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Biosorption of cadmium (II), copper (II) and lead (II) ions by citric acid modified and unmodified cocoa pod shell: Equilibrium, kinetics and thermodynamics

Alabi, A. H.,* Awoyemi, R. F. and **Ayedogbon, A. S.**
Department of Chemistry, University of Ibadan, Ibadan, Nigeria
Correponding author: helenalabie3@yahoo.com

Abstract

Chemical modification of biosorbent is a common practice in wastewater treatment when using adsorption technology. Thioglycollic acid has been used for the modification of cocoa pod without any significant improvement in its adsorption capacity for lead, cadmium and copper. This study is aimed at improving the sorption of these metal ions from aqueous solution using citric acid as the modifying agent for cocoa pod shell. The dried cocoa pod shell was ground and reacted with citric acid according to the method in the literature. Batch adsorption studies were conducted to examine the influence of pH, temperature, initial metal ion concentration; sorbent dose and contact time on the biosorption of Pb^{2+}, $Cu^{2+}$and Cd^{2+}ions by modified and unmodified cocoa pod shell. Langmuir, Freundlich, Temkin and Dubinin-Radushkevich models were used for fitting the equilibrium data. The amount of metal ion sorbed was determined using flame atomic absorption spectrophotometer (FAAS). The result for the adsorption of the metal ions under varying pH showed that sorption was pH dependent. The trend in biosorption was in the order of $Cd^{2+} > Cu^{2+} > Pb^{2+}$ on unmodified cocoa pod shell (UCPS); while the trend in biosorption of the ions onto modified cocoa pod shell (MCPS) was in the order of $Pb^{2+} > Cu^{2+} > Cd^{2+}$. The amount of Pb^{2+} adsorbed increased from 4.62-33.56 mg/g after modification as shown by values obtained using the Langmuir equation to fit the biosorption data. Langmuir isotherm gave R^2 values which shows that it satisfactorily describe the biosorption process for Pb^{2+}, $Cu^{2+}$and Cd^{2+} ions on UCPS and MCPS. The kinetics of the sorption process was best described by the pseudo-second order kinetic model (R^2>0.9922). Thermodynamic parameters showed that biosorption process was feasible and spontaneous for Pb^{2+}, $Cu^{2+}$and Cd^{2+}ions onto UCPS and MCPS. The process is exothermic for Cu^{2+} and Cd^{2+} ions; but endothermic for Pb^{2+}. This study has shown that citric acid modified cocoa pod shell is a good biosorbent especially for Pb^{2+} ions.

Keywords: Biosorption; cocoa pod shell; citricacid; pseudo-second order kinetics.

Introduction

The use of agricultural wastes for the treatment of polluted water via adsorption is an attractive and promising option for the removal of pollutants from the environment [1]. Agricultural waste materials are highly efficient, cheap and renewable source of biomass that can be exploited for heavy metal remediation [2]. This also helps to minimize the disposal problem caused by them. Some of the agricultural waste materials which are being used as low-cost alternatives to expensive adsorbents includes, *Theobroma cacao* [3, 4], *Moringa oleifera* bark [5], sawdust [6], bagasse flyash [7], rubber leaf powder [8], rice husk [9], tree fern [10], *Saraca indica* leaf powder [11], lalang *(Imperata cylindrica*) leaf powder [12], *Melocanna baccifera* (bamboo) [13] and maize leaf [14]. A number of complex mechanisms are involved in the binding of heavy metals to agro-biomass. These mechanisms include adsorption, complexation, chelation and entrapment in capillaries and spaces within the polysaccharide network due to concentration gradient causing diffusion through the cell walls and membranes.

However, crude agricultural by-products are known to have generally low adsorption capacity. To increase the ion exchange capacity and physical stability (partial

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solubility) of agricultural wastes, they can be modified chemically for better efficiency and multiple re-use to enhance their applicability for industrial scale use [15-17]. Several chemicals have been reported for modifying different agricultural materials. Ngah and Hanafiah [18] classified the chemicals used for modifying the plant materials as mineral and organic acids, bases, oxidizing agents, organic compounds, and so on. It was also stated that the application of untreated plant wastes as adsorbents can also cause high chemical oxygen demand (COD), and biochemical oxygen demand (BOD) as well as total organic carbon (TOC) due to release of soluble organic compounds contained in the plant materials. This increase in COD, BOD and TOC can cause depletion of oxygen content in water and can threaten aquatic life. Therefore, plant materials needs to be modified or treated before being applied for the decontamination of waste waters.

The biosorption of some metal ions onto cocoa pod (modified and unmodified) has been reported [3, 4]. The unmodified cocoa pod was shown to have higher adsorption capacity for copper (II), cadmium (II) and lead (II) than the thioglycollic acid ($HSCH_2COOH$) modified cocoa pod [4]. So far, there is dearth of information on the modification of cocoa pod using citric acid as the modifying agent. However, it has been used for other agricultural wastes like corn cob [19], soybean hulls [20], *Moringa oleifera* [15] leaves and so on with enhanced adsorption. In this study, the use of citric acid to attach free carboxyl groups onto the hydroxyl of the polysaccharide matrix of the cellulosic agricultural materials is investigated. The modified and unmodified cocoa pod shell was used to for the adsorption of cadmium (II), copper (II) and lead (II) under different operating conditions like time, adsorbent dose, pH, temperature and adsorbate concentrations.

Materials and method

Reagents

All chemicals used in this work were of analytical reagent grade (BDH, England) and were used without further purification. Stock solutions (1,000 mg/L) of lead, copper and cadmium were prepared from lead (II) trioxonitrate (V), copper (II) tetraoxosulphate (VI) andcadmium trioxonitrate (V) tetrahydrate respectively. Working solutions of initial concentration (100 mg/L) of each metal were prepared by pipetting 10 mL of the stock solution into a 100 mL standard flask and making up to the mark with deionised water. Other concentrations ranging from 10-90 mg/L) were prepared by serial dilution of the stock solution.

Biomass collection and preparation

The cocoa pods were obtained from a cocoa farm at Igbesi in Isin Local Government Area of Kwara State, (8°14′0′′N 5°62′0′′E). The samples were mixed to form a composite from which a representative sample was taken for sorption studies.

The biosorbent was prepared according to the method described by Odoemelam *et al* [4]. The pod shells were air-dried and ground into powder using a mechanical grinder. The ground sample was dried further in the oven at 50^{o}C for 12 hours. The dried sample was sieved using a 300 µm sieve.

Activation of cocoa biomass

The chemical activation of the cocoa pod shell aids the removal of any soluble biomolecules or debris that might interact with metal ions during sorption. The chemical activation described by Odoemelam *et al* [4] was adopted. The cocoa pod shell was activated by treating the biomass with 2% v/v trioxonitrate (V) acid solution and was soaked at room temperature for 24 hours. The biomass was further filtered through a Whatman No. 4 filter paper and rinsed with deionised water. The rinsed biosorbent (biomass) was air dried for about 12 hours. The biomass was again dried in the oven for about 6 hours at temperature of about 105^{o}C. The biomass was then removed from the oven, and divided into two parts. One part was stored in an air-tight plastic container and this represented the unmodified cocoa pod shell (UCPS) while the other part was further treated by chemical modification using citric acid.

Chemical modification of biosorbents

The methods of Marshall *et al* [21] and Marshall and Wartelle [22] were used with some modifications. Two hundred and forty grammes (240 g) of the activated cocoa pod shells were mixed with 1,680 mL of 0.3 M citric acid. The cocoa pod shells were allowed to absorb citric acid for 30 minutes at 25^{o}C, and then the slurry was dried at 60^{o}C overnight. It was further dried at 120^{o}C for 90 minutes in the oven. The dried slurry was stored in an air-tight plastic container and this represented the modified cocoa pod shell (MCPS).

