



## Sequestering of Cu(II) from aqueous solution using cassava peel (*Manihot esculenta*)

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### ABSTRACT

Cassava peel is a prospective cheap biosorbent for metal ions sequestration. In this research, the ability of cassava peel to remove Cu(II) from aqueous solution was evaluated. Its physical characteristics were probed by nitrogen adsorption measurements and scanning electron microscopy while its biosorption mechanism was studied by Fourier Transform Infrared (FTIR), Scanning Electron Microscopy/Energy Dispersive using X-ray analysis–(SEM/EDX), X-ray mapping and X-ray Photoelectron Spectroscopy (XPS). Biosorption experiments were carried out isothermally at three different temperatures (30 °C, 45 °C and 60 °C) in a static mode. The maximum adsorption capacity (41.77 mg g<sup>-1</sup>) was attained at the highest temperature. The pH and particle size effects in relation to biosorption capacity were also discussed. In addition, Langmuir, Freundlich, Sips and Toth equations were tested for data correlation. Langmuir and Freundlich models were the best choices since they contained less parameter with equally good fitting performance in comparison to the other three parameters equations. For kinetic studies, sorption rates were better represented using a pseudo second-order expression in comparison to a more commonly used pseudo first-order equation. Also, thermodynamic variables showed that the process was spontaneous ( $\Delta G < 0$ ), endothermic ( $\Delta H > 0$ ) and irreversible ( $\Delta S > 0$ ).

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### 1. Introduction

Heavy metal contamination has become a major issue for the past decades until now. They originated mainly from the discharge of metal containing effluents into water bodies. Undeniably, heavy metals are still in demand in most industries for their technological importance. Therefore, improper treatment of these industries' waste products would seriously bring deterioration impacts toward human health and environment [1,2]. Copper is an important metal widely incorporated in metal plating, paper board mills [3], porcelain enameling, mine drainage [4], etc. Its excessive presence in the environment causes human health problems, for instance excessive intake results in its accumulation within the liver resulting in gastrointestinal problems, kidney damage and anaemia. To that end, complete removal of heavy metal from industrial effluents is justified [5,6]. According to EPA (USA, 2004) the highest tolerated concentration of Cu in water is 0.25 mg L<sup>-1</sup> [7].

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Heavy metal removal from contaminated wastewater can be accomplished by conventional techniques [1,2,8–10] which has drawbacks associated with their high energy requirements, ineffectiveness for low metal concentration case and inherent large quantity of toxic waste sludge [2,10–12]. These technologies are perfect in conditions where the heavy metal ions concentration is relatively high [2]. For dilute concentrations of copper, the adsorption process still prevails. An effective adsorbent such as activated carbon, however imparts considerable economic constraint. Optionally, adsorption onto cheap adsorbent would be preferred to reduce metal concentrations below levels established by the legislation [5,13]. The search for alternative adsorbents, mainly from natural resources has been pioneered by Tsezos and Volesky [14] in early 1980s. To date, a number of studies have been conducted; most have concentrated on finding unconventional adsorbents including the most effective methods. Given that plenty of studies have been devoted in biosorption for heavy metal removal, this research is still prevalent and required due to the following reasons:

- Methodology of biosorption study based on an interdisciplinary approach [15].

- Different biomass type contains distinct types of functional groups so that the metal-binding mechanism as well as biosorption affecting parameters in each case is different.
- Biomass materials are heterogeneous to the extent that their chemical compositions largely depend on its origin, type, seasonal variation, geographic location, etc.
- Several metal-binding mechanisms occurs during the sorption process.
- Abundantly available [16–20].
- Currently, biosorbent use has not been scaled up and applied for heavy metal removal in industry.

These points justify the search and study for more effective alternative biosorbents. Current studies showed that Cu(II) can be effectively removed using low cost biological materials from agricultural and forest residues [13,21–30].

Cassava (*Manihot esculenta*) is an important commodity in Indonesia, and commonly consumed in rural areas and also employed in industrial applications as raw material for traditional food, snack and cassava starch [31]. These industries produce a large amount of solid cassava peel waste of which the direct discharge into the environment is illicit. Several research group has successfully converted cassava peel into high surface area activated carbon [31,32]. However, high consumption of energy makes it infeasible from an economic perspective. As a result, employing cassava peel as biosorbent might be a more practical answer.

This paper aims to investigate the possibility to use cassava peel as an alternative adsorbent for Cu(II) removal while also covers most aspects in biosorption studies. Cassava peel contains cyanogenic glucosides, mainly linamarin; which released hydrogen cyanide after hydrolysis by an endogenous linamarase; however it is considered safe to use this agricultural waste as an alternative adsorbent since cassava peel also contains a cyanide detoxification enzyme ( $\beta$ -cyanoalanine synthase) which sufficiently fast to maintain cyanide at safe concentration [33]. Characterizations of pristine and metal loaded cassava peel were performed using different methods and the results were then compared to determine the biosorption mechanism. Several parameters that influence sorption behaviour were discussed. Biosorption equilibria and kinetic studies were subsequently correlated using a few well-known adsorption and kinetic models. The thermodynamic biosorption data was also reported. This study revealed that cassava peel has potential application of copper removal since it has quite high adsorption capacity and comparable with the other low cost bio-based sorbents [13,21–30].

