Equilibrium and Kinetic Studies of Cu (II), Cd (II), Pb (II) and Fe (II) Adsorption from Aqueous Solution Using Cocoa (*Theobroma cacao*) Pod Husk

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ABSTRACT: The potentials of cocoa pod husk to adsorb Cu (II), Cd (II), Pb (II) and Fe (II) ions from aqueous solutions was investigated in a batch system. The effects of contact time, initial metal ion concentration and adsorbent dose on the adsorption capacity of the adsorbent were examined. The percent adsorbed increased as initial metal ion concentration, contact time and adsorbent dose was increased until equilibrium was reached. Langmuir isotherm and pseudo-second order models were used to analyse the equilibrium and kinetic experimental data respectively. Equilibrium experimental data of Cu (II), Cd (II), Pb (II) and Fe (II) adsorption onto cocoa pod fitted well to Langmuir model and the kinetic data also fitted well to the pseudo-second order model, as indicated by the correlation coefficients. The maximum sorption capacity (q_{max}) ranged as 4.16, 4.42, 4.69 and 4.83 mg/g for Fe (II), Cd (II), Cu (II) and Pb (II) respectively. This study demonstrated that the waste cocoa pod could be used as a potential adsorbent for toxic metals such as Cu (II), Cd (II), Pb (II) and Fe (II).

Heavy metals have been identified as very dangerous class of environmental pollutants. Heavy metals are natural elements that have been extracted from the earth and harnessed for industrial raw materials and products (Kanamadi *et al*., 2006). The increased use of metals and chemicals in industries has resulted in the generation of large quantities of effluents containing high levels of toxic heavy metals (Abia and Asuquo, 2006; Liang *et al*., 2007). Among these heavy metals, copper, cadmium, lead and iron are notable for their wide environmental dispersion from various industrial activities. This in effect increases their tendency to accumulate in selected tissues of the human body and their overall potential to be toxic even at relatively low levels of exposure (Kanamadi *et al*., 2006; Abia and Asuquo, 2006). Cadmium has been implicated in kidney dysfunction, hepatic damage and hypertension (Klaassen, 2001). Toxic levels of lead affect neurobehavioral development, brain function (Goldstein, 1990; Dietrich *et al*., 1990) and have been associated with encephalopathy, seizures and mental retardation (Schumann, 1990). Excess copper accumulates in the liver, brain, skin, pancreas and myocardium (Davis, 2000) and the most toxic form of copper is thought to be Cu (I) (Ho *et al*., 2002). Iron is a toxic heavy metal that is commonly found in industrial effluents. The presence

of iron in water results in undesirable color, odour and taste which makes water unfit for industry use and domestic consumption (Pavani and Sunil Kumar, 2013). The effects of iron exposure on human health include respiratory problems, heart attack, seizures, tissue damage and depression (Kamarudzaman *et al.,* 2013).

Following the need to remove Cu (II), Cd (II), Pb (II) and Fe (II) from industrial wastewater effluents to reduce environmental pollution, various conventional methods have been developed over the years. These methods include chemical precipitation, ion exchange, oxidation and reduction, fixation or cementation and solvent extraction (Kratochvil *et al*., 1998; Acosta-Rodriquez *et al*., 2018). These methods are economically unfavourable or technically complicated (Idris *et al*., 2012) and are used only in special cases of wastewater treatment (Kratochvil et al., 1998; Sharma, 2003). Recently, attention has been directed towards biosorption as a new technology for removing toxic metals from wastewaters (Acosta-Rodriquez *et al*., 2012). This is based on the binding capacities of various biological materials (Kanamadi *et al*., 2006). Biosorption technique is one of the preferred methods for the removal of heavy metals because of its efficiency and