Characterization of biosorbents

Fourier transform infrared (FT-IR) spectroscopy was used to determine the vibrational frequencies of the functional groups in the biosorbents. The spectra were determined using Perkin-Elmer spectrometer (Perkin-Elmer Spectrum version 10.03.07, USA) within the range of 400-4000 cm^{-1}. A fine powdered dry sample was first mixed with KBr and then ground in an agate mortar at an approximate ratio of 1/100 for the preparation of pellets (weight of 100 mg). The resulting mixture was pressed at 5 ton for 5 minutes and cast into disk prior to FT-IR analysis.

Biosorption experiments

Biosorption experiments were optimised at the desired pH value and contact time in a plastic centrifuge tube containing 50 mL of standard solution of the metal ions and 1g of the biosorbent (UCPS and MCPS). The pH was adjusted with either 0.1M HNO_3 or 0.1M NaOH. The centrifuge tubes were shaken in a temperature controlled shaker (Edmund Bühler SM25, Germany) at 300 rpm for 60 minutes. The solutions were filtered using Whatman filter paper No. 4. The residual equilibrium concentrations of the filtrates were analysed using Atomic absorption spectrophotometer (Buck Scientific model 210 VGP, USA). The amount of metal ions biosorbed at equilibrium condition,q_e(mg/g) was calculated using equation (1):

$$q_e = (C_o - C_e)\frac{V}{W} \quad .... \ (1)$$

where, V is the volume of the solution used (L), W is the mass of biosorbent used, C_o and C_e are the initial and equilibrium metal ion concentration (mg/L) in solution respectively.

The contact time was varied from 15 to 180 minutes for the study, while the pH was varied from 2 to 10 for the effect of pH on the biosorption process. The initial metal ion concentration used was from 10 to 100 mg/L and the adsorbent dose was varied from 500 mg to 1000 mg. All the biosorption experiments were done in duplicate using plastic centrifuge tubes that have been previously washed with 10% HNO_3.

Results and discussion

FT-IR analysis

The FT-IR spectra for MCPS and UCPS in their raw state and where the biomasses have sorbed copper, cadmium and lead ions are presented in Figures 1, 2 and 3, respectively. Wave numbers (cm^{-1})were assigned to the various functional groups in the raw, citric acid modified and metal loaded biomass. The broad peaks at 3401 (cm^{-1}) in (Figure 1a, UCPS) and 3411 (cm^{-1}) in (Figure 1b, MCPS) were assigned to –OH stretch due to inter and intra-molecular binding of polymeric compounds such as alcohols, phenols, and carboxylic acids, as in pectin, cellulose and lignin [3]. The peaks at 2925 and 2855 cm^{-1} on MCPS (Figure 1b) corresponded to the symmetric and assymetric C-H stretching vibrations of aliphatic acids [23]. Only one peak was observed in UCPS (Figure 1a) at 2927cm^{-1}. The peaks at 2344-2315$cm^{-1}$for UCPS (Figure 1a) and 2344-2313 $cm^{-1}$for MCPS (Figure 1b) were assigned to $C \equiv N$ stretching vibration frequency. The peaks at 1627, 1517 cm^{-1} for UCPS (Figure 1a) and MCPS (Figure 1b) represented the asymmetric stretching vibrations of ionic carboxylic group $–COO^-$ while the peak at 1,426 cm^{-1} represented –OH bend vibration frequency. The pectin peaks at 1,384 and 1,385 cm^{-1}were identified in both biosorbents UCPS (Figure 1a) and MCPS (Figure 1b) respectively. The 1033 to 1055 cm^{-1} band in Figure1a and 1,034 to 1,055 cm^{-1} band in Figure 1b, were assigned to C-OH stretching in alcohols. The peaks at 1,152 to 1,260 cm^{-1} on UCPS (Figure 1a) and 1,109 to 1,266 cm^{-1} on MCPS (Figure 1b) are due to C-O stretching vibrations. The C=O stretching vibration was observed at 1,727 cm^{-1} in MCPS (Figure 1b) which is absent in UCPS (Figure 1a). This was introduced on the sample as a result of modification by citric acid; a carboxylic acid (Figure 1).

The spectra of the biosorbents (UCPS and MCPS) used for biosorption of Pb^{2+}, Cu^{2+} and Cd^{2+} ions are shown in Figures 2 and 3. Significant shifts in specific peaks either to higher wave number or to lower wave number on adsorption of the metal ions were recorded. The active groups that play a significant role in the biosorption of Pb^{2+}, Cu^{2+} and Cd^{2+} ions were hydroxyl ($O–H_{stretch}$), ionic carboxyl group ($–COO^–$), nitrile ($C \equiv N_{stretch}$), alcohols ($–C–OH_{stretch}$), ($C–O_{stretch}$) and carbonyl ($C = O_{stretch}$). The carbonyl group C=O was highly responsible for the biosorption of Pb^{2+}, Cu^{2+} and Cd^{2+} ions on MCPS.

Effect of pH

The pH of the aqueous solution is an important controlling parameter in biosorption process because it affects the degree of dissociation of the functional groups on biosorbent surface, speciation and solubility of metal ions in aqueous solution [24, 25]. Figure 4 shows the effect of pH in the range of 2.0 to 10.0 on the biosorption of 100 mg/L Pb^{2+}, Cu^{2+} and Cd^{2+} ions by UCPS and MCPS, respectively. There was a continuous increase in the biosorption of all the metals until they all reached maximum uptake. The biosorption capacity of Pb^{2+}, Cu^{2+} and Cd^{2+} ions increased until they reached equilibrium pH 5, 7, and 4, respectively. The result clearly showed that the metal binding capacity was highly pH dependent. The low uptake of the metal onto the biosorbents (UCPS and MCPS) at pH 2 was due to the excess proton (H^+ ions) and these ions also compete effectively with metal ions for binding sites. These subsequently inhibit the binding of Pb^{2+}, Cu^{2+} and Cd^{2+} ions to the surface functional groups of the adsorbents (UCPS and MCPS) due to the decrease of negative surface charge of the sorbent. As the pH of the system increased, the negatively charged sites enhanced the electrostatic attraction of the metal ions by adsorbent (UCPS and MCPS) which led to a favourable sorption [26, 27].

