

# Lead Adsorption of Activated Carbon Synthesized from Durian Peel

SARAWUT SRIKUN, SAMORN HIRUNPRADITKOON, KAMCHAI NUIHITIKUL\*

Department of Chemical Engineering, Center of Eco-Materials and Cleaner Technology

King Mongkut's University of Technology North Bangkok

1518 Piboonsongkram Road, Bangsue, Bangkok 10800

THAILAND

Kamchai\_fius@yahoo.co.uk <http://www.kmutnb.ac.th>

*Abstract:* - In this study, activated carbons have been produced from durian peel and used for the removal of lead (II) ions from water. The activated carbons were synthesized with physical activation using CO<sub>2</sub> as the activating agent at 900 °C. Prior to the activation process, durian peel was carbonized under either nitrogen atmospheric or vacuum pyrolysis in order to compare the properties of the synthesized activated carbons. The results showed that the activated carbons synthesized under vacuum pyrolysis had higher adsorption capacity for lead ions than those synthesized under nitrogen atmospheric pyrolysis. Langmuir adsorption isotherm better fitted to the experimental data than Freundlich adsorption isotherm. The adsorption kinetics followed pseudo-second order model.

*Key-Words:* - Activated carbon, Durian peel, Physical activation, Vacuum pyrolysis, Lead adsorption, Adsorption isotherm, Adsorption kinetics.

## 1 Introduction

Lead, a toxic and non-biodegradable heavy metal, is often contaminated in the effluent of wastewater from several industries, especially battery manufacturing, plating, paint, paper and pulp industries. Lead poisoning can destroy nervous system and organs and tissues such as heart, bones, intestines and kidneys [1]. Since lead has become one of the major environmental pollutants [2], it is necessary to remove it from wastewater before releasing into rivers and other water bodies.

To date, there have been several methods to separate lead and other heavy metals from wastewater such as ion exchange, chemical precipitation, ultra filtration, electrochemical deposition and adsorption. Among these, adsorption is considered as an inexpensive and high efficient method to remove trace amount of heavy metals [3-4]. Adsorption is also a simple and feasible method which requires low consumption of energy.

In the adsorption process, activated carbon is a good adsorbent for the removal of toxic substances from water and wastewater. However, commercial activated carbon is quite expensive. Therefore, the production of activated carbon from agricultural wastes is promising since these wastes can be acquired with no cost and they are environmentally friendly.

Durian peel is an agricultural and zero-cost waste that can be used as a raw material to produce

activated carbon [5-7]. Chandra and co-workers [5] produced activated carbon from durian peel with KOH activation and used it for the removal of methylene blue from aqueous solution. Tham and co-workers [6] synthesized activated carbon from durian peel with H<sub>3</sub>PO<sub>4</sub> activation and used it for the removal of toluene vapor. In our previous study [7], durian peel-based activated carbon was synthesized and used for the removal of Basic Green 4 dye. Therefore, this study was the first investigation in the adsorption capacities of durian peel-based activated carbons for the removal of lead ions (Pb<sup>2+</sup>) from aqueous solution. The activated carbons were synthesized with physical activation using CO<sub>2</sub> as the activating agent. Prior to the activation process, durian peel was carbonized under either nitrogen atmospheric or vacuum pyrolysis in order to compare the properties of the synthesized activated carbons. Adsorption kinetics and isotherms of lead ions onto the synthesized activated carbons were also investigated.

## 2 Experimental

### 2.1 Preparation of activated carbons

Activated carbons were synthesized according to the procedure described in the previous study [7]. Durian peel was acquired locally, washed, cut into approximately 1 x 1 cm<sup>2</sup> and dried at 80 °C for 24 h.

Carbonization of 100 g of dried durian peel was performed in a furnace (Model N7 Naber) under either nitrogen atmospheric (150 mL/min) or vacuum (56 kPa) pyrolysis. Heating was initiated from room temperature to 900 °C with the rate of 5 °C/min. Activation with CO<sub>2</sub> (300 mL/min) was immediately followed and maintained for 1 h. Next, the products were cooled under a nitrogen flow, immersed in an aqueous solution of HCl (2 M) for 24 h, washed with deionized water, dried at 110 °C for 3 h and grounded to a required mesh size of less than 0.18 mm. In this study, activated carbons synthesized under nitrogen atmospheric and vacuum pyrolysis were denoted as ACN and ACV respectively.