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low cost (Li *et al*., 2007). Biomass viability does not affect the metal uptake. Therefore, any active metabolic uptake process is currently considered to be a negligible part of biosorption (Acosta-Rodriquez *et al*., 2012). Recent studies have shown that heavy metals can be removed using biosorption materials, like agricultural by-products (Gardia-Torresday *et al*., 1999; Sun and Shi, 1998); hazelnut shell (Comino *et al*., 2000); orange waste (Perez-Marin *et al.,* 2007); tamarind peel (Acosta et al., 2010); groundnut shell (Idris *et al*., 2012; Choudhury et al., 2012) ; maize cob and husk (Igwe and Abia, 2003); modified corn stalks (Chen *et al*., 2011); boiler fly ash (Okoronkwo *et al*., 2008; Okoronkwo *et al*., 2011); sawdust (Vinodhini and Das, 2010); *Zea mays* Tassel (Zvinowanda *et al*., 2010) and so on. Cocoa pod husk has also been used for the sorption of Al (III), As (V), Cr (VI) and Ni (II) (Igwe, 2011). The major advantages of these agricultural by-products are that they are economical, eco-friendly, abundant, renewable and more efficient (Manject *et al.,* 2009). Therefore, the present research studied the removal of Cu (II), Cd (II), Pb (II) and Fe (II) from synthetic aqueous wastewater using cocoa (*Theobroma Cacao*) pod husk by investigating some process conditions.

MATERIALS AND METHODS

Preparation of Synthetic Wastewater: Stock solutions (1000 mg/L) of Cu (II), Cd (II), Fe (II) and Pb (II) metal ions were prepared by dissolving 3.931 g of $CuSO_4.5H_2O$; 6.84 g of $CdSO_4.8H_2O$; 4.973 g of $Fe_2SO_4.7H_2O$ and 1.831 g of $PbOOCCH_2.3H_2O$ respectively in 1 L of de-ionised water. Serial dilutions were made from the respective stock solutions to obtain the working solution concentrations.

Preparation of Biosorbents: Cocoa pod husks were obtained from a cocoa farm in Isuikwuato L.G.A of Abia State, Nigeria. The cocoa pod husks were washed with distilled water, cut into small pieces and dried under the sun for 15 days. The dried cocoa pod husks were milled in a grinder. It was sieved through 1000 µm sieve size and then through 500 µm sieve size. The adsorbents retained on the 500 µm size were stored in an air-tight plastic container for further use as the adsorbent without any chemical treatment.

Biosorption Experiment: Batch biosorption experiments were carried out using modified method by Qaiser et al., (2007). Average values of all experiments were used in all calculations. To find the equilibrium time for sorption of Cu (II), Cd (II), Pb (II) and Fe (II) on cocoa pod husk, 1g of the prepared biosorbent, cocoa pod husk, was mixed with 50 mL

of Cu (II), Cd (II), Pb (II) and Fe (II) 100 mg/L solutions separately. The mixtures were shaken with a mechanical shaker for different time intervals of 10 to 60 minutes. The samples were filtered thereafter with a suction pump.

The effect of biosorbent dose was determined by varying the adsorbent loading from 1 g to 12 g in 100 mL of the metal ions solutions of 100 mg/L initial concentration and the biosorption experiment carried out using constant metal ion-substrate contact time of 90 min at ambient temperature of 35 °C. At the end of the experiments, the samples were filtered with a suction pump.

The initial concentrations of the metal ions solutions were varied from 10 mg/L to 100 mg/L. Using an adsorbent dose of 1 g, constant pH of the solutions of 7.5, and constant metal ion-substrate contact time of 90 mins, the biosorption experiment was carried out to determine the effect of initial metal ion concentration on the adsorption. The samples were filtered thereafter with a suction pump. A control flask containing only the Cu (II), Cd (II), Pb (II) and Fe (II) solutions with no adsorbent were used to determine the initial concentrations of the metal solutions and eliminate any sorption that might have occurred by the glass wares.

Analytical Method: The filtrates in all the experimental runs and the control were analyzed using a Shumadzu 6650 AAS model to determine the concentration of metal left after sorption.
The amount of metal removed was calculated by:

$$\% \text{ Removal } = 100 \times (C_i - C_e)/C_i \quad (1)$$

Where C_i= Initial concentration and C_e= Final concentration. The sorption capacity 'q' was calculated with the formula:

$$q = V(C_i - C_e)/m \qquad (2)$$

Where V = Volume of the solution; C_i = Initial concentration; C_e = Final concentration and m = Dry weight of the biosorbent.

