



Original Article

Removal of copper from aqueous solutions by adsorption using modify *Zalacca edulis* peel modify

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Abstract

The removal of Cu^{2+} ions by adsorption using biomass derived from *Zalacca edulis* peel was studied in a batch system. The effects of pH and chemical pre-treatment of the biomass by the use of CaCl_2 with different thermal conditions and initial concentrations were also determined. The results showed that chemical pre-treatment by CaCl_2 enhanced the capacity of Cu^{2+} ions biosorption. The equilibrium sorption data of untreated *Zalacca edulis* peel and *Zalacca edulis* peel pre-treated with CaCl_2 were fitted well by both Langmuir and Freundlich isotherms equations. According to the Langmuir equation, the maximum uptake of Cu^{2+} ions by the use of *Zalacca edulis* peel pre-treated with CaCl_2 was found to be 27.03 mg g^{-1} at pH 5. The rate of adsorption was found to conform to pseudo-second order kinetics with good correlation. The binding between heavy metal Cu^{2+} ions and chemically pre-treated biosorbent was confirmed by the use of scanning electron microscope combined with energy dispersive X-ray analysis and electron probe microanalyser.

Keywords: biosorption, Cu^{2+} ions, chemical pre-treatment, fruit peel

1. Introduction

Copper is a metal that is widely used in industry and is an essential element in human health. However, like all heavy metals, it is potentially toxic (Nuhoglu *et al.*, 2003). Exposure to copper can lead to liver damage causing gastrointestinal problems, Wilson Disease, and insomnia (Baraket, 2010; Farooq *et al.*, 2010). To reduce the risk of these conditions, it is desirable to minimize the amount of copper ions in industrial runoff by such methods as chemical precipitation,

ion exchange, reverse osmosis, adsorption, membrane processes, and floatation. However, these methods are uneconomical and inefficient, especially at metal concentrations in the range from 10 to 100 mg L^{-1} (Basci *et al.*, 2004). Biosorption has been found to be economically feasible, rapid, reversible, and ecologically friendly in the removal of heavy metals from aqueous solutions, especially when used in the treatment of high volumes and very low concentrations of wastewater containing heavy metals (Tunali *et al.*, 2006; Gupta and Ratstogi, 2008; Yazici *et al.*, 2008; Melckova and Ruzovix, 2010).

Agricultural waste or by-products have been investigated for biosorption both in batch and continuous systems. The biomass from this waste and/or by-products can be

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treated to improve its sorption ability. Literature has shown that metal ions' affinity to the biomass can be improved by its pre-treatment with alkalis, acids, salt, detergents, and heat to increase the amount of metal absorbed (Kaewsarn and Yu, 2002; Salatania *et al.*, 2004; Yang and Chen, 2008). The objective of this study was to investigate Cu^{2+} ions biosorption by low cost adsorbent developed from the plant material *Zalacca edulis* peel.

Zalacca edulis, known as 'Salacca,' is grown extensively in South-East Asia. In Thailand, for *Zalacca edulis* the major fruit season is from December to February, following a minor fruiting seasoning from June to July. The fruit is egg-shaped, contains three seeds covered with white flesh, and has a reddish-brown scaly skin or peel. A mature fruit weighs up to 70 g and most of the fruits are consumed fresh with some processed into fruit juice, canned fruit, and jam (Shela *et al.*, 2009). The peel, after removal, is waste material. In this study this peel was used as a biosorbent in the removal of Cu^{2+} ions.

2. Material and Methods

2.1 Preparation of samples

Samples of *Zalacca edulis* peel were collected from a local market near Ubon Ratchathani University in Northeast Thailand. The preparation of the adsorbents was carried out using a similar as described previously by Matheickal and Yu (1999). The peel was washed with de-ionized water, dried at room temperature, cut into small pieces, blended, and passed through a sieving machine, producing untreated *Zalacca edulis* peel biomass. Twenty grams of this biomass was then pre-treated by slowly stirring in 0.1 M calcium chloride solution (CaCl_2) (400 ml) for 24 hours at room temperature. Afterwards, the material was washed with de-ionized water and dried in a hot air oven (Memmert Model 600) at 60°C for 24 hours and sieved with a 200 mesh stainless steel sieve to a selected particle size of 300-600 μm .