## 2. Isotherm and kinetic studies

Equilibrium data is a vital piece of information to design a particular adsorption process. At equilibrium condition, the chemical potential of the solute in liquid phase is equal to that in solid phase. Numerous adsorption equilibrium models which were originally developed for gas phase adsorption can also be employed to correlate equilibrium data for liquid phase adsorption [34]. A number of isotherms available are purely empirical while some others are derived on the basis of thermodynamic approaches. In the biosorption area, the most popular equations are Freundlich, Langmuir and some other two or three parameters models [1,35–37].

Freundlich isotherm is an empirical equation. It can represent well the adsorption of organic and inorganic compounds onto a wide variety of adsorbents as well as biosorbent. The equation has the form

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

where  $q_e$  is the amount adsorbed ( $\text{mg g}^{-1}$ ),  $C_e$  is the equilibrium concentration ( $\text{mg L}^{-1}$ ),  $K_F$  is a characteristic constant related to the adsorption affinity ( $\text{mg g}^{-1} (\text{mg L}^{-1})^{-n}$ ) and  $n$  is a characteristic constant related to adsorption intensity or degree of favourability of adsorption.

Langmuir isotherm model is another classical equation in biosorption area. It was derived on three simple assumptions (1) a homogeneous surface, (2) monolayer coverage and (3) no secondary interaction between solute and sorbent (i.e. that the presence of Cu already bound to some sites does not have an impact on Cu uptake by other sites.). Although simple, it can describe many biosorption systems very well [37]. Langmuir equation relates the coverage of molecules on a solid surface to the concentration of a medium above the solid surface at a fixed temperature. It can be written in the following form:

$$q_e = q_{\max} \frac{K_L C_e}{1 + K_L C_e} \quad (2)$$

where  $q_{\max}$  and  $K_L$  are the saturated monolayer adsorption capacity and the sorption equilibrium constant, respectively.

For some cases where as-available two parameters models are not competent enough, more than two parameters models can be preferred upon [37]. For example, Sips in 1948 proposed an expression with a similar form to Freundlich isotherm [38].

$$q_e = q_{\max} \frac{(K_S C_e)^\gamma}{(1 + (K_S C_e)^\gamma)} \quad (3)$$

Eq. (3) is almost similar to Langmuir equation. Their difference is the addition of parameter  $\gamma$  to Sips equation which can be regarded as a parameter characterizing the system's heterogeneity or indicating different sorption stoichiometries. Parameter  $K_S$  in Eq. (3) is Sips equilibrium constant. Another three parameters equation that can be employed is Toth equation. It can be classified as an empirical equation. Toth isotherm is developed from potential theory and has been proven powerful to represent sorption in heterogeneous systems. It assumes a quasi-Gaussian energy distribution, i.e. most sites have adsorption energy lower than the peak of maximum adsorption energy [37]. Toth model is shown as

$$q_e = q_{\max} \frac{b_T C_e}{(1 + (b_T C_e)^{n_T})^{1/n_T}} \quad (4)$$

where  $b_T$  and  $n_T$  are Toth parameters and specific for a particular adsorbate–adsorbent pairs.

With the aim to obtain biosorption mechanism based on its potential rate-controlling steps that incorporate mass transport and chemical reaction processes, kinetic models are required for comparison with the experimental data. Pseudo first-order and second-order models are largely employed to study the kinetics of biosorption. Lagergren pseudo first-order rate expression is derived from the solid capacity. It assumes that the rate of occupation onto biosorption sites is proportional to the number of unoccupied sites [2,39]. It is expressed as

$$\frac{dq}{dt} = k_1(q_e - q) \quad (5)$$

Integration of Eq. (5) with boundary conditions at  $t=0$ ,  $q=0$  and at  $t=t$ ,  $q=q$  gives

$$\ln(q_e - q) = \ln q_e - k_1 t \quad (6)$$

Eq. (6) can also be written in non-linear form

$$q = q_e(1 - \exp(-k_1 t)) \quad (7)$$

where  $q_e$  and  $q$  are the amounts of metal ions adsorbed on biosorbent at equilibrium and at time  $t$  ( $\text{mg g}^{-1}$ ), respectively while  $k_1$  is the equilibrium rate constant of pseudo first-order adsorption ( $\text{min}^{-1}$ ).

Pseudo second-order model on the other hand is developed upon the sorption capacity of the solid phase [40] which is expressed as

$$\frac{dq}{dt} = k_2(q_e - q)^2 \quad (8)$$

Integration of Eq. (8) with the boundary conditions at  $t=0$ ,  $q=0$  and at  $t=t$ ,  $q=q$ , results in

$$\frac{1}{q_e - q} = \frac{1}{q_e} + k_2 t \quad (9)$$

Eq. (9) as well, can be stated in the non-linear form as

$$q = q_e - \frac{q_e}{(1 + q_e k_2 t)} \quad (10)$$

where  $k_2$  is the equilibrium rate constant of pseudo second-order adsorption ( $\text{g mg}^{-1} \text{min}^{-1}$ ).

### 3. Materials and methods

#### 3.1. Materials

Copper sulphate ( $\text{CuSO}_4 \cdot 6\text{H}_2\text{O}$ ; AR grade) was purchased from Shimakyu's Pure Chemicals, Taiwan and used directly without any pretreatment.

#### 3.2. Preparation of biosorbent

Cassava peel was collected from a cassava starch factory located near Surabaya, East Java, Indonesia. Firstly, cassava peel was washed with tap water repeatedly to eliminate surface dirt. It was subsequently dried under the sun for at least 24 h before dried further in oven at  $100^\circ\text{C}$  for another 24 h to reduce its water content. Biomass size was then reduced using JANKE & KUNDEL hammer mill and further sieved to obtain desirable particle size (125–500  $\mu\text{m}$ ). Final products was later stored in airtight plastic containers for further experimental use.