## 2.2 Characterization of activated carbons

Yields of the synthesized activated carbons were determined by weighing compared to the weight of dried bamboo precursor. Nitrogen adsorption of ACN and ACV at -196 °C was performed with Autosorb I (Quantachrome Corporation) in order to determine BET specific surface area, pore volume and average pore diameter of the synthesized activated carbons. Iodine numbers of the activated carbons were determined based on ASTM D4607-94. Adsorption capacities of the activated carbons for methylene blue were evaluated according to JIS K1474-1991.

## 2.3 Lead adsorption of activated carbons

Adsorption capacities of ACN and ACV for lead ions (Pb<sup>2+</sup>) were investigated in a batch mode. Aqueous solutions (25 mL) of lead ions were prepared from lead nitrate [Pb(NO<sub>3</sub>)<sub>2</sub>] with the concentrations of 10-30 mg/L. The solutions were mixed with 0.05 g of ACN or ACV. The mixtures were placed in a thermostatic shaker bath and stirred with the speed of 150 rpm for the required contact time. The adsorption temperature was maintained at 30 °C. After the adsorption, the activated carbons were rapidly separated from the mixtures with centrifugal method. The clarified supernatant solutions were used to determine the concentrations of lead ions according to dithizone colorimetric method [8-9]. After forming lead-dithizone complexes, the colour solutions were measured photometrically using a double beam UV/vis spectrophotometer (UV500 model, UNICAM). The optimum wavelength was 540 nm. The lead concentrations of the color solutions were calculated from a prepared calibration curve.

For the study of adsorption equilibrium, amounts of ACN and ACV were varied from 0.01 to 0.13 g. The initial concentrations of lead solutions (25 mL)

were fixed at 10 mg/L. The adsorption temperature was maintained at 30 °C. The contact time was 5 h to ensure the adsorption equilibrium.

# 3 Results and Discussion

## 3.1 Properties of the synthesized activated carbons

The properties of ACN and ACV are shown in Table 1. The yield of the activated carbon synthesized under vacuum pyrolysis was lower than that synthesized under nitrogen atmospheric pyrolysis. However, the BET specific surface area, pore volume and average pore size of the activated carbon synthesized under vacuum pyrolysis were greater than those of the activated carbon synthesized under nitrogen atmospheric pyrolysis. This is due to the greater degree of reactions between CO<sub>2</sub> and char obtained from vacuum pyrolysis. The lower yield of ACV compared to ACN supports this fact. In comparison to nitrogen atmospheric pyrolysis, volatilization occurs more under vacuum pyrolysis, leaving the surface of the char with less amount of deposits. When this char is brought to contact with CO<sub>2</sub> in the activation process, the reactions take place to a greater extent. Consequently, greater BET surface area, pore volume and average pore size are obtained. With greater BET specific surface area and pore volume, ACV had higher adsorption capacities for iodine and methylene blue than ACN.

Table 1 Properties of ACN and ACV

Properties	ACN	ACV
Yield (wt%)	21.32	18.74
BET specific surface area (m <sup>2</sup> /g)	748	1015
Pore volume (cm <sup>3</sup> /g)	0.46	0.66
Average pore diameter (nm)	2.488	2.602
Iodine number (mg/g)	580	739
Adsorption capacity for methylene blue (mg/g)	176	253

## 3.2 Lead adsorption of the synthesized activated carbons

The adsorption capacities of ACN and ACV for lead ions (Pb<sup>2+</sup>) when the initial concentrations of lead ions (C<sub>0</sub>) were varied between 10-30 mg/L are shown in Fig. 1. Adsorption of lead ions onto the activated carbons occurred rapidly during the first one minute owing to a great number of sites available for the sorption operation at the beginning. The adsorption rates then decreased and the equilibrium was obtained after 120 min. When the initial concentrations of lead ions increased from 10

to 30 mg/L, the equilibrium adsorption capacities of both ACN and ACV increased significantly. This trend corresponds to the previous studies [10-11]. It is important to note that ACV had higher adsorption capacities for lead ions than ACN. This is likely to be due to the greater surface area of ACV for lead ions to adsorb.