In this study the yield ($W\%$) of biomass after pre-treatment with CaCl_2 was determined by following equation:

$$W\% = \frac{W_f}{W_i} \times 100(\%) \quad (1)$$

in which W_i is the dry weight of the biomass before pretreatment with CaCl_2 and W_f is the dry weight of the biomass after pretreatment with CaCl_2 . The amount of biomass remaining after the pretreatment step were 84.15 %.

2.2 Determination of pH of zero charge

The point of zero charge (pH_{pzc}) was also investigated to explain the effect of pH on biomass adsorption. In this study, the pH_{pzc} determination method described by Rivera *et al.* (2001) was applied. In brief, 50 mL of 0.01 M NaCl solutions were placed in Erlenmeyer flasks. The initial pH solu-

tions were adjusted to 2, 4, 6, 8, 10, and 12 by adding HCl 0.1 M or NaOH 0.1 M solutions. Then 0.1 g of adsorbent was added to each flask and agitated at room temperature for 48 hours and then finally the final pH solutions were measured. The pH_{pzc} was determined by plotting $\text{pH}_{\text{initial}}$ versus pH_{final} (not shown). (Rivera *et al.*, 2001; Khormaei *et al.*, 2007). The obtained pH_{pzc} was 4.8 and 3.9 for untreated *Zalacca edulis* peel and pre-treated *Zalacca edulis* peel by CaCl_2 , respectively.

2.3 Microstructure studies

2.3.1 Scanning electron microscope images

Dried samples of this pre-treated material were glued onto 1 cm diameter metal stubs. The samples were then coated with gold particle by a sputtering coater unit. The coated samples were examined by the use of a scanning electron microscope (SEM) (Quata 200 Model, USA) combined with an energy dispersive X-ray (EDX) analysis, (EDX Oxford Instrument FEI couple Quata 200 3 D Dual Beam).

2.3.2 Electron probe micro-analyzer study

Samples of the biomass with heavy metal ions were prepared by slowly stirring 2 g of the biomass in 100 ml nitrate solution of copper concentration 70 mg L^{-1} for a period of 24 hours and then rinsed with de-ionized water and dried in an oven at 60°C for 24 hours. The presence of Cu^{2+} was measured by the use of an electron probe micro-analyzer (Yu *et al.*, 2000).

Dried sample were glued onto 1 cm diameter carbon stubs. The sample were coated with carbon then brought into a seal sputtering unit where the coating of the biomass with carbon took place. The coated samples were brought into the EPMA unit under vacuum. Once a certain pressure had been reached in the EPMA unit the sample could be viewed using the focus, movement and zoom facilities of the EPMA. When the desired view of the biomass structure was obtained, a graph was taken by using a printer attached to the EPMA (JXA 8100, JOEL).

2.4 Biosorption test

A Cu^{2+} ion solution was prepared by dissolving solid copper nitrate ($\text{CuNO}_3 \times 2.5\text{H}_2\text{O}$) in de-ionized water. The biosorption experiment was conducted in 250 ml Erlenmeyer flasks containing 0.1 g of biomass with 100 ml of Cu^{2+} ion solution with an initial concentration of 100 mg L^{-1} . The flasks were agitated on a shaker at 100 rpm at room temperature for 24 hours. During the experiment, a constant pH was maintained by using 0.1 N NaOH and HNO_3 . After the pre-set contact time was reached, the solutions were separated from the biomass by filtration through GF/C filter paper (Whatman 0.45 μm). The Cu^{2+} ion concentrations in the solutions before and after investigation were determined by the use of a flame

atomic absorption spectrometer (Perkin-Elmer Analyze 200). The analytical wave length was 324.8 nm.

The effect of pH on the biosorption of metal ions was measured in the range of pH 2-6, the range that would be influenced by metal precipitation. The solution pH was adjusted to the desired value by adding 0.1 N NaOH and 0.1 N HNO₃ solution.

