

Full Length Research Paper

Papaya (*Carica papaya*) seed as a low-cost sorbent for zinc removal

Siew-Teng Ong^{1*}, Shiau-Ping Yip¹, Pei-Sin Keng², Siew-Ling Lee³ and Yung-Tse Hung⁴

¹Department of Chemical Science, Faculty of Science, Universiti Tunku Abdul Rahman, Jalan Universiti, Bandar Barat, 31900 Kampar, Perak, Malaysia.

²Department of Pharmaceutical Chemistry, International Medical University, No.126, Jalan 19/155B, Bukit Jalil, 57000 Kuala Lumpur, Malaysia.

³Ibnu Sina Institute for Fundamental Science Studies, Universiti Teknologi Malaysia, 81310 Skudai, Johor Malaysia.

⁴Department of Civil and Environmental Engineering, Cleveland State University, Cleveland, Ohio, USA.

Accepted 6 December, 2011

The potential of using papaya seed as a sorbent for the removal of Zn from aqueous solution was investigated. The sorption characteristics of the sorbent was studied under various experimental conditions, such as pH, contact time, concentration of Zn(II), agitation rate and sorbent's particle size. The equilibrium data have been studied using Langmuir, Freundlich and Brunauer-Emmett-Teller equations. The best correlation was obtained using Langmuir isotherm with the regression coefficient value of 0.9799 and maximum sorption capacity of 19.88 mg/g. The effective pH for the maximum uptake of Zn(II) was at pH 5.0. An increase in percentage uptake of Zn(II) can be observed with increasing contact time and agitation rate. Decrease in sorbent particle size led to an increase in the sorption of Zn(II) and this could be explained by an increase in surface area and hence binding site. Equilibrium was attained around 60 min indicating this sorbent could be a potential material for continuous flow system.

Key words: Papaya seed, sorption, zinc, heavy metal removal, kinetics, modelling.

INTRODUCTION

Heavy metals are broadly referred to a group of toxic metals and metalloids associated with pollution and toxicity. As, Cd, Cr, Co, Cu, Fe, Pb, Ni, Ag, Sn, and Zn are some of the toxic elements listed by The Agency for Toxic Substances and Disease Registry (ATSDR). Zn exists in nature as sulphide, carbonate and silicate. In view of human metabolism, Zn is vital for the stabilization of DNA and the expression of genes as well as for the transfer of nervous signals. In fact Zn is an essential element for the functioning of various enzyme systems, including alkaline phosphate, carbonic anhydrase and alcohol dehydrogenase (Karl et al., 2004). However, the increasing accumulation of Zn in the environment from industrial outputs has caused great concern. Effluent

discharges from the industries of galvanising; electroplating, iron and steel are the major contributors to Zn pollution in the aquatic environment (Agarwal, 2009). Soil can be poisoned by Zn smelting or by Zn-contaminated sewage sludge.

Conventional technologies for the removal of heavy metals from industrial wastewater include chemical precipitation, ion exchange, membrane separation and adsorption by activated carbon. Most of these commonly practiced processes suffer from drawback such as high capital and operational cost or the disposal of the residue metal sludge (Low et al., 1999). Biological treatment methods have many advantages due to economical acceptance and simplicity of treatment facility. However, in certain extent they are often unsuitable for the treatment of wastewater containing heavy metals because of the poor biodegradability.

Despite the versatility of activated carbon as an adsorbent in wastewater treatment, it remains costly and

*Corresponding author. E-mail: ongst_utar@yahoo.com or ongst@utar.edu.my. Tel: +605-4688888. Fax: + 605-4661676.

problems with the spent carbon limit its large-scale application. Thus, extensive research has been directed to the investigation of low cost materials such as agricultural and industrial waste or by-products for the removal of heavy metals. These materials including corncobs (Zacaria, 2002), grape stalk wastes (Villaescusa et al., 2004), tea waste (Malkoc and Nuhoglu, 2006), strawberry lead powder (Liu et al., 2010), peanut hull pellets (Johnson et al., 2002), heavy metal sludge (Hsieh et al., 2006), waste beer yeast (Han et al., 2006) and granular slag (Dimitrova, 2002) have the advantage of being readily available and inexpensive.

According to Hameed et al. (2009), Malaysia is now capable of producing up to 72,000 tonnes of papaya annually. As a result, solid wastes such as peel, skin and seeds are excessively produced from papaya fruits. In general, over 50% of the papayas weight during processing appears as waste materials whereby papaya seeds consist of about 22% of the weight. The usage of the waste materials generated from this process could result in waste minimization and tremendous cost saving. Therefore, in the continued effort to use low-cost materials for the removal of heavy metals, the potential of papaya (*Carica papaya*) seed (PS) was explored under batch conditions.

MATERIALS AND METHODS

Preparation of sorbent and sorbate

The PS were collected from a local market and washed several times to remove dirt and other impurities. PS were boiled for 8 h to get rid of transparent gelatinous aril and then washed with deionised water. The washed materials were then oven-dried at 60°C for 48 h to ensure the removal of moisture content. The dried PS was then ground into fine particles. The powdered form of PS was stored in a container in a cool dry place for further use. No other physical or chemical treatments were employed prior to sorption experiments.

The synthetic metal ion solution was prepared from A.R. grade $Zn(NO_3)_2 \cdot 6H_2O$. A stock solution of 1000 mg/L was prepared and subsequently diluted when necessary. The percentage uptake of Zn(II) was calculated according to the following equation:

$$\text{Percentage uptake (\%)} = \frac{C_o - C_t}{C_o} \times 100 \quad (1)$$

Where C_o is the initial concentration and C_t is the concentration at time t .

