Research Article

Equilibrium and kinetics modeling biosorption of Zn(II) in aqueous solution using durian (*Durio zibethinus*) seed as low-cost biosorbent

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ABSTRACT

The research of biosorption Zn(II) in aqueous solution using durian seed powder has been conducted. The capability of durian seed powder to biosorption of Zn(II) in aqueous solution is affected by the solution pH, contact time, stirring speed, biosorbent mass and initial concentration in the solution. Experiments conducted in a batch at room temperature. The biosorption capacity increases with increasing initial concentration of Zn (II). The optimum condition biosorption obtained at pH 4, contact time of 60 minutes, stirring speed of 150 rpm, 0.1 g biosorbent mass and initial concentration of 200 mg/L. The equilibrium data was calculated using equation model of Langmuir, Freundlich and Temkin isotherm. The kinetic data were analyzed using Lagergren kinetics equation pseudo-first-order, pseudo-second-order and diffusion intra particles.

Keywords: Biosorption, durian (*Durio zibethinus*) seed, Equilibrium and kinetics.
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INTRODUCTION

The increasing concentrations of heavy metals in the waste water are generally caused because of some industrial waste disposal. Pollution of natural waters naturally by the metal ions become a major issue because of the concentration of heavy metals passes the threshold value permitted [1]. Heavy metals can not be degraded in the environment can be harmful to some species of living cell in waters, can accumulate through the food chain so that it can affect human health [2].

These Heavy metals can cause changes in human health such as the accumulation of poisoning, cancer, brain damage, lung damage, hepatic and renal damage [3]. Zinc in trace amount sneeded by the body as a physiological function of a living tissue and regulation in biochemical processes, but at a very high concentration of 100-500 mg/g per day can lead to serious health problems such as stomach cramp, skin irritations, vomiting, nausea, and anemia [4].

Several methods that have been used for the absorption of heavy metals is adsorption, complexation, chemical oxidation or reduction, chemical precipitation, reverse osmosis, ion exchange and solvent extraction [5-8]. adsorption is a method commonly used for easier low-cost and little use of reagents [9].

Some agricultural waste has been used as biosorbent by many researchers including sugarcane bagasse modified and sawdust [10], Carica papaya seed [11], Akkee apple (*Bligia sapida*) seed [8] and durian peel [12].

Durian is known as a preferred fruit in Southeast Asia because of the taste and flavor. It's unique odor and taste of so many processed into food such as candy, ice cream and cakes. One known durian species found in a local area is Durio zibethinus. Because of the high consumption of durian, it can cause problems waste shell and seed durian. It has been reported that *Durio zibethinus* largely consists of holocellulose (73.5%), α-cellulose (60.5%) and hemicellulose (13.1%) [13]. This characteristic makes it attractive as a adsorbent for the removal of metal ions. Therefore, in the present work, biosorption of Zn(II) from aqueous solution onto durian seed was examined. The equilibrium and kinetics modeling of the adsorption were also studied in detail.

EXPERIMENTAL SECTION

Biomass Preparation
Durian seeds were obtained from a local market in Padang City, Indonesian. Durian seed were thoroughly washed with distillated water and air-dried at room temperature   for 7 days. After drying the durian seed dry in an oven maintained at a temperature of 60°C. The oven-dried seed were later ground and sieved using sieve of mesh sizes 71 μm. This was stored in desiccator and used in further experiments.

Chemical and Equipment
All chemical used were of analytical reagent grade. Deionized double distilled water was used throughout the experimental studies. A stock solution of Zn 1000 mg/L was prepared by dissolving as much 4.39 grams of Zn $(SO_4)_2$ in 1L volumetric flask slightly acidized distilated water. Standard solution prepared by diluting the stock solution. HNO_3 and NaOH solution were used to adjust the solution pH. The concentration of metal ions initially and at equilibrium in the samples is measured by Atomic Absorption Spectrophotometer. Analysis functional group by FTIR spectrophotometer was used for IR spectral studies (4000-400 cm-1) of adsorbent and characterization morphology sorbent by SEM-EDX.

Biosorption Studies
Experiments conducted in a batch process biosorption in 100 mL conocal flasks containing 20 mL Zn(II) solution using a thermostatic water bath shaker operated at a constant speed. Effect of pH, contact time, stirring speed, mass and concentration of metal ions studied on the biosorption process was investigated by equilibrating 0.1 g of DS (particle size of 71μm) in a series of conical flasks, containing $10mgL^{-1}$of Zn(II) solution with pH ranging from2.0 to 6.0 The effect of contact time on the removal of Zn(II) was conducted at different contact times ranging from 5 to 120 minutes, agitation speed from 100-300 rpm and concentration from 10-250 mg/L Zn(II) solution and temperature 300°K. The mixture of the sorbent and the solution was filtration after agitation and the concentration of metal ion present in the supernatant was determined using atomic absorption spectrometer (AAS). The amount of metal ions adsorbed per unit mass of sorbent was determined according to the following equation:

$$Qe = \frac{Co - Ce \cdot V}{M} \tag{1}$$

Where m is the mass of DS(g), V is the volume of the solution(L), C_0 is the initial concentration of metal (mgL^{-1}), Ce is the equilibrium concentration of the adsorbate in the liquid phase (mgL^{-1}), and qe is the amount of metal adsorbed at Equilibrium (mgg^{-1}).

