/g), n is the Freundlich constant and K_F is the adsorption capacity (mg/g). K_F and n can be determined from a linear plot of $\log q_e$ against $\log C_e$.

Langmuir isotherm model deals with adsorption at monolayer surface with a finite number of identical sites. The linear form of the Langmuir equation is rendered as Equation (3) [30]

$$\frac{C_e}{q_e} = \frac{C_e}{Q} + \frac{1}{Qb} \tag{3}$$

where C_e is the equilibrium concentration of metal ion (mg/L), q_e is the amount of metal ion adsorbed per unit weight of adsorbed at equilibrium (mg/g), b is the Langmuir constant (L/mg), and Q is the maximum adsorption at monolayer (mg/g).

The calculated results of the Freundlich and Langmuir isotherm constants are given in **Table 1**. As presented in **Table 1**, the adsorption of Zn(II) onto biosorbents was correlated well with the Freundlich isotherm model. Meanwhile, the adsorption data for Cu(II) and Pb(II) were best described by either the Freundlich or Langmuir isotherm model. The maximum adsorption capacities (Q) estimated from the Langmuir isotherm model for Cu(II), Pb(II), and Zn(II) were 3.89, 25.00 and 23.81 mg/g for CTS, 34.48, 90.0, and 35.71 mg/g for ES, and 3.65, 21.28, and 40.0 mg/g for SB, respectively.

The Q values estimated from the Langmuir isotherm model were in the order of: Pb(II) > Zn(II) > Cu(II) for CTS and ES, and Zn(II) > Pb(II) > Cu(II) for SB. The stronger affinity of biosorbents towards Pb(II) than Cu(II) and Zn(II) may be due to ion electronegativity and ionic radius. Pb(II) has the highest ion electronegativity (2.33) than Cu(II) (1.93) and Zn(II) (1.63). Furthermore, Pb(II) has the largest ionic radius (0.132 nm) than Zn(II) (0.083 nm) and Cu(II) (0.072 nm). These characteristics increase the attraction force between metal ions and active sites of the biosorbents [31]. Therefore, the amount of metal ion bound to the biosorbents increased.

From **Table 1**, the n values from application of the Freundlich isotherm model lie between 1 and 10 indicating the metal ions were favourably adsorbed by the biosorbents. The interaction of metal ions and biosorbents was further evaluated by separation factor (R_L). R_L is a dimensionless constant separation factor, an equilibrium parameter derived from the Langmuir model. The R_L was defined by Hall *et al*. [32], and is expressed as Equation (4)

$$R_L = \frac{1}{1 + bC_o} \tag{4}$$

As described by Hall *et al*. [32], the R_L values indicate whether the isotherm is favourable ($0 < R_L < 1$), unfavourable ($R_L > 1$), linear ($R_L = 1$) or irreversible ($R_L = 0$). The R_L values for Cu(II), Pb(II) and Zn(II) adsorption

Table 1. Freundlich and Langmuir isotherm constants for metal ion adsorption by CTS, ES and SB.

Biosorbent	Metal ion	Freundlich			Langmuir		
		K_F (mg/g)	n	R^2	Q (mg/g)	b (L/mg)	R^2
CTS	Cu(II)	2.26	7.87	0.768	3.89	4.36	0.998
	Pb(II)	5.75	3.38	0.995	25.00	0.13	0.955
	Zn(II)	0.53	1.47	0.999	23.81	0.01	0.913
ES	Cu(II)	4.10	2.45	0.908	34.48	0.04	0.718
	Pb(II)	18.92	3.13	0.465	90.90	0.44	0.998
	Zn(II)	1.28	1.58	0.990	35.71	0.02	0.900
SB	Cu(II)	1.30	4.65	0.883	3.65	0.21	0.988
	Pb(II)	2.12	2.19	0.979	21.28	0.05	0.948
	Zn(II)	0.31	1.23	0.999	40.00	0.00	0.877

onto biosorbents are in the range of 0-1, suggesting that the adsorption of metal ions was favourable.

The maximum adsorption capacity (Q) of CTS, ES and SB for Cu(II), Pb(II) and Zn(II) was compared with other low-cost adsorbent. As presented in **Table 2**, it is apparent that the adsorption capacity of biosorbents studied was comparable with other adsorbents. The difference in adsorption capacity can be related to the difference in physical and chemical characteristic of the adsorbents.