#### 3.3. Biosorption studies

$\text{Cu(II)}$  solution was prepared by diluting 0.3930 g of  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  in 500 mL of deionized distilled water (DDW). The isotherm study was conducted by adding desired amount of adsorbent (0.1–12 g) into several Erlenmeyer flasks, each of which contained 200 mL metal solution with initial Cu concentration of  $200 \text{ mg L}^{-1}$ . Afterwards, the flask was placed in an orbital shaker incubator LM-570. The incubator was then set to rotate at 200 rpm until equilibrium condition was achieved. This procedure was conducted at three different temperatures (30, 45, and  $60^\circ\text{C}$ ).

To investigate the adsorption kinetics, 200 mL of  $\text{Cu(II)}$  solutions with initial concentration of  $200 \text{ mg L}^{-1}$  was mixed with 0.5 g of cassava peel in an Erlenmeyer flask. The flask was then set in an incubator-shaker and shaken at 200 rpm at a temperature of  $60^\circ\text{C}$  for a certain period of time. After each certain time interval, 2 mL volume of solution was taken to analyze its metal content using spectrophotometer (JASCO V-550 UV/vis spectrometer).

The pH effect was studied at pH range of 1.0–4.5 since metal precipitation to its hydroxide take place at a pH above 5.0. To adjust the pH, appropriate amounts of  $\text{H}_2\text{SO}_4$  solution (0.1 N) was added to the solution.

To determine metal concentration, samples were centrifuged at 4000 rpm for 3 min to separate biosorbent from the solution and then filtered using Whatman filter paper (No. 42). The metal concentration in solution was determined using a spectrophotometer.

The amount of metal uptake was obtained by the following equation:

$$q = \frac{(C_0 - C_e)}{m} V \quad (11)$$

where  $q$  ( $\text{mg g}^{-1}$ ) is the amount adsorbed,  $C_0$  ( $\text{mg L}^{-1}$ ) and  $C_e$  ( $\text{mg L}^{-1}$ ) are the initial and the equilibrium concentration, respectively while  $m$  (g) is the mass of adsorbent and  $V$  (L) is the volume of solution.

#### 3.4. FTIR spectroscopy

FTIR spectroscopy was used to probe the functional groups on the surface of the cassava peel (both pristine and loaded cassava peel). The spectra were collected with a FTS-3500 GX (Bio-Rad) spectrometer within the range  $400\text{--}4000 \text{ cm}^{-1}$  using a KBr window. Pure KBr background was automatically subtracted from the sample spectra. Spectra were plotted using the same scale on the absorbance axis.

#### 3.5. Nitrogen adsorption

The pore structure characteristics of cassava peel was determined by nitrogen adsorption at  $-196^\circ\text{C}$  by a Quadrasorb SI. Prior to gas adsorption measurements, the cassava peel was degassed at  $150^\circ\text{C}$  in a vacuum for a period of at least 24 h. Nitrogen sorption isotherm was measured over a relative pressure ( $P/P_0$ ) range from approximately 0.005–0.994. The BET surface area was determined by means of the standard BET equation applied in the relative pressure range from 0.06 to 0.3. The total pore volume was calculated at a relative pressure of approximately 0.994 and at this relative pressure all pores were completely filled with nitrogen gas.

#### 3.6. Scanning electron microscopy (SEM) analysis

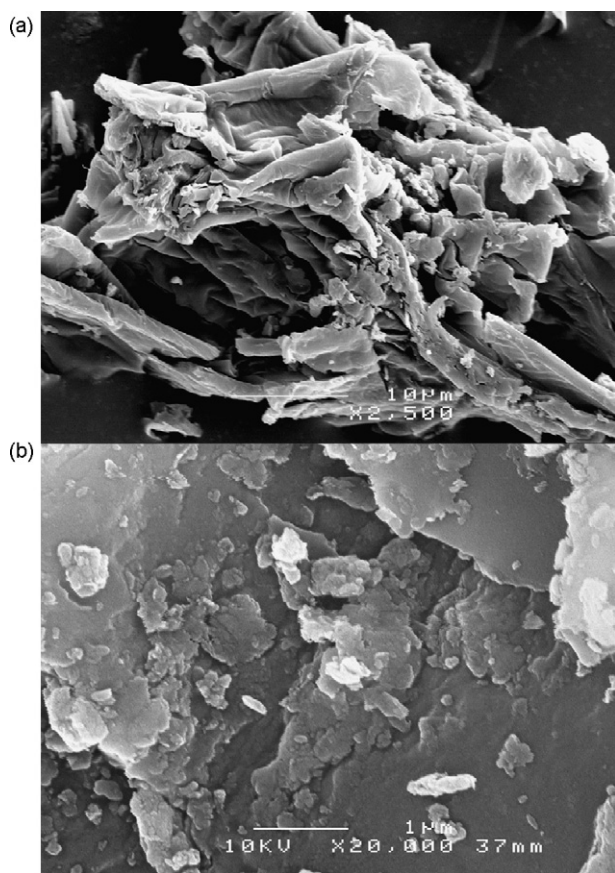
SEM images were recorded using JEOL JSM-6400F field emission SEM. A thin layer of platinum was sputter-coated on the samples for charge dissipation during FESEM imaging. The sputter coater (Eiko IB-5 Sputter Coater) was operated in an argon atmosphere using a current of 6 mA for 4 min. The coated samples were then transferred to the SEM specimen chamber and analyzed at an accelerating voltage of 10 kV, eight spot size, four aperture and 37 mm working distance.