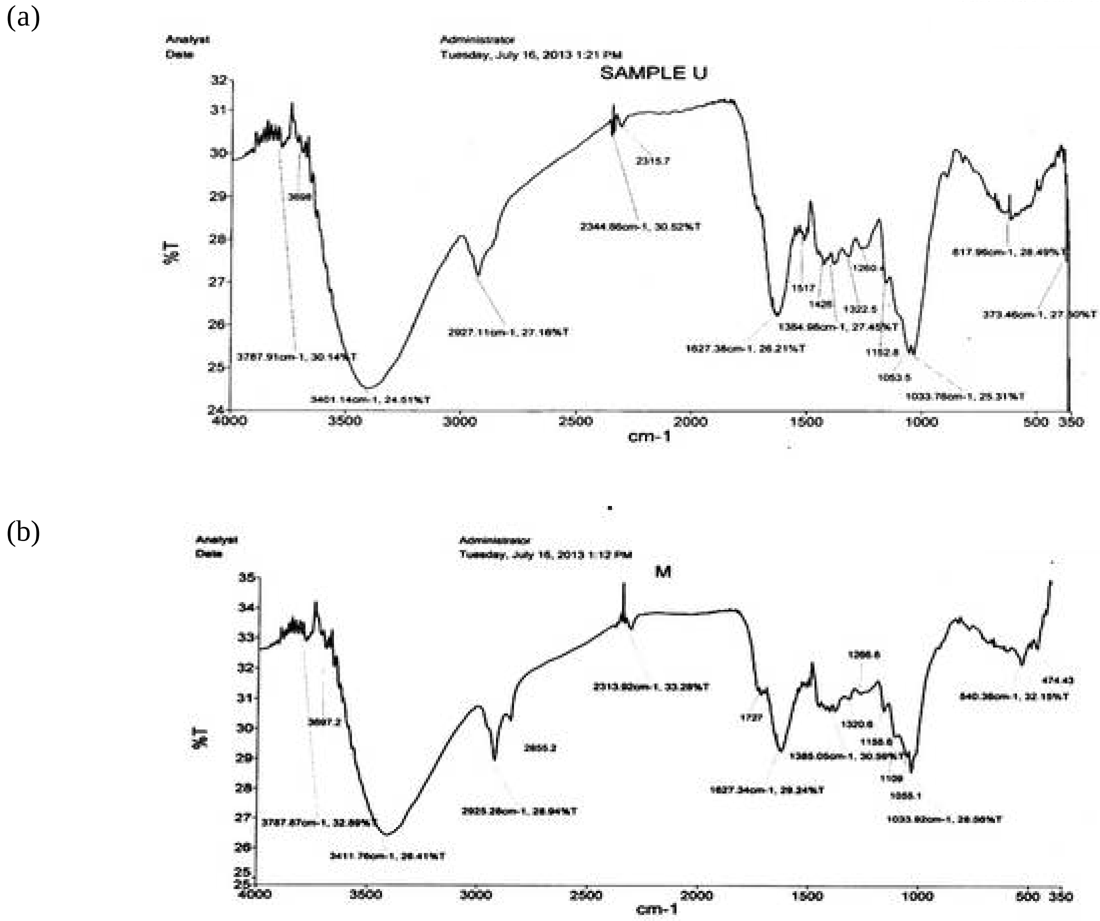
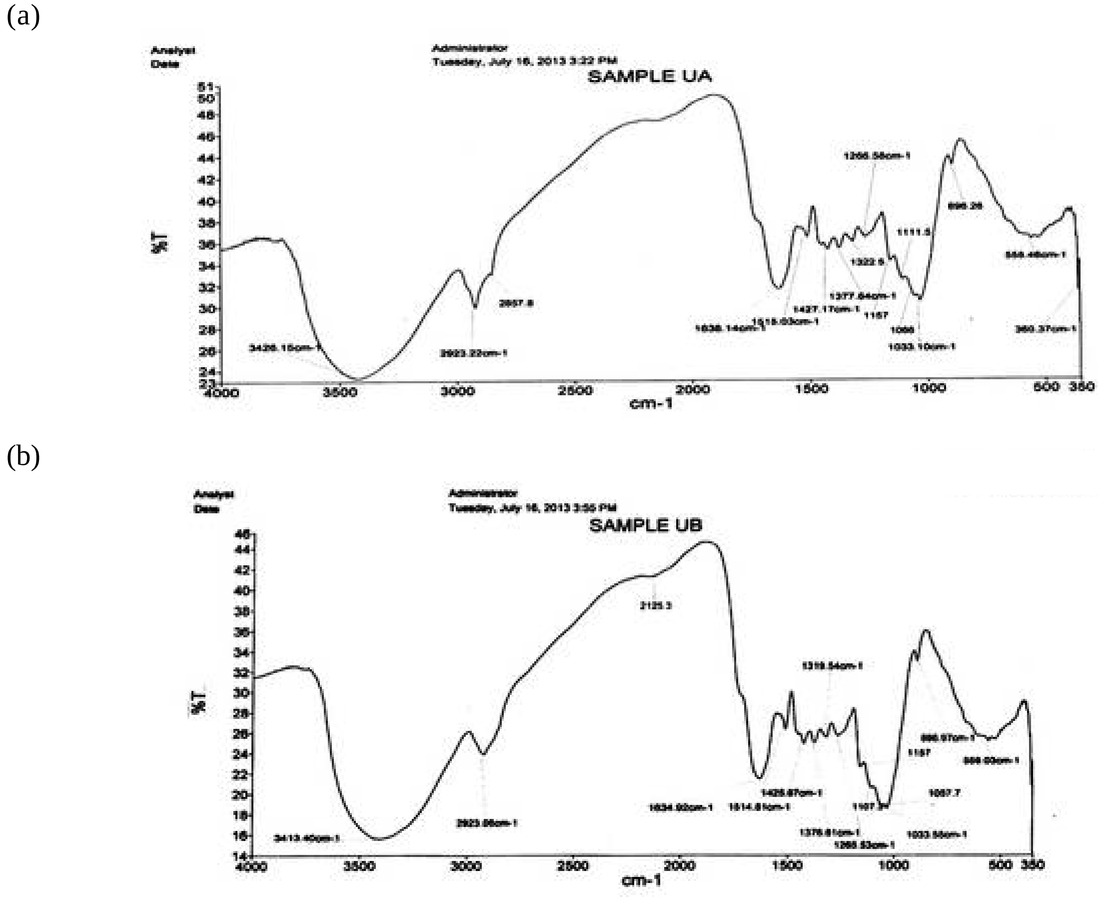


Figure 1. FT-IR spectrum of (a) unmodified cocoa pod shell (UCPS) (b) modified cocoa pod shell (MCPS).



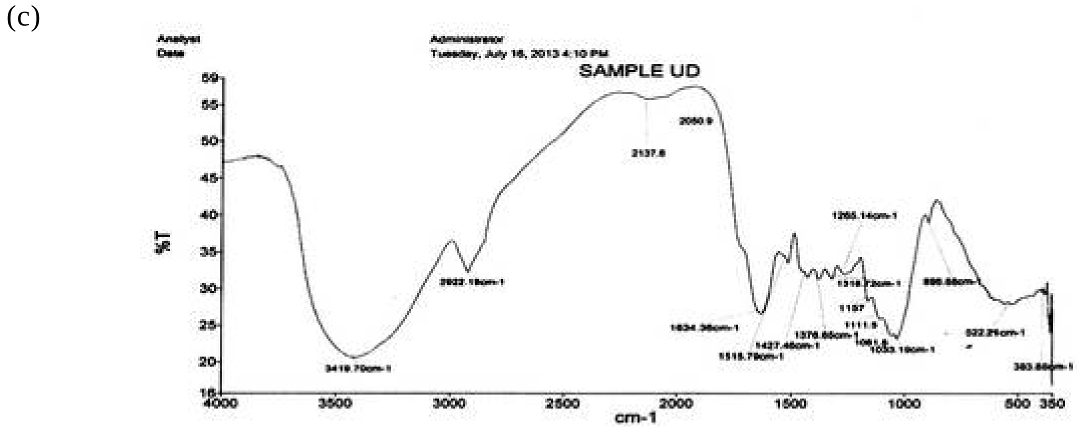


Figure 2. FT-IR spectrum of UCPS loaded with metal (a) Pb^{2+}, (b) Cu^{2+} and (c) Cd^{2+}.