RESULTS AND DISCUSSION

Effect of Adsorbent Dose: The effect of adsorbent dose on Cu (II), Cd (II), Pb (II) and Fe (II) adsorption onto cocoa pod husk are shown in Figure 1. It could be observed that the percentage removal of each metal increased rapidly to 1 g after which further

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increase in adsorbent dose showed no significant effect on the percentage removal. However, for Cu (II) there was a slight decrease between 1 g to 4 g after which percentage removal became fairly constant. Initial increase in adsorption with adsorbent dose can be attributed to increased adsorption surface area and availability of more adsorption sites (Wasewar et al., 2009). The percentage adsorbed remain fairly constant even at increasing adsorbent dosage could be attributed to small concentration of metal ions remaining in solution available for biosorption and exhaustion of the adsorbents as seen in Figure 1. Similar results have been reported (Choudhury et al., 2012; Nameni *et al.*, 2008; Elaigwu *et al.*, 2010; Igwe *et al.,* 2011). Saueprasearsit et al., (2010), reported that increasing adsorbent dose increases amount adsorbed but decreases adsorption density. This is mainly because of unsaturation of adsorption sites (Pehilivan et al., 2008). This could also be due to particle interaction such as aggregation resulting from high adsorbent dose. This leads to decrease in total surface area of the adsorbent and an increase in diffusion path length (Shukla *et al.,* 2002). Hence, the decrease in adsorption at high adsorbent dose.
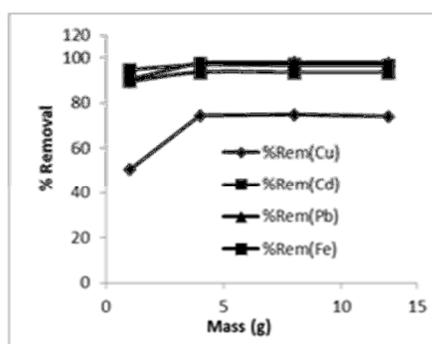

Fig 1: Effect of adsorbent dose on adsorption onto cocoa pod husk

Effect of Contact Time: Biosorption of Cu (II), Cd (II), Pb (II) and Fe (II) at various contact time of 10 to 60 mins onto cocoa pod husk are shown in Figure 2. The initial adsorptions for the four metals were rapid within 10 mins after which change in contact time yielded no significant change in the adsorption. However, the percentage removal of Cu (II), Cd (II) and Pb (II) were higher than Fe (II). The initial rate of adsorption of the metals may be explained by the fact that initially for adsorption, large vacant sites were available which slowed down later due to exhaustion of remaining surface site (Saravanane *et al.*, 2002) and sorption process could be said to have attained equilibrium. Further increase in contact time did not increase the percent (%) adsorption capacity

of the metal ions as seen in Figure 2. Hussain et al., (2009) reported initial rapid adsorption and attainment of equilibrium at about 50 mins for sorption of Pb (II) using non-living biomass of *Spirogyra neglecta.* Similar results have also been reported (Okoronkwo et al., 2008; Okoronkwo et al., 2011). Zvinowanda et al (2009) in the removal of Cr (VI) using maize tassel reported that equilibrium was established at the surface of the adsorbent after sometime or it can be spontaneous. Hassan et al., (2008) in removal of Cr (VI) using maize bran reported that the extent of sorption increased rapidly in the initial stages but became slow in the later stages until the attainment of equilibrium and that equilibrium time was independent of initial sorbate concentration. Also, the rate of biosorption of metal ions has been reported to be biphasic (Liu et al., 2006). The initial fast phase occurs due to surface adsorption on the biomass. The subsequent slow phase occurs due to diffusion of the metal ions into the inner part of the biomass (Babarinde et al., 2007).
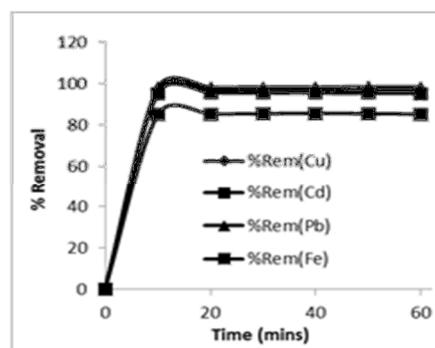

Fig 2: Effect of contact time on adsorption of metal ions onto cocoa pod husk.