The equilibrium isotherm was determined by mixing 0.1 g of untreated *Zalacca edulis* peel and *Zalacca edulis* peel pre-treated with CaCl₂ in a range of different concentrations of CuNO₃·2.5H₂O solutions from 10-100 mg g⁻¹. Agitation mixing time was maintained for 24 hours, sufficient to reach equilibrium with a constant agitation speed of 100 rpm at room temperature. The pH was adjusted by adding 0.1 N NaOH or 0.1 N HNO₃ before, during, and after each experiment. All samples were tested three times and the averages calculated.

The amounts of Cu²⁺ ions biosorbed by untreated *Zalacca edulis* peel and *Zalacca edulis* peel pre-treated with CaCl₂ were calculated by the application of the equation:

$$q = \frac{(C_i - C_f)}{M} \times V \quad (2)$$

in which C_i is the initial concentration (mg L⁻¹) and C_f is the final metal concentration, (mg L⁻¹), M is the dry weight of the biomass (g), V is the volume of metal solution (ml), and q is mg of metal ion bioadsorbed per g of biomass.

3. Results and Discussion

3.1 Microstructures of the biomass

SEM is a primary tool for characterizing the surface morphology and fundamental physical proportion of the adsorbent. It is useful for determining the particle shape, porosity, and appropriate size distribution of the adsorbent. The biomass was scanned by the electron microscope at a magnification of 700x.

The microstructure of untreated *Zalacca edulis* peel examined by the use of SEM images is shown in Figure 1(a). It was observed that the surface was a thick and rough and the inside was lumpy, dense, and there were a series of overlaps. The microstructure of *Zalacca edulis* peel pre-treated with CaCl₂ was studied by SEM and is shown in Figure 1(b). It was found that there were differences between samples of untreated *Zalacca edulis* peel and *Zalacca edulis* peel pre-treated with CaCl₂. The structure of the latter was uniform, leaf-like, shrunken, and ruptured. The pores were formed by connecting structure. The porous structure could be observed in various shapes (oval, lotus, and cylinder) and diameters. These differences may be due to the pre-treatment by CaCl₂ and heat (Sirilamduan and Kaewsarn, 2009).

The *Zalacca edulis* peel pre-treated with CaCl₂ loaded with Cu²⁺ was examined by using the same technique and comparisons were made between the loaded and unloaded pre-treated samples, see Figure 1(c). It was observed that

there were no differences between the loaded and unloaded biomass samples. The SEM image could not show the presence of Cu²⁺ ions. The cylinder-like shapes were in the same range with those of loaded and unloaded samples.

The presence of Cu²⁺ ions on the surface of *Zalacca edulis* peel pre-treated with CaCl₂ biomass was confirmed by the use of EDX and EPMA analyzers (see Figure 2). However, the presence of Cu²⁺ ions in the inner structure could not be identified. The distribution of Cu²⁺ ions was detected at about 0.049 (mass %).

3.2 Effects of pH

The pH of the solution was an important parameter in the biosorption process (Kaewsarn and Yu, 2001). The effects of pH on the biosorption capacity of Cu²⁺ ions by untreated *Zalacca edulis* peel biomass and *Zalacca edulis* peel pre-

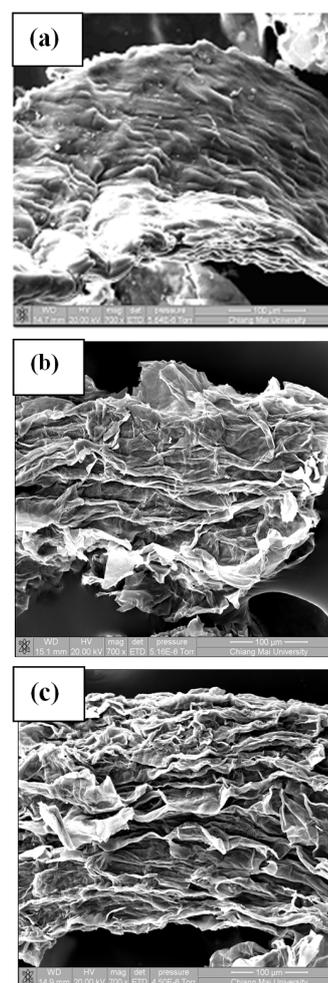


Figure 1. SEM images of *Zalacca edulis* peel (a) untreated *Zalacca edulis* peel (b) *Zalacca edulis* peel pre-treated with CaCl₂ and (c) *Zalacca edulis* peel pre-treated with CaCl₂ loaded with Cu²⁺ ions. All images are at magnification of 700x (scales indicated in each image).

