Dried Biosorbent Derived from Banana Peel: A Potential Biosorbent for Removal of Cadmium Ions from Aqueous Solution

Pairat Kaewsarn[1,3]* Wanna Saikaew[2,3]* Surachai Wongcharee[1,3]*

[1] Department of Chemical Engineering, Faculty of Engineering, Ubon Ratchathanee University, 34190

[2] D.Eng. Candidate in Environmental Engineering, Faculty of Engineering, Ubon Ratchathanee University, 34190

[3] National Center of Excellence for Environmental and Hazardous Waste Management (NCE-EHWM), 34190

E-mail: COKE.wongcharee@gmail.com, P_kaewsarn@hotmail.com, kosanlavitw_0@hotmail.com

Abstract

Banana peel, an agricultural waste, was used as biosorbent for the biosorption of cadmium ions from aqueous solution. The important parameters such as particle sizes, initial solution pH and initial cadmium ion concentration were evaluated on the biosorption studies, in a batch scale at 25°C. Fourier transform infrared spectroscopy revealed that carboxyl, hydroxyl and amide groups on the banana peel surface was involved in the adsorption of the cadmium ions. The particle size of banana peel had no effect on the removal of cadmium ions. The cadmium ion removal increased significantly as pH of the solution increased rapidly from 1 to 5. At pH of about 5, cadmium ion removal reached a maximum value of 17.94%. Biosorption isotherms showed an S-shaped isotherm, that did not follow the Langmuir and Freundlich isotherm model. The result shows that banana peel could be used as biosorbent for removing cadmium ions from aqueous solution. A low cost material that shows potential use in wastewater technology for removing of heavy metal.

Keywords— Banana peel Biosorption Cadmium Wastewater

1. Introduction

Effluents from metal mining, melting, plating, batteries, pesticide, oil paint, pigments, and alloy at small and large-scale sector contains considerable amounts of cadmium ions. Cadmium has been well recognized for its negative effect on the environment where it accumulates readily in living systems [1]. Cadmium contamination in human was first reported in Japan in the 1950s where the municipal sewage sludge was used as a fertilizer through the rice crop [2]. Therefore the removal of cadmium ions from process or waste effluents becomes environmentally important.

The conventional technologies includes chemical and surface chemistry processes such as precipitation, adsorption, membrane processes, ionic exchange, floatation, and others [3-4]. Some of them are expensive like ion exchange or can produce refractory residues like the oxidation by chemical precipitation [5]. In addition, those techniques are not economically feasible for small-scale industries prevalent in developing economies due to huge capital investment [6]. These disadvantages, together with the need for more economical and effective method for recovery of metal from wastewater, have resulted in the development of alternative separation technologies. One such alternative is biosorption [7], where certain types of biomass are used to bind and concentrate metals from even very dilute aqueous solution. A biosorption process offers a number of advantages when compared to the conventional methods currently used. These include low operational costs and minimizing the volume of chemical and/or biological waste sludge as well as a high degree of efficiency in decontamination very diluted effluents [8]. The mechanisms of biosorption are generally based on physico-chemical interactions between metal ions and the functional groups present on the cell surface, such as electrostatic interactions, ion exchange and metal ion chelation or complexation. Functional groups most commonly implicated in such interactions include carboxylate, hydroxyl, amine and phosphoryl groups present within cell wall components such as polysaccharides, lipids and proteins [9]. Whereby factors like pH, size of biosorbent, ionic strength, and temperature influence metal biosorption [10].

Therefore, the purpose of this study was to explore the feasibility of using banana peel for cadmium ion removal from aqueous solutions. The effect of various operating parameters such as particle size, solution pH, and initial cadmium ions concentration on cadmium ions removal were investigated.

2. Materials and Methods

2.1 Biomass preparation

Banana peel, mature banana with yellow peel, was collected as solid waste. The collected material was then washed with deionized water which was prepared by the technique of reverse osmosis for several times to remove heavy metal. The washed material was cut into small pieces (1-2 cm) then dried in a hot air oven (Memmert Model 600) at 60°C until it reached a constant weight, which was accomplished after 48 hrs. In the final stage these material was dried, ground, and screened with sieves of the cut of size of > 850, 600-850, 425-600, 300-425, 212-300 and 150-212 μm.