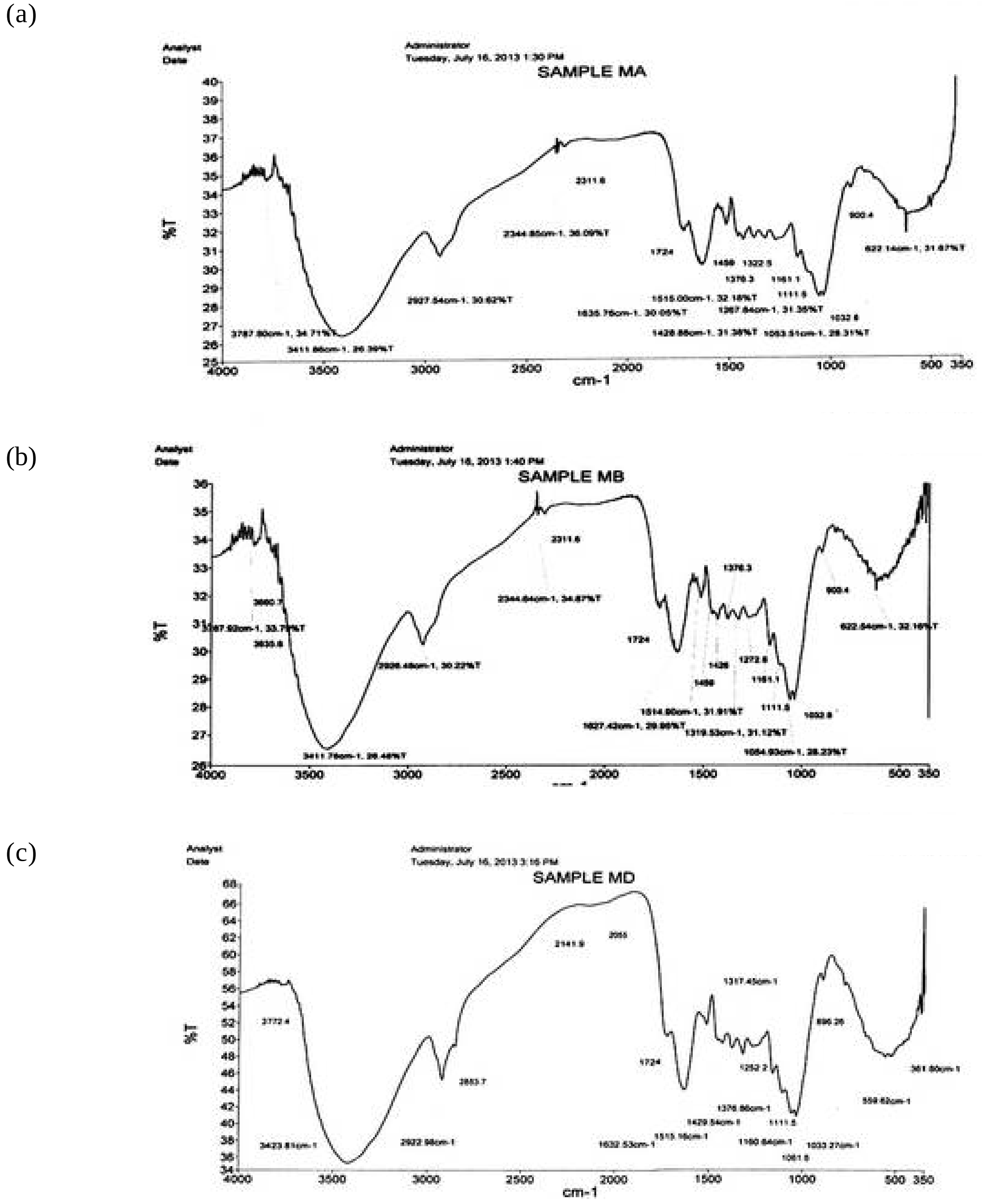


Figure 3. FT-IR spectrum of MCPS loaded with metal (a) Pb^{2+}, (b) Cu^{2+} and (c) Cd2+.

However, with a further increase in pH, the formation of anionic hydroxide complexes decreased the concentration of free cations (Pb^{2+}, Cu^{2+} and Cd^{2+}) and thereby the biosorption capacity of Cd^{2+} decreased. Figure 4 showed that modified cocoa pod shell adsorbed Pb^{2+} ions better than the unmodified cocoa pod shell. Lead biosorption increased significantly between pH 3 and 5. This implies that the –COOH group on the MCPS could have contributed to the adsorption of Pb^{2+} ions from aqueous solution by complexing with the Pb^{2+} ions through the lone pairs of electron on the oxygen atom of the –COOH group. Similar results were reported in literature for different biomass materials [26, 28].

The biosorption capacities of copper from water onto UCPS were increased from 2.686 mg/g to 4.835 mg/g with the increase in pH from 2 to 7 while for MCPS increased from 4.397 to 4.461 mg/g. Copper biosorption increased significantly between pH 2 to pH 7. This was probably due to the availability of Cu^{2+}, $Cu(OH)^+$, and $Cu_2(OH)^{2+}$ species for biosorption as pH increased according to the report by Du *et al* [29]. Above pH 7, the copper begins to precipitate as $Cu(OH)_2$ so, the removal was not completely by biosorption [30]. Similar results have been reported in the literature [24, 31, 32]. Figure 4 showed that the optimum pH for cadmium removal from aqueous solution was pH 4. This study is in agreement with the results previously reported by other authors [3, 28, 33]. From this study, the UCPS adsorbed Cu^{2+} and Cd^{2+} ions better than the MCPS, probably due to the inability of these ions to displace H^+ from the –COOH group. This is in agreement with the results of Odoemelam *et al* [4]. The modified cocoa pod shell adsorbed Pb^{2+} better than unmodified cocoa pod shell as also observed by Jimoh *et al* [34]. Thus, the citric acid modification of cocoa pod shell increased the binding capacity of Pb^{2+} ions.

Effect of contact time

The amount of Pb^{2+}, Cu^{2+} and Cd^{2+} ions adsorbed by the UCPS and MCPS calculated using equation (1) are presented in Figure 5. The results showed that 45, 180 and 60 minutes were sufficient contact time for UCPS to achieve equilibrium with Pb^{2+}, Cu^{2+} and Cd^{2+}ions respectively. However, there was a slight drop in the amount of metal adsorbed between 45-60 minutes for the two ions Pb^{2+} and Cu^{2+}, hence the trend of sorption capacities remained fairly constant and almost close to each other as time increased. The uptake of Pb^{2+}, Cu^{2+} and Cd^{2+} ions by UCPS at equilibrium were found to be 4.709, 4.997 and 4.358 mg/g at equilibrium contact time of 45, 180 and 60 minutes, respectively. According to Figure 5, the study also show the unmodified cocoa pod shell adsorbed Cu^{2+} ions better than Pb^{2+} and Cd^{2+} ions, although both ions reached equilibrium at the contact time of 45 and 60 minutes respectively, when compared to Cu^{2+} ions which reached equilibrium at the contact time of 180 minutes. Cu^{2+}may have been adsorbed better than $Pb^{2+}$and Cd^{2+} ions because of its small ionic size. This observation has been reported earlier by Abia *et al* [35], Horsfall *et al* [36], and Egila *et al* [37]. Therefore, the smaller the ionic size, the greater its affinity to reaction sites.