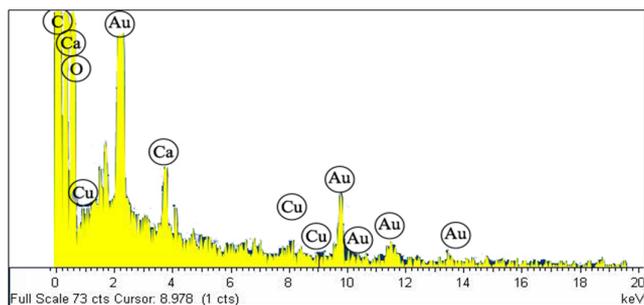
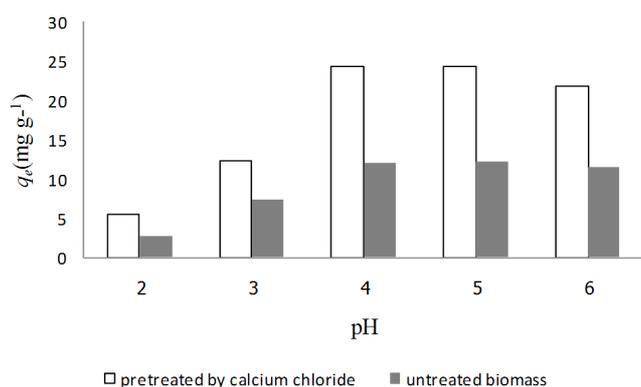


Figure 2. EDX surface analysis.

Figure 3. Effect of pH on Cu²⁺ ions in untreated peel and *Zalacca edulis* peel pre-treated with CaCl₂ (biomass 0.1 g, Cu²⁺ ions 100 mg L⁻¹, contact time 24 hours, speed 100 rpm).

treated with CaCl₂ are shown in Figure 3. There was an increase in Cu²⁺ ion sorption as the pH values increased from 2 to 6. The maximum adsorption capacity was observed at pH 4-5, results that were in accordance with the results for the optimum pH for biosorption of Cu²⁺ ions in the studies of Matheickal and Yu (1997), Basci *et al.*, (2004), and Ucun *et al.* (2009). These results may be explained by the fact that at lower pH values, H³⁺ ions compete strongly with metal ions for exchange sites in the adsorbent. The surface charge of the biomass was positive and cations adsorption was not favorable. Cu²⁺ ion uptake was small because the surface area of the adsorbent was protonated of hydrogen ions (Ertugay *et al.*, 2010).

The effect of pH can be described in terms of pH_{pzc} of the adsorbent and species of Cu (II) formed in the solution. When pH=pH_{pzc}, the surface charge of adsorbents is neutral, it is negligible of electrostatic attraction existing between the adsorbent surface and metal cations in solution. When pH is lower than pH_{pzc}, the surface charge of adsorbents is positive, which inhibits the approach of positively charged cations. Rivera *et al.* (2003) stated that an increase in the negative surface charge of the adsorbent that augments it to adsorb positively charged species. At pH greater than pH_{pzc}, the surface charge of adsorbents is negative. Thus, cations adsorption on adsorbent is favorable at pH values greater

than pH_{pzc} while anion adsorption is favorable at pH value lower than pH_{pzc} (Adedirin *et al.*, 2011).

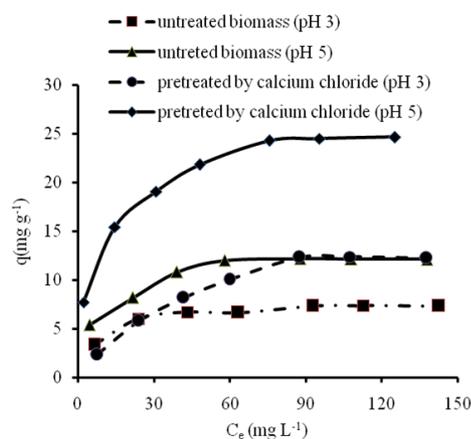
3.3 Effects of initial metal concentrations