2.2 Effect of particle size

The effect of particle size, > 850, 600-850, 425-600, 300-425, 212-300 and 150-212 μm, was determined by agitation 0.1 g of banana peel and 100 ml of $Cd(NO_3)_2.4H_2O$ solution at the concentration of 50 mg/l. Agitation contact time was kept for 24 hrs which is sufficient to reach equilibrium with a constant agitation speed of 150 rpm at 25 °C. A pH value of 3to 6 were maintained throughout the experiment by adding 0.1 N NaOH or HNO_3 before each the experiment.

2.3 Effect of solution pH

The effect of initial solution pH, ranging 1 to 8, was determined by agitation 0.1 g of banana peel and 100 ml of $Cd(NO_3)_2.4H_2O$ solution at the concentration of 50 mg/l. Agitation contact time was kept for 24 hrs which is sufficient to reach equilibrium with a constant agitation speed of 150 rpm at 25 °C. The pH was adjusted by adding 0.1 N NaOH or HNO_3 before each experiment. The pH measured by using a pH meter (WTW. inoLab pH level 1).

2.4 Isotherm experiments

The equilibrium isotherms were determined by contacting a constant mass 0.1 g of 150-212 μm. banana peel material with a range of different concentrations of $Cd(NO_3)_2.4H_2O$ solution from 25-100 mg/l. Agitation contact time was kept for 24 hrs which is sufficient to reach equilibrium with a constant agitation speed of 150 rpm at 25 °C. A pH value of 3.0 and 5.0 were maintained throughout the experiment by adding 0.1 N NaOH or HNO_3 before each the experiment.

2.5 Metal analysis

After biosorption, biosorbents were separated from the solution by passing through a Watman 0.45 μm GF/C filter and the filtrate was subjected to residual cadmium concentration determination. The residual concentrations of the cadmium ions were analyzed by flame atomic absorption spectrophotometer (Perkin Elmer AAnalyst 200).

The percent removal of cadmium ion by banana peel material was calculated using the equation:

$$\% R = (C_0 - C_e)*100/C_0 \quad (1)$$

Where;

R = cadmium ion removal

C_0 = initial cadmium ion concentration cadmium in solution used (mg/l);

C_e = cadmium ion concentration in solution at equilibrium (mg/l)

2.6 FT-IR spectroscopy

The samples of the biomass before and after cadmium ion biosorption were analyzed with a FT-IR (Perkin Elmer System 2000) spectrometer under ambient conditions.

3. Result and discussion

3.1 Effect of particle size

The percentage of cadmium ions removal using banana peel at different particle sizes are shown in Fig 1. It was seen that the influence of the particle size was similar at different solution pH ranging from 2 to 6. The particle sizes of banana peel had no effect on the removal of cadmium ions. The higher biosorption level achieved by smaller particle size of the biosorbents may not be connected to the fact that smaller particle sizes give large surface areas. There was tendency that smaller particle sizes produce shorter time to equilibrate [11]. Although this is contrary to expect for an intrapaticle diffusion controlled process, it is necessary to point out that the two sizes of biomass are actually of the same thickness (dimension which determines the diffusion distance). This is due to size grading of ground biomass particle by standard sieves works on the length and width dimensions [12]. The behavior has been reported by others [13], although Leusch et al. 1995 [14] showed that larger biomass particles of Sargassum fluitans and Ascophylum nodosum had higher metal uptake than smaller particles in the case of cadmium, copper, nickel, lead and zinc. Then, the influence of biosorpbent size on metal uptake seems to be function of both the type of biomass and the metal ion.

