

# Pomelo Peel: Agricultural Waste for Biosorption of Cadmium Ions from Aqueous Solutions

Wanna Saikaew, Pairat Kaewsarn, and Wuthikorn Saikaew

**Abstract**—The ability of pomelo peel, a natural biosorbent, to remove Cd(II) ions from aqueous solution by biosorption was investigated. The experiments were carried out by batch method at 25 °C. The influence of solution pH, initial cadmium ion concentrations and contact times were evaluated. Cadmium ion removal increased significantly as the pH of the solution increased from pH 1 to pH 5. At pH 5, the cadmium ion removal reached a maximum value. The equilibrium process was described well by the Langmuir isotherm model, with a maximum biosorption capacity of 21.83 mg/g. The biosorption was relatively quick, (approx. 20 min). Biosorption kinetics followed a pseudo-second-order model. The result showed that pomelo peel was effective as a biosorbent for removing cadmium ions from aqueous solution. It is a low cost material that shows potential to be applied in wastewater technology for remediation of heavy metal contamination.

**Keywords**—Pomelo peel, biosorption, Cadmium ions.

## I. INTRODUCTION

CADMIUM, a non-essential and non-beneficial element to plants and animals, is non-biodegradable and travels through the food chain. The kidneys are the critical target organ after ingestion (renal dysfunction, hypertension and anaemia) [1]-[3]. The major sources of cadmium release into the environment by waste streams are electroplating, smelting, alloy manufacturing, pigments, plastic, batteries, mining and refining processes [4]-[6]. This metal is a serious cause of environmental degradation. Therefore, it is necessary to alleviate cadmium ion from industrial effluents. Many methods for treatment have been described include chemical and surface chemistry processes such as precipitation, adsorption, membrane processes, ionic exchange, floatation, and others [7]-[8]. However, those techniques have their own inherent limitation such as less efficiency, sensitive operating conditions, and production of secondary sludge requiring further, costly disposal [9]. These disadvantages, together with

the need for more economical and effective methods for recovery of metal from wastewater, have resulted in the development of alternative separation technologies. One such alternative is biosorption [10], where certain types of biomass are able 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.

Biosorption, the passive uptake of heavy metals by biomaterials, can be both highly efficient and cost effective. A low cost biosorbent is defined as one which is abundant in nature, or is a by-product or waste material from another industry. Agriculture biosorbent such as orange wastes [11], olive stones [12], papaya wood [13], grape stalk waste, peas, broad bean, and medlar peels [14], lemon peels, orange peels, grapefruit peels, apple peels, apple kernel, apple core, and grape skins [15], coconut shell powder [16], coconut copra meal [17] have been evaluated for their biosorption properties. Most of the studies showed that agricultural waste either in natural form or modified form is highly efficient for the removal of cadmium ions. Agricultural by-products usually are composed of lignin and cellulose as major constituents and may also include other polar functional groups of lignin, which includes alcohols, aldehydes, ketones, carboxylic, phenolic, and ether groups. These groups have ability to some extent to bind heavy metal ions by donation of an electron pair from these groups to form complexes with the metal ions in solution [18].

Pomelo peel, agricultural waste, was selected because of its high pectin content and the fact that it is an agricultural by-product. The by-products resulting from processing represent a major disposal problem for industry and the environment. Therefore, the purpose of this study was to explore the feasibility of using pomelo peel for cadmium ion removal from aqueous solutions by conducting batch experiments as a function of solution pH, initial cadmium ions concentration and contact times.

## II. MATERIALS AND METHODS

### A. Biosorbents Preparation

Pomelo peel was collected as solid waste. The collected material was then washed with deionized water which was prepared by the technique of reverse osmosis several times to

Wanna Saikaew is with the Engineering Department, Ubon Ratchathani University, Ubon Ratchathani, 34190 Thailand (corresponding author to provide phone: (0066) 045-353-311; fax: (0066) 045-353-333; e-mail: kosanlavitw\_0@hotmail.com).

Pairat Kaewsarn is with the Engineering Department, Ubon Ratchathani University, Ubon Ratchathani, 34190 Thailand (e-mail: p\_kaewsarn@hotmail.com).