The effects of initial Cu²⁺ ions on the biosorption capacity were investigated at pH 5. Figure 4 illustrates the relationship between uptake capacities (q_e) and metal concentrations (C_e), showing that in untreated *Zalacca edulis* peel biomass the biosorption of Cu²⁺ ions increased with increasing initial Cu²⁺ ion concentrations from 10 to 150 mg L⁻¹, until equilibrium was achieved at 100 mg L⁻¹ and became constant with further increase in C_e , similarly in case of the pretreated *Zalacca edulis* peel by CaCl₂. This relation showed the adsorption isotherm of Cu²⁺ on the adsorbents. In the cases of the CaCl₂ pre-treated *Zalacca edulis* peel. Bhatti *et al.* (2009) reported that the surface saturation was dependent on the initial metal ion concentrations.

The experimental data at optimum conditions were applied to the Langmuir and Freundlich models. These two isotherms view q_e as a function of C_e , in accordance to the equilibrium distribution of ions between aqueous and solid phase as the initial concentration (C_i) rises. In order to calculate each isotherm constantly C_i was varied (10-100 mg L⁻¹) for adsorption by the constant 0.1 g of sorbents for the contact time of 24 hours. The Langmuir isotherm model is based on three assumptions: (1) a homogeneous surface, (2) a monolayer coverage, and (3) no second interaction between solute and sorbent. The mathematical description of this model is as follows:

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

where q_e (mg g⁻¹) is the amount of metal ions adsorbed per unit mass of adsorbent, C_e the equilibrium metal concentration in the solution (mg L⁻¹), q_{\max} the Langmuir constant

Figure 4. Adsorption isotherm of Cu²⁺ ions on untreated *Zalacca edulis* and *Zalacca edulis* peel pre-treated with CaCl₂. (biomass 0.1 g, Cu²⁺ ions 10-150 mg L⁻¹, constant time 24 hours, speed 100 rpm at room temperature).

related to the maximum monolayer adsorption capacity (mg g^{-1}), and b is the equilibrium constant. The Freundlich isotherm model considers the non-ideal sorption on heterogeneous surfaces in a multiple layer way. The mathematical description of this model is as follows:

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

where K_F (L g^{-1}) and n are Freundlich constants representing the adsorption capacity and adsorption intensity or degree of favorability of adsorption, respectively. Equation 4 can also be written in the linear form:

$$\ln q_e = \ln K_F + \frac{1}{n} C_e \quad (5)$$

The results obtained from the adsorption isotherms were analyzed by the use of the Langmuir and Freundlich models. The experimental data point for biosorption of Cu^{2+} ions at pH 3 and pH 5 are shown in Figure 5 and 6. The values of the regression coefficients obtained from these models were used as the appropriate criteria to discover these isotherms. The biosorption data for Cu^{2+} ions of untreated and pre-treated *Zalacca edulis* peel were in agreement with both the Langmuir and Freundlich models. This implied the possibility of Cu^{2+} ion adsorption by untreated *Zalacca edulis* and *Zalacca edulis* peel pre-treated with CaCl_2 by monolayer biosorption and heterogeneous surface conditions (Donmez and Akzu, 2002).

Table 1 shows the isotherm model constant for biosorption Cu^{2+} ions by untreated *Zalacca edulis* peel and *Zalacca edulis* peel pre-treated with CaCl_2 . The uptake capacity (q_{\max}) of *Zalacca edulis* peel pre-treated with CaCl_2 was higher than the untreated samples. According to the results of other researchers (Schiewer and Santosh, 2007; Saikaew and Kaewsarn, 2010), the pH solution significantly affected the biosorption equilibrium, for example, at pH 5 the uptake capacity was higher than that at pH 3 (Table 1). The findings were probably due to the fact that at low pH values, there was a high concentration of proton in the solution and this competed with metal ions in the formation of bonds with active sites on the surface of the biomass (Pavasarnt *et al.*,

2006). On the other hand, a decrease in proton concentration at pH 5 caused a decrease the competition between protons and metal ions for the same binding sites, resulting in an increase in sorption capacity (Kaewsarn and Yu, 2001).