Batch experiments

The batch studies were carried out at room temperature ($25 \pm 2^\circ\text{C}$) by mixing 0.1 g of sorbent with 25.0 ml metal ion solution in a centrifuge tube and shaken on an orbital shaker at 150 revolutions per minutes (rpm) for two hours unless otherwise stated. The reaction mixture was then centrifuged at 3000 rpm for phase separation. All the batch experiments were carried out in duplicate and the results given are the means with a relative standard

deviation (RSD) of less than 5%. Control experiments without sorbent was carried out to ascertain that the sorption was due to the sorbent and not the wall of the container. The supernatant was analyzed for its metal content using atomic absorption spectrometer (AAAnalyst 200, Perkin-Elmer).

To study the effect of pH on the sorption, the pH of metal ion solution was adjusted to the range of 2 to 10 by adding HCl or NaOH prior to experiment. Time course experiments were investigated by shaking the sorption mixture at various predetermined intervals and analyzing the metal ion concentration at the end of the contact time. The effect of agitation rate was investigated by varying the agitation rates from 50 to 200 rpm at various time intervals. The effect of particle size was studied using four different sizes (106 μm , 250 μm , 425 μm and 1 mm). For sorption isotherm, the concentrations were varied from 30 mg/L to 90 mg/L.

RESULTS AND DISCUSSION

Effect of pH

Figure 1 shows the effect of pH in the range of 2.0 to 10.0 on the uptake of 10 mg/L Zn(II) by PS. A continuous increase in the metal uptake was observed in the pH range of 2 to 5 and the maximum uptake of 98.33% was achieved at pH 5. It is clear that the metal-binding capacity was highly pH dependent. Introduction of strong acids or bases could typically modify the surface properties of PS, the solubility as well as the degree of ionization of metal ions. The low percentage uptake of Zn(II) onto PS at pH 2 was due to the excess H^+ ions surrounding the sorption sites. The active sites are being protonated in the presence of excess H^+ ions and these ions also compete effectively with metal cations for binding sites. This subsequently inhibit the binding of Zn(II) cations to the surface functional groups of PS due to the decrease of negative surface charge of sorbent.

As the pH of system increase, the negatively charged sites enhanced the electrostatic attraction force of the metal cations with the PS which led to a favorable sorption. At higher pH values, a diminution of the percentage uptake for Zn(II) was observed. This could be due to the hydrolysis reaction of metal cations. The formation of soluble hydroxylated complexes of metal ions hindered the metal-binding capacity (Rengaraj et al., 2001).

In the study conducted by Rocha et al. (2009) on the adsorption of divalent heavy metal cations Cu(II), Zn(II), Cd(II) and Hg(II) by rice straw, they also observed that an increase in pH led to a favorable adsorption. Maximum sorption capacity was recorded at pH 5 and at higher pH, a slight decrease occurred in metal cations sorption (pH 6 to 7).

Effect of initial concentration

The effect of initial concentration and contact time on the uptake of Zn(II) metal solution by PS at room temperature

