



Study of lead adsorption on activated carbons

Yao Urbain KOUAKOU, Aimé Serge ELLO*, Aboua Jacques YAPO,
Irié Marc GOULI-BI and Albert TROKOUREY

Laboratoire de Chimie Physique, Université Felix Houphouët-Boigny,
22 BP 582 Abidjan 22 Côte d'Ivoire.

*Corresponding author; E-mail : elloserge@gmail.com; Tel: +225-08789230,

ABSTRACT

In this study, the removal of lead (II) from water using commercial activated carbons from wood and coconut shell were investigated in acidic medium (pH = 4). Atomic absorption spectrometer (AAS) was used to investigate initial (C_0) and (equilibrium) (C_e) solution concentrations. Powder and granular activated carbons showed different adsorption capacity. The amount of Pb^{2+} adsorbed reached 44.58, 38.96 and 39.06 mg/g for CPA, CGA 830 and CGA 1230 respectively at 25 °C. Langmuir and Freundlich adsorption models were used to represent the equilibrium data. Despite the high value of coefficient (R^2) from Freundlich model, the best interpretation for the experimental data was given by the Langmuir model. The work showed that using powder activated carbon from wood exhibited relatively high adsorption capacity than activated carbon from coconut shell.

© 2014 International Formulae Group. All rights reserved.

Keywords: Lead, activated carbon, adsorption, Langmuir, isotherm.

INTRODUCTION

The toxicity of heavy metals has been often observed even at low concentrations such as arsenic (As), chromium (Cr), lead (Pb), mercury (Hg) and cadmium (Cd). They had non-biodegradable form, and untreated effluents from these heavy metals caused an adverse impact on the environment and public health (Papanikolaou et al., 2005). Drinking water containing lead caused serious disorders, such as anemia, kidney disease, and nervous system damages (Papanikolaou et al., 2005; Fu and Wang, 2011). As organic pollutants, lead must be removed from wastewater. The removal of this metal from contaminated water has been attempted by

several scientists employing a wide variety of techniques including chemical precipitation, ion-exchange, electroflotation, membrane filtration, reverse osmosis, ... (Barakat, 2011 ; Sreejalekshmia et al., 2009). All these methods are generally expensive. For this reason, developing countries needed economical and eco-friendly methods to overcome wastewater treatments costs. Therefore, many approaches such as the development of cheaper and effective adsorbents from agricultural by-products, called biosorbent were used to remove heavy metals from wastewaters by adsorption. Then several activated carbons as adsorbents from plant origin were obtained. According to lead

adsorption, using activated carbon prepared from renewable plant material showed high amount of lead(II) ions adsorbed 279.72 mg/g at 40 °C (Gerçel and Gerçel, 2007). Pb²⁺ adsorption capacities were of 10.66 mg/g and 53.73 mg/g with charcoal and activated raw charcoals respectively were also observed (Lalhrualtuanga et al., 2010). The use of coconut shell showed the maximum of lead adsorption capacity at 26.50 mg/g with the Langmuir adsorption model (Sekar et al., 2004). Amount of 44 mg/g of Pb (II) was adsorbed by activated carbon obtained from Tammarin wood (Acharya et al., 2009). Adsorption of lead Pb²⁺ on sugar beet pulp, a low-cost material was studied and adsorption reached 43.5 mg/g at pH 5.0 (Pehlivan et al., 2008). The high amount of 12.6 and 34.72 mg/g of lead were adsorbed respectively on rice husk ash (Feng et al., 2004) and carbon aerogel (Goel et al., 2005). Activated carbon from apricot stone showed 22.85 mg/g for lead adsorption (Kobyta et al., 2005). The adsorption capacity up to 15.96 mg/g was obtained for initial concentrations between 25 and 40 mg/L and at pH = 2 and 6 respectively for activated prepared from van apple pulp (Tolga et al., 2012). Generally, metal adsorption depends on the following parameters: the initial concentration, the pH and temperature which help to optimize the adsorption capacity. This capacity (amount) changed very often with the initial concentration and temperature. The pH of the mixture was linked to the adsorbent but maximum adsorption was observed in acid medium. The adsorption mechanism was very complex. It was also demonstrated that adsorbents played an important role during the adsorption and their capacity depended on the nature of these adsorbents. The description developed to reflect the adsorption mechanism is ion exchange and surface complexation. Several isotherm adsorption models such as Langmuir (Bayrak, 2006), Freundlich (Agarwal et al., 2014), Temkin (Günay et al., 2007), Redlich-Peterson (Foo and Hameed, 2010) and Elovich (Wu, 2009) are used to describe

adsorption. No model describes the adsorption before but Langmuir and Freundlich models were more used and suitable to show adsorption phenomena. The aim of this work is the study of the use of industrial activated carbon obtained from African plant origin such as wood and coconut shell for adsorption of lead in the strong acid medium (pH = 4) in order to compare their adsorption capacities with other plant origin material.