3.4 Adsorption kinetics

Kinetic information is required for modeling and the design of the adsorption process. Figure 7(a) illustrates the

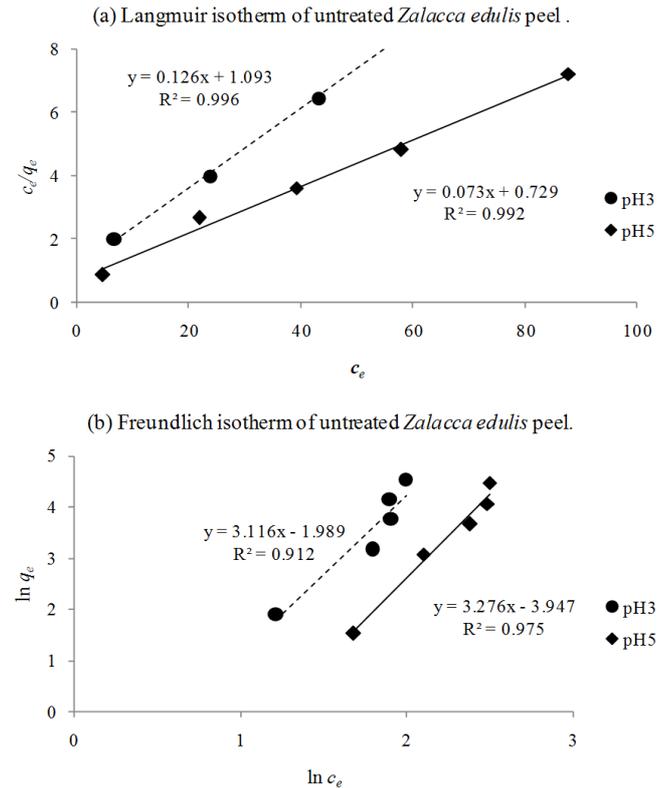


Figure 5. Langmuir and Freundlich isotherm plots for the biosorption of Cu^{2+} ions by untreated *Zalacca edulis* peel (biomass 0.1 g, Cu^{2+} ions concentration 100 mg L^{-1} , speed 100 rpm, contact time 24 hours).

Table 1. Langmuir and Freundlich isotherm parameters for Cu^{2+} ion uptake by untreated *Zalacca edulis* peel and *Zalacca edulis* peel pre-treated with CaCl_2 .

Sample	Langmuir model			Freundlich model		
	b (L mg^{-1})	q_{\max} (mg g^{-1})	R^2 (L g^{-1})	K_F	n	R^2
Untreated biomass						
pH 3	0.115	7.937	0.996	0.137	0.321	0.912
pH 5	0.100	13.70	0.992	0.019	0.305	0.975
Pre-treated with CaCl_2						
pH 3	0.018	20.83	0.995	0.486	0.687	0.992
pH 5	0.109	27.03	0.991	0.005	0.333	0.993