Effect of Initial Metal Ion Concentration: The effect of initial metal ion concentration of Cu (II), Cd (II), Pb (II) and Fe (II) adsorption onto cocoa pod husk are shown in Figure 3. From the plots, it could be seen that the percentage removal of the four metals increased with increase in initial metal ion concentration. The increase was rapid from 10 mg/L to 20 mg/L for all metal ions. For Cu (II), Pb (II) and Fe (II), the increase slowed down from 20 mg/L to 30 mg/L. For Fe (II) and Pb (II), there was a slight decrease from 30 mg/L to 40 mg/L after which further increase in metal ion concentration had no significant effect on the percentage removal. As initial metal ion concentration increased from 20 mg/L and 30 mg/L for Cd (II) and Fe (II) respectively, there was no significant change in the percentage removal. The initial increase in the percentage removal could be attributed to the decrease in resistance for the uptake of solute from

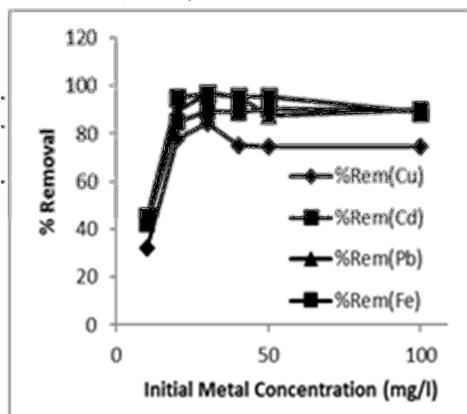solution with increase in metal concentration (Wasewar *et al.*, 2009).

Fig 3: Effect of initial metal ion concentration on adsorption onto cocoa pod husk

Also, this sorption characteristic indicated that surface saturation was dependent on the initial metal ion concentration (Babalola et al., 2008). At low concentrations, sorption sites took up the available metals quickly. But at higher concentrations, metal ions needed to diffuse to the biomass surface by intraparticle diffusion and greatly hydrolyzed ions will diffuse at a slower rate (Zafar *et al.*, 2006), hence reduced sorption rate.
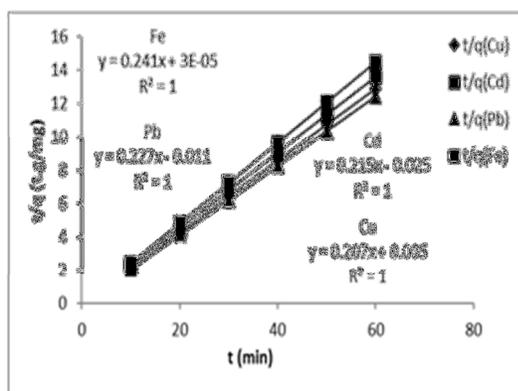

Fig 4: Pseudo second order plot Cu (II), Cd (Ii), Pd (II) and Fe (II) adsorption onto cocoa pod husk.