MATERIALS AND METHODS

Three commercial activated carbons were used as adsorbents: commercial powder activated carbon (CPA) supplied by Polychimie Company from Côte d'Ivoire is produced from wood, and granular activated carbons Norit 830 and 1240 labeled in this study as CGA 830 and CGA 1240 supplied by Netherlands industry and produced from coconut shell. The only characteristics given for these adsorbents were total pore volume $V_p = 0.6 \text{ cm}^3/\text{g}$, randomly particle sizes from 2 to 60 nm and $S_{\text{BET}} = 1500 \text{ m}^2/\text{g}$ for CPA. CGA 830 and 1240 particle sizes were 0.6 - 2.36 and 0.425 - 1.70 mm respectively and $S_{\text{BET}} = 1150 \text{ m}^2/\text{g}$. Metal ions Pb²⁺ or Pb(II) are from: Pb(NO₃)₂ with $p = 97\%$, (Merck).

Batch adsorption experiments

Batch adsorption experiments were performed using 250 mL glass bottles. Solutions contained 0.1 g of activated carbon and 20 mL of initial concentrations (C_0) increasing from 100 to 500 mg/l. The glass bottles were sealed with Teflon and were mounted on a shaker. The shaker was placed within a temperature control box and operated at 27 °C and 500 rpm for 2 h. The suitable pH was adjusted with nitric acid 0.1 M and sodium hydroxide 0.1 M. When the adsorption procedure was completed, the solutions were centrifuged at 4500 rpm for 2 min and the supernatants were filtered then analyzed for the equilibrium lead (II) ion concentrations. The initial and equilibrium concentrations of lead (II) were determined by absorption atomic spectrometer (AAS, Varian

AA20) dosing solution up to concentration limits of $1\mu\text{g}$. The amount of metal adsorbed is calculated with equation 1: $q_e \text{ (mg/g)} = (C_0 - C_e) V/m$ (1) where q_e is the amount of metal adsorbed by activated carbon (mg/g); C_0 is the initial metal concentration (mg/L); C_e is the equilibrium metal concentration after filtration (mg/l); V is the initial solution volume (L); m is the activated carbon weight (g).

RESULTS

The effect of contact time and pH

Adsorption of Pb (II) on to CPA, CGA830 and 1240 at 27 °C with the contact time is shown in Figure 1. The amount of lead adsorbed increased with time. The high amount was adsorbed within 70 min. CPA adsorbed 82 mg/g against 62 and 63 mg/g respectively for CGA 830 and 1240. The equilibrium time reached around 100 min but high amount of lead is adsorbed after 70 min.

Adsorption isotherms

Adsorption of Pb (II) was studied with concentration range of 20-500 mg/L. The amount of Pb (II) adsorbed q_e has been plotted

against the equilibrium concentration C_e . Figure 2 showed the plot for the adsorbents CPA, CGA 830 and 1240. The maximum amounts adsorbed were 44.68, 38.96 and 39.06 mg/g for CPA, CGA 830 and 1240 respectively. The powder activated carbon showed a great adsorption capacity than granular activated carbon. Several isotherms models were available to describe adsorption and the most common used are: Langmuir, Freundlich, for this field. The plots of C_e/q_e versus C_e and $\ln q_e$ versus $\ln C_e$ were used to determine values for Langmuir Freundlich adsorptions respectively summarized in Table 1.

Isotherm constants were very useful parameters because they predicted adsorption capacities. The coefficients (R^2) of adsorption model isotherm showed 0.99 according to Langmuir model for CPA, CGA 830 and CGA 1240. Freundlich model showed 0.99; 0.95; 0.98 for CPA, CGA 830 and CGA 1240 respectively.