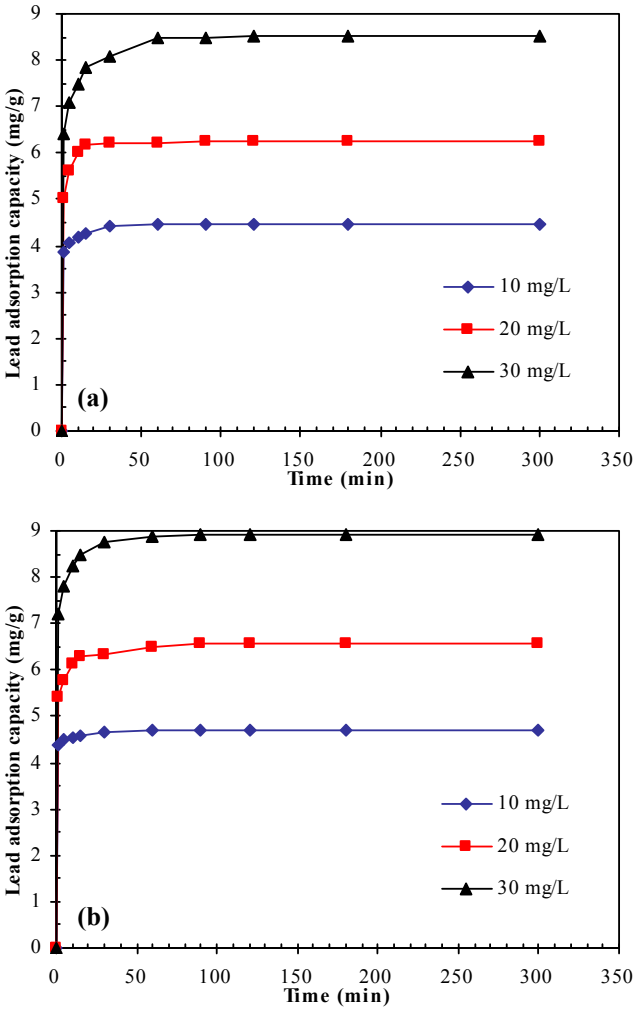


Fig. 1 Lead adsorption capacities of: (a) ACN, (b) ACV at 30 °C

### 3.2.1 Adsorption kinetics

The experimental data during the first 30 min. of contact time was used for the study in adsorption kinetics. In this research, pseudo-first order [12] and pseudo-second order [13] kinetic models were used as shown in Eqs. (1) and (2), respectively.

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303}t \quad (1)$$

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

$q_e$  (mg/g) and  $q_t$  (mg/g) represent amounts of lead ions adsorbed onto activated carbon per unit mass of activated carbon at equilibrium and any time  $t$ .  $k_1$  ( $\text{min}^{-1}$ ) and  $k_2$  ( $\text{g}/\text{mg}/\text{min}$ ) are the rate constants of pseudo-first order and pseudo-second order kinetic models, respectively.

Comparison between the experimental data with the two kinetics models for lead adsorption of ACN and ACV was made as shown in Figs. 2 and 3.