Equilibrium Studies
Equilibrium isotherm studies were conducted by agitating 0.1 g of DS with 20mL of zinc solution of pH 2 for 60 minutes. The initial metal concentration ranged from 10 to 250 mgL^{-1}.The samples were then filtration and analyzed as described earlier.

RESULTS AND DISCUSSION

Effect of pH
The effect of Ph on the biosorption of Zn(II)by durian seed is presented in Figure 1.

It is obvious from the figure 1 that the biosorption capacities of Zn^{2+}increased from 0,.3864 to 1.8452 when the pH was raised from 2 to 4.The pH dependence of metal uptake can be related to the functional groups of the sorbent and also to solution chemistry. At pH values less than 4 metals are in their free ionic form (Zn^{2+}) and as such the sharp increase in metal uptake between pH 2 and 4 cannot be described by the change in metal speciation. One would expect a very low metal uptake at this region because of the repulsive forces that exit between the H^+ and Zn^{2+}ions. This can make one assumes that the functional groups present on the surface of the sorbent and their associated ionic state are responsible for this extent of biosorption [14,15].
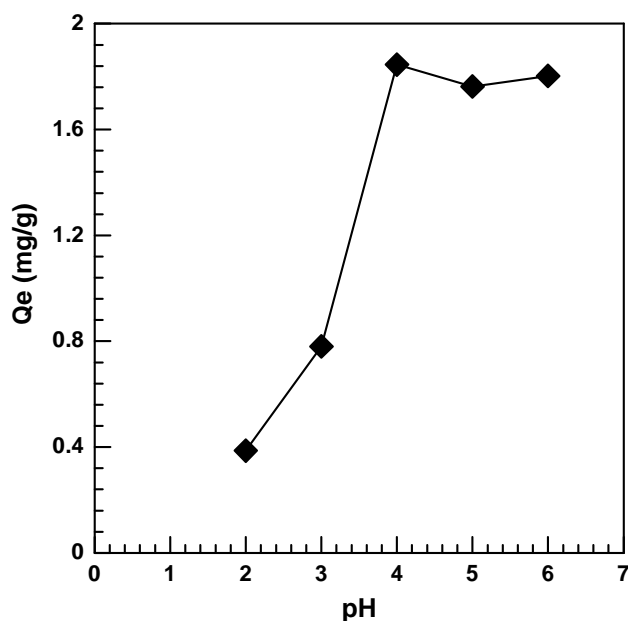
Figure 1. Effect of pH on the sorption of Zn(II)

At low pH there is high concentration of hydrogen ions resulting in competition with metal ions, causing the absorption capacity is low. By increasing the pH, the hydrogen ion concentration is reduced and the cause of functional groups on the surface biosorbent becomes negatively charged so that can cause interactions with metal ions and produce a sufficiently high absorption capacity. The absorption capacity of the optimum Zn metal ion obtained at pH 4. At pH higher than 4 a decrease in the amount of zinc removed was noticed this could be due to the formation of anionic hydroxide complexes and lower polarity of zinc ions at higher pH values [16]. Literature reports have it that maximum uptake of Zn^{2+} for most sorbent takes place between pH 4 and 5 [16-18].
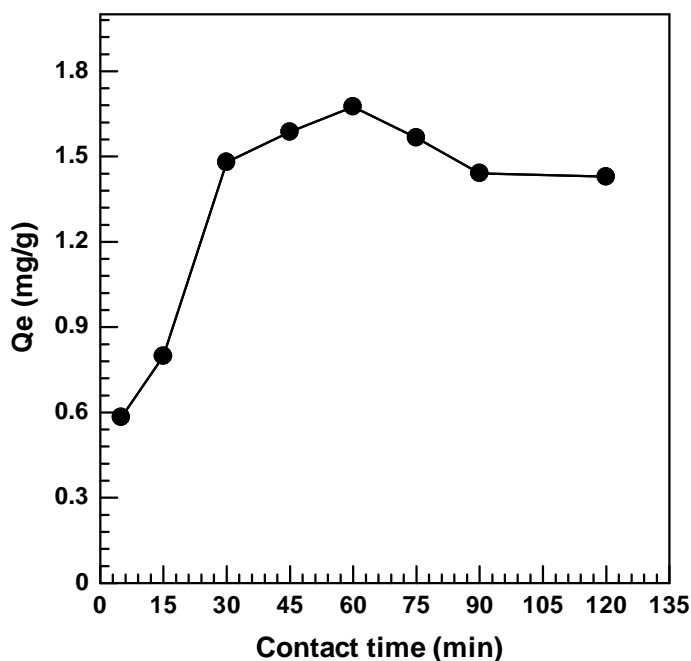