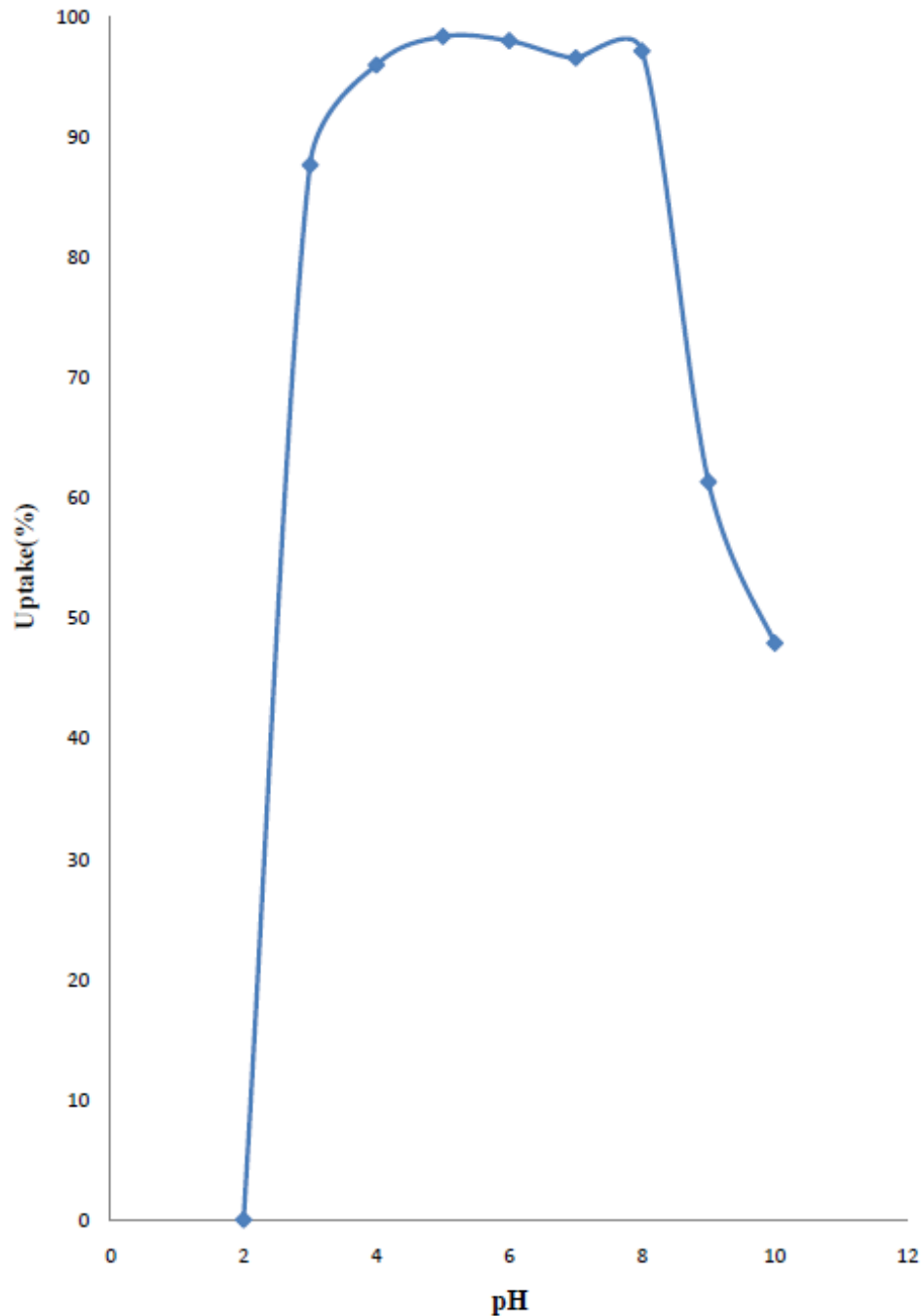


Figure 1. Effect of pH on the uptake of Zn(II) by PS.

was shown in Figure 2. The results showed that the percentage uptake of Zn(II) decreased gradually as the concentration increased from 10 to 80 mg/L. The metal uptake was rapid for the first 30 min and it proceeded at a slower rate and finally reached equilibrium at 120 min. Adsorption process with a relatively short contact time would indicate that most probably chemisorption is important (Ong et al., 2010a). The initial rapid stage was most likely attributed to the high number of available

vacant sites on the adsorbent surface. The second slower stage required a longer time periods in order to attain equilibrium due to the penetration of metal ions to the inner active sites of the adsorbent.

Sorption kinetics study

Sorption kinetics study in wastewater treatment is vital as

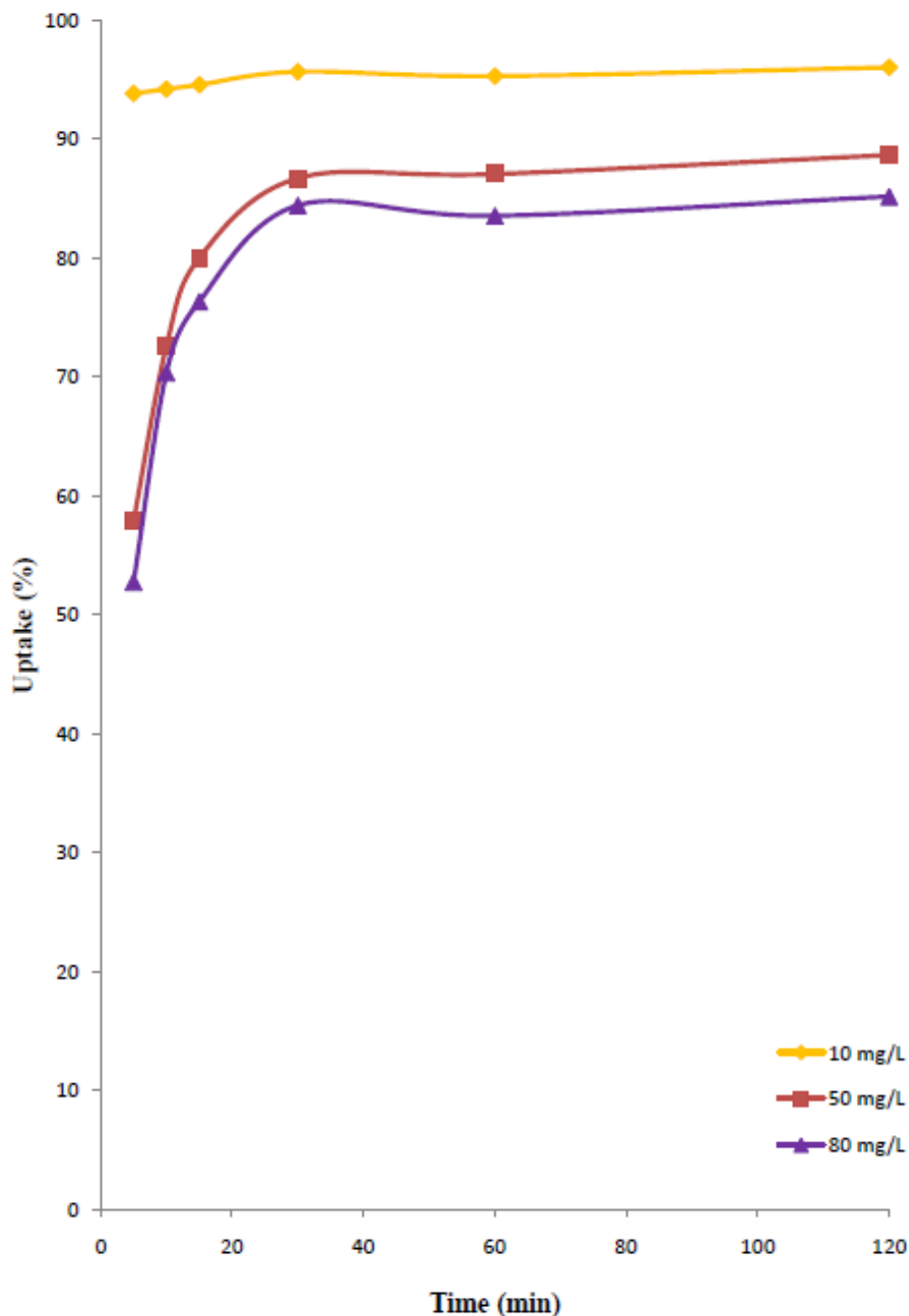


Figure 2. Effect of initial concentration and contact time on the uptake of Zn(II) by PS.

it describes reaction pathways along times to reach the equilibrium, which is an important factor for efficiency of the process optimization. In addition, sorption kinetics revealed a large dependence on the physical and chemical characteristics of the sorbent which also influences the sorption mechanism (Singh et al., 2009; Iqbal et al., 2008).