#### 3.7. Energy dispersive X-ray (EDX) and X-ray elemental mapping analysis

EDX and X-ray mapping analysis was performed on JEOL JSM-6460 LA low vacuum analytical Scanning Electron Microscope equipped with an integrated JEOL Hyper mini-cup, 133 eV resolution, ultra thin window (UTW), SiLi crystal and energy dispersive X-ray spectrometer. Integrated JEOL Analysis Station (v3.2) software was used to collect and analyze the X-ray data. Samples were coated with custom-made carbon coater with carbon fiber. Acquisition conditions on the scanning electron microscope (SEM) were 20 kV, 10 mm working distance and 30 s live time acquisition at approximately 10–15% dead time.

#### 3.8. X-ray photoelectron spectroscopy (XPS) analysis

XPS spectra were acquired using a Kratos Axis ULTRA X-ray Photoelectron Spectrometer incorporating a 165 mm hemispherical electron energy analyzer. The incident radiation was Monochromatic Al  $K\alpha$  X-rays (1486.6 eV) at 150 W (15 kV, 15 mA). Survey (wide) scans were taken at analyzer pass energy of 160 eV and multiplex (narrow) high-resolution scans at 20 eV. Survey scans were



**Fig. 1.** SEM pictures of cassava peel with magnification of (a) 2,500 $\times$  and (b) 20,000 $\times$ .

carried out over 1200–0 eV binding energy range with 1.0 eV steps and a dwell time of 100 ms. Narrow high-resolution scans were run with 0.05 eV steps and 250 ms dwell time. Base pressure in the analysis chamber was  $1.0 \times 10^{-9}$  Torr which increased to  $1.0 \times 10^{-8}$  during sample analysis.

## 4. Results and discussion

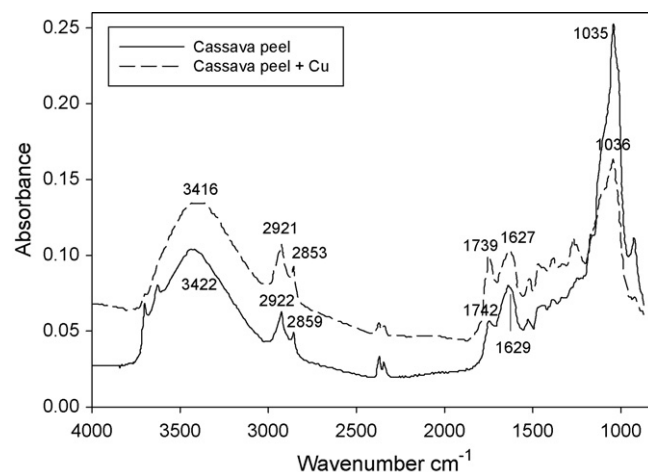
### 4.1. Surface and pore characteristics of pristine cassava peel

Surface morphology of cassava peel at two different magnifications is displayed in Fig. 1. Fig. 1 confirms the heterogeneity characteristics of cassava peel's surface. Additionally, it can be seen from Fig. 1(b) that the surface is non-porous. Its nitrogen adsorption capacity is very low ( $20.20 \text{ cm}^3 \text{ g}^{-1}$  STP) with BET surface area of  $3.72 \text{ m}^2 \text{ g}^{-1}$ . The physical adsorption process does not seem to play a substantial role on Cu(II) adsorption onto cassava peel. Combination of ion exchange, coordination, chelation, complexation and other mechanisms in this case tends to be more dominant. These characteristics were also noticed by other research groups [41–43].

### 4.2. Characteristic of cassava peel loaded with Cu(II)

#### 4.2.1. FTIR analysis

Table 1 shows the FTIR results of the original and metal loaded cassava peel. There are several functional groups on cassava peel's surface, namely hydroxyl, carboxyl, carboxylate, etc. as listed in Table 1. It is obvious from Table 1 that for Cu(II) loaded cassava peel, some peaks are shifted in terms of wave number denoting that these functional groups are involved or participating in metal



**Fig. 2.** Fourier Transform Infrared (FTIR) spectra for cassava peel before and after loaded with Cu.

binding. Fig. 2 is also included to provide clear comparison of FTIR results before and after adsorption.

The peak around  $3422 \text{ cm}^{-1}$  indicates the existence of free and intermolecular bonded OH groups. The peak corresponds to this functional groups was altered after Cu(II) adsorption indicating their involvement in Cu binding. The inclusion of hydroxyl groups on the metal binding was also observed by Prasad and Freitas [44] and Aydin et al. [16]. The oxygen on each hydroxyl group acts as a strong Lewis base because of the presence of its vacant double electrons, and this hydroxyl group undergoes a complex coordination with metal (Cu(II)) which is electron deficient. Further detail about the mechanism can be found elsewhere [16,44]. The peaks observed at 2922–2859 can be assigned to aliphatic C–H groups. A peak at 1742 represents the stretching of carboxyl groups, these groups associated with carboxylic acids. Carboxylate groups are observed at a peak of 1629. The peak present at 1035 indicates the presence of OH groups (cellulosic compounds).

### 4.2.2. Energy dispersive X-ray spectroscopy, X-ray mapping and XPS methods

SEM and EDX spectra of Cu(II) loaded cassava peel is depicted in Fig. 3. Cu K and L lines' presence indicates that a remarkable amount of Cu was adsorbed on the surface. The Cu elemental mapping was also performed to probe Cu distribution on the surface. SEM and Cu element mapping at another fixed position are shown in Fig. 4. The adsorbed Cu ions were not distributed uniformly on the surface. In some particular parts of cassava peel, Cu ions seems to be more concentrated. These observations confirm the heterogeneous nature of cassava peel on which the existence of distinct functional groups responsible for metal binding was not uniform.