Table 1: Pseudo Second Kinetics' Parameters

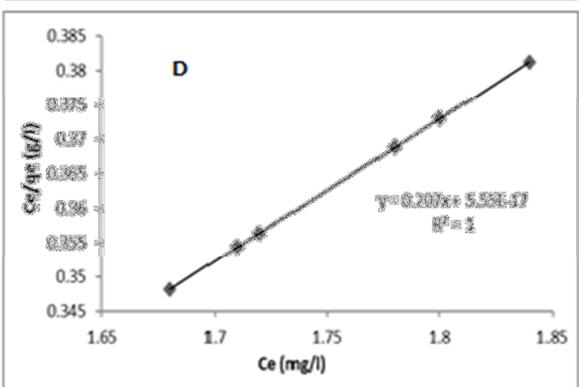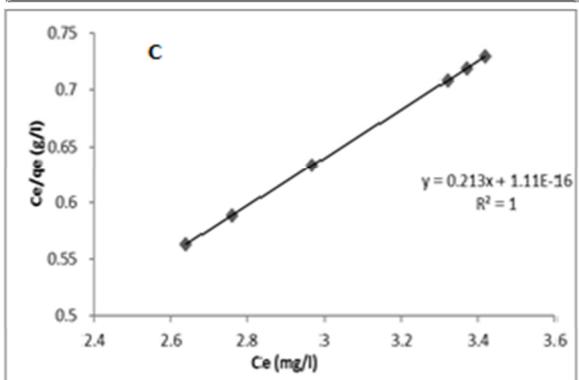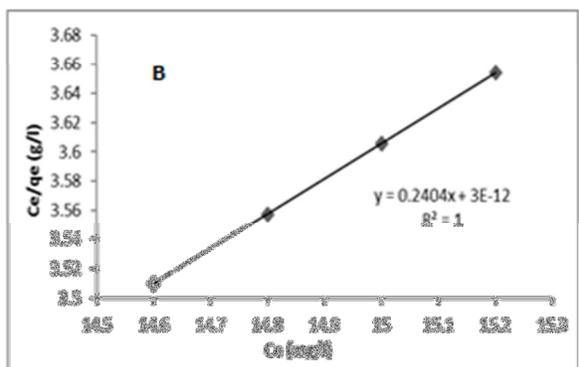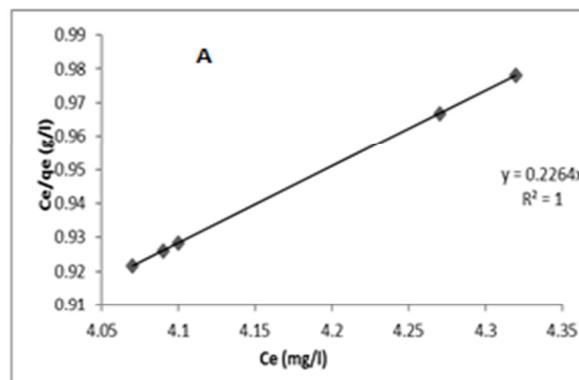| Metal	$K_{2.ads}$	q_e	R^2
Cu(II)	8.5731	4.83	1.000
Cd(II)	-1.8499	4.65	1.000
Pb(II)	-4.6957	4.40	1.000
Fe(II)	1.9335×10^3	4.15	1.000

Fig 5: Langmuir isotherm plot of (a) Cd (II), (b) Cu (II), (c) Fe (II) and (d) Pb (II) adsorption onto cocoa pod husk.

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Again, this could be due to the increase in the number of ions competing for the available functional groups on the surface of the biomass (Agarwal et al., 2006). Similar results have also been reported such as in the adsorption of hexavalent chromium using wheat bran (Nameni et al., 2008); adsorption of Cr (VI), Ni (II) and Al (III) ions using cocoa pod husk (Igwe et al., 2011); biosorption of Zn (II) on maize wrapper (Babarinde et al., 2008); hexavalent chromium removal using *Litchi chinensis* (Acosta-Rodriquez et al., 2012)

Adsorption Kinetics: The kinetics of metal ion sorption has been described as a very important parameter for designing sorption systems. The reactor configuration also depends on the rate of sorption in addition to sorption capacity.

A rapid kinetics will facilitate smaller reactors while a slow rate of uptake will require long columns to utilize maximum potential of the biosorbent. The rate of sorption onto a sorbent surface depends on a number of factors such as structural properties of the sorbent, initial concentration of the solute and the interaction between the solute and the active sites of the sorbent (Vinodhini and Das, 2010).

The experimental data were analysed using pseudo second order kinetics model (Ho, YS; McKay, 2004), which can be expressed as follows:

$$t/q_t = 1/K_{2ads} \cdot q_e^2 + t/q_e \qquad (3)$$

Where $K_{2.ads}$ is the pseudo-second order kinetics constant (g.mg^{-1}.min^{-1}). The linear plot of t/q_t versus t for Cu (II), Cd (II), Pb (II) and Fe (II) are shown in Figure 4.

The values of $K_{2.ads}$ and q_e were calculated from the slopes and intercepts of the plot. The values obtained are depicted in Table 1.

Adsorption Isotherm: The analysis of equilibrium adsorption data by fitting them to different isotherm models is an important step to find the suitable model

that can be used for design purposes (Haghseresht and Lu, 1998).

The Langmuir model was employed in this study. The linearized form of the Langmuir isotherm model is represented by the equation (Langmuir, 1918):

$$C_e/q_e = 1/K_L \cdot q_{max} + C_e/q_{max} \qquad (4)$$

Where q_e is the equilibrium solid phase metal ion concentration on the adsorbent (mg.g^{-1}), C_e is the equilibrium liquid phase metal ion concentration in the solution (mg.l^{-1}), q_{max} in the maximum biosorption capacity of adsorbent (mg.g^{-1}) and K_L is the Langmuir biosorption constant (L.mg^{-1}

It is well known that the Langmuir equation is intended for a homogeneous surface. A good fit of this equation reflects monolayer adsorption (Fytianos et al., 2000).