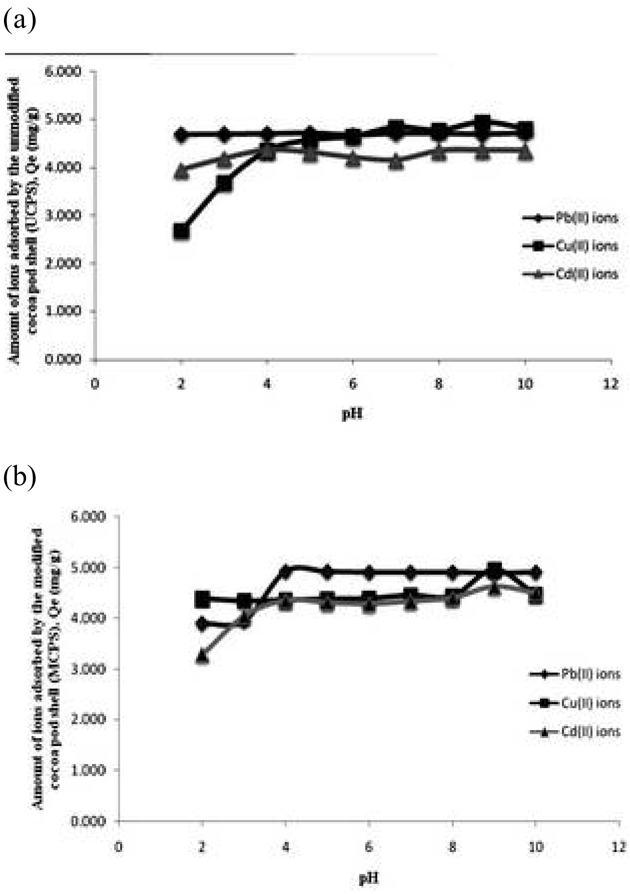
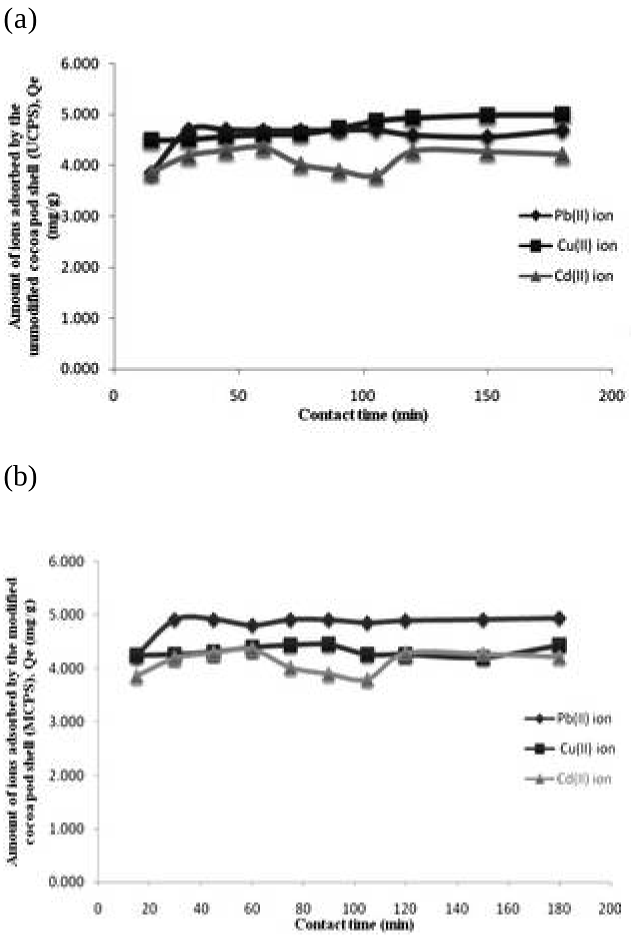


Figure 4. Effect of pH on the biosorption of Pb^{2+}, Cu^{2+}, and Cd^{2+} ions on (a) UCPS and (b) MCPS.

From Figures 5, there was rapid uptake of the metal ions during the first 15 minutes of agitation after which the rate of adsorption became slower. The uptake of Pb^{2+}, Cu^{2+} and Cd^{2+} ions by MCPS was found to be 4.919, 4.445 and 4.355 mg/g at equilibrium contact time of 45 minutes, 60 minutes and 90 minutes for Pb^{2+}, Cu^{2+} and Cd^{2+}ions, respectively. This suggested large number of vacant active binding sites available at the first phase of experiment and large amount of Pb^{2+}, Cu^{2+} and Cd^{2+}ions were bound rapidly to the cocoa pod shell at a faster adsorption rate. The binding site shortly became limited and the remaining vacant surface sites were difficult to be accessed by Pb^{2+}, Cu^{2+} and Cd^{2+} ions due to the formation of repulsive forces between the ions on the solid surface and the ones in the liquid phase. The results showed that for an initial concentration of 100 mg/L of Pb^{2+}, Cu^{2+} and

Cd^{2+} ions, there was a progressive increase in the amount of metal ions bound as the contact time increased for both UCPS and MCPS. This trend has also been reported for the removal of Pb^{2+}, Cu^{2+} and Cd^{2+} ions from aqueous solution by agricultural wastes: rice husks [26], crab shell [31], Neem oil cake [33], *Gmelina arborea* leave [34], mango stone and cocoa pod [3]



Figures 5. Effect of contact time on the biosorption of Pb^{2+}, Cu^{2+}, and Cd^{2+} ions on (a) UCPS and (b) MCPS.

Furthermore, Figures 5 show clearly that MCPS gave a better adsorption of Pb^{2+} than Cu^{2+} and Cd^{2+} ions. This may be due to the fact that the carboxyl groups on the biosorbent surface contributed by the citric acid chelate the metal ions, thereby improving the adsorption of Pb^{2+} on MCPS. Thus, the acid modification increased the binding capacity of the cocoa pod shell for the Pb^{2+} ions. This finding agrees with Jimoh *et al* [34] which reported that the modified biosorbent adsorbed Pb^{2+} than Cu^{2+} ions. The UCPS gave a better adsorption for Cu^{2+} than Pb^{2+} and Cd^{2+} ions. This study agrees with Odoemelam *et al* [4]. Nonetheless, maximum equilibrium capacity was achieved by the cocoa pod shell (UCPS and MCPS) except for Cu^{2+} on UCPS.

Biosorption isotherm models

The equilibrium study is an important aspect of biosorption process as it reveals the biosorption capacity of the biosorbent and as well, describes the surface properties and affinity of the biosorbent. The isotherms that are most conveniently used for describing the biosorption of metal ions from aqueous solution include the Langmuir, Freundlich, Temkin, and Dubinin-Radushkevich isotherms. These four isotherms were used to explain the performance of the biosorbents and the equilibrium distribution of metal ions between the biosorbent and the metal ion solution and also to estimate the biosorbent efficiency.

Langmuir biosorption isotherm model was successfully adopted for homogeneous biosorption and was used successfully in monomolecular adsorption process. The Langmuir isotherm is assumed valid for monolayer sorption on a surface containing a finite number of binding sites. It assumes uniform energies of sorption on the surface and no transmigration of sorbate in the plane of the surface.

The Langmuir equation is:

$$q_e = \frac{q_{\max} b C_e}{1 + b C_e} \qquad \text{. . . . (2)}$$

The Lineweaver-Burk linearized form of the equation is shown below:

$$\frac{1}{q_e} = \left(\frac{1}{b q_{\max}}\right) \frac{1}{c_e} + \frac{1}{q_{\max}} \qquad \text{. . . . (3)}$$

where, q_e is the biosorption capacity (mg/g), q_{max} is the Langmuir monolayer biosorption capacity (mg/g), C_e is the concentration of the solute in the bulk solution (mg/L) at equilibrium and b is the Langmuir isotherm constant (L/g) and it is related to the free energy of biosorption.

Table 1 shows good correlation for the biosorption of Pb^{2+}, Cu^{2+} and Cd^{2+} ions on both biosorbents (UCPS and MCPS) with a regression value, R^2, ranging between 0.9646 and 0.9993. This indicates that Pb^{2+}, Cu^{2+} and Cd^{2+} ions on MCPS and UCPS form monolayer coverage over the interface between the biosorbent. It was observed that the Langmuir isotherm gave a good fit for the adsorption of Pb^{2+}, Cu^{2+} and Cd^{2+} ions on MCPS and UCPS. The equilibrium parameter often referred to as dimensionless separation factor which was calculated for the biosorption of the metal ions on UCPS and MCPS showed that the biosorption process was favourable as all the values of R_L were within 0 and 1 ($0 < R_L < 1$). A similar result was presented by Olu-Owolabi *et al* [3]; Adediran *et al* [38]; Ejikeme *et al* [39].

Table 1. Isotherm parameters for Pb^{2+}, Cu^{2+} and Cd^{2+} ions biosorption by UCPS and MCPS.