Fig. 5 shows XPS spectra for Cu-loaded cassava peel. The characteristic peak of copper (Cu  $2p_{3/2}$ ) appears at 932.88 eV which corresponds to either  $\text{Cu}_2\text{O}$  [45] or CuCN (at 932.80 eV) [46] or  $\text{Cu}_2\text{S}$  (at 932.90 eV) [47], further verifying its presence within the surface depth.

### 4.3. Effect of solution pH on biosorption

The pH is an important factor affecting the biosorbent performance, as it influences both solution chemistry of metals and activity of functional groups on biomass [48]. The pH effect on metal uptake is shown on Fig. 6. The uptake rate increases steadily with pH rise to reach the maximum at pH 4.5. This pH also served as the optimum point since an increase above this value is likely to bring metal precipitation into effect. Again, this trend is in accordance

**Table 1**  
Major functional groups in Cassava Peel and Cassava Peel + Cu.

Functional groups	Cassava peel wave number (cm <sup>-1</sup> )	Cassava peel + Cu wave number (cm <sup>-1</sup> )
Bonded OH groups	3422	3416
Aliphatic C–H groups (C–H stretching of the CH <sub>2</sub> groups)	2922	2921
Aliphatic C–H groups	2859	2853
Carboxyl stretching groups	1742	1739
Carboxylate groups	1629	1627
–OH groups (cellulosic compounds)	1035	1036

with other reports on Cu(II) sorption using several biosorbents [3,49–51].

At low pH, the surface charge becomes positive due to high concentration of H<sup>+</sup> and H<sub>3</sub>O<sup>+</sup> ions [48,52]. Their presence (H<sup>+</sup> and H<sub>3</sub>O<sup>+</sup> ions) inhibits biosorption as Cu(II) ions need to compete with protons to form a bond with active sites of functional groups on biosorbent's surface [48,52]. With an increase in pH however, the amount of protons decreases leading to less restriction from repulsive forces. As a result, metal uptake is enhanced.

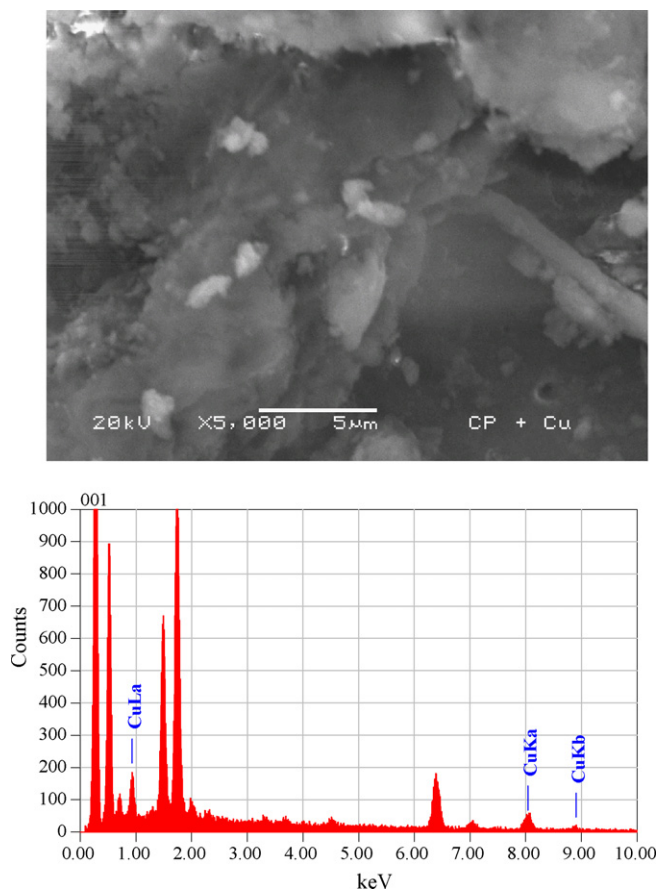
#### 4.4. Isotherm studies

Experimental adsorption equilibrium data of copper sorption onto cassava peel at different temperature are depicted in Fig. 7. Model parameters were determined using non-linear regression toolbox in Sigma Plot v.9. Table 2 summarizes the results. It is apparent that all models can represent the equilibrium data adequately. Aside from the good correlation coefficient values obtained, the physical meaning of parameters should be explored further to get better interpretation.