In this study, the modeling of the kinetics of sorption Zn(II) onto the PS was studied with respect to different initial concentrations by applying two different kinetic models, namely pseudo-first-order (Langergren, 1898)

and pseudo-second-order (Ho and McKay, 1999):

$$\log(q_e - q_t) = \log(q_e) - \frac{k_1 t}{2.303} \quad (\text{pseudo-first-order}) \quad (2)$$

And

$$\frac{t}{q_t} = \frac{1}{h} + \frac{t}{q_e} \quad (\text{pseudo-second order}) \quad (3)$$

Where q_e = the amount of Zn(II) sorbed at equilibrium

Table 1. Pseudo-first and pseudo-second-order kinetic model parameters for different initial Zn(II) concentrations.

Initial Zn(II) concentration (mg/L)	$q_{e, \text{exp}}$ (mg/g)	Pseudo-first-order kinetic model			Pseudo-second-order kinetic model			
		$q_{e, \text{cal}}$ (mg/g)	k_1 (1/min)	R^2	$q_{e, \text{cal}}$ (mg/g)	k_2 (g/mg min)	h (mg/mg min)	R^2
10	3.522	0.069	0.023	0.449	3.525	1.296	16.103	1.000
50	17.056	4.437	0.052	0.600	17.393	0.026	7.943	0.999
80	18.387	4.483	0.055	0.792	18.762	0.024	8.382	0.999

(mg/g), q_t = the amount of Zn(II) sorbed at time t (mg/g), k_1 = the rate constant of pseudo-first-order kinetics (1/min), h ($k_2 q_e^2$) = the initial sorption rate (mg/g min) and k_2 = the rate constant of pseudo-second order kinetics (g/mg min).

The various rate parameters associated with Zn(II) at various concentrations are shown in Table 1. It was found that the pseudo-second order kinetics provides a better correlation with the experimental data than the pseudo-first order model for all the concentrations being studied. In addition, the equilibrium sorption capacities determined from the first order kinetic model were lower than those determined experimentally. It thus appears that the system under study is more appropriately described by the pseudo-second order model which is based on the assumption that the rate limiting step may be chemical sorption or chemisorption involving valency forces through sharing or exchange of electron between sorbent and sorbate (Ho and McKay, 2000).

The values of q_e , k_2 and h against C_0 in the corresponding linear plots of the pseudo-second order equation were regressed to obtain expressions for these values in terms of the initial dye concentration. The generalized predictive models for Zn(II) sorbed at any contact time and initial concentration within the given range with relationship of q_t , C_0 and t can be represented by substituting into the Equation 4 (Ho and McKay, 2000):

$$q_t = \frac{C_0 t}{A_h C_0 + B_h + (A_q C_0 + B_q) t} \quad (4)$$

The theoretical model for Zn(II)-PS system can be represented as follows after substitution of the constant values into Equation 4:

$$q_t = \frac{C_0 t}{0.1358 C_0 - 1.0796 + (0.0052 C_0 + 4.0836) t} \quad (5)$$

The theoretical model derived for Zn(II) sorption by PS was applied to obtain the sorption capacity, q_t at any given C_0 and t . A comparison of the experimental data and the predicted theoretical values by using Equation 5 was shown in Figure 3. It was found that the theoretically

generated curves showed good agreement with the experimental data for sorption of Zn(II) cations by PS for all the concentrations under studied.

Effect of agitation rate

In adsorption process, agitation rate plays a significant role in affecting the external boundary film as well as the distribution of the solute in the bulk solution. Thus, agitation rate is one of the parameters being investigated in this study. The results revealed that the percentage of Zn(II) uptake increased gradually as the agitation rate increased from 50 to 200 rpm (Figure 4). The uptake of Zn(II) cations at the first 5 min for 50, 100 and 200 rpm were 69.35, 88.08 and 91.77%, respectively. The uptake was then increased in the following 10 min and the difference in percentage uptakes for the three agitation rates was minimal after achieving equilibrium at about 60 min.

Typically the agitation rate has an effect on the distribution of the solute in the bulk solution and the formation of external boundary film. The increasing agitation rates would lead to the diminution of the boundary layer resistance followed by the increase of the mobility of the sorbent. Consequently, the diffusion of metal cations toward the surface binding sites of the sorbents was enhanced. Similar trend has been reported by Saifuddin and Kumaran (2005) in the removal of heavy metal from industrial wastewater using chitosan coated oil palm shell charcoal and Ong et al., (2010b) in the removal of methylene blue using tartaric acid modified rice hull.

Sorption isotherms

In order to obtain information about the homogeneity and heterogeneity of the sorbent surface and to design sorption process effectively, the sorption data in this study was analyzed by employing three widely used isotherms, Langmuir, Freundlich and Brunauer, Emmet and Teller (BET).