Wuthikorn Saikaew is with the Science and Technology Department, Rajabhat Maha Sarakham University, Maha Sarakham, 44000 Thailand (e-mail: k.saikaew@thaimail.com).

remove heavy metals. The washed materials was cut into small pieces (1-2 centimeter; cm) then dried in a hot air oven at 60°C until they reached a constant weight, which was accomplished after 48 hours (hrs). In the final stage the material was dried, ground and screened to a cut-off size of 150-212 micrometer ( $\mu\text{m}$ ).

#### B. Effect of Solution pH

The effect of initial solution pH was determined by agitation 0.1 g of pomelo peel and 100 ml of  $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  solution concentration 50 mg/l using a shaker at different solution pH values ranging from pH 1 to pH 6. Agitation contact time was kept for 24 hrs which was 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 0.1  $\text{HNO}_3$ .

#### C. Isotherm Experiments

The equilibrium isotherms were determined by contacting a constant mass 0.1 g of pomelo peel material with a range of different concentrations of  $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  solution from 25-100 mg/l. Contact time with agitation was constant at 24 hrs which was sufficient to reach equilibrium with an agitation speed of 150 rpm at 25 °C. A pH value of either pH 3.0 or pH 5.0 was maintained throughout the experiment by adding 0.1 N NaOH or 0.1  $\text{HNO}_3$ .

#### D. Kinetic Experiments

The kinetic studies were conducted by combining a constant mass (0.1 g) of pomelo peel material and 100 ml of  $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  solution concentration 50 mg/l using a shaker for different contact times ranging from 0 to 240 min with a constant agitation speed of 150 rpm at 25 °C. A pH value of either pH 3.0 or pH 5.0 was maintained throughout the experiment by adding 0.1 N NaOH or 0.1  $\text{HNO}_3$ .

#### E. Metal Analysis

After biosorption, biosorbent was separated from the solution by passing through a 0.45  $\mu\text{m}$  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 spectrophotometry (Perkin Elmer AAnalyst 200).

The cadmium ions capacity per gram of pomelo peel material was determined by employing the mass balance. The equilibrium cadmium ions capacity was calculated as (1)

$$q_e = V(C_i - C_e)/m \quad (1)$$

Where;

- $q_e$  = equilibrium cadmium ions capacity (mg/g);
- $V$  = suspension volume (l);
- $m$  = mass of pomelo material (g);
- $C_e$  = cadmium ions concentration at equilibrium (mg/l);
- $C_i$  = initial cadmium ions concentration (mg/l)

### III. RESULT AND DISCUSSION

#### A. Effect of pH

The pH of the aqueous solution was an important controlling parameter in the biosorption process [19]. Most research conducted on heavy metal biosorption indicates that the decrease in metal ion biosorption at acid pH could be due to the increase in competition with protons for active sites [20]–[22]. At alkaline pHs, however, other effects could arise that also alter the process, such as the predominant presence of hydrated species of heavy metal, changes in surface charge or the precipitation of the appropriate salt [12]. Effect of pH solution on the biosorption of cadmium ions by using pomelo peel material was studied and the results are shown in Fig 1. There was increasing cadmium ion removal with increasing pH from pH 1 to pH 5. The cadmium ion removal increased rapidly. At pH of around 5, cadmium ion removal leveled off at a maximum value. The biosorption of cadmium in a highly acidic solution (pH 1) was observed to be negligible. According to several authors [3], [23] biosorption below pH 2 is negligible due to the competition of hydrogen ions for the active sites. The dependence of cadmium capacity on pH was similar to the cadmium ion sorption on *Hydrilla verticillata* and Cystine-modified biomass [24]–[25]. Then the cadmium ion capacity increases as the pH continue increasing. Due to proton ( $\text{H}^+$ ) vies with cadmium ions in lower pH, the sorbent surface taken up more  $\text{H}^+$ , consequently reducing cadmium ions binding on the biosorbent surface. At higher pH, the biosorbent surface takes more negative charges, thus attracting more cadmium ions. However, with further increases in pH the formation of anionic hydroxide complexes decreases the concentration of free cadmium ions, thereby the biosorption capacity of cadmium ions decreases [26].