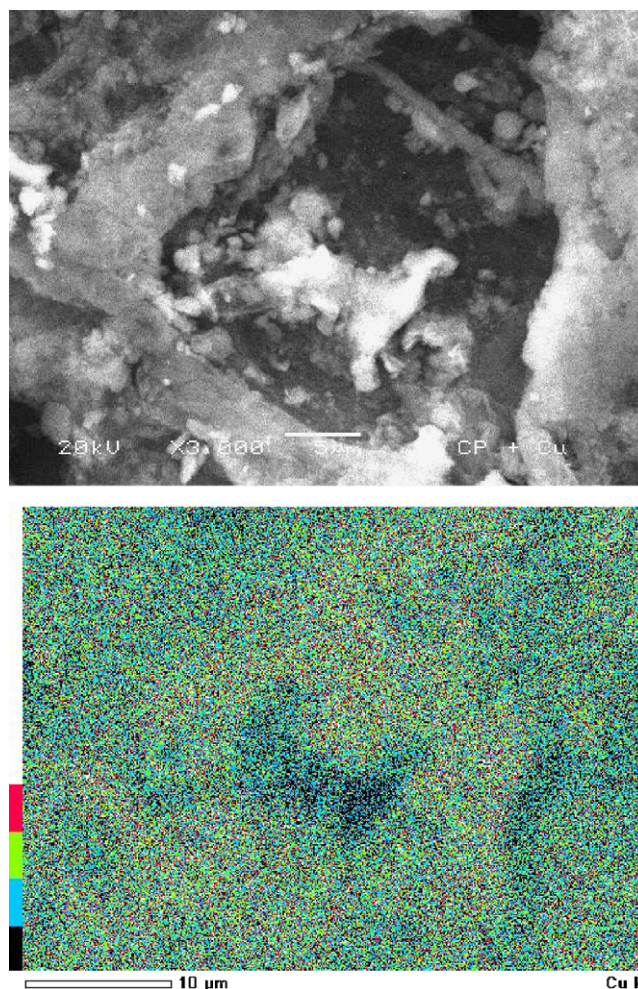
The magnitude of  $K_F$  in Freundlich equation increases with increasing temperature which may imply that the biosorption capacity is governed by temperature so that the sorption process will be more enhanced at higher temperature. Additionally, larger values of  $n$  imply stronger interaction between biosorbent and the heavy metal.

The trend of biosorption capacity predicted by Langmuir model is similar to that acquired from Freundlich. Adsorption capacity enlarges with temperature rise as noted in Table 2. In the Langmuir model, higher values of  $K_L$  signify higher affinity for metal ions binding. Table 2 shows that  $K_L$  increases with increasing temperature so that high temperature biosorption process is more favourable. Moreover, enhancement of  $K_L$  with temperature denotes that biosorption is an endothermic process.

Given that Freundlich and Langmuir models already adequately represent the experimental data, the capability of three parameters equations will still be interesting to test. Therefore, Sips and Toth



**Fig. 3.** SEM and EDX spectra of Cu-loaded cassava peel.



**Fig. 4.** SEM image and X-ray elemental mapping for Cu on Cu-loaded cassava peel.

**Table 2**  
Isotherm constants of Freundlich, Langmuir, Sips and Toth model for copper biosorption onto cassava peel (*Manihot esculenta*).

Isotherm model	Parameter	Temperature		
		30 °C	45 °C	60 °C
Freundlich	$K_F$ ( $\text{mg g}^{-1}$ ) ( $\text{mg L}^{-1}$ ) <sup>-n</sup>	0.64	1.40	2.11
	$n$	1.53	1.75	1.91
	RMSE	0.99	1.55	1.69
Langmuir	$q_{\text{max}}$ , $\text{mg g}^{-1}$	37.83	39.88	41.77
	$K_L$ , $\text{L mg}^{-1}$	0.006	0.011	0.015
	RMSE	0.91	1.17	1.27
Sips	$q_{\text{max}}$ , $\text{mg g}^{-1}$	41.59	38.20	44.44
	$K_S$ , $\text{L mg}^{-1}$	0.005	0.012	0.013
	$\gamma$	0.95	1.04	0.94
	RMSE	1.00	1.27	1.38
	Toth	$q_{\text{max}}$ , $\text{mg g}^{-1}$	23.93	40.05
	$b_T$ , $\text{L mg}^{-1}$	0.007	0.010	0.015
	$n_T$	1.98	0.99	0.78
	RMSE	0.99	1.28	1.36

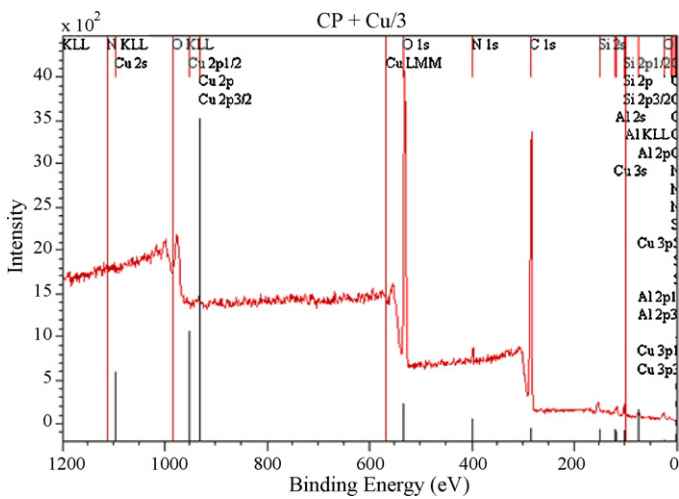


Fig. 5. XPS spectra of Cu-loaded cassava peel.

equations are chosen. As represented in Fig. 7 and Table 2, both these models also end up with good correlation coefficient values. Both parameters,  $\gamma$  of Sips and  $n_T$  of Toth equation characterize the system's heterogeneity. Since obtained  $\gamma$  values are close to