Figure 2. Effect of contact time of biosorption Zn(II) by durian seed

Effect of Contact Time

Contact time is one of the important parameter for successful use of the biosorptions for practical application and rapid sorption is among desirable parameter [5]. The result for the effect of contact time on the removal of Zn^{2+} by DS is presented in Figure 2. The result shows that the rate of metal removal occurred rapidly within the first 60 minutes of the biosorption process, and after this the process proceeded slowly. This indicates that most of the biosorption occurs on the surface rather than the pores of the durian seed [19]. The figure also reveals that maximum uptake of zinc took place after 60 minutes of agitation beyond which there was no appreciable increase in uptake of zinc; instead there was a small decrease in biosorption rate. This might be due to saturation of the sorbent surface with zinc followed by adsorption and desorption after saturation [4].

Biosorption kinetics study

In order to investigate the mechanism of sorption, the rate constants for sorption of Zn(II) determinate using some kinetic models [20]. The kinetics studied of Zn(II) adsorption were carried out by batch adsorption that formerly were used to determine optimum condition of contact time[21].

For pseudo first-order rate equation of Lagergren [22]. The pseudo first-order rate:

$$\frac{dQ}{dt} = k_1 (Qe - Qt) \tag{2}$$

The linear first-order rate expression was generally expressed as:

$$-\ln (Qe - Qt) = k_1 \cdot t - \ln Qe \tag{3}$$

For pseudo second-order rate, samples were taken until 60 min for Zn(II). The pseudo second order rate:

$$\frac{dQ}{dt} = k_2 (Qe - Q_t)^2 \tag{4}$$

The linear form of pseudo second-order can be written [23]:

$$\frac{t}{Qt} = \frac{1}{k_2 Qe^2} + \frac{t}{Qe} \tag{5}$$

where Qe and Qt were the amount of Zn(II) ions adsorbed at equilibrium and at time t (mg/g), k_1 was the pseudo first-order rate constant (min^{-1}) and k_2 was the pseudo second order rate constant (g/mg min). The pseudo first- and second order kinetic models consider that the rate of occupation of adsorption site to be proportional to the number of unoccupied sites and the concentration of adsorbate, while the rate of desorption to be proportional of the occupied sites. If the initial adsorbate concentration was high it produced the pseudo first order reaction [eqns. (2) and (3) [21].

The intraparticle diffusion equation is expressed as [24]:

$$Qt = Kid. \, t^{1/2} + C \tag{6}$$

Where Qt (mg/g) is the amount adsorbed at time t (min), Kid ($mgg^{-1}min^{-0,5}$) is the rate constant of intraparticle diffusion. C is the value intercept which gives an idea about the boundary layer the thickness, i.e. the larger intercept, the greater is the boundary effect [24]. If the intra particle diffusion is the sole rate the determining step, the plot of Qt Vs. $t^{1/2}$ should be linier passing through the origin. The plot in the figure is multiline with the three distinct regions. The initial curved region correspondents to the external surface uptake, the second stage related the gradual uptake reflecting intraparticle diffusion as the rate limited step and final plateau region indicates equilibrium uptake [25]. Based on the result it may be concluded the intraparticle diffusion is not only the determining factor.
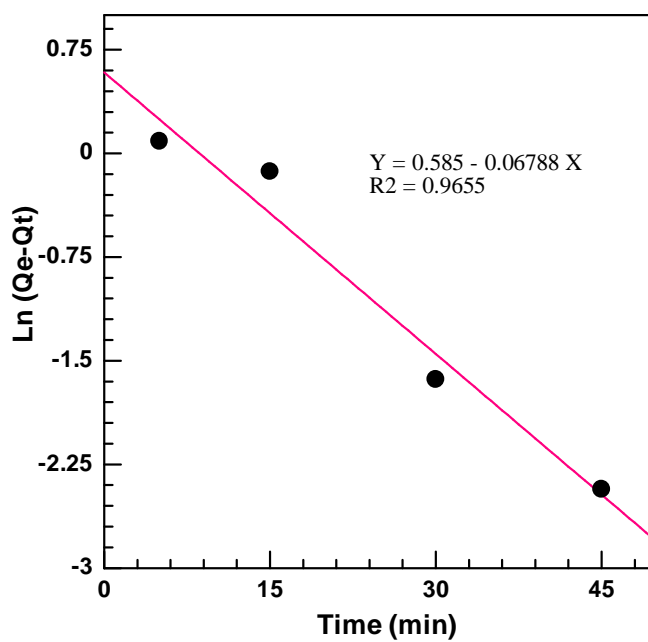
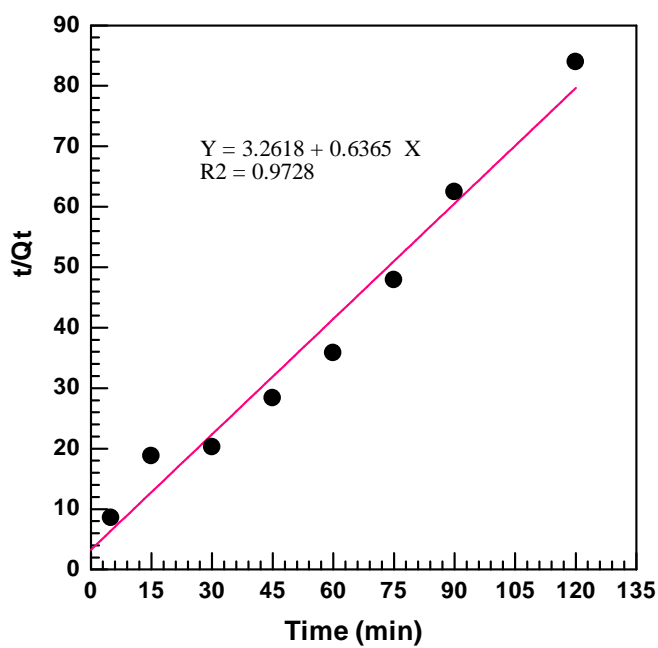**Figure 3. Pseudo-first order kinetic model for Zn(II)**