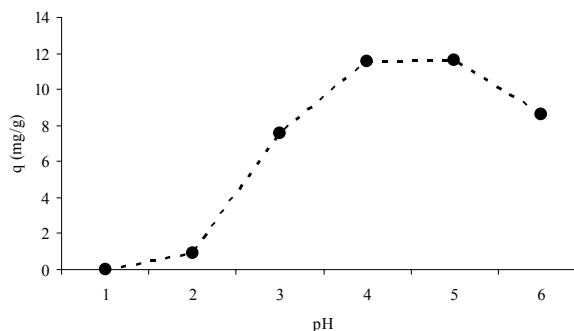


Fig. 1 Effect of pH for pomelo peel biosorption of cadmium ions from aqueous solution. Conditions: 0.1 g; initial  $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  concentration 50 mg/l; contact time, 24 hrs; 150 rpm; 25±2°C

#### B. Biosorption Isotherms

Biosorption isotherms can be generated based on numerous theoretical models where Langmuir and Freundlich models are commonly used to fit experimental data when solute uptake occurs by a monolayer biosorption [27]–[28]. Langmuir isotherms assume monolayer biosorption, and are described by equation (2):

$$q_e = q_{max}bC_e / 1+bC_e \quad (2)$$

The Freundlich isotherm is described by equation (3):

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

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

The equilibrium biosorption of Langmuir and Freundlich isotherms for the biosorbent from pomelo peel material are presented in Figs. 2 and 3 respectively. The model parameters were tabulated in Table I. The experimental data was better described by the Langmuir isotherm than Freundlich isotherm. The regression coefficient ( $R^2$ ) was 0.97 for the Langmuir isotherm. In contrast, the Freundlich isotherm model was less precise, with a lower  $R^2$  value of 0.86 at pH 5. Based on the Langmuir isotherm, the maximum capacity of cadmium was 21.83 mg/g. In addition, the comparison of the maximum biosorption capacities for cadmium ions obtained in this study with some using different low-cost biosorbents reported in the literature is shown in Table II. The results show that the biosorption capacity for cadmium ion using pomelo was greater than that which has been found using other biosorbents.

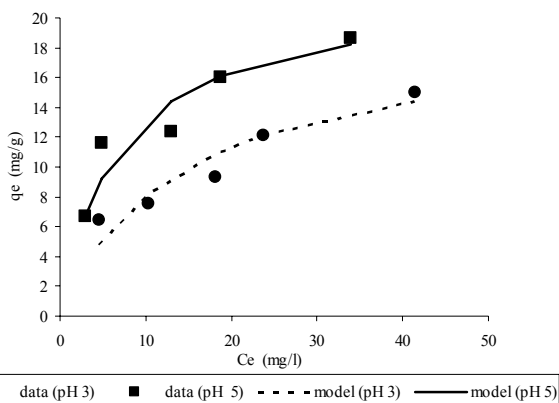


Fig. 2 Equilibrium biosorption isotherms of pomelo peel at pH 3 and pH 5 (data and Langmuir model)

Conditions: 0.1 g; initial cadmium nitrate concentration 25-100 mg/l; particle size, 150-212  $\mu$ m; contact time, 24 hrs; 150 rpm; 25 $\pm$ 2 $^\circ$ C

TABLE I

LANGMUIR AND FREUNDLICH ISOTHERM CONSTANTS FOR CADMIUM IONS BIOSORPTION ONTO PUMMELO PEEL

pH	Langmuir Model			Freundlich Model		
	b (l/g)	$q_{max}$ (mg/g)	$R^2$	$k_f$ (mg/l)	n	$R^2$
3	0.072	19.23	0.93	3.27	2.53	0.94
5	0.149	21.83	0.97	5.29	2.84	0.88