Model	Pb		Cu		Cd	
	U	M	U	M	U	M
Langmuir						
Q_e(mg/g)	4.62	33.56	5.10	5.40	12.09	4.29
K_L (L/mg)	0.8272	0.0249	0.3835	0.1177	0.0656	0.0969
R^2	0.9769	0.9993	0.9946	0.9646	0.9962	0.9965
R_L	0.1079-0.0119	0.8006-0.2863	0.2068-0.0254	0.4594-0.0783	0.6040-0.1323	0.5079-0.0935
Freundlich						
K_F (mg/L)	1.88	0.81	1.26	0.57	0.75	0.45
n	1.51	1.04	1.56	1.36	1.16	1.57
1/n	0.66	0.96	0.64	0.73	0.86	0.64
R^2	0.9462	0.9986	0.9881	0.9528	0.9891	0.9813
Temkin						
K_T (L/mg)	6.8946	1.673	3.6675	1.2457	1.6186	0.9534
b_T(KJ/mol)	2.019	1.508	2.042	1.987	1.699	2.505
R^2	0.8038	0.9197	0.9416	0.8333	0.9374	0.9205
Dubinin-Radushkevich						
Q_D (mg/g)	3.25	3.04	3.09	2.74	2.89	2.38
B_D (mol^2/J^2)	8×10^{-8}	3×10^{-7}	1×10^{-7}	5×10^{-7}	4×10^{-7}	8×10^{-7}
E_D (KJ/mol)	2.5	1.29	2.24	1.00	1.12	0.79
R^2	0.8177	0.8368	0.8226	0.7707	0.8302	0.7701

U= unmodified; M=modified.

The biosorption capacity, Q_{max} of 4.62, 5.10 and 12.09 mg/g for Pb^{2+}, Cu^{2+} and Cd^{2+}ions respectively show that UCPS sorbed most of Cd^{2+}ions and less of Pb^{2+} ions. The trend in biosorption is in order of $Cd^{2+}>Cu^{2+}>Pb^{2+}$. The result conforms to the report of Olu-Owolabi *et al* [3] and Jimoh *et al* [27]. The Q_{max} of 33.56, 5.40 and 4.29 mg/g for Pb^{2+}, Cu^{2+} and Cd^{2+} ions respectively showed that citric acid modified cocoa pod adsorbed most of Pb^{2+} ions and less of Cd^{2+} ions. Therefore, the biosorption trend is in the order $Pb^{2+}>Cu^{2+}>Cd^{2+}$. More so, the Q_{max} values for Pb^{2+} and Cu^{2+} ions on MCPS (33.56 and 5.40 mg/g) were higher than on UCPS (4.62 and 5.10 mg/g) respectively. Therefore, the citric acid modification of cocoa pod shell improved the biosorption capacity of cocoa pod shell for Pb^{2+} and Cu^{2+}ions while it does not improve the biosorption capacity for Cd^{2+} ions.

Freundlich isotherm is based on multilayer biosorption on heterogeneous surface. Freundlich isotherm model was chosen to estimate the adsorption intensity of the metal ion on the biosorbent surface. The Freundlich equation is given as:

$$q_e = K_F C_e^{1/n} \quad \ldots . (4)$$

and the linearized form of the equation is given as:

$$\log_{10} q_e = \log_{10} K_F + \frac{1}{n}\log_{10} C_e \quad \ldots . (5)$$

where, q_e is the amount of metal ion adsorbed on biosorbent at equilibrium (mg/g), C_e is metal ion concentrations in solution at equilibrium (mg/L), K_F is the Freundlich biosorption constant; it is an indication of the biosorption capacity (mg/g) and *n* is biosorption intensity.

The biosorption of Pb^{2+}, Cu^{2+} and Cd^{2+} ions onto UCPS and MCPS were equally fitted to the Freundlich isotherm. The Freundlich equation parameter, $1/n$ for all metal ions as shown in Table 1 was found to be less than unity, indicating that they have higher biosorption intensity. Based on the R^2 value which ranged from 0.9986 to 0.9462, the linear form of Freundlich isotherm appears to produce a reasonable model for the sorption of the three metalions on UCPS and MCPS. The biosorption capacity values for Pb^{2+}, Cu^{2+} and Cd^{2+} ions using UCPS are 1.88, 1.26 and 0.75 mg/g while MCPS biosorption capacities gave 0.81, 0.57 and 0.45 mg/g for Pb^{2+}, Cu^{2+} and Cd^{2+} ions respectively. The trend in biosorption as seen in Table 1 is in order of $Pb^{2+}> Cu^{2+}> Cd^{2+}$for both MCPS and UCPS. This agrees with Langmuir adsorption isotherm for MCPS.

This isotherm which was first developed by Temkin and Pyzhev in 1940 to describe the adsorption of hydrogen on platinum electrodes within acidic solutions and it was based on the assumption that the heat of adsorption as a function of temperature was linear rather than logarithmic, as implied in the Freundlich equation [40]. The Temkin isotherm equation is as shown in equation 6:

$$q_e = \frac{RT}{b_T}\ln K_T + \frac{RT}{b_T}\ln C_e \quad \text{. . . . (6)}$$

where, T is the absolute temperature in Kelvin, R is the universal gas constant 8.314 Jmol^{-1} K, b_T is the Temkin constant related to heat of sorption (J/mg), and K_T is the Temkin isotherm constant (L/mg). The linear form of Temkin equation is:

$$q_e = \beta \ln \alpha + \beta \ln C_e \quad \text{. . . . (7)}$$

where, $\beta = \frac{RT}{b_T}$ and $\alpha = K_T$ . . . . (8)

The biosorption of Pb^{2+}, Cu^{2+} and Cd^{2+} ions onto UCPS and MCPS were equally described by the Temkin isotherm. The heat of biosorption, b_T, decreased from 2.505 to 1.508 KJ/mol for Cd^{2+} ion on MCPS to Pb^{2+} ion on MCPS respectively as shown in Table 1. The R^2 value ranges from 0.9416 to 0.8038.

The heat of biosorption, b_T, for Pb^{2+}, Cu^{2+} and Cd^{2+} ions on UCPS are 2.019, 2.042 and 1.699 KJ/mol while b_T on MCPS gave 1.508, 1.987 and 2.505 KJ/mol for Pb^{2+}, Cu^{2+} and Cd^{2+} ions, respectively. It can be seen that the trend in heat of biosorption as seen in Table 1 is in the order Cu^{2+}> Pb^{2+}> $Cd^{2+}$for MCPS while that of UCPS is Cd^{2+}> Cu^{2+}> Pb^{2+}. The trend of b_T obtained with the metal ions on UCPS agrees with the trend of Q_{max} obtained in Langmuir adsorption isotherm for UCPS.

Dubinin-Radushkevich (DR) equation is a mathematical model capable of describing the (q_e) vs (C_e) relationship as observed experimentally. Dubinin-Radushkevich isotherm was used to determine the characteristic porosity of the biomass and the apparent free energy of biosorption. D-R isotherm is more general as it does not assume a homogeneous surface or constant biosorption potential but is based on the heterogeneous nature of the sorbent surface. The D-R isotherm can be written as:

$$Q_e = Q_D e^{-K_{DR}\varepsilon^2} \quad \text{. . . . (9)}$$

where Q_D is the maximum biosorption capacity (mg/g), K_{DR} is the Dubinin-Radushkevich isotherm constants related to the mean free energy of biosorption (mol^2/J^2) and is the Polanyi potential (J/mol), which is related to the equilibrium concentration C_e (mg/g) as follows:

$$e = RT\ln\left(1 + \frac{1}{C_e}\right) \quad \text{. . . . (10)}$$

The linear form of the model is represented as follows:

$$\ln Q_e = \ln Q_D - K_{DR}\varepsilon^2 \quad \text{. . . . (11)}$$

The linear Dubinin-Radushkevich isotherm was plotted for the biosorption of Pb^{2+}, Cu^{2+} and Cd^{2+} ions on UCPS and MCPS and the Dubinin-Radushkevich isotherm constants are shown in Table 1. The data for the plots revealed that the linearized Dubinin-Radushkevich isotherm provides a good description of the data for the metal ions with a regression value,, ranging from 0.7701 to 0.8368. Table 1 revealed that the theoretical biosorption capacity, Q_D, were lower than the experimental biosorption capacity values.