The linear form of Langmuir isotherm can be expressed as Equation 6:

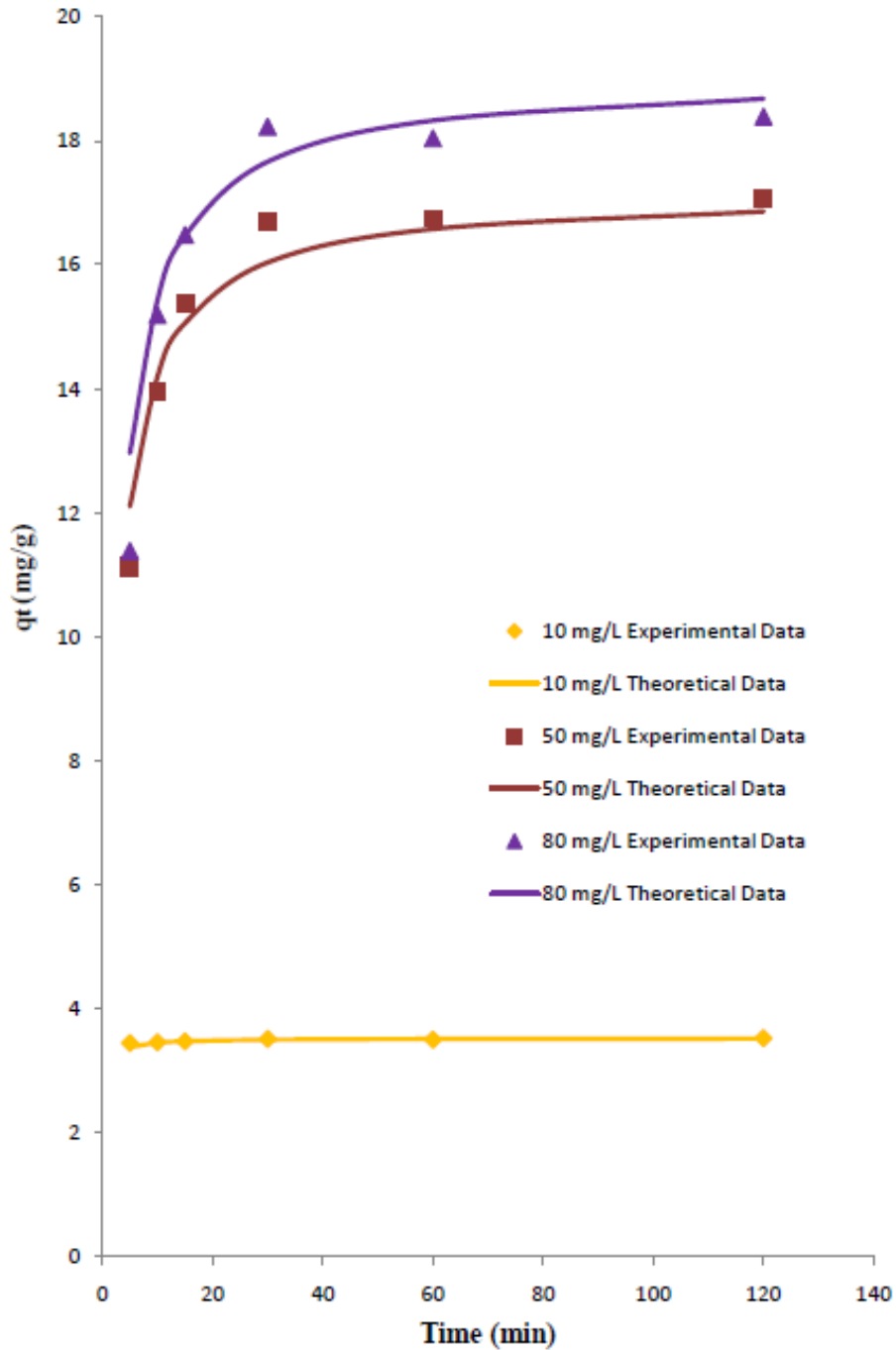


Figure 3. Comparison between the measured and pseudo-second order modelled time profiles for Zn(II) sorption by PS.

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{K_a q_m} \tag{6}$$

Whereas the linear form of Freundlich can be represented as:

$$\log q_e = \log K_f + (1/n) \log C_e \tag{7}$$

And the linear form of BET equation as follows:

$$\frac{C_e}{(C_{eq} - C_e)N_e} = \frac{1}{Ax_m} + \frac{A-1}{Ax_m} \left(\frac{C_e}{C_{eq}} \right) \tag{8}$$

Where C_e = concentration of Zn(II) at equilibrium (mg/L), q_e = amount of Zn(II) sorbed at equilibrium (mg/g), q_m =