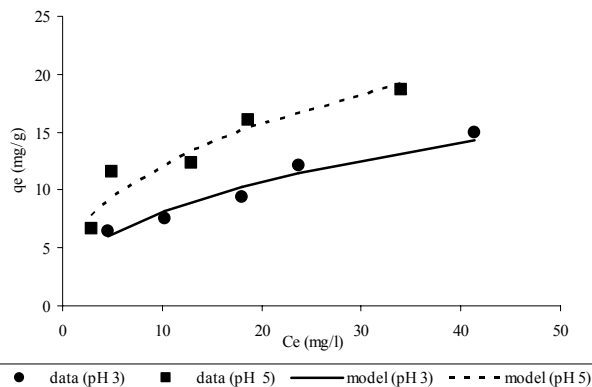


Fig. 3 Equilibrium biosorption isotherms of pomelo peels at pH 3 and pH 5 (data and Freundlich model)  
Conditions: 0.1 g; initial  $Cd(NO_3)_2 \cdot 4H_2O$  concentration 25-100 mg/l; particle size, 1.5-2.12 $\times 10^5$  nm; contact time, 24 hrs; 150 rpm; 25 $\pm$ 2 $^\circ$ C

TABLE II  
BIOSORPTION CAPACITIES FOR CADMIUM IONS USING DIFFERENT BIOSORBENTS

Biosorbent	Biosorption Capacity (mg/g)	Reference
Pomelo peel	21.83	This study
Papaya wood	17.22	[13]
Cystine-modified biomass	11.63	[31]
<i>H. verticillata</i>	15.00	[24]
Tea industry waste	11.30	[4]
Olive pomace	6.97	[12]

The solution pH had a significant effect on biosorption equilibrium; at pH 5 the biosorption capacity was consistently higher than at pH 3 (see Table II). Similar results were observed for orange peel [24] lemon and grapefruit peels [29]. It is likely that 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 [30].

### C. Biosorption Kinetics

Various models can be used to analyze the kinetics of the sorption process. The pseudo-first-order rate equation of the Lagergren is one of the most widely used for the biosorption of solutes from a liquid solution [31]-[32] and is represented in equation (4):

$$\ln(1 - qt/q_e) = -k_1 t \quad (4)$$

Another model for the analysis of biosorption kinetics is pseudo-second-order. The rate law for this system is expressed as (5):

$$t/qt = (1/k_2 q_e^2) + (t/q_e) \quad (5)$$

where  $qt$  and  $q_e$  are the grams of solute sorbed per gram of biosorbent at any time and at equilibrium, respectively, and  $k_1$  and  $k_2$  are the rate constant of pseudo-first-order sorption and pseudo-second-order sorption, respectively.

Biosorption kinetics of cadmium ions on pomelo at two pH values could be explained with the pseudo-second order equation (Fig. 4). The  $R^2$  values for the second-order kinetic

model were 1 for either pH value, while those for the first-order kinetic model were 0.98 and 0.87 for pH 3 and pH 5 respectively (Table III). A very fast increase in the biosorption rate of cadmium ion to the pomelo peel may be observed in the first 30 minutes for both pH-values studies, followed by a less rapid increase and a practically constant plateau after 60 min, in both cases. The results showed that at pH 5 the equilibrium capacity was higher than at pH 3. This is a typical phenomenon in biosorption when acidic sites were involved. Metal binding is usually higher at higher pH due to reduced competition by protons for the same binding sites [33].

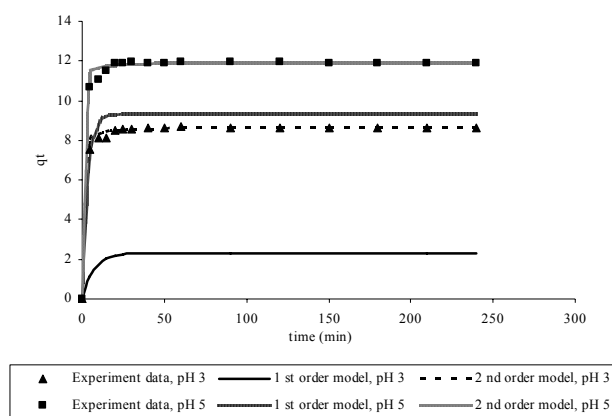


Fig. 4 Biosorption kinetics of pomelo peel at pH 3 and pH 5. (data and predictions of first- and second-order models)