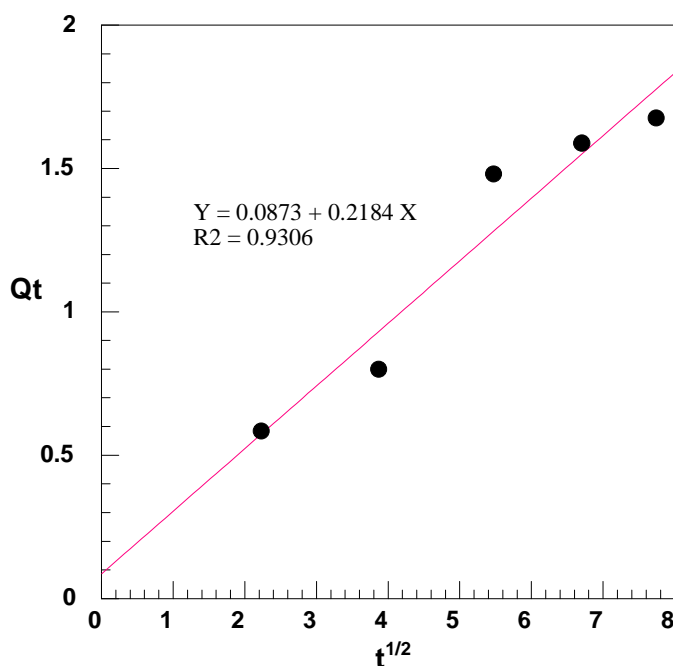**Figure 4. Pseudo-second order kinetic model for Zn(II)**

Figure 5. Diffusion intra–particle Zn(II)

The value of rate constants and correlation coefficients for each model are shown in Table 1. The correlation coefficients R^2 show that the adsorption process follow pseudo-second-order model. Its observed from Table 1 that the pseudo –second-order model gives a better fit that the two other models (pseudo-first-order and intraparticle diffusion models). Model suggesting a chemicals reaction mechanism [26]. This would indicate that the metal cation sorption is complex mix of surface chemisorption occurring on the boundary layer of the durian seed particle and intra-particle diffusion.

Table 1. Parameters of pseudo-first-order, pseudo-second-order and intraparticle diffusion models for Zn (II)

Pseudo-first-order			Pseudo-second-order			Weber and Morris			
K_1 (min^{-1})	Qe (th) mgg-1	R^2	K_2	Qe	R^2	K_{id}	Qe	R^2	Q_{exp} (mg/g)
-0.0679	0.557	0.9655	0.124	1.571	0.9728	0.2184	0.0873	0.9306	1.675

Effect of string speed
Biosorption studies were carried out in shaker at pH 4 for Zn (II). The stirring speed varied from 100-300 rpm. Figure 6 illustrated the influence of the stirring speed on the biosorption, showed that an optimum value was obtained at the highest biosorption capacity 1.864 mg/g was recorded at 150 rpm and declined slightly as the speed increased to 300 rpm. The increased in biosorption capacity at a high string speed could be explained in term of boundary layer thickness. By increasing the string speed, a good degree of mixing could be achieved, and the boundary layer thickness around the sorbent particles could be reduced [27]. Hence, the concentration of Zinc ion near the surface of sorbent would be increased. However, a more vigorous stirring speed resulted in more zinc ion being desorbed from the sorbent surface, which suggests a possible breaking of newly formed bonds between zinc ion and bio sorbent surface [21]. Therefore, stirring speed of 150 rpm was selected for subsequent biosorption analysis.