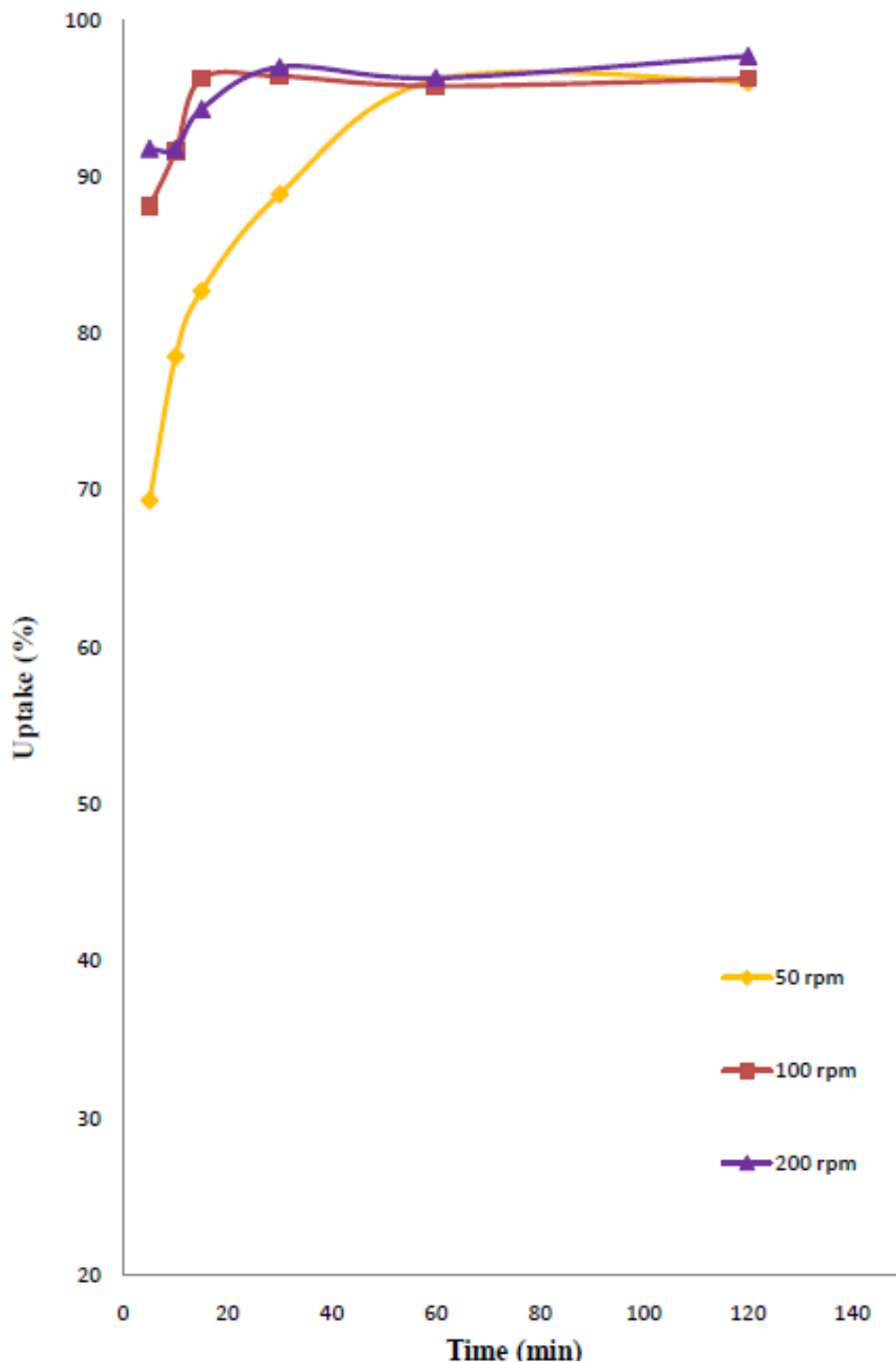


Figure 4. Effect of agitation rate on the uptake of Zn(II) by PS.

maximum sorption capacity of PS (mg/g), K_a = sorption equilibrium constant (L/mg), K_f = Freundlich equilibrium constant, n = Freundlich exponent, C_{eq} = saturation concentration of solute (mg/L), A = a constant describing the energy of interaction between the solute and the sorbent surface and x_m = amount of solute in forming a complete monolayer (mg/g).

The values obtained from the intercept and slope for each plot was summarized in Table 2. By comparing the linear square regression correlation coefficient, R^2 (Table 2), the experimental data fitted well to Langmuir isotherm model. Assumptions made for Langmuir isotherm model:

1. Adsorption takes place only at the specific localized

Table 2. Comparison between Langmuir, Freundlich and BET isotherm parameters.

Isotherm model	q_m (mg/g)	K_a (L/mg)	R^2
Langmuir	19.88	0.025	0.979
	K_f	n	R^2
Freundlich	6.928	2.802	0.842
	A	x_m (mg/g)	R^2
BET	-4.314	0.0083	0.804

Table 3. Comparison of the sorption capacity for Zn(II) onto various low-cost sorbents.

Sorbent	Maximum sorption capacity, q_m (mg/g)	Author
Rice bran	14.17	Wang et al. (2006)
<i>Caulerpa lentillifera</i>	2.66	Pasavant et al. (2006)
EDTA modified maize husk	769.23	Igwe and Abia (2007)
Activated sludge	15.69	Hammaini et al. (2007)
Lignocellulosic substrate	16.02	Dupont et al. (2005)
Carbonated tricalcium substrate	52.10	Chen et al. (2008)
PS	19.88	Present study

sites on the surface and the saturation coverage corresponds to complete occupancy of these sites.

- Each site can accommodate one and only one molecule or atom.
- The surface is energetically homogenous and there is no interaction between neighboring adsorbed molecules or atoms.
- There are no phase transitions.

The maximum sorption capacity of various sorbents for Zn(II) was shown in Table 3 and it is clear that PS can serve as an attractive alternative for the removal of Zn(II) ions.

Effect of particle size

The effect of particle size acts as one of the significant variables to be investigated in wastewater treatment, as the efficiency of a sorption process is closely related to the surface area of the sorbent. Figure 5 illustrated the sorption of Zn(II) for different particle sizes of PS at room temperature as a function of contact time. The results indicated that the metal uptake increased as the particle size of adsorbent decreased. At the first 5 minutes, the uptake of Zn(II) by the adsorbent with the size of 1 mm, 425 μm , 250 μm , 106 μm were 35.37%, 83.42%, 92.89% and 97.81%, respectively.

The difference in the metal uptake revealed that the removal of Zn(II) onto PS was particle size dependent. Smaller particle size of adsorbent in the metal solution provided a greater availability of the metal ions to

penetrate to the internal pore structure of the adsorbent. The lower metal uptake with larger adsorbent particles was due to the high diffusion resistance to mass transport. Similar results were reported in the removal of; basic dyes by sugarcane bagasse (Ong et al., 2010c); Cu(II) and Zn(II) by red rose distillation sludge (Bhatti et al., 2009); Cr(III) by activated carbon (Fahim et al., 2006) and Ni(II) by Cassia fistula biomass (Hanif et al., 2007).