TABLE III  
RATE CONSTANTS AND EQUILIBRIUM CADMIUM IONS CAPACITY AT PH 3 AND PH 5 WITH  $Cd(NO_3)_2 \cdot 4H_2O$  CONCENTRATION

pH	Pseudo-First Order Model			Pseudo-Second Order Model			Experimental qe (mg/g)
	$k_1$	qe (mg/g)	$R^2$	$K_2$	qe (mg/g)	$R^2$	
pH 3	0.14	2.31	0.98	0.26	8.67	1	8.62
pH 5	0.28	9.33	0.87	0.33	11.93	1	11.93

#### IV. CONCLUSION

The use of pomelo peel waste could be an environmentally friendly method of cadmium ion adsorption from aqueous solution. Further studies will help to evaluate the economic implications of using this biosorbent. Pomelo peel biosorption of cadmium ions was dependent on solution pH, initial ion concentrations and contact time.

#### ACKNOWLEDGMENT

The authors are grateful to Ubon Ratchathani Rajabhat University for financial support and to Ubon Ratchathani University for providing laboratory facilities.

#### REFERENCES

[1] C.W. Cheung, J.F. Porter and G. McKay, "Sorption kinetic analysis for the removal of cadmium ions from effluents using bone char," *Water Resource.*, vol. 35, pp. 605-612, 2001.