Effect of biomass dosage
Biomass dosage is an important parameter because this determines the capacity of sorbent for a given initial concentration. The biosorption as a function of biomass dosage was investigated in Figure 7. It is clear from the figure that uptake capacity in mg/g decreased from 1.039- 0.252 mg/g with the increased the sorbent dose of DS used. This may due to increase in the number of binding sites available at high concentration of the sorbent [4-5]. This result can be explained by the fact that the biosorption sites remain unsaturated during the biosorption reaction whereas the number of sites available for the biosorption site increases by increasing the sorbent dose [5]. Therefore, the optimum biomass dosage was taken as 0,1 g for further experiments.
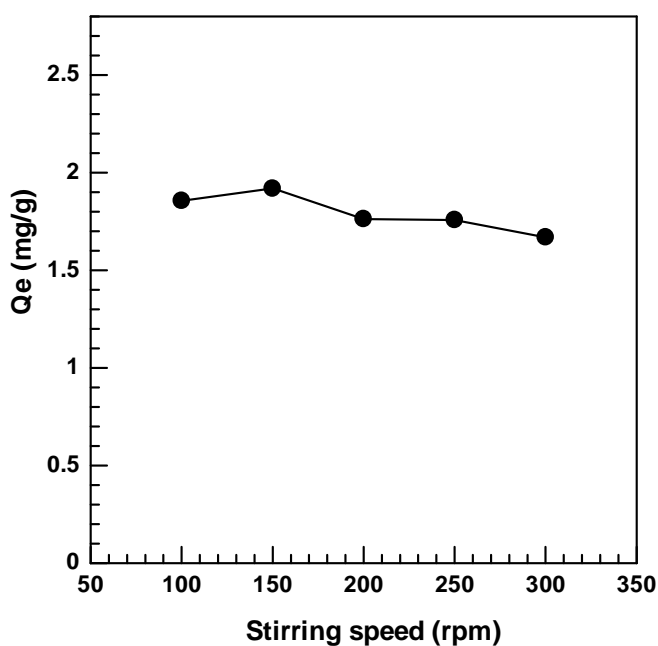
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Figure 6. Effect of the stirring speed on Zn(II) biosorption
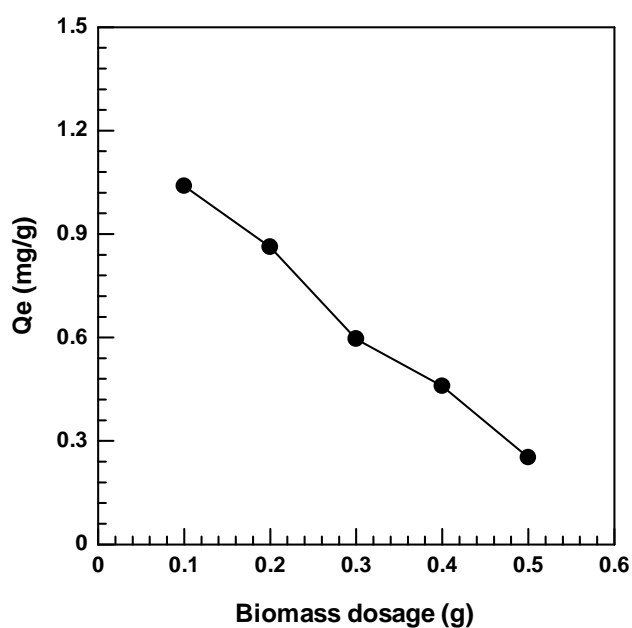

Figure 7. Effect of biomass dosage (g) on Zn(II) biosorption

Effect of initial metal ion concentration
The influence of initial metal ion concentration on biosorption was studied at room temperature and pH 4. Figure 8 shows that all the curves have the same trend, i.e. initial quick decreased followed by a final stability, with the increasing of biomass dose. This was due to the interference between binding site and higher biomass dose or insufficiency of metal ion in solution with respect to available binding sites [28].