Conclusion

This study identified that PS could be used as a potential adsorbent for the removal of Zn(II) from aqueous solution. The optimal pH for metal uptake was at pH 5.0. The percentage uptake of Zn(II) increased with increasing agitation rate. A smaller particle size and lower initial metal concentration favoured the metal uptake. Langmuir isotherm model appeared to be the most appropriate model to describe the equilibrium of the sorption process with the maximum sorption capacity of 19.88 mg/g. The results of kinetic studies revealed that the sorption conformed to pseudo-second-order kinetic model, suggesting the chemisorption of Zn(II) onto PS. The sorption profiles derived based on the pseudo-second-order kinetic model showed a good conformity with the experimental curves.

ACKNOWLEDGEMENTS

The financial support by the International Foundation for

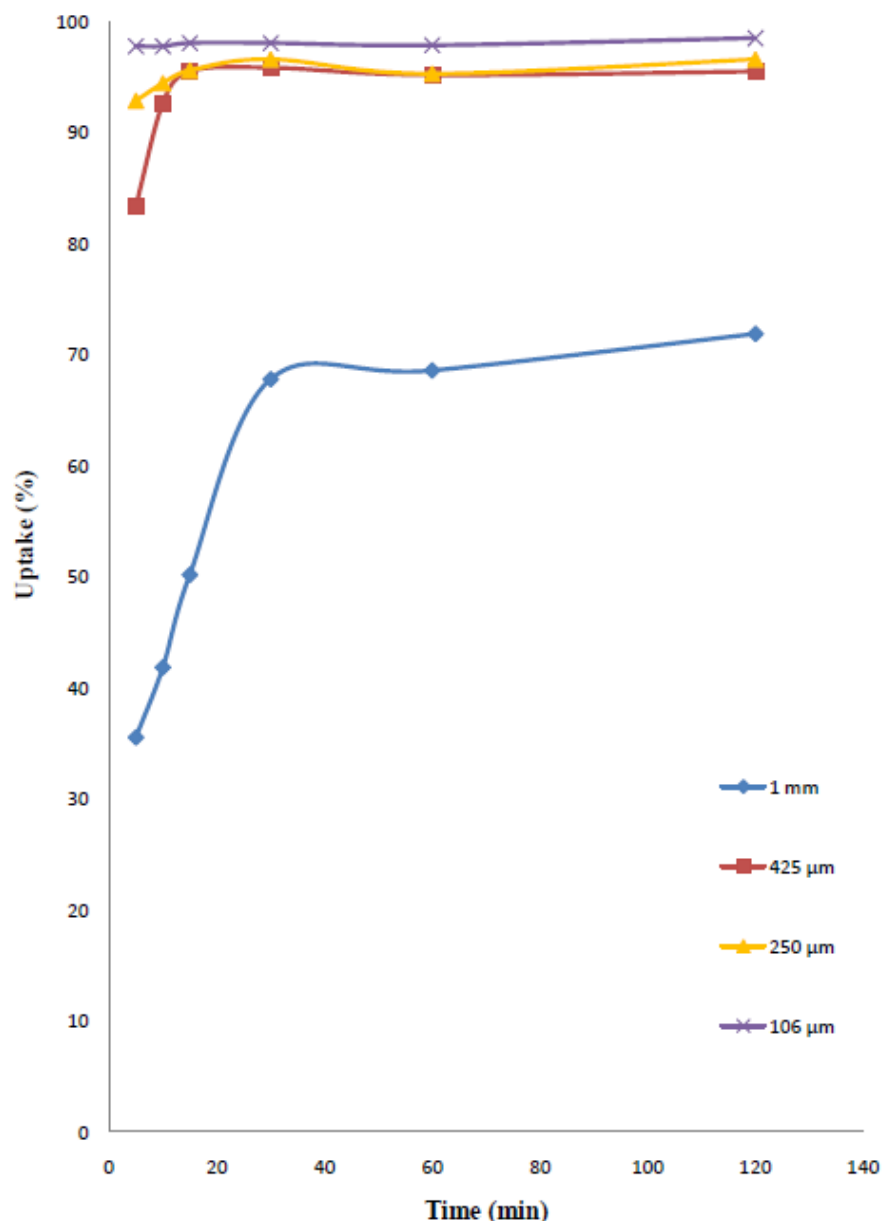


Figure 5. Effect of particle size for the sorption of Zn(II) by PS.

Science, Stockholm, Sweden, and the research facilities by Universiti Tunku Abdul Rahman are acknowledged.

REFERENCES

- Agarwal SK (2009). Heavy Metal Pollution. (pp 39-53). APH Publishing Corporation, New Delhi.
- Bhatti HN, Khalid R, Hanif MA (2009). Dynamic biosorption of Zn(II), Cu(II) using pretreated *Rosa gruss an teplitz* (red rose) distillation sludge. Chem. Eng. J., 148: 434-443.
- Chen QY, Hills CD, Yuan MH, Liu HH, Tyrer M (2008). Characterization of carbonated tricalcium silicate and its sorption capacity for heavy metals: A micron-scale composite adsorbent of active silicate gel and calcite. J. Hazard. Mat., 153: 775-783.
- Dimitrova SV (2002). Use of granular slag columns for lead removal. Water Resour., 36: 4001-4008.
- Dupont L, Bounanda J, Dumonceau J, Aplincourt M (2005). Biosorption of Cu(II) and Zn(II) onto a lignocellulosic substrate extracted from wheat bran. Environ. Chem. Lett., 2: 165-168.
- Fahim NF, Barsoum BN, Eid AE, Khalil MS (2006). Removal of chromium(III) from tannery wastewater using activated carbon from sugar industrial waste. J. Hazard. Mat., B136: 303-309.
- Hameed BH (2009). Evaluation of papaya seed as a novel non-conventional low-cost adsorbent for removal of methylene blue. J. Hazard. Mater., 162: 939-944.
- Hammami A, Gonzalez F, Ballester A, Blazquez ML, Munoz JA (2007). Biosorption of heavy metals by activated sludge and their desorption characteristics. J. Environ. Manage., 84: 419-426.
- Han RP, Li HK, Li YH, Zhang JH, Xiao HJ, Shi J (2006). Biosorption of copper and lead ions by waste beer yeast. J. Hazard. Mat., 137: 1569-1576.