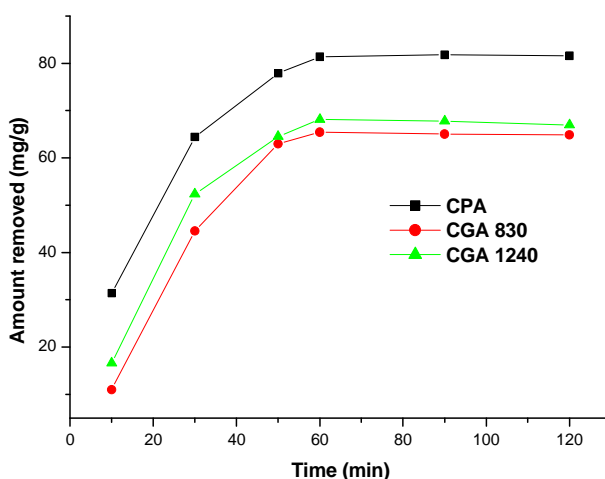


Figure 1: Effect of equilibrium contact time of adsorption of lead onto CPA, CGA 830 and 1240 at T = 27 °C, m = 1 g. CPA: commercial powder activated carbon; CGA: commercial granular activated carbon.

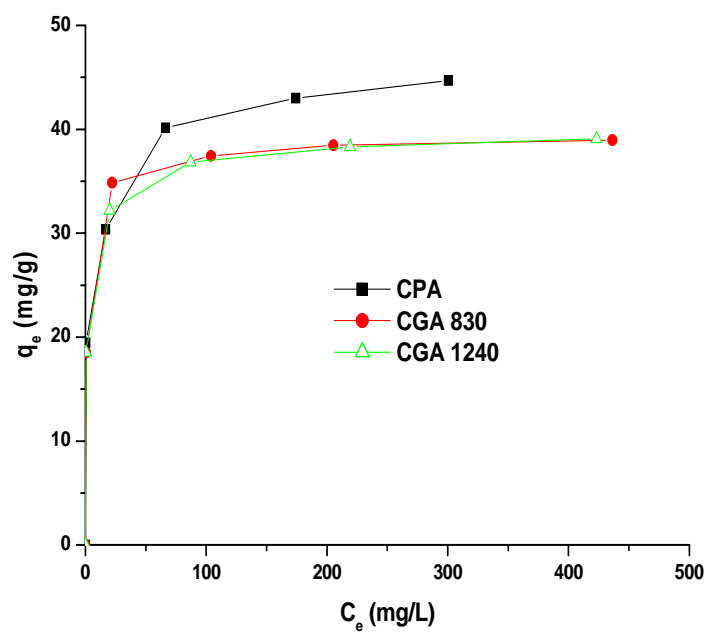
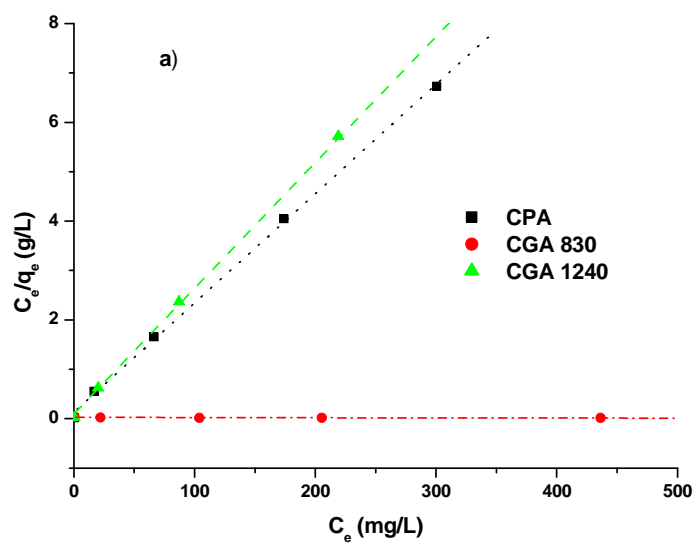


Figure 2: Adsorption isotherms of lead on 0.1 g of CPA, CGA 830 and 1240 at $T = 27\text{ }^\circ\text{C}$ and $\text{pH} = 4$. CPA: commercial powder activated carbon; CGA: commercial granular activated carbon.