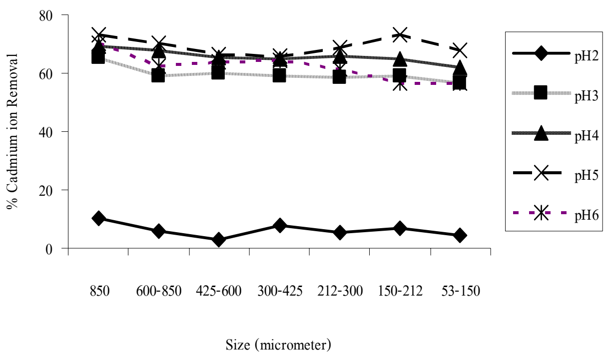

Fig. 1 Effect of particle sizes of banana peel on different pH Conditions: 0.1 g; initial Cadmium nitrate concentration 50 mg/l; contact time, 24 hrs; pH, 2-6; 150 rpm; 25±2°C.

2.2 Effect of solution pH

The pH of the aqueous solution is an important controlling parameter in the biosorption process [15]. This factor is capable of influencing not only the binding site dissociation state, but also the solution chemistry of the target metal in terms of hydrolysis, complexation by organic and/or inorganic ligands and redox potentials [16]. Most research conducted on heavy metal biosorption indicates that the decrease in ion biosorption at acid pH may be due to the increase in competition with protons for active sites.[17-19] At alkaline pHs, however, other effects may arise that also alter the process, such as the predominant presence of hydrated species of heavy metal, changes in surface change or the precipitation of the appropriate salt [8].

Effect of pH solution on the biosorption of cadmium ion by using banana peel material was studied and results are shown in Fig 2. The influence of the pH value was the same at different particle size used as follows: > 850, 600-850, 425-600, 300-425, 212-300 and 150-212 µm. There was an increase in cadmium ion removal with increasing pH from 1 to 5. The cadmium ion removal increased rapidly. At pH of around 5, the cadmium ion removal leveled off at a maximum value. The biosorption of cadmium in a very highly acidic (pH 1) was negligible. According to several authors [20-21] the biosorption below pH 2 was little due to the competition of hydrogen ions for the active sites. It is clear that cadmium ion was effectively adsorbed for the pH 4 to 8 and the maximum biosorption of cadmium ion on banana peel material occurred at pH 5. The dependence of percent cadmium removal on pH is similar to the cadmium ion sorption on *Hydrilla verticillata* and Cystine-modified biomass [22-23]. Then decreases as the pH continue increasing. Because proton (H^+) vies with cadmium ion in lower pH, the sorbent surface takes up more H^+, consequently reducing cadmium ions binding on the sorbent surface. In higher pH, the sorbent surface takes more negative charges, thus attracting greater cadmium ions. But with further increase in pH, the formation of anionic hydroxide complexes decreases the concentration of free cadmium ion, thereby the biosorption capacity of cadmium ion was decreased [24].

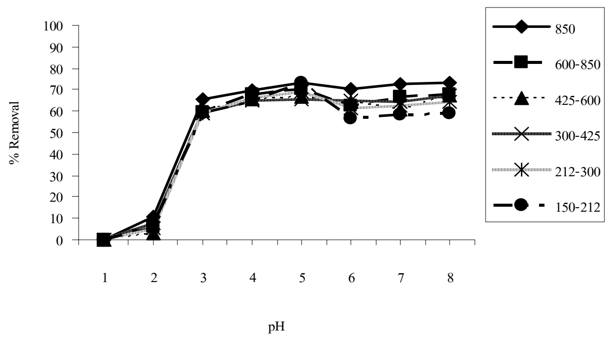

Fig. 2 Effect of pH of banana peel on different particle sizes Conditions: 0.1 g; initial Cadmium nitrate concentration 50 mg/l; particle size, : > 850, 600-850, 425-600, 300-425, 212-300 and 150-212 µm; contact time, 24 hrs; 150 rpm; 25±2°C.

3.3 Adsorption isotherms

The relationship between equilibrium uptake and final concentrations of cadmium ion was plotted as sorption isotherms in Fig. 3. Since solution pH has a significant effect on biosorption equilibrium, at pH 5 the uptake capacity was consistently higher than at pH 3. Similar results were observed for orange peel [25] lemon and grapefruit peels [26]. This occurred because of a decrease in proton concentration at pH 5 and thus decreased competition between protons and cadmium ions for the same binding site. Cadmium adsorption capacity attains maximum under this condition with the maximum capacity of 17.94 mg/g. The results showed that the adsorption capacity for cadmium ion using banana peel is greater than that has been found using other adsorbents listed in Table 1.