- Hanif MA, Nadeem R., Bhatti HN, Ahmad NR, Ansari TM (2007). Ni(II) biosorption by *Cassia fistula* (Golden Shower) biomass. *J. Hazard. Mat.*, 139: 345–553.
- Hsieh CH, Lo SL, Kuan WH, Chen CL (2006). Adsorption of copper ions onto microwave stabilized heavy metal sludge. *J. Hazard. Mater.*, 136: 338-344.
- Ho YS, McKay G (1999). Pseudo second order model for sorption process. *Process Biochem.*, 34: 451-465.
- Ho YS, McKay G (2000). The kinetics of sorption of divalent metals ions onto sphagnum moss peat. *Water Res.*, 34: 735-742.
- Igwe JC, Abia AA (2007). Equilibrium sorption isotherm studies of Cd(II), Pb(II) and Zn(II) ions detoxification from waste water using unmodified and EDTA modified maize husk. *Electron. J. Biotechnol.*, 10: 536-548.
- Iqbal M, Saeed A, Saeed IZ (2008). FTIR spectrophotometry, kinetics and adsorption isotherms modeling, ion exchange, and EDX analysis for understanding the mechanism of Cd^{2+} and Pb^{2+} removal by mango peel waste. *J. Hazard. Mat.*, 164: 161-167.
- Johnson PD, Watson MA, Brown J, Jefcoat IA (2002). Peanut hull pellets as a single use sorbent for the capture of Cu(II) from wastewater. *Waste Manage.*, 22: 471-480.
- Karl JP, Kathleen AS (2004). *Handbook of Lead-Free Solder Technology For Microelectronic Assemblies*. 1st Edition.. Marcel Dekker, Inc, New York, pp. 49-51.
- Langergren S, Svenska BK (1898). Zur theorie der sogenannten adsorption gelöster stoffe. *Veternskapsakad Handlingar*, 24: 1-39.
- Liu HW, Dong YH, Wang HY, Liu Y (2010). Ammonium adsorption from aqueous solutions by strawberry lead powder: Equilibrium, kinetics and effects of coexisting ions. *Desalination*, 263: 70-75.
- Low KS, Lee CK, Ng AY (1999). Column study on the sorption of Cr(VI) using quarterized rice hulls. *Bioresour. Technol.*, 68: 205-208.
- Malkoc E, Nuhoglu Y (2006). Removal of Ni(II) ions from aqueous solutions using waste of tea factory: Adsorption on a fixed-bed-column. *J. Hazard. Mat.*, 135: 328-336.
- Ong ST, Keng PS, Lee SL, Leong MH, Hung YT (2010a). Equilibrium studies for the removal of basic dye by sunflower seed husk (*Helianthus annuus*). *Inter. J. Phys. Sci.*, 8: 1270-1276.
- Ong ST, Keng PS, Chong AW, Lee SL, Hung YT (2010b). Tartaric acid modified rice hull as a sorbent for Methylene Blue removal. *Am. J. Environ. Sci.*, 6: 244-248.
- Ong ST, Khoo EC, Hii SL, Ha ST (2010c). Utilization of sugarcane bagasse for removal of basic dyes from aqueous environment in single and binary systems. *Desalination Water Treat. J.*, 20: 86-95.
- Pasavant P, Apiratikul R, Sungkhum V, Suthiparinyanont P, Wattanachira S, Marhaba TF (2006). Biosorption of Cu^{2+} , Cd^{2+} , Pb^{2+} , and Zn^{2+} using dried marine green macroalga *Caulerpa lentillifera*. *Bioresour. Technol.*, 97: 2321-2329.
- Rengaraj S, Yeon KH, Moon SH (2001). Removal of chromium from water and wastewater by ion exchange resins. *J. Hazard. Mater.*, B87: 273-287.
- Rocha CG, Zaia DAM, Alfaya RVdS, Alfaya AAdS (2009). Use of rice straw as biosorbent for removal of Cu(II), Zn(II), Cd(II) and Hg(II) ions in industrial effluents. *J. Hazard. Mater.*, 166: 383-388.
- Saifuddin MN, Kumaran P (2005). Removal of heavy metal from industrial waste water using chitosan coated oil palm shell charcoal. *Elect. J. Biotechnol.*, pp. 717-3458.
- Singh KK, Hasan SH, Talat M, VK Singh, Gangwar SK (2009). Removal of Cr(VI) from aqueous solutions using wheat bran. *Chem. Eng. J.*, 151: 113-121.
- Villaescusa I, Fiol, Marti'nez M, Miralles, Pocj J, Serarols J (2004). Removal of copper and nickel ions from aqueous solutions by grape stalks wastes. *Water Resour.*, 38: 992-1002.
- Wang X, Qin Y, Li Z (2006). Biosorption of zinc from aqueous solutions by rice bran: kinetics and equilibrium studies. *Separation Sci. Technol.*, 41: 747-756.
- Zacaria R (2002). Adsorption of several metal ions onto low-cost biosorbent: kinetic and equilibrium studies. *Environ. Sci. Technol.*, 36: 2067-2073.