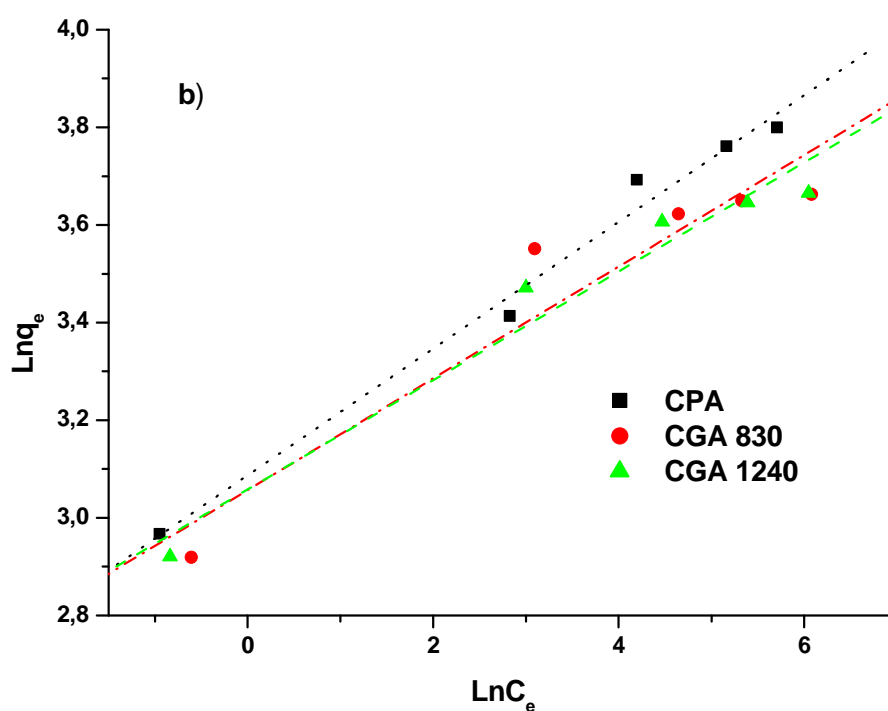


Figure 3: a) Langmuir and b) Freundlich linear forms are plotted for the adsorption of Pb^{2+} ions on CPA, CGA 830 and CGA 1240. CPA: Commercial Powder activated carbon; CGA: Commercial granular activated carbon.

Table 1: Langmuir and Freundlich isotherms parameters for the adsorption of Pb^{2+} on CPA, CGA 830 and 1240.

Adsorbents	CPA	CGA830	CGA 1240
Langmuir			
q_m (mg/g)	45,2	39,12	39,27
b (m/g)	0,169	0,377	0,269
R^2	0,99	0,99	0,99
Freundlich			
K_f (mg/g)	21,91	21,25	21,29
n	7,7	8,73	8,95
R^2	0,99	0,95	0,98

CPA : Commercial powder activated carbon; CGA: Commercial granular activated carbon; q_m : amount adsorbed(mg/g); b : coefficient of Langmuir(Lmg^{-1}); K_f : coefficient of Freundlich (mg/g); n : constant of Freundlich; R : coefficient of the straight.

Table 2: Comparison of biosorption capacity of Pb²⁺ by CPA, CGA 830 and 1240 and other plant origin materials.

Adsorbentorigin	q _m (mg/g)	References
EuphorbiaRigida	279.72	Gerçel and Gerçel, 2007
charcoal	10.6	(LalhrUITluanga et al., 2010)
Activated charcoal	53.7	(LalhrUITluanga et al., 2010)
Coconut shell	26.5	(Sekar et al., 2004)
Tammarin wood	44.4	(Acharya et al., 2009)
Sugar beet pulp	43.5	(Pehlivanet al., 2008).
Rice husk ash	12.6	(Feng et al., 2004)
Carbon aerogel	34.7	(Goel et al., 2005)
Apricot stone	15.9	KobyA et al., 2005
Van apple pulp	40	(Tolga et al., 2012)
CPA (wood)	44.6	This study
CGA 830 (coconut shell)	38.9	This study
CGA 1240 (coconut shell)	39	This study

CPA : Commercial Powder activated carbon; CGA: Commercial granular activated carbon.