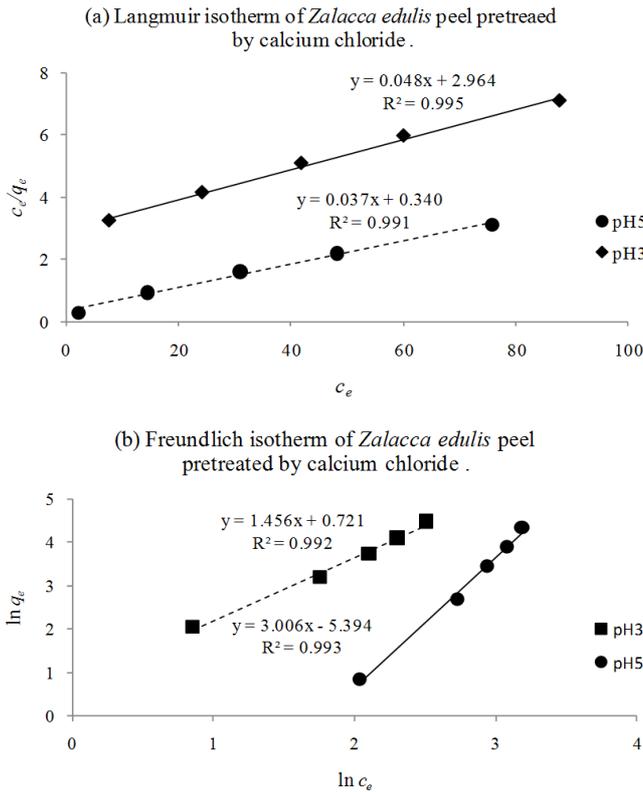


Figure 6. Langmuir and Freundlich isotherm plots for the biosorption of Cu^{2+} ions by *Zalacca edulis* peel pre-treated with CaCl_2 (biomass 0.1 g, Cu^{2+} ions concentration 100 mg L^{-1} , speed 100 rpm, contact time 24 hours).

time profiles of the adsorptions of Cu^{2+} ions by the untreated *Zalacca edulis* peel and *Zalacca edulis* peel pre-treated with CaCl_2 . It can be observed that the adsorption was rapid during 30 min. and then equilibrium within 60 min. The curve showed that sorption took place in two main stages – a very rapid stage in which biosorption was fast as a result of available binding sites on the external surface of the biomass and a second slow stage due to diffusion of metal ions into the inner part of the biomass. Similar results for copper and other biosorbents have been reported in other literature, for example, Cu (II) in *Aspergillus flavus* biomass (Akar and Tunali, 2006), copper in sour orange residue (Khormaei *et al.*, 2007), and Cu (II) in disintegrated aerobic granules (Wang *et al.*, 2010).

To characterize kinetic behavior, pseudo-first order model has been widely used. This can be expressed as:

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \tag{6}$$

where q_e and q_t are the amounts of metal adsorbed at equilibrium and at a given time t respectively, and k_1 is the first order rate constant. The linear form is:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \tag{7}$$

A plot of “ $\ln(q_e - q_t)$ ” versus “ t ” should generate a

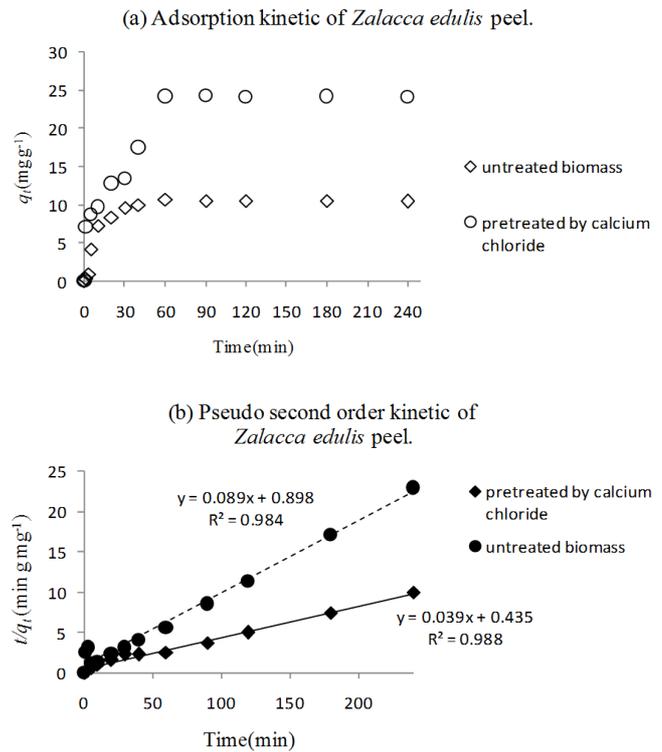


Figure 7. Adsorption kinetics and pseudo second order model of Cu^{2+} ion adsorption by *Zalacca edulis* peel (0.1 g biomass, 100 ml of 100 mg L^{-1} Cu^{2+} ion solution, pH 5, 100 rpm and room temperature).

straight line with an intercept of “ $\ln q_e$ ” and the slope of “ $-k_1$ ” value of “ q_e ” can be calculated and compared with that experiment. The pseudo-second order kinetic equation proposed by Ho and McKay (1999) is:

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \tag{8}$$

where k_2 is the second order rate constant. The linear form is:

$$\frac{t}{q_t} = \frac{1}{k_2(q_e^2)} + \frac{t}{q_e} \tag{9}$$

A plot of (t/q_t) versus t should generate a straight line with an intercept of $1/k_2 q_e^2$ and slope of $1/q_e$. The value of q_e can be calculated and compared with that obtained in the experiment.