Table 1. Biosorption capacities for cadmium ions using different biosorbents

Biosorbent	Biosorption capacity (mg/g)	Reference
Banana peel	17.94	This study
Papaya wood	17.22	[27]
Cystine-modified biomass	11.63	[28]
H. verticillata	15.00	[22]

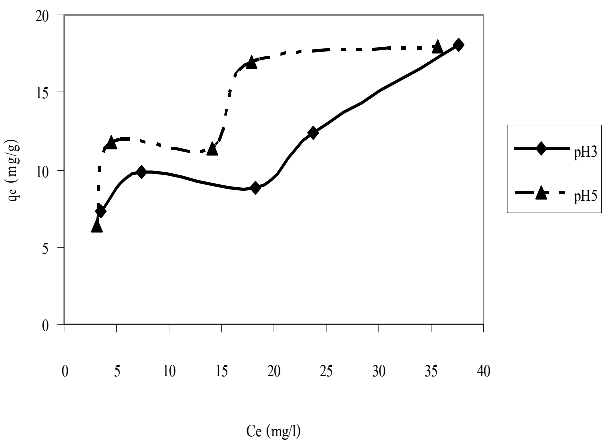

Fig. 3 Experiment data isotherms for cadmium ions on banana peel at pH 3 and 5

Conditions: 0.1 g; initial Cadmium nitrate concentration 25-100 mg/l; particle size, 150-212 μm; contact time, 24 hrs; 150 rpm; 25±2°C.

Biosorption isotherms can be generated based on numerous theoretical models where Langmuir [29] and Freundlich [30] models are commonly used to fit experimental data when solute uptake occurs by a monolayer biosorption. Langmuir isotherm assume monolayer biosorption, and is presented by the following equation:

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

And the Freundlich isotherm has the form

$$q_e = K_F C_e^{1/n} \quad (3)$$

Where q_e and q_{max} are the equilibrium and maximum uptake capacities (mg/g biosorbent); C_e the equilibrium concentration (mg/l solution); K the equilibrium constant; K_F and n are Freudlich constants characteristic of the system.

The Langmuir and Freudlich isotherms for the biosorbent using banana peel material are presented in Fig. 4 and 5 respectively. The models parameters are tabulated in Table 2. Especially biosorption by banana peel could not be predicted well by both models. According to Schiewer and Santosh [26] who found the anomalous two-stage-shape behavior occurred for untreated. It could have been due to a combination of the following factors:

1. Heterogeneity of biosorbent material (e.g. inner peel vs. outer peel) at different equilibrium points; that, is “scattering” of data. Since each data point was obtained from an individual experiment, the biosorbent properties could have differed between flasks.

2. Two binding sites with different affinities for cadmium ions. The binding site with the strongest affinity for cadmium ions became saturated at the first plateau, then cadmium ions bound to a less favored binding site.

3. Conformational changes in the polygalacturonate gel, whereby increasing cadmium ions binding changes the pectin gel structure from a less ordered state to an ordered form. Such an ordered configuration has been described by Grant et al. as the “egg box” model, for the gel structure in the presence of ions like calcium. The ordered gel structure could facilitate binding of additional cadmium ions by providing suitable “pockets” with the right spatial configuration for cadmium ions binding.

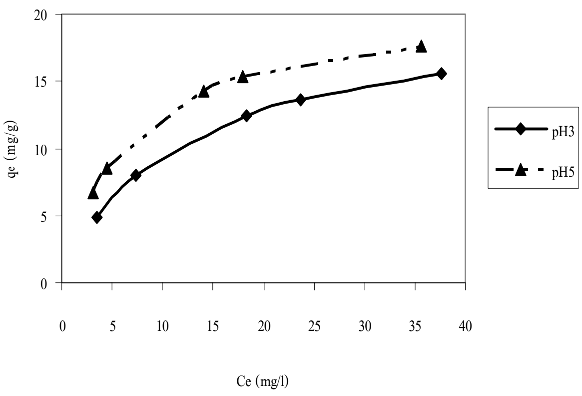

Fig. 4 Langmuir isotherm at different solution pH 3 and 5 Conditions: 0.1 g; initial Cadmium nitrate concentration 25-100 mg/l; particle size, 150-212 μm; contact time, 24 hrs; 150 rpm; 25±2°C.