- [2] A.B. Prez-Marín, V. Meseguer Zapata, J.F. Ortuno, M. Aguilar, J. Saez and M. Llorens, "Removal of cadmium from aqueous solutions by adsorption onto orange waste," *Hazardous Materials.*, vol. 136, no. 1, pp. 122-131, 2007.
- [3] C.C.V. Cruz, C.A. Antonio, C.A. Henriques, and A.S. Luna, "Kinetic modeling and equilibrium studies during cadmium biosorption by dead *Sargassum* sp. biomass," *Bioresource Technol.*, vol. 91, pp. 249-257,
- [4] E. Malkoc and Y. Nuhoglu, 2005. "Investigations of nickel (II) removal from aqueous solutions using tea factory waste," *Hazardous Material.*, vol. 127, pp. 120-128, 2004.
- [5] C. Guiziu, Z. Guangming, T. Lin, D. Chunyan, J. Xiaoyun, H. Guohe, L. Hongliang and S. Guoli, "Cadmium removal from simulated wastewater to biomass byproduct of *Lentinus edodes*," *Bioresource Technology*, vol. 99, pp. 7034-7040, 2008.
- [6] L. Xiaomin, T. Yanru and X. Zhexian, "Study on the preparation of Orange peel cellulose adsorbents and biosorption of  $Cd^{2+}$  from aqueous solution," *Separation Purification and Technology*, vol. 55, pp. 69-75, 2007.
- [7] M.I. Kefala, A.I. Zouboulis and K.A. Matis, "Biosorption of cadmium ions by actinomycetes and separation by flotation," *Environmental Pollution.*, vol. 104, pp. 283-293, 1999.
- [8] 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," *Hydrometallurgy.*, vol. 75, pp. 11-24, 2004.
- [9] S.S. Ahluwalia, and D.Goyal, "Removal of heavy metals from waste tea leaves from aqueous solution," *Engineering of Life Science.*, vol. 5, pp. 158-162, 2005.
- [10] B. Volesk, "Review Biosorption and me," *Water Research.*, vol. 41, pp. 4017 - 4029, 2007.
- [11] A.B. Prez-Marín, A. Ballester, F. González, M.L. Blázquez, J.A. Muñoz, J. Sez and V. Meseguer Zapata, "Study of cadmium, zinc and lead biosorption by orange wastes using the subsequent addition method," *Bioresource Technology.*, vol. 99, no. 17, pp. 8101-8106, 2008.
- [12] G. Blázquez, F. Hernández, M. Calero and L.F. Ruiz-Núñez, "Removal of cadmium ions with olive stones: the effect of some parameters," *Process Biochemistry.*, vol. 40, pp. 2649-2654, 2005.
- [13] S. Asma, A.M. Washeed, and I. Muhammed, "Removal and recovery of heavy metals from aqueous solution using papaya wood as a new biosorbent," *Separation and Purification Technology.*, vol. 45, pp. 25-31, 2005.
- [14] H. Benaisa, "Screening of new sorbent materials for cadmium removal from aqueous solutions," *Hazardous Materials.*, vol. 132, 189-195, 2006.
- [15] S. Schiewer and S.B. Patil, "Pectin-rich fruit wastes as biosorbents for heavy metal removal: Equilibrium and kinetics," *Bioresource Technology.*, vol. 99, pp. 1896-1903, 2008.
- [16] G.H. Pino, L.M.S. De Mesquita, M.L. Torem and G.A.S. Pinto, "Biosorption of cadmium by green coconut shell powder," *Minerals Engineering.*, vol. 19, pp. 380-387, 2006.
- [17] E. Augustine and H. Yuh-Shan, "Effect of pH on cadmium biosorption by coconut copra meal," *Hazardous Materials.*, vol. 139, pp. 356-362, 2007.
- [18] F. Pagnanelli, S. Mainelli, F. Veglio and L. Toro, "Heavy metal removal by olive pomace: biosorbent characterization and equilibrium modeling," *Chemistry Engineering of Science.*, vol. 58, pp. 4709-4717, 2003.
- [19] Q. Yu and P. Kaewsarn, "Biosorption of copper(II) from aqueous solution by pre-treated biomass of marine alga *Padina* sp.," *Chemosphere.*, vol. 47, pp. 1081-1085, 2002.
- [20] Q. Yu and P. Kaewsarn, "A Model for pH Dependent Equilibrium of Heavy Metal Biosorption," *Korean Journal of Chemistry Engineering.*, vol. 16, no. 6, pp. 753-757, 1999.
- [21] Q. Yu and P. Kaewsarn, "Cadmium Removal from Aqueous Solutions by Pre-treated Biomass of Marine Macro-Alga *Padina* sp.," *Environmental Pollution.*, vol. 112, pp. 1-5, 2000.
- [22] Z.R. Holan, B. Volesky and I. Prasetyo "Biosorption of cadmium by biomass of marine algae," *Biotechnology and Bioengineering.*, vol. 41, pp. 819-825, 1993.
- [23] J.S. Chang, R. Law and C. Chang, "Biosorption of lead copper and cadmium by biomass of *Pseudomonas aeruginosa* PU 21," *Water Resource.*, vol. 31, pp. 1651-1658, 1997.

- [24] S. Bunluesin, M. Kruatrachue and P. Pokethitiyook, "Batch and continuous packed column studies of cadmium biosorption by *Hydrilla verticillata* biomass," *Bioscience and Bioengineering*, vol. 103, pp. 509-513, 2007.
- [25] M. Junxia and Xiaomei, "Cystine-modified biomass for Cd (II) and Pb (II) biosorption," *Hazardous Materials*, vol. 143, 277-284, 2007.
- [26] B. Stephen and N. Sulochana, "Carbonised jackfruit peel as an adsorbent for the removal of Cd (II) from aqueous solution," *Bioresource and Technology*, vol. 94, pp. 49-52, 2004.
- [27] V. Christian, F. Henri, P. Catherine and D. Alain, "Removal of Cd(II) and Pb(II) ions, from aqueous solutions, by adsorption onto sawdust of *Pinus sylvestri*," *Hazardous Materials*, vol. 105, 121-142, 2003.
- [28] S. Schiewer and B. Santosh, "Modeling the effect of pH on biosorption of heavy metals by citrus peels," *Hazardous Materials*, vol. 157, pp. 8-17, 2008.
- [29] S. Schiewer and B. Santosh, "Pectin-rich fruit wastes as biosorbents for heavy metal removal: Equilibrium and kinetics," *Bioresource Technology*, vol. 40, pp. 1896-1903, 2007.
- [30] P. Kaewsarn and Q. Yu, "Cadmium removal from aqueous solutions by pre-treated biomass of marine macro-alga *Padina* sp." *Environmental Pollution*, vol. 112: pp. 1-5, 2001.
- [31] J. Yu, M. Tong, X. Sun and B. Li, "Cystin-modified for Cd(II) and Pb(II) biosorption," *Hazardous Materials*, 143, pp. 277-284, 2007.
- [32] B. Benguella and H. Benaissa, "Cadmium removal from aqueous solution by chitin: kinetic and equilibrium studies," *Water Resource*, vol. 36, pp. 2463-2474, 2002.
- [33] S. Schiewer, B. Volesky, "Modeling of the proton-metal ion exchange in biosorption" *Environmental Science and Technology*, vol. 29, pp. 3049-3058, 1995.