Values of Langmuir parameters q_{max} and K_L were calculated from the slopes and intercepts of the linear plot of C_e/q_e against C_e as shown in Figures 5, 6, 7 and 8 for Cu (II), Cd (II), Pb (II) and Fe (II) respectively.

The parameters obtained are listed in Table 2. It could be seen that the Langmuir isotherm gave a very good fit to the equilibrium sorption experimental data, going by the values of the coefficient of determination (R^2) shown in Table 2.

Langmuir isotherm model have been used to model sorption experiments (Sirajudeen et al., 2013; Sharawy et al., 2013) and have been reported to give a good fit to some sorption systems (Nameni et al., 2008; Hassan et al., 2008). Table 3 below shows a summary of the comparism between the results of the maximum sorption capacity from this study and that reported in the literature.

It could be seen that the values of the maximum sorption capacity q_{max} from this work, compares favourably with that reported in literature by other researchers.

Table 2: Langmuir Isotherm Parameters

Metal ions	K_L (dm^3/mg)	q_{max} (mg/g)	R^2
Cu(II)	1.92×10^{15}	4.69	1.000
Cd(II)	2.82×10^{12}	4.42	1.000
Pb(II)	3.73×10^{15}	4.83	1.000
Fe(II)	2.40×10^{11}	4.16	1.000

Table 3: Comparism of q_{max} reported in literature and that from this study

S/N	Adsorbent	Metal ions (q_{max}) (mg/g)				Reference
		Cu (II)	Cd (II)	Pb (II)	Fe (II)	
1	*Luffa cylindrical* fibre	-	-	4.63	-	(Sauepraseaarsit et al., 2010)
2	Almond shells	-	-	2.00	-	(Mehrasbi et al., 2009)
3	Orange peel	44.28	-	-	-	(Feng et al., 2009)
4	Dried sunflower leaves	89.37	-	-	-	(Benaissa and Elouchdi, 2007)
5	Olive cake	-	65.4	-	-	(Al-Anber and Matoug, 2008)
6	Sugar beet pulp	-	46.1	43.5	-	(Pehlivan et al., 2008)
7	Lady fern (*Athyrium-felix-femina*)	0.073	-	-	-	(Asiagwu et al., 2012)
8	Maize leaf	-	10.179	-	-	(Babarinde et al., 2007)
9	Calcium carbonate	569.93	1068.63	1551.62	502.98	(Ahmad et al., 2012)
10	Modified Loquat (*Eriobotrya japonica*) leaves	29.67	-	-	-	(Awwad and Salem, 2012)
11	*Basella alba* L	-	-	149.25	-	(Babalola et al., 2008)
12	Grape stalk	-	-	9.15	-	(Martinez et al., 2006)
13	Peat	8.4	83.5	-	-	(Koivula et al., 2009)
14	Tea waste	48.0	-	65.0	-	(Amarasinghe and Williams, 2007)
15	*Psidium guvajava* leaf powder	-	31.15	-	-	(Rao et al., 2010)
16	Wheat bran	-	15.71	-	-	(Nouri et al., 2007)
17	Spent tea leaves	90.00	-	-	-	(Bajpai and Jain, 2010)
18	Maize cob	-	1.98	1.89	-	(Igwe and Abia, 2007)
19	Cocoa pod husk	4.69	4.42	4.83	4.16	(This study)

*Conclusion***:** Adsorption studies for the removal of Cu (II), Cd (II), Pb (II) and Fe (II) from synthetic wastewater were carried out using cocoa pod as adsorbent. The effects of various parameters; contact time, adsorbent dose and initial metal ion concentration were studied. The study showed the adsorption potentials of cocoa pod for the removal of the four metals studied. Using the correlation coefficient, R^2, Kinetics studies showed that the adsorption of the four metals followed pseudo second order kinetics. On the basis of correlation coefficient, R^2, it was clear that the Langmuir isotherm fitted the sorption of the four metals studied onto cocoa pod. The results of this study showed that cocoa pod can be efficiently used as a low-cost alternative for the removal of Cu (II), Cd (II), Pb (II) and Fe (II) from aqueous solutions.

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