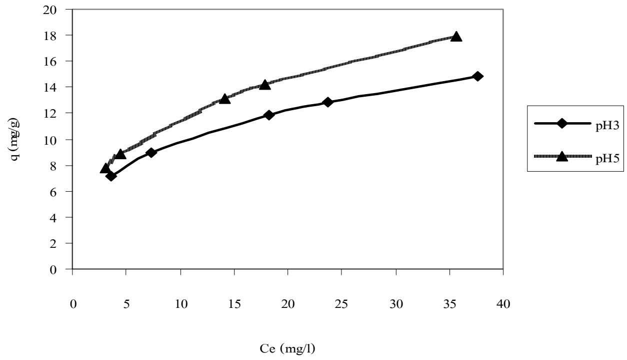

Fig. 5 Freudlich isotherm at different solution pH 3 and 5 Conditions: 0.1 g; initial Cadmium nitrate concentration 25-100 mg/l; particle size, 150-212 μm; contact time, 24 hrs; 150 rpm; 25±2°C.

Table 2. Langmuir and Freundlich isotherm constants for cadmium ion biosorption onto banana peel

Biosorbent	Langmuir model			Linearization of Freundlich model			Non-linearization of Freundlich model		
	K (l/g)	q_{max} (mg/g)	R^2	K_F (mg/l)	n	R^2	K_F (mg/l)	1/n	SSE
pH 3	0.088	20.20	0.75	4.81	3.22	0.72	3.889	0.390	18.467
pH 5	0.154	20.88	0.94	5.32	2.94	0.76	5.659	0.320	14.07

3.4 FT-IR analysis

The FT-IR spectra of banana peel material before and after cadmium ion biosorption are shown in Figs. 6 to 7. These spectra were obtained from scanning in the range of 400-4000 cm^{-1}. The band of banana peel represented overlapping of O-H and N-H stretching vibration at 3365 cm^{-1} While the band represented C=O stretching vibration of carboxylic acids at 1731 cm^{-1}.

The significant shifts of these specific peaks to the higher wave number after the cadmium ions biosorption suggested that chemical interactions between the cadmium ions and the amide groups occurred on the biomass surface. The band of banana peel shifted to 3416 cm^{-1} indicating that hydroxyl, carboxyl and amide groups were involved in the biosorption. The spectra of banana peel at 1731 cm^{-1} become smoother and a band of banana at 1427 cm^{-1} appeared, which would resulted from the complexation of cadmium ions with the functional groups from protein. These results indicated that carboxyl, hydroxyl and amide groups on the banana peel surface were involved in the biosorption of the cadmium ions.