Kinetics parameters were determined using linear regressive method with the least sum of squares of difference. The kinetic information obtained from the model is summarized in Table 2. Plots for the pseudo-first order equation, see Equation 6, of Cu^{2+} ions in samples pre-treated with CaCl_2 are not shown because the correlation coefficient for the pseudo-first order model were lower than that of the pseudo second order model (Equation 8). As seen in Table 2, the pseudo-first order model is not suitable for modeling the

Table 2. Results of Cu²⁺ ion biosorption kinetic modeling.

Type of biosorbent	Kinetic model			
	Pseudo first order equation		Pseudo second order equation	
	untreated	pretreated by CaCl ₂	untreated	pretreated by CaCl ₂
Fitted model	2.339-0.079t	2.405-0.025t	0.898+0.089t	0.435+0.039t
R ²	0.969	0.637	0.984	0.988
Constant	$k_1 = 0.079 \text{ min}^{-1}$	$k_1 = 0.025 \text{ min}^{-1}$	$k_2 = 0.010 \text{ g mg}^{-1} \text{ min}^{-1}$	$k_2 = 0.004 \text{ g mg}^{-1} \text{ min}^{-1}$
Calculated $q_e (q_{e,cal})$	10.37 mg g ⁻¹	11.08 mg g ⁻¹	11.24 mg g ⁻¹	25.64 mg g ⁻¹
Experimental $q_e (q_{e,exp})$	10.66 mg g ⁻¹	24.26 mg g ⁻¹	10.66 mg g ⁻¹	24.26 mg g ⁻¹

adsorption of Cu²⁺ ions by untreated *Zalacca edulis* and *Zalacca edulis* peel pre-treated with CaCl₂. In contrast, application of the pseudo-second order model yields best fits to the experiment data of samples pre-treated with CaCl₂, see Figure 7(b). Beside the highest regression coefficients of 0.984 and 0.988 in cases of untreated samples and samples pre-treated with CaCl₂, respectively, the closeness of the calculated values ($q_{e,cal}$) to the actual values ($q_{e,exp}$) for this model indicates the ability of the pseudo second-order model to describe the kinetics of Cu²⁺ ion uptake by untreated *Zalacca edulis* and *Zalacca edulis* peel pre-treated with CaCl₂. The estimated model parameters (k_1 , k_2 and q_e) in Table 2 indicate that they depend on the type of biomass. Similar results have been obtained by Schiewer and Santosh (2007), Ibrahim *et al.* (2006), and Olivares *et al.* (2011), who compared a pseudo-first order and pseudo-second order model. They found that the pseudo-second order model was superior for the binding of divalent cations. Base on the adsorption kinetic assumption that the rate limiting step might be chemical biosorption (Ho, 2006).

4. Conclusion

This study showed the bioadsorption ability of untreated *Zalacca edulis* peel biomass and *Zalacca edulis* peel pre-treated with CaCl₂. SEM analysis demonstrated that the structure of the biomass was uniform due to the pre-treatment by CaCl₂. This pre-treatment enhanced the bioadsorption capacity of the *Zalacca edulis* peel biomass. pH played an important role in Cu²⁺ ion adsorption in both untreated *Zalacca edulis* peel and *Zalacca edulis* peel pre-treated with CaCl₂. The sorption capacity was significantly affected by the initial metal concentration. Sorption data of untreated *Zalacca edulis* peel in this study is in accordance with the Langmuir model. The Langmuir and Freundlich Isotherm models were the more appropriate models for Cu²⁺ ion in *Zalacca edulis* peel pre-treated with CaCl₂. Isotherm studies show that Cu²⁺ ion sorption in untreated *Zalacca edulis* and *Zalacca edulis* peel pre-treated with CaCl₂ was good even at pH 5. Sorption kinetics was found to be more appropriate with the pseudo-second order in the both adsorbents. The results of this study indicate that *Zalacca edulis* peel is a

suitable choice for the adsorption of Cu²⁺ ions from aqueous solutions.

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