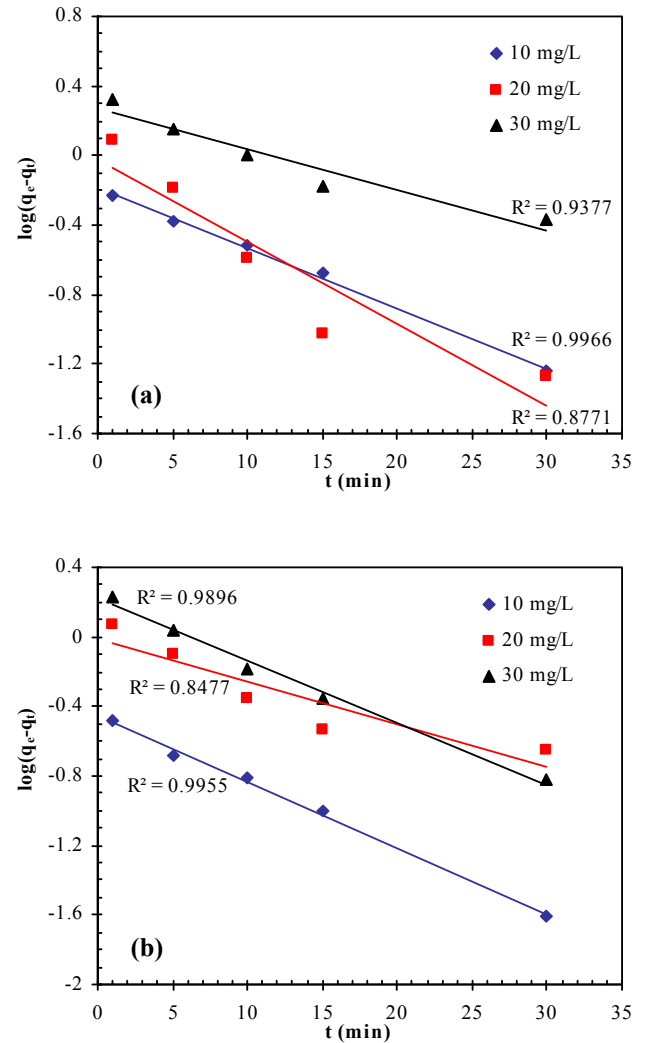


Fig. 2 Pseudo-first order kinetics of: (a) ACN, (b) ACV at 30 °C

As can be seen from Figs. 2 and 3, pseudo-second order model better fitted to the experimental data for both ACN and ACV than pseudo-first order model. The rate constants and equilibrium adsorption capacities of ACN and ACV were evaluated from the intercepts and slopes of the graphs and reported in Table 2. The values of  $q_e$  calculated from pseudo-second order model were closed to the experimental values of  $q_e$  than those from pseudo-first order model.

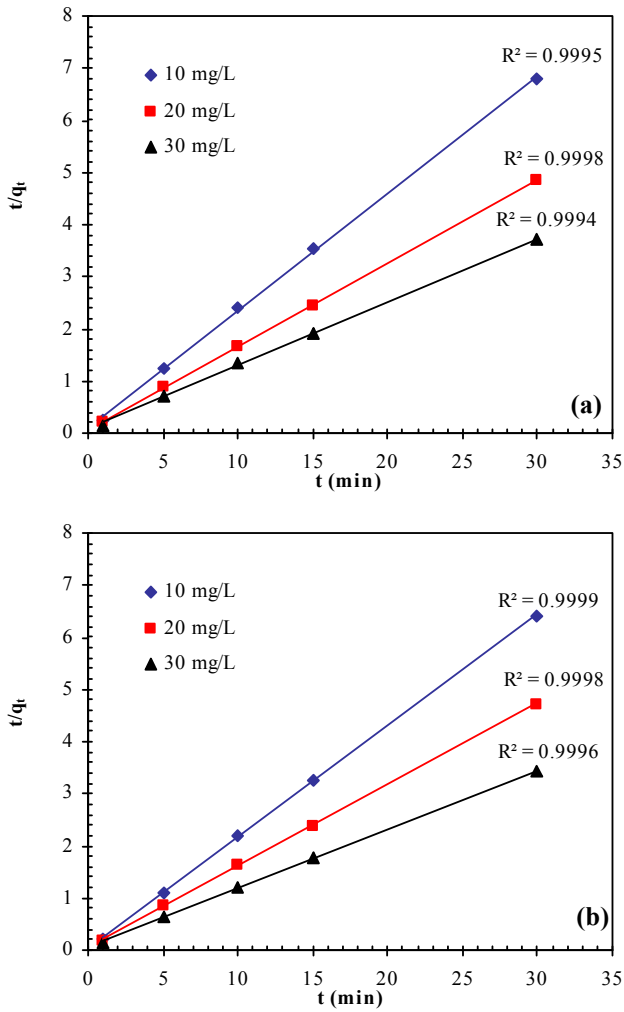


Fig. 3 Pseudo-second order kinetics of: (a) ACN, (b) ACV at 30 °C

Table 2 Adsorption kinetics of ACN and ACV at various initial concentrations of lead ions