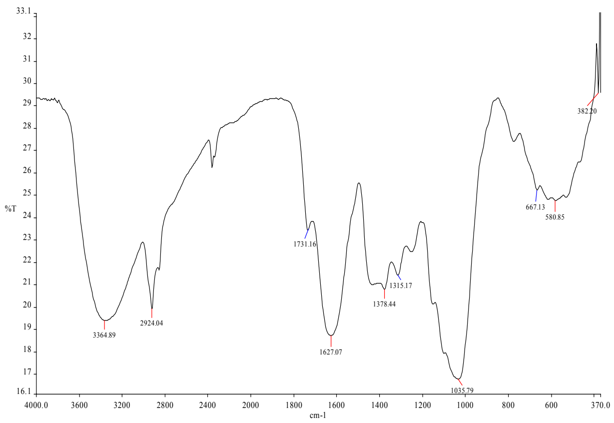

Fig. 6 FT-IR of banana peel

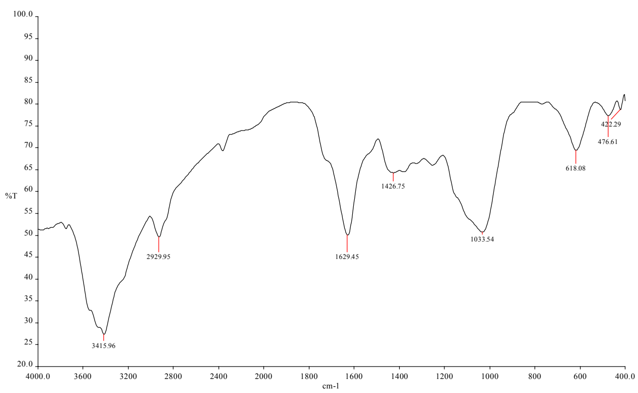

Fig. 7 FT-IR of banana peel with of cadmium ions biosorption

4. Conclusions

The use of banana peel which is waste in this study will be environmental friendly and can adsorb cadmium ion from aqueous solution. The banana peel material is a potential candidate for biosorption and further studies will help to evaluate economical use of this biosorbent. The biosorption was dependent on particle size, solution pH and initial cadmium ion concentration. The particle size of banana peel had no influence on the removal of cadmium ions. As the pH of around 5, the cadmium ion removal leveled off at a maximum value. The Langmuir and Freundlich isotherms did not fit the experimental data. The experimental data displayed an unusual S-shaped isotherms. FT-IR spectroscopy revealed that carboxyl, hydroxyl and amide groups on the banana peel surface were involved in the biosorption of the cadmium ions.

5. Acknowledgment

The authors are grateful for the financial support of Ubon Ratchathani Rajabhat University and Department of Chemical Engineering Ubon Ratchathani University for providing laboratory facilities.

6. REFFERENCE

[1] H. Benaissa, Screening of new sorbent materials for cadmium removal from aqueous solutions, *J. Hazard. Mater*. B132, 2006, 189-195.

[2] M.D. Mashitah, Y. Yus Azila and S. Bhatia, Biosorption of cadmium (II) ions by immobilized cells of *Pycnoporus sanguineus* from aqueous solution, *J. Bioresour Technol*., In press.

[3] Li. Xiaomin, T.Yanru and X. Zhexian, Study on the preparation of Orange peel cellulose adsorbents and biosorption of Cd^{2+} from aqueous solution, *J. Sep. Purif. Technol*. 55, 2007, 69-75.

[4] A. Selatnia, M.Z. Bakhti, A. Madani, L. Kertous and Mansouri, Biosorption de Cd^{2+} from aqueous solution by a NAOH-treated bacterial dead *streptomyces rimosus* biomass, *J. Hydrometallurgy*. 75, 2004, 11-24.

[5] T.G.P. Vasquez, C.A.E. Botero, L.M.S. Mesquita and M.L. Torem, Biosorption removal of Cd and Zn from liquid streams with a *Rhodococcus opacus* strain, *J. Miner Eng*., In prees.

[6] H. Michael and I. Ayebaemi, Effect of metal ion concentration on the biosorption of Pb^{2+} and Cd^{2+} by Caladium bicolor (wild cocoyam), *J. African J. of Biotechnol*. 4, 2005, 191-196.

[7] B. Volesky, Biosorption of Heavy Metals CRC press, Boca Ratton, USA., 1990.

[8] G. Blazquez, F. Hernainz and M. Calero, Removal of Cadmium ions with olive stones: the effect of somes parameters, *J. Process Biochem*. 40, 2005, 2649-2654.

[9] S. Dhiraj, M. Garima and M.P. Kaur, Argriculture waste material as Potential biosobent for sequestering heavy metal ions from aqueous solutions- A review. *Bioresour. Technol.*, Inpress.

[10] B. Volesky, and S. Schiewer, Biosorption of metal in Encyclopedia of bioprocess Technology: fermentation, Biocatalysis, and Bioseparation, John Wiley & Sons,1999.

[11] E. Demirbas, M. Kobya, and E.Senturkl, Adsorption Kinetics for the removal of chromium (VI) from aqueous solution on the activated carbons prepared from agricultural wastes, *J. Water SA*. 30, 2004, 533-539.