DISCUSSION

The equilibrium time is in accordance with the literature where the equilibrium time is generally between 60 and 120 min (Gouli et al., 2008; Ouattara and al., 2012). Lead existed in different forms, including cationic, anionic and neutral forms. These forms existed or coexisted under acid or basic conditions. In this study, the adsorption of lead was carried out at pH = 4, strong acidic medium. At this pH only non-complex such as Pb²⁺ or Pb (II) existed. In this condition, there was a competitive adsorption between Pb²⁺ and H⁺ ions at the surface of activated carbon. It was shown that the optimal pH for lead adsorption was between 4 and 6, because when the pH increases, the H⁺ decreases causing less competitive effect (Al-Degset al., 2008; Doğan et al., 2007). The pH of the study allowed adsorption of Pb²⁺ useful for the removal of heavy metal pollution. The initial concentration influenced amount of lead adsorbed. The increasing of Pb²⁺ concentration enhanced the diffusion of the ions to the adsorbent due to the increasing of the concentration gradient (Tolga et al., 2012). Langmuir model was represented

mathematically by the following equation 2: $q_e = q_m b C_e / (1 + b C_e)$ (2) Where q_e (mg/g) the amount of Pb (II) adsorbed per unit mass of adsorbent at equilibrium and q_m (mg/g) the amount of Pb (II) adsorbed per gram of solid required to cover the surface of the adsorbent layer of a monomolecular or the maximum adsorption capacity; C_e (mg/l) represented the equilibrium Pb (II) concentration, b (Lmg⁻¹) was a constant. There were five types of Langmuir equation linear forms. The most commonly used was linear form type 2: equation 3. $C_e/q_e = C_e/q_m + 1/bq_m$ (3). The Freundlich model was given by equation 4 hereafter: $q_e = K_F C_e^{1/n}$ (4) q_e was the amount of Pb adsorbed per unit mass of the adsorbent and K_F [(mg/g)(L/mg)] and were constants. The linear form of the Freundlich equation 5 was: $\ln q_e = \ln K_F + 1/n \ln C_e$ (5) The high coefficients obtained with Freundlich model did not show a better model to describe the adsorption of lead on CGA 830 than Langmuir model. Figures 3a and 3b showed a good harmony with theoretical (Langmuir) and experimental adsorption models. However, the maximum theoretical amounts adsorbed q_{max} were 45.2, 39.12 and 39.27

mg/g for CPA, CGA 830 and CGA 1240 respectively comparatively to 44.68, 38.96, and 39.06 mg/g respectively for CPA, CGA 830 and CGA 1240. Langmuir model was suitable for this application. We compared the results with the values found in literature in Table 2. Activated carbon from wood gave high capacity comparatively to using activated carbon from coconut shell, rice husk, apricot stone and van apple pulp. All these plant origins were used as raw carbon materials in order to develop local technology to remove Pb²⁺ from water. The large amount removed depends on the adsorption capacity of the carbon. The values observed have shown it was possible to use carbon from wood to remove lead but preferably in the powder form.

Conclusion

The present study showed the activated carbons CPA, CGA 830 and 1240 were effective adsorbents for the removal of Pd (II) ions from metal-containing aqueous solutions. The amount (mg/g) of metal uptake was found to increase up to 44.68 mg/g on CPA. The model of Langmuir was in agreement with experiment. The maximum amount of lead adsorbed is more than with other bio sorbents from van apple pulp, rice husk ash, apricot stone and coconut shell.

ACKNOWLEDGMENTS

This work is supported by the Laboratory of Physical Chemistry from the Houphouët-Boigny University of Abidjan, by the program for promoting scientific research for young students.

REFERENCES

Acharya J, Sahu JN, Mohanty CR, Meikap BC. 2009. Removal of lead (II) from wastewater by activated carbon developed from Tamarind wood by zinc chloride activation. *Chem. Eng. J.*, **149**: 249–262.

Agarwal AK, Kadu MS, Pandhurnekar CP, Muthreja IL. 2014. Langmuir, Freundlich

and BET Adsorption Isotherm Studies for Zinc ions onto coal fly ash. *Inter. J. Appl. Innov. Eng. Manage*, **3**(1): 64-71.

Al-Degs YS, El-Barghouthi MI, El-Sheikh AH, Walker GM. 2008. Effect of solution pH, ionic strength, and temperature on adsorption behavior of reactive dyes on activated carbon. *Dyes and Pigments*, **77**(1): 16–23.

Barakat MA. 2011. New trends in removing heavy metals from industrial wastewater. *Arab. J. Chem.*, **4**: 361-377.