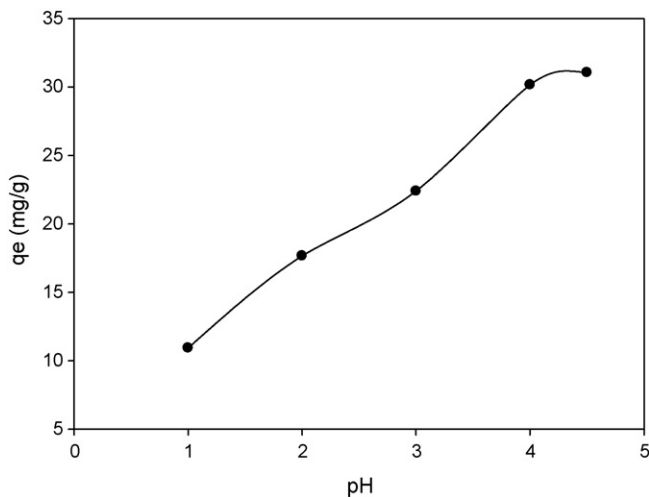


Fig. 6. Effect of pH on equilibrium Cu(II) sorption onto cassava peel. (Initial Cu(II) concentration of 200 mg/L and temperature of 60 °C.)

unity, it can be safely assumed that Langmuir isotherm is sufficient to describe the biosorption process. By looking at Toth equation, their  $n_T$  values at 30 °C and 60 °C reveal that the system is quite heterogeneous while the  $n_T$  value at 45 °C is close to unity; indicates the likelihood of monolayer adsorption. Due to this contradiction, Toth equation is considered not suitable to describe the biosorption process for Cu(II)-cassava peel system.

4.5. Kinetic studies

Kinetic data was fitted onto non-linear pseudo-first-order and -second-order models by SigmaPlot v.9 with acquired parameters listed in Table 3. Fig. 8 plots metal uptake rate versus time. It can be concluded that the particle size affects copper biosorption performance. As shown on Table 3, smaller particle size enhances the biosorption process evidenced by higher amounts of copper adsorbed. Reduction in particle size also enhances the reaction rate constant so that equilibrium is reached in shorter time. On the same amount of biosorbent, smaller particle size gives shorter distance from the surface to the binding site in the interior of the particle, and consequently faster reaction rate occurs [40]. These evidences clearly show that diffusion into the particle takes place and affects the overall kinetics.

By comparing the fitting result by pseudo first-order and second-order kinetic model, pseudo second-order model seems to give better representation (correlative coefficient >0.99). Moreover,

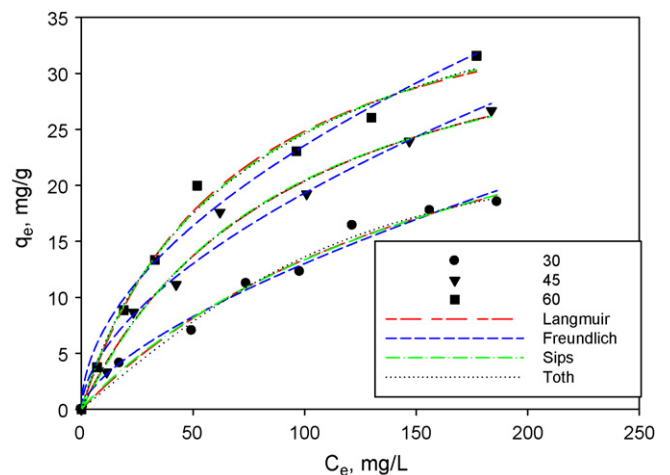


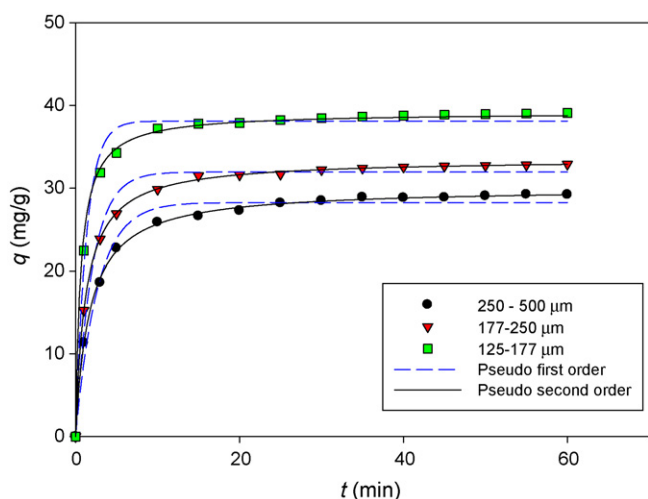
Fig. 7. Biosorption isotherms of copper on cassava peel.

**Table 3**  
Comparison of pseudo first-order and second-order model parameters at different particle size.

Particle size ( $\mu\text{m}$ )	$q_e$ (exp)	Pseudo first-order			Pseudo second-order		
		$k_1$ ( $\text{min}^{-1}$ )	$q_e$ ( $\text{mg g}^{-1}$ )	$R^2$	$K_2$ ( $\text{g}(\text{mg min})^{-1}$ )	$q_e$ ( $\text{mg g}^{-1}$ )	$R^2$
125–177	39.083	0.431	38.522	0.870	0.035	39.503	0.999
177–250	32.883	0.339	32.247	0.871	0.025	33.539	0.999
250–500	29.235	0.295	28.462	0.817	0.020	29.960	0.999

**Table 4**  
Thermodynamic parameters for copper biosorption on cassava peel.

$T$ ( $^{\circ}\text{C}$ )	$b$ ( $\text{L mol}^{-1}$ )	$\Delta G^{\circ}$ ( $\text{kJ mol}^{-1}$ )	$\Delta H^{\circ}$ ( $\text{kJ mol}^{-1}$ )	$\Delta S^{\circ}$ ( $\text{kJ mol}^{-1} \text{K}^{-1}$ )
30	348.035	−14.750	27.424	0.133
45	664.075	−17.189		
60	930.978	−18.935		



**Fig. 8.** Biosorption kinetics of Cu(II) ions on cassava peel (Co: 200 mg/L, temperature 60  $^{\circ}\text{C}$ , agitation rate 200 rpm and solution pH of 4.5) and model fitted using pseudo first-order and second-order model.

calculated  $q_e$  values from pseudo second-order model agree quite well with experimental data. Potential advantages of the pseudo second-order equation as an expression estimating the  $q_e$  value is its small sensitivity for the influence of the random experimental error, also the  $q_e$  value can be determined from the plot independently of the kinetic mechanism which governs the adsorption process [53].