[12] S. Eneida, R. Célia, and M. Teresa, Biosorption of chromium(III) by *Sargassum* sp. Biomass, *J.Process Technol***.** 5, 2002, 133-140,.

[13] N. Kuyucak, and B. Volesky, Accumulation of cobalt by marine alga, *J. Biotechnol. and Bioeng*. 33, 1989, 809-814.

[14] A. Leusch, Z.R. Holan and B. Volesky, Biosorption of heavy metals (Cd, Cu, Ni, Pb, Zn) by chemically-reinforced biomass of marine algae, *J. of Chem and Technol Biotech*. 62, 1995, 279-288.

[15] A.B. Perez-Marin, V. Meseguer Zapata, J.F. Ortuno, M. Aguilar, J. Saez and M. Llorens, Removal of Cadmium from aqueous solutions by adsorption onto orange waste, *J. Hazard Mater*. B139, 2007, 122-131,.

[16] N. Fiol, I. Villaescusa, and M. Martinez, Sorption of Pb(II), Ni (II), Cu (II) and Cd (II) from aqueous solution by olive stone waste, *J. Sep. Purif Technol*. 50, 2006, 132-140.

[17] Q. Yu and P. Kaewsarn, A Model for pH Dependent Equilibrium of Heavy Metal Biosorption, *J. Korean J. of Chem. Eng*. 16, 1999c, 753-757.

[18] P. Kaewsarn, and Q. Yu, Cadmium Removal from Aqueous Solutions by Pre-treated Biomass of Marine Macro-Alga *Padina* sp., *J. Environ. Poll*. 112, 2000, 1-5.

[19] Z.R. Holan, B. Volesky, and I. Prasetyo, Biosorption of cadmium by biomass of marine algae, *J. Biotechnol. Bioeng*. 41, 1993, 819-825.

[20] J.S. Chang, R. Law and C. Chang, Biosorption of lead copper and cadmium by biomass of *Pseudomonas aeruginosa* PU 21, *J. Water Res*. 31, 1997, 1651-1658.

[21] C.C.V. Cruz, A.C.A. DA Costa and C.A. Henrique, Kinetic modeling and equilibrium studies during cadmium biosorption by dead *Sargassum* sp. Biomass, *J. Bioresour. Technol.* 91, 2004, 249-257.

[22] Bunluesin., Kruatrachue., and Pokethitiyook, Batch and Continuous packed Column Studies of Cadmium Biosorption by *Hydrilla verticillata* Biomass, *J. Biosci. and Bioeng*. 103, 2007, 509-513.

[23] M. Junxia and Xiaomei, Cystine-modified biomass for Cd (II) and Pb (II) biosorption,. *J. Hazard. Mater*. 143, 2007, 277-284.

[24] B. Stephen and N. Sulochana, Carbonised jackfruit peel as an adsorbent for the removal of Cd (II) from aqueous solution, *J. Bioresour. Technol*. 94, 2004, 49-52.

[25] S. Schiewer, and B. Santosh, Modeling the effect of pH on biosorption of heavy metals by citrus peels*, J. Hazard. Mater*., Inpress.

[26] S.Schiewer, and B. Santosh, Pectin-rich fruit wastes as biosorbents for heavy metal removal: Equilibrium and kinetics, *J. Bioresour. Technol*., Inpress.

[27] S. Asma, A.M. Washeed, and I.Muhammed, Removal and recovery of heavymetals from aqueous solution using papaya wood as a new biosorbents, *J. Sep. Purif. Technol*. 45, 2005, 25-31.

[28] J. Yu, M. Tong, X. Sun and B. Li , Cystin-modified for Cd(II) and Pb (II) biosorption, *J. Hazard Mater*. 143, 2007, 277-284.

[29] I. Langmuir, The constitution and fundamental properties of solids and liquids, *J. Am. Chem. Soc.* 38, 1916, 2221-2295.

[30] H. Freundlich, Over the adsorption in solution, *J. Phys. Chem.* 57, 1906, 385-470.