Kinetics models	ACN			ACV		
	$C_0 = 10$	20	30	10	20	30
<b>Pseudo-first order</b>						
$k_1 \times 10^2$ ( $\text{min}^{-1}$ )	7.99	10.85	5.41	8.75	5.62	8.22
Calculated $q_e$ (mg/g)	0.65	0.94	1.88	0.35	0.97	1.66
<b>Pseudo-second order</b>						
$k_2 \times 10$ (g/mg/min)	4.94	3.86	1.83	9.99	4.02	2.01
Calculated $q_e$ (mg/g)	4.45	6.29	8.22	4.69	6.43	8.88
Experimental $q_e$ (mg/g)	4.47	6.25	8.51	4.70	6.57	8.91

### 3.2.2 Adsorption isotherm

Two well-known adsorption isotherms: Langmuir [14] and Freundlich [15], were used to correlate the experimental data at the equilibrium. The linear forms of Langmuir and Freundlich isotherms are shown in Eqs. (3) and (4), respectively.

$$\frac{C_e}{q_e} = \frac{1}{Q_o b} + \left(\frac{1}{Q_o}\right) C_e \quad (3)$$

$$\log q_e = \log K_F + \left(\frac{1}{n}\right) \log C_e \quad (4)$$

$Q_o$  (mg/g) and  $b$  (L/mg) are Langmuir constants in relevant to maximum adsorption capacity (monolayer capacity) and energy of adsorption, respectively.  $K_F$  and  $n$  are Freundlich constants in relevant to adsorption capacity and how favorable the adsorption process (adsorption intensity), respectively.

The plots of the experimental data according to Langmuir and Freundlich adsorption isotherms are shown in Figs. 4 and 5, respectively. As can be seen from the values of the correlation coefficients ( $R^2$ ) above 0.9, both models well described the adsorption of lead ions. However, Langmuir adsorption isotherm better fitted to the experimental data than Freundlich adsorption isotherm for both ACN and ACV. This indicates monolayer adsorption of lead ions on the homogeneous surface of the activated carbons prepared from durian peel with  $\text{CO}_2$  activation. Moreover, the binding of lead ions onto the surface of activated carbons is primarily by a chemical adsorption reaction.