The biosorption of Zn(II) ion by DS increased by increasing initial metal ion concentration, and became saturated at 200 mg/L. The maximum Zn(II) uptake capacity were determined as 18.3298 mg/g. These results may be explained that the initial metal concentration provides a driving force to overcome all mass transfer resistances between the

sorbent and the biosorption medium. Hence higher sorption capacities were obtained at higher initial metal concentration.
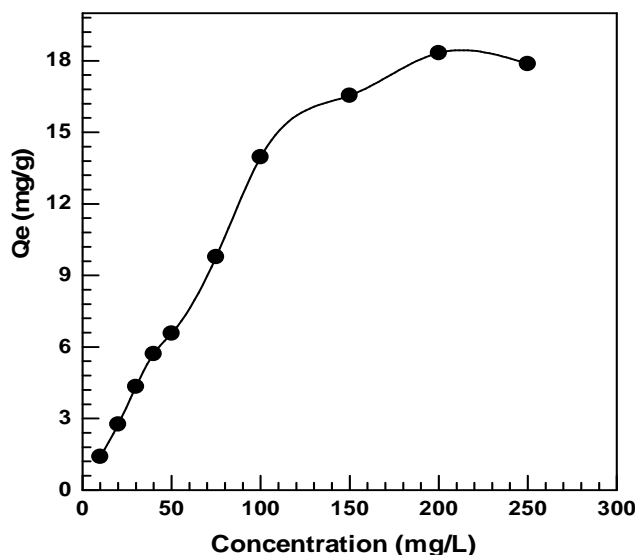

Figure 8. Effect of initial concentration on biosorption capacity of Zn(II)

Biosorption isotherm models
The capacity biomass can be described by equilibrium sorption isotherm, which is characterized by certain constants whose values express the surface properties and affinity of the biomass. The biosorption isotherms were investigated using three equilibrium models, which are namely the Langmuir, Freundlich and Temkin isotherm models analysis [5].

Langmuir isotherm
The Langmuir sorption isotherm has been successfully applied to many pollutant biosorption processes and has been the most widely used isotherm for the biosorption of a solute from a liquid solution. A basic assumption of the Langmuir theory is that sorption takes place at specific homogenous sites within the sorbent. This model can be written in non linier form [29].

$$Qe = \frac{Qm.K_L.Ce}{1 + K_L.Ce} \tag{7}$$

Where Qe is the equilibrium metal ion concentration on the adsorbent (mg/g), Ce is the equilibrium metal ion concentration in the solution (mg/L), Qm is the monolayer biosorption capacity of the sorbent (mg/g) and K_L is the Langmuir biosorption by constant (L/mg) related with the free energy of biosorption. Value of Langmuir parameters Q_{max} and K_L were calculated from the slope and intercept of the linier plot of Ce versus Ce/Qe as show in figure 9. Values of Q_{max}, K_L and regression coefficient R^2 are listed in Table 2.

Freundlich isotherm
The Freundlich isotherm model is the well-known earliest relationship describing the adsorption process. This model applies to adsorption on heterogeneous surfaces with interaction between adsorbed molecule and the application of the Freundlich equation also suggest that sorption energy exponentially decreases on completion of the sorption centers of an adsorbent. This isotherm is an empirical equation and can be employed as follow in linier form [30].

$$Ln\ Qe = Ln\ K_F\ +\ 1/n\ Ln\ Ce \tag{8}$$

Where K_F is the Freundlich constant related to the bonding energy, 1/n is the heterogeneity factor and n (g/L) is a number of deviation from linearity of adsorption [31].
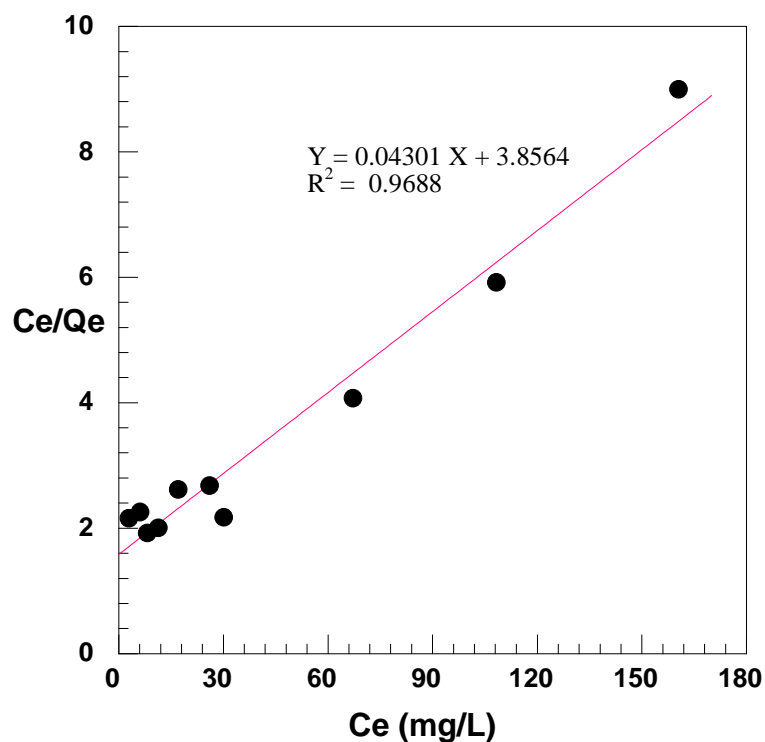
Figure 9. Langmuir Isotherm plots for the biosorption of Zn(II)

Freundlich equilibrium constant were determinate from the plot of ln Qe versus ln Ce, figure 10 on the basis of the linier of Freundlich equation (8). The n value indicated degree of non-linearity between solution concentration and adsorption as follow: if n = 1, then adsorption is linier, if n<1, then adsorption is a chemical process, if n>1 then adsorption is a physical process.