"Heavy metal uptake capacities of common marine macro algal biomass," *Water research*, vol. 33, no. 6, pp. 1534-1537, 1999.

His current research which under study is "Biosorption of Cadmium Ions by Using Biomass Derived from Fruit Peel Wastes" and expected to complete in 2010.

Assistant Professor Dr. Pairat Kewsarn is a member of Thailand Chemical Engineers and Applied Chemists Association.

**Saikaew Wk.** (M'76-SM'81-F'87) was born in Prachinburi, Thailand in 1970. He got B. Sc. (Public Health) from Mahidol University and M.Sc. (Environmental Science) from Burapha University, Thailand.

He has worked as Lecturer since 2001 in Faculty of Science and Technology, Rajabhat Maha Sarakham University. His current research is focused on membrane technology and biosorption. At the present he has acted as doctor candidate in Environmental Engineering as well.

**Saikaew W.** (M'76-SM'81-F'87) was born in Thailand in 1968. She graduated and received bachelor degree from Ram Kham Hang University in 1992 in Chemical Science. Her master degree in Environmental Science from Burapha University was conferred in 1998.

She has worked as Lecturer since 2001 in Ubon Ratchathani Rajabhat University. Her current research which under study is "Biosorption of Cadmium Ions Using Biomass Derived from Fruit Peel Wastes" and expected to complete in 2010.

**Kaewsarn P.** (M'76-SM'81-F'87) was born in Thailand in 1964. He graduated and received bachelor degree from Khon Kaen University in 1978 in Chemical Engineering. His master degree in Chemical and Metallurgical Engineering from Royal Melbourne Institute of Technology was conferred in 1988 and then he got Ph. D. in Environmental Engineering from Griffith University, Australia in 1999. His major field of study and research is biosorption.

He has worked as Lecturer since 1987 in Ubon Ratchathani University and at present he has acted as Lead of Chemical Engineering Department. His major publications were

"Biosorption of copper(II) from aqueous solutions by pre-treated biomass of marine algae *Padina* sp.," *Chemosphere*, vol. 47, no.10, pp. 1081-1085, June 2002.,

"Cadmium(II) removal from aqueous solutions by pre-treated biomass of marine alga *Padina* sp.," *Environmental Pollution*, vol.112, no. 2, pp. 209-213, April 2001.,

"Adsorption of nickel from aqueous solutions by pretreated biomass of marine macro alga *Durvillaea Potatorum*," *Separation Science and Technology*, vol. 35, no. 5, pp. 689-701, 2000.,

"Electron Microscopy study of biosorbents from marine alga *Durvillaea Potatorum*," *Chemosphere*, vol. 41, pp. 589-594, 2000.,

"A Model for pH Dependent Equilibrium of Heavy Metal Biosorption," *Korean Journal of Chemistry Engineering*, vol. 16, no. 6, pp. 753-757, 1999.,

"Binary adsorption of copper and cadmium from aqueous solution by biomass of marine alga *Durvillaea Potatorum*," *Separation Science and Technology*, vol. 34, no. 8, pp. 1595-1605, 1999.,

"Fixed-bed study for copper removal from aqueous solution by marine alga *Durvillaea Potatorum*," *Environmental Technology*, vol. 20, pp. 1005-1008, 1999.,