3.2. Characterisation Studies

3.2.1. SEM Analysis

The surface morphology of the biosorbents before and after metal ion adsorption was observed using SEM analysis. There are significant changes to the surface morphology of the biosorbents, as well as the formation of discrete aggregates on their surfaces following metal ion adsorption. The SEM images of ES before and after metal uptake at 10,000 × magnification are shown in **Figure 3**, as an example.

As presented in **Figure 3**, ES displayed a dense and porous surface texture. Interaction of ES with Cu(II) has resulted in the formation of flake-like deposits on its surface (**Figure 3(b)**). Meanwhile, cube-like deposits were observed on the surface of ES after Pb(II) uptake (**Figure 3(c)**). Lump-like deposits were formed after contact with Zn(II) (**Figure 3(d)**).

CTS had a smooth and dense surface texture (data not shown). Interaction with metal ions changed the surface morphology of CTS to rough texture. Zn(II) had a significant effect to the surface of CTS of which the surface became irregular. Lump- and twist-like deposits were observed on the surface of CTS following Cu(II) and Pb(II) adsorption.

SB had a smooth, dense and porous surface texture (data not shown). The porous texture disappeared after contact with Cu(II), Pb(II) and Zn(II). Interaction with Cu(II) and Zn(II) changed the surface texture of SB to rough and irregular. Grooves were observed on its surface after Zn(II) uptake. Meanwhile, tiny nodules were observed after contact with Pb(II).

3.2.2. EDX Analysis

EDX analysis was performed to determine the elemental composition of the biosorbents before and after metal ion adsorption. As described in Section 2.2, samples were coated with platinum prior to EDX analysis to avoid charging. The features of platinum were observed at 2.05 and 9.44 keV. Carbon and oxygen are the major constituents in the biosorbents. Their features can be observed at 0.277 and 0.523 keV, respectively. It is known that eggshell consists of calcium carbonate. The features of calcium were appeared at 3.691 and 0.341 keV.

Figure 4 presents the EDX spectrum of SB following Zn(II) adsorption, as an example. As shown in **Figure 4**, new peaks appeared at 1.012 and 8.637 keV represent the features of Zn. The characteristic peaks for Cu can be observed at 0.830 and 8.040 keV. Meanwhile, interaction with Pb(II) has resulted in the appearance of EDX features at 2.342 and 10.550 keV (data not shown). Overall, the appearance of EDX features of Cu, Pb and Zn on the surface of biosorbents implies the ability of CTS, ES and SB for metal ions binding.

3.2.3. FTIR Analysis

The presence of functional groups on the surface of biosorbents was confirmed using FTIR analysis. In addition, FTIR analysis provides information on possible mechanism(s) involved in metal ion adsorption.

Table 2. Comparison of maximum adsorption capacity (Q) estimated from Langmuir isotherm model for various low-cost adsorbents.