The mean free energy of biosorption, $E_D$$Pb^{2+}$, Cu^{2+} and Cd^{2+} ions on UCPS and MCPS range from 0.79 to 2.50 KJ/mol. It can be inferred that the trend in biosorption energy as seen in Table 1 is in order of Pb^{2+}>Cu^{2+}>Cd^{2+} for both UCPS and MCPS. The biosorption energy, obtained for Pb^{2+}, Cu^{2+} and Cd^{2+} ions compares favourably with those obtained from the Temkin isotherm. This finding agrees with the trend obtained for linearized Freundlich isotherm for both UCPS and MCPS and linearized Langmuir isotherm for MCPS. The mean free energy of biosorption gives information about biosorption mechanism, physiosorption or chemisorption [41]. If E_D value is between 8 and 16 KJ/mol, the biosorption process follows chemisorption and if E < 8 KJ/mol, the biosorption process is of physiosorption [41]. The biosorption energy, E_D, in this study ranged from 0.79 to 2.50 KJ/mol. Therefore for a biosorption process whose E_D is less than 8 KJ/mol, the process is likely to follow physiosorptionas observed for the sorption of Pb^{2+}, Cu^{2+} and Cd^{2+} ions onto UCPS and MCPS [41].

Biosorption kinetics

The rate of biosorption can be described by the kinetic studies and this rate controls the equilibrium time. These kinetic models are useful for the design and optimization of effluent treatment models. Pseudo-first order, Pseudo-second order, Elovich and Intra-particle diffusion kinetic models were analysed for the mechanism of metal ions biosorbed by cocoa pod shell.

The Lagergren's pseudo-first order rate equation is generally expressed as:

$$\frac{dq_t}{dt} = K_1(q_e = q_t) \quad \text{. . . . (12)}$$

The integrated linear form of the model can be written as:

$$\log_{10}(q_e - q_t) = \log_{10} q_e - \frac{K_1 t}{2.303} \quad \text{. . . . (13)}$$

where, q_t is the biosorption capacity at time t (mg/g),

Table 2. Kinetics parameters for the biosorption of Pb^{2+}, Cu^{2+} and Cd^{2+} ions by cocoa pod shell (UCPS and MCPS).

Ions	Pb^{2+}		Cu^{2+}		Cd^{2+}	
Model	**U**	**M**	**U**	**M**	**U**	**M**
Pseudo-first order kinetics						
Q_e(mg/g)	1.96	1.10	1.65	17.90	1.03	1.45
K_1 (min)	-0.02372	-0.0322	-0.0290	-0.0364	-0.0131	-0.0083
R^2	0.8489	0.9496	0.7780	0.7405	0.5098	0.7847
Pseudo-second order kinetics						
Q_e(mg/g)	4.68	4.96	5.11	4.33	4.22	3.91
h_0(mg/g/min)	8.15	3.67	1.02	55.87	2.30	8.41
K_2(g/mg/min)	0.3729	0.1488	0.0392	2.9759	0.1291	0.5486
R^2	0.999	0.9998	0.9988	0.9973	0.9928	0.9922
$Q_{e\ experimental}$ (mg/g)	4.71	4.92	5.00	4.44	4.36	4.36
Elovich						
α (mg/g.min)	6.42×10^6	6.30×10^7	2.47×10^6	4.71×10^{16}	1.1×10^{25}	6.8592
β (g/mg)	4.68	5.1099	4.31	10.26	16.03	1.93
R^2	0.3901	0.5145	0.8157	0.8029	0.0547	0.7283
Intra-particle diffusion						
K_d(g/mg/min)	0.0436	0.0428	0.0625	0.0237	0.0143	0.0932
C (mg/g)	4.20	4.45	4.18	4.17	3.99	3.678
R^2	0.2481	0.377	0.9068	0.7013	0.0437	0.6969

U = Unmodified; M = modified.

q_e is the biosorption capacity at equilibrium (mg/g) and K_1 is the rate constant (min^{-1}) of pseudo-first order biosorption.

The rate constants, predicted equilibrium uptakes and the corresponding correlation coefficient for Pb^{2+}, Cu^{2+} and Cd^{2+} ions were computed into Table 2. The R^2 values in Table 2 reveals that the biosorption mechanisms of Pb^{2+}, Cu^{2+} and Cd^{2+} ions on both biosorbents (UCPS and MCPS) do not follow the pseudo-first order kinetic model. For all the metal ions, the calculated Q_e is not equal to the experimental Q_e, suggesting the inadequacy of pseudo-first order model to fit the kinetic data for the biosorption of the metal ions. The differences between the Q_e values might have been due to the time lag, possibly due to a boundary layer or external resistance at the beginning of the sorption process [42]. Vijayaraghavan *et al* [31] reported that in most cases in the literature, the pseudo-first order model does not fit the kinetic data well for the whole range of contact time, and generally underestimate the Q_e values even when the R^2 value is relatively high.

The pseudo-second order kinetics can be expressed as:

$$\frac{dq_t}{dt} = K_2(q_e = q_t)^2 \quad \ldots . (14)$$

The linearized form of the above model is:

$$\frac{t}{q_t} = \frac{t}{q_e} + \frac{1}{K_2 q_e^2} \quad \ldots . (15)$$

where, q_e is the amount of metal ion biosorbed per unit mass of biosorbent at equilibrium (mg/g), is the amount of the metal ion biosorbed at contact time *t* (mg/g) and K_2 is the rate constant of pseudo second order biosorption mg/gmin^{-1}. The pseudo-second order model is based on the sorption capacity on the solid phase, contrary to other well established models, it predicts the behaviour over the whole range of studies and it can be used to determine whether the rate determining step involves chemisorption [42]. The R^2 values as shown in Table 2 are very high and the range is 0.9928 to 0.9998. The values of R^2 show that the pseudo-second order model equation gave a better fit to the biosorption process than the pseudo-first order. Also, the theoretical Q_e values were closer to the experimental Q_e values. In this model, the rate-determining step is a biosorption mechanism involving chemisorption, where metal removal from solution is due to physicochemical interactions between biomass and metal solution [43]. Similar results have been reported by Hadi *et al* [32]; Odoemelam *et al* [4]; Olu-Owolabi *et al* [3]; Rao and Khan [33].

The Elovich equation is given as:

$$\frac{dq_t}{dt} = \alpha e^{-\beta} \quad \ldots . (16)$$

The linear form is as shown in equation (17):

$$q_t = \frac{1}{\beta}\ln(\alpha\beta) + \frac{1}{\beta}\ln(t) \quad \ldots .\,(17)$$

where, α is the initial biosorption rate ($mg/gmin^{-1}$) is the desorption rate constant ($mg/gmin^{-1}$). Table 2 showed that the regression value, R^2, ranges between 0.0547 and 0.8157. This implies that Elovich model does not satisfactorily fit the data.

The intra-particle diffusion model is expressed as:

$$q_t = K_d t^{1/2} + C \quad \ldots .\,(18)$$

where, K_d is the intra-particle diffusion rate constant , q_t is the amount of metal ion at time t (mg/g) and C is the intercept (mg/g). Pb^{2+} ions had the highest C values signifying high biosorption capacity for ions with the biosorbents and in the order $Pb^{2+} > Cu^{2+} > Cd^{2+}$ for both UCPS and MCPS respectively.