Bayrak Y. 2006. Application of Langmuir isotherm to saturated fatty acid adsorption. *Microporous Mesoporous Mater.*, **87** (3): 203-206.

Depci T, Kul AR, Önal Y. 2012. Competitive adsorption of lead and zinc from aqueous solution on activated carbon prepared from Van apple pulp: Study in single- and multi-solute systems. *Chem. Eng. J.*, **200-202**: 224–236.

Doğan M, Özdemir Y, Alkan M. 2007. Adsorption kinetics and mechanism of cationic methyl violet and methylene blue dyes onto sepiolite. *Dyes and Pigments*, **75**(3): 701–713.

Feng Q, Lin Q, Gong F, Sugita S, Shoya M. 2004. Adsorption of lead and mercury by rice husk ash. *J. Colloid Interface Sci.*, **278**: 1–8.

Foo KY, Hameed BH. 2010. Insights into the modeling of adsorption isotherm systems. *Chem. Eng. J.*, **156**(1): 2–10.

Fu F, Wang Q. 2011. Removal of heavy metal ions from wastewaters: A reviews. *J. Environ. Manage*, **92**(3): 407-418.

GerçelÖ, Gerçel FH. 2007. Adsorption of lead (II) ions from aqueous solutions by activated carbon prepared from biomass plant material of *Euphorbia rigida*. *Chem. Eng. J.*, **132**: 289–297.

Goel J, Kadirvelu K, Rajagopal C, Garg VK. 2005. Removal of lead (II) from aqueous solution by adsorption on carbon aerogel using a response surface methodological approach. *Indus. Eng. Chem. Research*, **44**: 1987–1994.

- Gouli BIM, Yapo AJ, Ello AS, Diabaté D, Trokourey A. 2008. Adsorption of Acetic and Benzoic Acids from Aqueous Solutions on Activated Carbon. *J. Soc. Ouest-Afr. Chim.*, **26**: 53 – 57.
- Günay A, Arslankaya E, Tosun İ. 2007. Lead removal from aqueous solution by natural and pretreated clinoptilolite: Adsorption equilibrium and kinetics. *J. Hazard. Mater.*, **146**(1–2): 362–371.
- Kobyas M, Demirbas E, Senturk E, Ince M, 2005. Adsorption of heavy metal ions from aqueous solutions by activated carbon prepared from apricot stone. *Bioresour. Technol.*, **96**: 1518–1521.
- Lalhrualtuanga H, Jayaram K, Prasad MNV, Kumar KK. 2010. Lead(II) adsorption from aqueous solutions by raw and activated charcoals of *Melocannabaccifera* Roxburgh (bamboo)- A comparative study. *J. Hazard. Mater.*, **175**: 311–318.
- Liu C, Bai R, San LQ. 2008. Selective removal of copper and lead ions by diethylenetriamine - functionalized adsorbent: behaviors and mechanisms. *Water Res.*, **42**: 1511–1522.
- Ouattara K, Gouli M, Ello S, Yapo A, Trokourey A. 2012. Adsorption of acetic acid on different carbons. *Inter. J. Eng. Sci. Technol.*, **4**(10): 4398-4403.
- Papanikolaou NC, Hatzidaki EG, Belivais S, Tzanahakis GN, Tsatsakis AM. 2005. Lead toxicity update. A brief Review. *Med. Sci. Monit.*, **11**(10): 329-336.
- Pehlivan E, Yanik BH, Ahmetli G, Pehlivan M. 2008. Equilibrium isotherm studies for the uptake of cadmium and lead ions onto sugar beet pulp. *Bioresour. Technology*, **99**: 3520-3527.
- Sekar M, Sakthi V, Rengaraj S. 2004. Kinetics and equilibrium adsorption study of lead(II) onto activated carbon prepared from coconut shell. *J. Colloid Interface Sci.*, **279**: 307–313.
- Sreejalekshmi KG, Anoop KK, Anirudhan TS. 2009. Adsorption of Pb (II) and Pb (II)-citric acid on sawdust activated carbon: Kinetic and equilibrium isotherm studies. *J. Hazard. Mater.*, **161**(30): 1506–1513.
- Wu F, Tseng R, Juang R. 2009. Characteristics of Elovich equation used for the analysis of adsorption kinetics in dye-chitosan systems. *Chem Eng. J.*, **150**(2-3): 366–373.