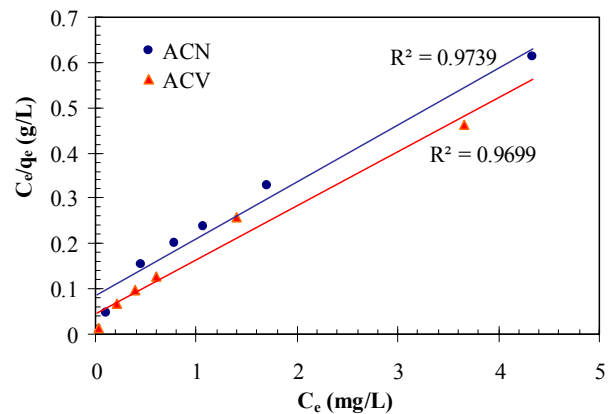


Fig. 4 Langmuir adsorption isotherm of ACN and ACV at 30 °C

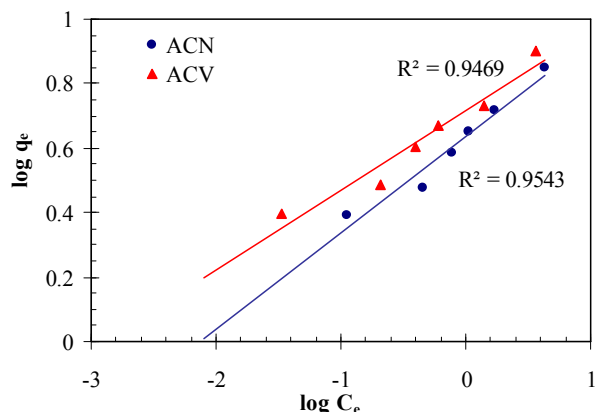


Fig. 5 Freundlich adsorption isotherm of ACN and ACV at 30 °C

The constants in Langmuir and Freundlich adsorption isotherms were determined from the slopes and intercepts of the graphs in Figs. 4 and 5. Table 3 represents the values of such constants. The maximum adsorption capacities ( $Q_o$ ) of durian peel-based activated carbons in this study are similar to those of coconut shell-based activated carbon [11] and sugar cane bagasse-based activated carbon [16].

Table 3 Langmuir and Freundlich isotherm constants for lead adsorption onto ACN and ACV

Adsorption isotherms	ACN	ACV
<b>Langmuir isotherm</b>		
$Q_o$ (mg/g)	7.97	8.43
$b$ (L/mg)	1.45	2.52
$R_L$	0.065	0.038
<b>Freundlich isotherm</b>		
$n$	3.34	4.04
$K_F$ (mg/mg <sup>1/n</sup> ·L <sup>1/n</sup> /g)	4.33	5.21

$R_L$  is an important characteristic of Langmuir isotherm which is called separation factor. The definition of  $R_L$  is given by Eq. (5). Its value can suggest whether the isotherm is favorable based on the following criteria:  $R_L > 1$  for unfavorable adsorption,  $0 < R_L < 1$  for favorable adsorption,  $R_L = 0$  for irreversible adsorption, and  $R_L = 1$  for linear adsorption [17-19]. As can be seen from Table 3, the values of  $R_L$  were less than 1 for both ACN and ACV, suggesting that the adsorption process of lead ions on durian peel-derived activated carbons was favorable and rather irreversible. Moreover, the values of  $1/n$  below 1 in Freundlich isotherm for both ACN and ACV could indicate favorable adsorption [20].

$$R_L = \frac{1}{1 + bC_o} \quad (5)$$

## 4 Conclusion

Activated carbon synthesized under vacuum pyrolysis had higher adsorption capacity for lead ions than that synthesized under nitrogen atmospheric pyrolysis. Langmuir adsorption isotherm better fitted to the experimental data than Freundlich adsorption isotherm. The adsorption kinetics followed pseudo-second order model.

### References:

- [1] U.S. Department of Health and Human Services, Toxicological Profile for Lead, 2007, <http://www.atsdr.cdc.gov/toxprofiles/tp13.pdf>.
- [2] Eba, F., Biboutou, R.K., Nlo, J.N., Bibalou, Y.G. and Oyo, M., Lead Removal in Aqueous Solution by Activated Carbons Prepared from *Cola edulis* Shell (Alocacée), *Pentaclethra macrophylla* Husk (Mimosaceae) and *Aucoumea klaineana* Sawdust (Burseraceae), *African Journal of Environmental Science and Technology*, Vol. 5, 2011, pp. 197-204.
- [3] Park, G.P., Tae, W.K., Myeoung, Y.C. and Ik, K.Y., Activated Carbon Containing Alginate Adsorbent for the Simultaneous Removal of Heavy Metals and Toxic Organics, *Process Biochemistry*, Vol. 42, 2007, pp. 1371-1377.
- [4] Sampranpiboon, P. and Charnkeitkong, P., Equilibrium Isotherm, Thermodynamic and Kinetic Studies of Lead Adsorption onto Pineapple and Paper Waste Sludges, *International Journal of Energy and Environment*, Vol. 4, No. 3, 2010, pp 88-98.
- [5] Chandra, T.C., Mirna, M.M., Sudaryanto, Y. and Ismadji, S., Adsorption of Basic Dye onto Activated Carbon Prepared from Durian Shell: Studies of Adsorption Equilibrium and Kinetics, *Chemical Engineering Journal*, Vol. 127, No. 1-3, 2007, pp. 121-129.
- [6] Tham, Y.J., Latif, P.A., Abdullah, A.M., Shamala-Devi, A. and Taufiq-Yap, Y.H., Performances of Toluene Removal by Activated Carbon Derived from Durian Shell, *Bioresource Technology*, Vol. 102, No. 2, 2011, pp.724-728.
- [7] Nuithitikul, K., Srikhun, S. and Hirunpraditkoon, S., Kinetics and Equilibrium Adsorption of Basic Green 4 Dye on Activated Carbon Derived from Durian Peel: Effects of Pyrolysis and Post-treatment Conditions,