This trend agrees with the biosorption trend given by Freundlich model for both MCPS and UCPS and the trend given by Langmuir model for MCPS. It has also been reported that at a high temperature, the thickness of the boundary layer decreases due to the increased tendency of the metal ions to escape from the biomass surface to the solution phase which results in a decrease in biosorption as the temperature increases. However, R^2 values from Table 2 shows fairly high values by the MCPS while UCPS displayed very low R^2 values. In general terms, the sorption process did not give a satisfactory fit with intra-particle diffusion model and that particle diffusion is not the only major process in the rate determining step.

Biosorption thermodynamics

Normally, temperature stimulates the molecules, functional groups and surface morphology of the biosorbent and metals during the biosorption process [25]. The standard free energy change (ΔG^{ϕ}) was calculated using the expression:

$$\Delta G^{\phi} = RT\ln K_C \quad \ldots .\,(19)$$

Equation (19) is an important equation used in biosorption thermodynamics to predict the feasibility of biosorption process. At constant temperature, the thermodynamic parameters standard free energy change (ΔG^{ϕ}) is related to standard enthalpy change (ΔG^{ϕ}) and standard entropy change (ΔS^{ϕ}) through equation (20):

$$\Delta G^{\phi} = \Delta H^{\phi} - TS^{\phi} \quad \ldots .\,(20)$$

The thermodynamics parameters like standard enthalpy change (ΔH^0) and standard entropy change (ΔS^0) can be obtained from the Van't Hoff equation:

$$\ln K_C = \frac{\Delta H^{\phi}}{RT} + \frac{\Delta S^{\phi}}{R} \quad \ldots .\,(21)$$

where, T is the temperature in Kelvin, R is the ideal gas constant (8.314 $J/molK^{-1}$), is the thermodynamic

Table 3. Thermodynamic parameters for the biosorption of Pb^{2+}, Cu^{2+} and Cd^{2+} ions by UCPS and MCPS.

Metal ion		T (K)	$\frac{1}{T}(K^{-1})$	C_e	K_C	log K_C	ΔG^{ϕ} ($KJmol^{-1}$)	ΔH^{ϕ} ($KJmol^{-1}$)	ΔS^{ϕ} (J/mol/K)
Pb^{2+}	**U**	303	0.00319	3.66	26.32	1.4203	-8.103	70.06	249.64
		323	0.00310	2.48	39.32	1.5946	-9.097		
		333	0.00300	0.77	128.9	2.1102	-12.038		
	M	303	0.00319	3.18	30.45	1.4835	-8.463	71.29	254.51
		323	0.00310	2.35	41.55	1.6186	-9.234		
		333	0.00300	0.65	152.86	2.1843	-12.461		
Cu^{2+}	**U**	303	0.00330	7.85	11.74	1.0696	-6.102	-9.08	-9.756
		313	0.00319	9.42	9.62	0.9830	-5.608		
		333	0.00300	10.70	8.35	0.9215	-5.257		
	M	303	0.00330	9.39	9.65	0.9845	-5.617	-10.66	-16.360
		323	0.00310	11.95	7.37	0.8674	-4.948		
		333	0.00300	13.17	6.59	0.8191	-4.673		
Cd^{2+}	**U**	303	0.00319	6.94	13.41	1.1274	-6.432	-32.59	-83.265
		323	0.00310	12.68	6.89	0.8380	-4.781		
		333	0.00300	13.69	6.30	0.7997	-4.562		
	M	303	0.00330	25.40	2.94	0.4679	-2.669	-3.99	-4.135
		323	0.00310	26.72	2.74	0.4382	-2.450		
		333	0.00300	28.35	2.53	0.4027	-2.297		

U = unmodified; M = modified.

equilibrium constant, ΔS^0 is the standard entropy change and ΔH^0 is the standard enthalpy change.

Table 3 showed that the free energy change (ΔG^{ϕ}) values decreased from -8.103 to -12.038 KJ/mol and -8.463 to -12.461 KJ/mol for Pb^{2+} ion on UCPS and MCPS respectively. The ΔG^{ϕ} value of the processes decrease with increasing temperature and since $\Delta G^{\phi} < 0$, then the biosorption process is always feasible and spontaneous. More so, ΔH^{ϕ} values obtained for Pb^{2+} ion on UCPS and MCPS are +70.057 and +71.294 $\frac{\text{KJ}}{\text{mol}}$ respectively. The increase in sorption of Pb^{2+} ion with temperature might have been due to change in pore size and enhanced rate of intra particle diffusion. The positive value of ΔS^{ϕ} shows; that there is an increase in randomness at the solid/solution interface during the sorption of Pb^{2+} ion [33]. The result suggests that biosorption for Pb^{2+} ion on UCPS and MCPS was spontaneous, feasible and endothermically controlled and showing a decrease in the degree of disorderliness of the biosorption system.

Furthermore, Table 3 revealed that ΔG^{ϕ} values of Cu^{2+} and Cd^{2+} ions on UCPS ranges from -6.102 to -5.257 $\frac{\text{KJ}}{\text{mol}}$ and -6.431 to -4.561 $\frac{\text{KJ}}{\text{mol}}$ while ΔG^{ϕ} values of the same ions on MCPS ranges from -2.661 to -2.297 $\frac{\text{KJ}}{\text{mol}}$ respectively. Since, $\Delta G^{\phi} < 0$, the biosorption process is always feasible and spontaneous. The negative values of ΔH^{ϕ} for Cu^{2+} and Cd^{2+} ions suggest the exothermic nature of sorption and occur with a decrease in disorder at solid-liquid interface. The negative value of ΔS^{ϕ} as shown in Table 3 depicts that the biosorption was enthalpy driven and spontaneous in nature during the sorption of Cu^{2+} and Cd^{2+} ions. Therefore, the sorption for both cations was spontaneous, feasible and exothermically controlled.

The values of ΔG^{ϕ} are presented in Table 3 ranges between -2.297 to -12.461. In general, it is of note that $\Delta G^{\phi} \leq -20$ KJ/mol are consistent with electrostatic interaction between charged molecules and surface indicative of physiosorption while $\Delta G^{\phi} > -40$ KJ/mol involve chemisorption [44]. Therefore, the order of magnitude of the values indicates physiosorption mechanism for the adsorption of metal ions onto UCPS and MCPS.

Conclusion

The study reveals that the optimum binding of Pb^{2+}, Cu^{2+} and Cd^{2+} ions to the cocoa pod shell (UCPS and MCPS) was achieved at a pH of 5, 7 and 4 respectively. The equilibrium data for Pb^{2+}, Cu^{2+} and Cd^{2+} ions was better described by the Langmuir equation. Citric acid modified cocoa pod shell bind more Pb^{2+} ions than Cu^{2+} and Cd^{2+}. The trend in biosorption of Pb^{2+}, Cu^{2+} and Cd^{2+}ions on UCPS is in the order $Cd^{2+} > Cu^{2+} > Pb^{2+}$. The trend in biosorption of Pb^{2+}, Cu^{2+} and Cd^{2+} ions on MCPS is in the order $Pb^{2+} > Cu^{2+} > Cd^{2+}$. The biosorption energy,, which ranged between 0.79 and 2.50 KJ/mol was less than 8 KJ/mol, therefore, the process is likely to follow physiosorption (physical biosorption) for the biosorption of Pb^{2+}, Cu^{2+}, and Cd^{2+} ions onto UCPS and MCPS. The sorption of Pb^{2+}, Cu^{2+}, and Cd^{2+} ions on UCPS and MCPS conformed to pseudo-second order kinetic model. It can be inferred that cocoa pod shell; an agricultural waste is a good, cost-effective and naturally abundant biosorbent for the removal of heavy metal ions (especially Pb^{2+}, Cu^{2+} and Cd^{2+}) from aqueous solution. Also citric acid modified cocoa pod proved to be more effective for removing lead from aqueous solution.

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