Biosorbent	Q (mg/g)			Reference
	Cu(II)	Pb(II)	Zn(II)	
Bentonite	14.10	-	21.1	[33]
Pomegranate peel	1.31	13.87	-	[34]
Rice husk	-	0.62	19.61	[35]
Activated carbon derived from *Cicer arietinum*	17.77	20.69	19.93	[36]
Volcanic rock	10.87	9.52	4.46	[37]
Coir fibre	9.43	29.41	-	[16]
Phosphate rock	7.24	78.74	5.44	[38]
Poplar sawdust	3.24	-	-	[39]
Groundnut shells	4.46	-	7.62	[40]
Jute fibres	4.23		3.55	[41]
Polyporus tenoiculus	14.7	92	-	[42]
Tea waste	48	65	-	[11]
Cotton fibre	6.12	21.62	4.53	[43]
Chorella vulgaris	25.42	-	31.38	[44]
Residual biomass	28.34	92.20	25.37	[31]
CTS	3.89	25.00	23.81	This study
ES	34.48	90.90	35.71	This study
SB	3.65	21.28	40.00	This study
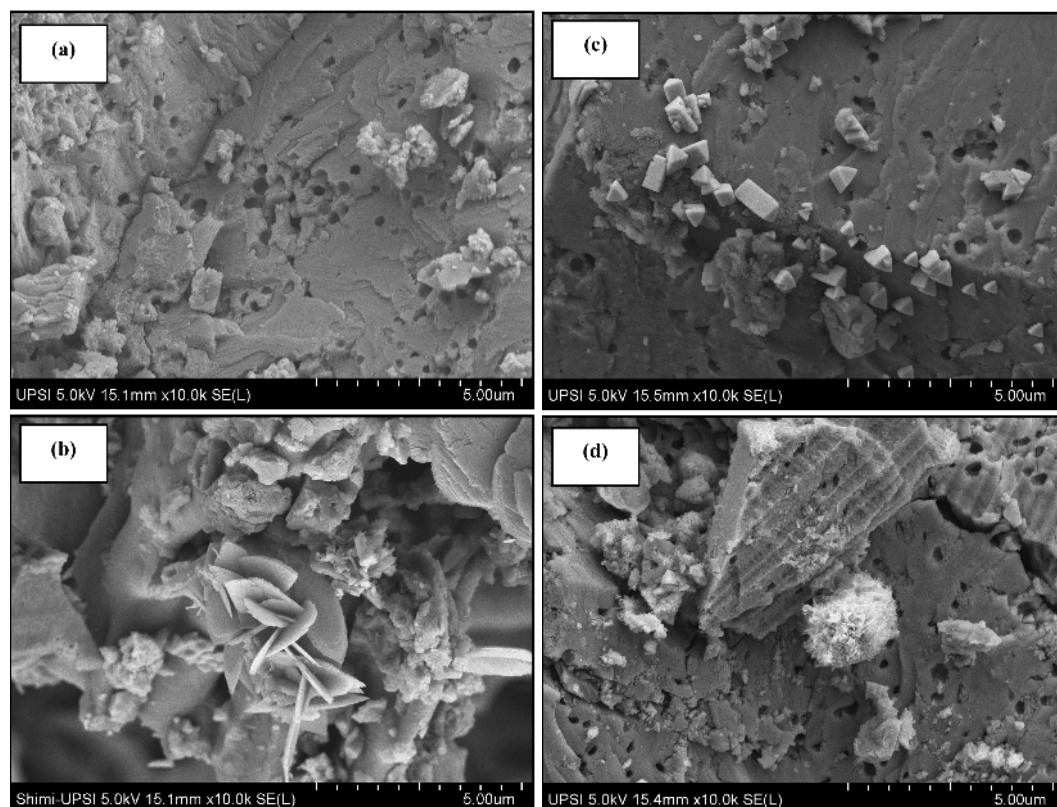
Figure 3. SEM images of ES before adsorption (a) and after adsorption of (b) Cu(II), (c) Pb(II) and (d) Zn(II).
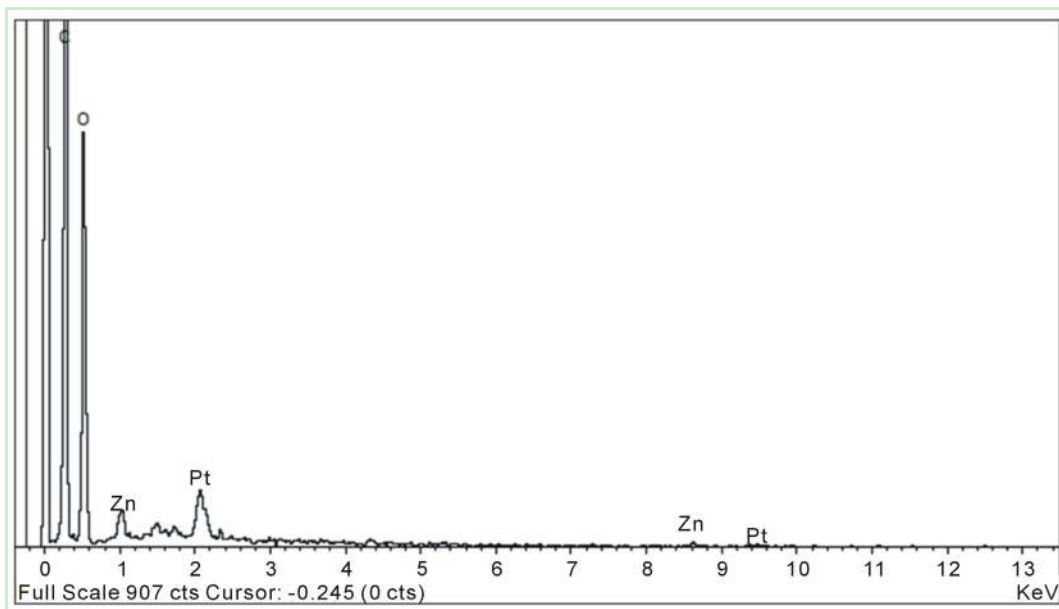
Figure 4. EDX spectrum of SB after interaction with Zn(II).