- Journal of the Taiwan Institute of Chemical Engineers*, Vol. 41, 2010, pp. 591-598.
- [8] Bassett, J., *Vogel's Textbook of Quantitative Inorganic Analysis*, 4<sup>th</sup> ed., Longman, London, 1978, pp.158-159.
- [9] Christian, G.D., *Analytical Chemistry*, 2<sup>nd</sup> ed., John Wiley, New York, 1977, pp.620-621.
- [10] Gerçel, Ö. and Gerçel, H.F., Adsorption of Lead (II) Ions from Aqueous Solutions by Activated Carbon Prepared from Biomass Plant Material of *Euphorbia rigida*, *Chemical Engineering Journal*, Vol. 132, 2007, pp. 289-297.
- [11] Sekar, M., Sakthi, V. and Rengaraj, S., Kinetics and Equilibrium Adsorption Study of Lead (II) onto Activated Carbon Prepared from Coconut Shell, *Journal of Colloid and Interface Science*, Vol. 279, 2004, pp. 307–313.
- [12] Lagergren, S., Zur Theorie der Sogenannten Adsorption Geloster Stoffe. 591. Kungliga Svenska Vetenskapsakademiens, *Handlingar*, Vol. 24, 1898, pp. 1-39.
- [13] Ho, Y.S. and G. McKay, Pseudo-Second Order Model for Sorption Processes, *Process Biochemistry*, Vol. 34, 1999, pp. 451-465.
- [14] Langmuir, I., The Constitution and Fundamental Properties of Solids and Liquids. Part I: Solids, *Journal of the American Chemical Society*, Vol. 38, 1916, pp. 2221-2295.
- [15] Freundlich, H.M.F., Over the Adsorption in Solution, *Journal of Physical Chemistry*, Vol. 57, 1906, pp. 385-470.
- [16] Giraldo-Gutiérrez, L. and Moreno-Piraján, J.C., Pb(II) and Cr(VI) Adsorption from Aqueous Solution on Activated Carbons Obtained from Sugar Cane Husk and Sawdust, *Journal of Analytical and Applied Pyrolysis*, Vol. 81, 2008, pp. 278–284.
- [17] Mall, I.D., Srivastava, V.C., Agarwal, N.K. and Mishra, I.M., Adsorptive Removal of Malachite Green Dye from Aqueous Solution by Bagasse Fly Ash and Activated Carbon – Kinetic Study and Equilibrium Isotherm Analyses, *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, Vol. 264, 2005, pp. 17-28.
- [18] Weber, T.W. and Chakraborty, R.K., Pore and Solid Diffusion Models for Fixed Bed Adsorbents, *American Institute of Chemical Engineering Journal*, Vol. 20, 1974, pp. 228-238.
- [19] Wang, L., Zhang, J., Zhao, R., Li, Y., Li, C. and Zhang, C., Adsorption of Pb (II) on Activated Carbon Prepared from *Polygonum orientale* Linn.: Kinetics, Isotherms, pH, and Ionic Strength Studies, *Bioresource Technology*, Vol. 101, 2010, pp. 5808-5814.
- [20] Treybal, R.E., *Mass-Transfer Operations*, 2<sup>nd</sup> ed., McGraw Hill, New York, 1968.