Temkin isotherm

The Temkin isotherm model assumes the adsorption energy decrease linearly with the surface coverage due to adsorbent-adsorbate interactions. The linier form of Temkin isotherm models is defined by:

$$Qe = RT \ Ln \ KT \ + \ \frac{RT}{bT} \ Ln \ Ce$$

Where bT is the Temkin constant related to heat of sorption (J.mol) and K_T is the Temkin isotherm constant (L/g). These constant were obtained from plotting Ln Ce versus Qe, figure 11. Value of bT and KT are listed in Table 2. The result comparison biosorption of Zn (II) with other biosorbent are listed in Table 3.

Table 2. Langmuir, Freundlich and Temkin constant for the biosorption of Zn (II)

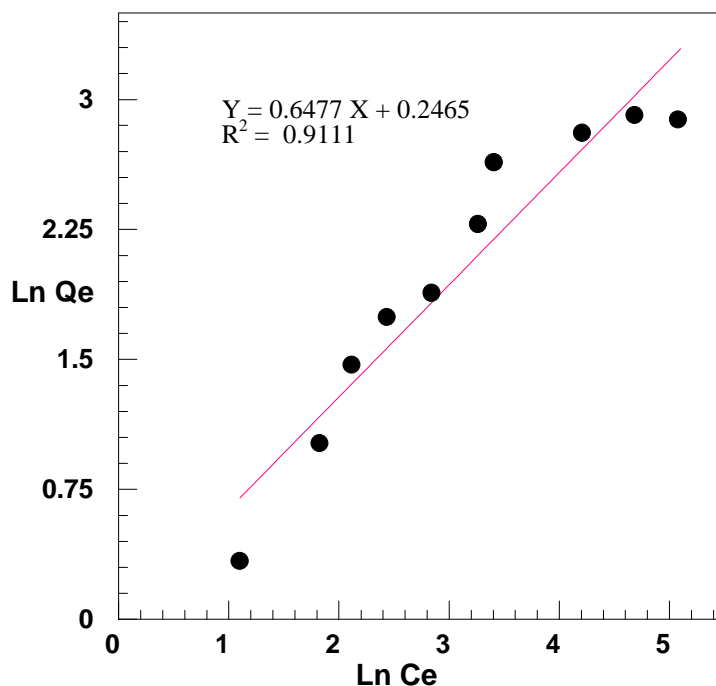| Metal	Langmuir			Freundlich			Temkin			
	Q_m	K_L	R^2	K_F	n	R^2	b_T	K_T	R^2	$Q_{m,exp}$
Zn	23.31	0.0279	0.9533	0.970	1.512	0.9024	5.0746	0.3246	0.9260	18.3298

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$$Y = 0.6477\ X + 0.2465$$
$$R^2 = 0.9111$$

Figure 10. Freundlich Isotherm plots for the biosorption Zn(II) onto DS

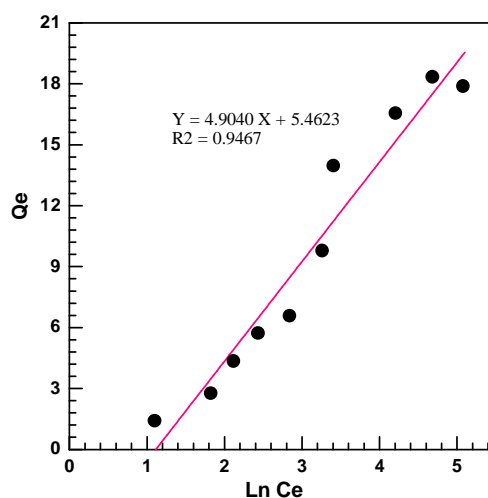$$Y = 4.9040\ X + 5.4623$$
$$R2 = 0.9467$$

Figure 11. Isotherm Temkin plots for the biosorption Zn(II)