The FTIR spectra of ES, before and after metal ion uptake are shown in **Figure 5**, as an example. Based on **Figure 5(a)**, the absorption bands observed at 1404, 875 and 711 cm^{-1} are characteristics of carbonate (CO_3^{2-}) [45]. The characteristics of carbonate at the aforementioned wavenumbers have been further discussed by Vagenas *et al*. [46] and Rehman and Bonfield [47]. The interaction of ES with Cu(II) has caused the absorption bands at 1404 cm^{-1} to split to two peaks, namely 1414 and 1352 cm^{-1} (**Figure 5(b)**). The adsorption of Cu(II) onto ES has also resulted in the appearance of new shoulder peaks at 875 and 711 cm^{-1} (**Figure 5(b)**). The absorption band at 1404 cm^{-1} shifted to 1345 cm^{-1} and the peak at 711 cm^{-1} split into two peaks at 759 and 680 cm^{-1} following Pb(II) uptake by ES (**Figure 5(c)**). Meanwhile, a new peak was appeared at 474 cm^{-1} after contact with Zn(II) (**Figure 5(d)**).

Both CTS and SB have similar functional groups on their surfaces. The absorption band at 3343 cm^{-1} corresponds to the stretching vibration of -OH and the extension vibration of -NH [45]. The band at 2874 cm^{-1} can be assigned to CH stretching, meanwhile the band at 1718 cm^{-1} represents carbonyl (C=O) groups [45]. The absorption bands at 1029 and 1031 cm^{-1} can be attributed to C-O stretching vibration of cellulose, lignin and hemicelluloses [45].

After interaction with metal ions, the absorption band of -OH and -NH groups at 3433 cm^{-1} shifted to 3320 cm^{-1}. Meanwhile, the absorption band represents carbonyl group shifted from 1718 cm^{-1} to 1723 cm^{-1}. In addition, the absorption intensity of this band was found to increase significantly. The wavenumber of C-O stretch shifted from 1029 cm^{-1} to 1024 cm^{-1} following interaction of CTS and SB with metal ions.

From FTIR study, the formation of new absorption bands, the change in absorption intensity, and the shift in wavenumber of functional groups could be due to interaction of metal ions with active sites of biosorbents. The metal ions bound to the active sites of the biosorbents through either electrostatic attraction or complexation mechanism. The electrostatic attraction was between metal ion and carbonate group. Meanwhile, the complexation mechanism involved electron pair sharing between electron donor atoms (O and N). Results from this study suggest carbonate, carbonyl, hydroxyl and amine are the main adsorption sites in ES, CTS, and SB.

4. Conclusion

Results from this study highlight the feasibility of CTS, ES and SB as alternative low-cost biosorbents for the removal of Cu(II), Pb(II) and Zn(II) ions from aqueous solution. The presence of functional groups in the biosorbents favours metal ion binding. Adsorption and characterisation studies however are preliminary evaluation of such utilisation for water treatment. It is also necessary to evaluate the effectiveness of CTS, ES and SB to treat real industrial effluents. Coconut tree sawdust, eggshell and sugarcane bagasse are abundantly available at
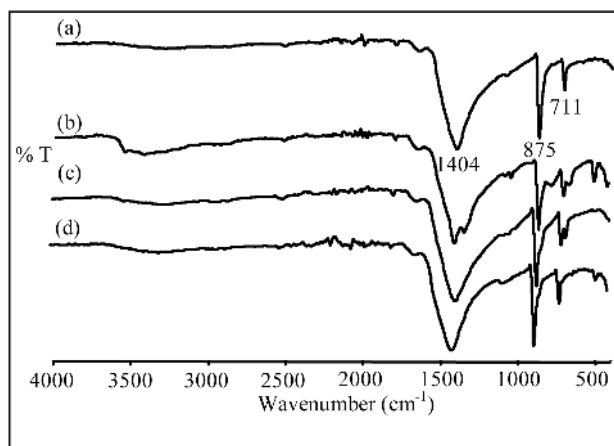
Figure 5. FTIR spectrum of ES before adsorption (a) and after adsorption of (b) Cu(II), (c) Pb(II) and (d) Zn(II).

low-cost. The use of these wastes will provide a solution to their disposal.

Acknowledgements

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