The failure of pseudo first-order to describe the kinetic data of adsorption Cu(II) onto cassava peel is due to the behavior of parameter  $k_1$ . The parameter  $k_1$  in pseudo first-order is the time scaling factor whose value decides how fast the equilibrium in the system can be reached; higher value of  $k_1$  results in shorter times required for the system to reach the equilibrium [53]. The applicability of the pseudo first-order equation depends on the range time at which the data recorded. If the data collected when the system is not very close to equilibrium (this condition is not fulfilled by our experimental data as indicated in Fig. 8), this model will give satisfy prediction result as indicated by Plazinski et al. [53]. Complete theoretical description and fundamental consideration on the pseudo first- and pseudo second-order models can be found on the recent review article by Plazinski et al. [53].

#### 4.6. Thermodynamics studies

Thermodynamic considerations can be investigated through Gibbs free energy, enthalpy and entropy. Standard free energy

change ( $\Delta G^{\circ}$ ) is calculated with the following relationship:

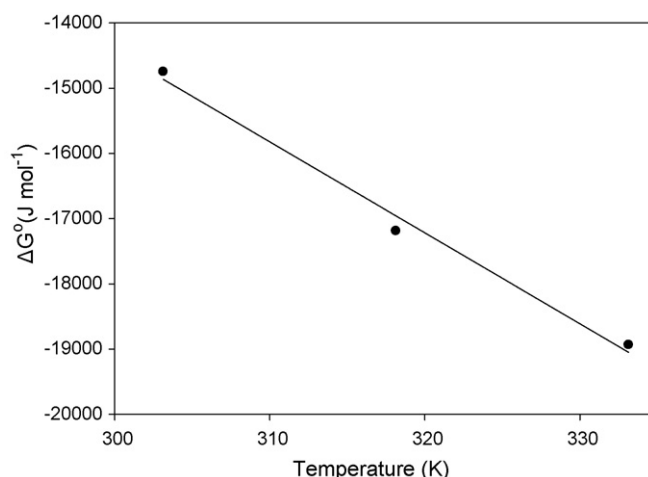
$$\Delta G^{\circ} = -RT \ln b \quad (12)$$

where  $b$  is the equilibrium constant obtained from Langmuir model ( $\text{L mol}^{-1}$ ),  $T$  is the absolute temperature (K) and  $R$  is the gas constant ( $8.314 \text{ J mol}^{-1} \text{ K}^{-1}$ ). The relationship between Gibbs free energy change, entropy change ( $\Delta S^{\circ}$ ) and enthalpy change ( $\Delta H^{\circ}$ ) can be expressed as

$$\Delta G^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ} \quad (13)$$

$\Delta S^{\circ}$  and  $\Delta H^{\circ}$  were obtained from the slope and intercept of plot of  $\Delta G^{\circ}$  versus  $T$ .

Thermodynamics parameters for copper sorption by cassava peel are tabulated in Table 4. Fig. 9 plots the Gibbs energy change versus temperature. The Gibbs free energy measures the degree of spontaneity for the adsorption process where more negative values reflect a more energetically favourable adsorption process [54]. A negative value of  $\Delta G^{\circ}$  indicates that the adsorption process is spontaneous in nature. In parallel with temperature rise, the Gibbs energy value becomes more negative leading to a conclusion that biosorption is more favourable at higher temperatures. On the other hand, positive value of enthalpy change suggests that copper biosorption onto cassava peel is endothermic. This point was further reinforced by the enhanced uptake capacity with higher temperature. Besides,  $\Delta H^{\circ}$  value also indicates the type of adsorption. Normally, adsorption process with heat of adsorption magnitude between 0.5 and 5  $\text{kcal mol}^{-1}$  ( $2.1\text{--}20.9 \text{ kJ mol}^{-1}$ ) can be classified as physical adsorption. Furthermore, the activation energy for chemical adsorption lies within



**Fig. 9.** Gibbs energy change versus temperature.

the same range as the heat of chemical reaction, between 5 and 100 kcal mol<sup>-1</sup> (20.9–418.4 kJ mol<sup>-1</sup>) [55]. As-acquired  $\Delta H^\circ$  value is 27.424 kJ mol<sup>-1</sup> which indicates that chemisorption is controlling the reaction. Additionally, as-calculated  $\Delta S^\circ$  value is 0.133 kJ mol<sup>-1</sup> K<sup>-1</sup>. A positive value of  $\Delta S^\circ$  denotes the increased randomness at the solid–solution interface during biosorption resulting in the irreversibility of the process.

## 5. Conclusion

Cassava peel is a potential biosorbent for copper biosorption. Its metal binding takes place through chemical interactions between Cu(II) ions and functional groups on the cassava peel's surface. Cu(II) biosorption process onto cassava peel was pH dependent which is optimized at pH 4.5. The isotherm data is best represented by Langmuir and Freundlich models with the maximum adsorption capacity achieved at 60 °C. Thermodynamic parameters indicate that the biosorption process is spontaneous, endothermic and irreversible.

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