Table 3. Comparison biosorption of Zn(II) with other bio sorbent

Biosorbent	Maximum Capacity of biosorption (mg/g)	Reference
Rice bran	14,17	34
Acinetobacter	36,6	35
Powder *Cow Hooves*	10,93	4
Caulerpa lentillifera	2.66	36
Pseudomonas strains	19,06	37
Lignocellulose substrate	16,02	38
Durian tree sawdust	22,78	39
Langsat (*Lansium domesticum corr*)	8,754	40
Pithecellobium jiringa	16,67	41
Durian (*Durio zibethinus*) seed	23,31	In this study

Sorbent Characterization

Scanning electron microscopy (SEM) connected with EDX represents another useful tool for studying mechanistic aspects of metal biosorption and for the qualitative visualization of metal sorbent interactions [32].Comparison of unloaded sorbent SEM images and images of DS after biosorption of Zn^{2+}ions (magnification 1000x) shows that in figure 12, there are morphological changes on the biomass surface and there did appear to be any specific

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localization of both metals on the sorbent surface. The cells before adsorption was characterized markedly a rather granular structure surface, while the post-adsorbed biomass was loose and had a rigid and folded appearance. Thus it could be suggested that the cell wall of durian seed acted as a defense against metal toxicity. EDXA is one of the useful tools to evaluate the chemical and elemental analysis of sorbents [33]. EDXA spectra taken in spot profile of Fig 13A mode recorded the signals of carbon, nitrogen, and oxygen which were likely present in polysaccharides and proteins on the cell wall of the biomass. An additional signal of Zn observed in EDXA profile of Fig. 13B indicated its presence due to the adsorption on the biomass was having smaller pores and therefore more specific surface area.
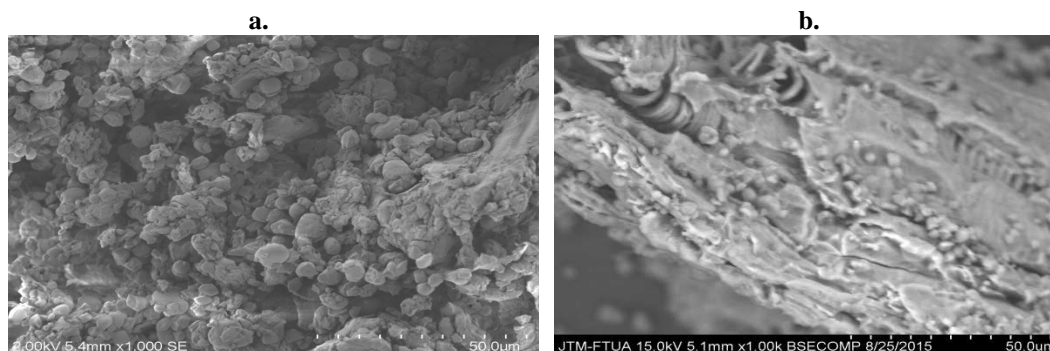
a.   b.

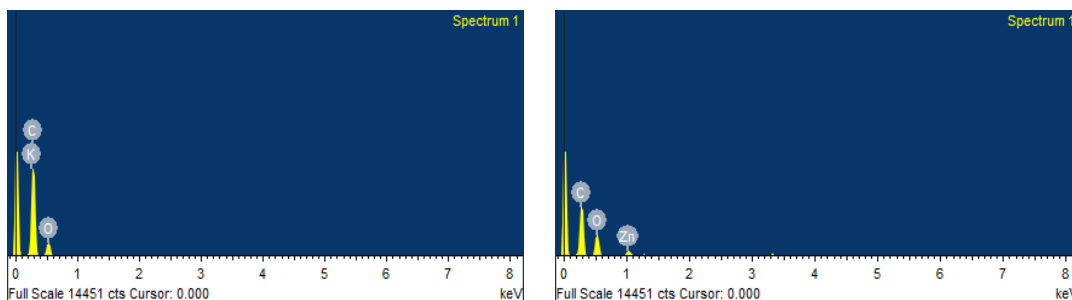**Figure 12. SEM before (a) and after (b) biosorption Zn (1000x magnification)**

FTIR Analysis

Figure 13. EDX before (a) and after biosorption of Zn(II)

CONCLUSION

In this study durian seed found to be a promising bio sorbent for the removal of Zn(II) from an aqueous solution because of its short equilibrium time, selectivity adsorption capacity and its high bio sorption capacity. The selective adsorption experiments were conducted and found that the durian seed has an excellent selective property to Zn (II). Adsorption has pH 4, adsorption increased with contact time and reaches equilibrium value at about 60 min. The biosorption is highly pH dependent and the maximum Zn (II) biosorption capacity is 18.3298 mg/g. The Langmuir isotherm model yields a much better fit than of Freundlich and Temkin isotherm models in describing Zn (II) adsorption. The kinetics of Zn(II) biosorption onto durian seed is follow by the pseudo-second-order equation. Compared to other sorbent reported in other literature, the durian seed shoe good promise for practical applications due to its easy to obtain nature, high biosorption capacity.

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