

## Continuous adsorption of lead ions in a column packed with palm shell activated carbon

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### Abstract

The continuous adsorption of lead ions from aqueous solution on commercial, granular, untreated palm shell activated carbon (PSAC) was studied. Effect of pH, flow rates and presence of complexing agents (malonic and boric acids) were examined. The breakthrough period was longer at pH 5 indicating higher adsorption capacity of lead ions at higher pH. Increase of the flow rate, expectedly, resulted in the faster saturation of the carbon bed. Presence of complexing agents did not improve adsorption uptake of lead ions. However, presence of malonic acid resulted in smoother pH stabilization of solution compared to single lead and lead with boric acid systems. The results on continuous adsorption of lead were applied to the model proposed by Wang et al. [Y.-H. Wang, S.-H. Lin, R.-S. Juang, Removal of heavy metals ions from aqueous solutions using various low-cost adsorbents, *J. Hazard. Mater. B* 102 (2003) 291–302]. The agreement between experimental and modelled breakthrough curves was satisfactory at both pHs.

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### 1. Introduction

High concentrations of heavy metals in the environment are extremely detrimental for the living organisms and ecosystems. It is well known that industrial discharges are the main sources of heavy metals pollution. In Malaysia, the electroplating and metal treatment/fabrication industries are the major contributors to the generation of hazardous wastes bearing heavy metals. The largest concentration of industrial operations is localized along the West coast of peninsular Malaysia including Klang Valley, Penang, Ipoh, and Johor Bahru [1].

Lead discharges into aqua-environment present a special concern, since this metal is bounded to bioaccumulation and excessive concentrations of lead are associated with various diseases in humans and animals.

Innovative practices for wastewater treatment bearing heavy metals often involve technologies directed towards either reduction of generated wastes' amount or recovery of reusable

resources [2]. The land disposal of the wastes with excessive heavy metal content faces more stringent legislative barriers. As a consequence, the implementation of new alternative approaches becomes a necessity in the primary metal industry nowadays.

The major economy sector of Malaysia is production of palm oil. It has greatly expanded in the last decades making Malaysia a leading exporter of the product. Palm shells are generated in great quantities in this economy sector, along with other wastes that are mostly disposed without further utilization. It is only in recent years the interest to palm shell has increased, mainly due to the research findings that this material can be an excellent source of high quality and low cost activated carbon. However, most of the studies on palm shell activated carbon (PSAC) are focused on the parameters of the activation/carbonization procedures [3–9] and so far only few examined the adsorption capacity of this material [10–12]. A recent study conducted by our research team [13] showed that palm shell activated carbon has high capacity to adsorb lead ions compared to other types of activated carbons. However, the study was only focused on the batch adsorption. In order to investigate adsorption potential of PSAC, a series of experiments on continuous adsorption was

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conducted, results of which are presented in this paper. Effects of such parameters as flow rate, pH, and presence of complexing agents on the breakthrough curve and bed capacity were investigated. Additionally, the obtained data were fit to a model [14] to predict the breakthrough curves under different operating conditions.

## 2. Materials and methods

Description of the experimental setup and relevant procedures is available elsewhere, including characterization data of the PSAC [13,15].

## 3. Results and discussion

### 3.1. pH profile in continuous adsorption of lead

#### 3.1.1. Single lead

Fig. 1 shows pH changes for single lead at pH 5 and 3. Overall, pH changes were such that pH increased in the first 20 min of adsorption up to pH 9 and then stabilized. The stabilization period for lead solution of pH 5 was longer compared to pH 3 solution (50 min vs. 30 min); the stabilized pH values were 6.3 and 3.2, respectively.

Observations on pH increase at the beginning of continuous adsorption of metals were also reported by Chen and Wang [16] and Dimitrova [17]. Two possible explanations for pH increase over initial value are proposed: adsorption of hydrogen ions from the solution, and dissolution of some impurities from the activated carbon [16]. In addition, a release of hydroxyl ions from adsorbent into aqueous phase is possible due to hydrolysis reaction [17]. Furthermore, when influent pH carries more hydrogen ions (lower pH) through the bed, the hydrolysis reaction is accompanied by an exchange reaction between substances from adsorbent and hydrogen ions from solution.

Since increase of pH in continuous adsorption is associated with reactions occurring within the carbon bed, such as adsorption, co-precipitation, hydroxide precipitation and ion exchange [18], it is possible that at the given bed thickness and pH 3 solution, the interference of these reactions is low and therefore pH settles within its initial value. In this regard [16], suggested that

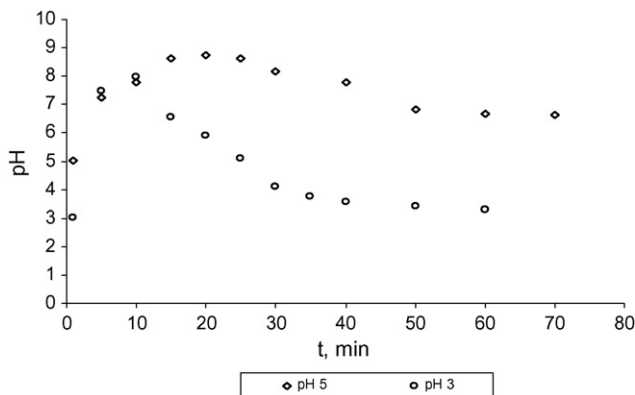


Fig. 1. pH profile in continuous adsorption of single lead, 1.0 L/h.

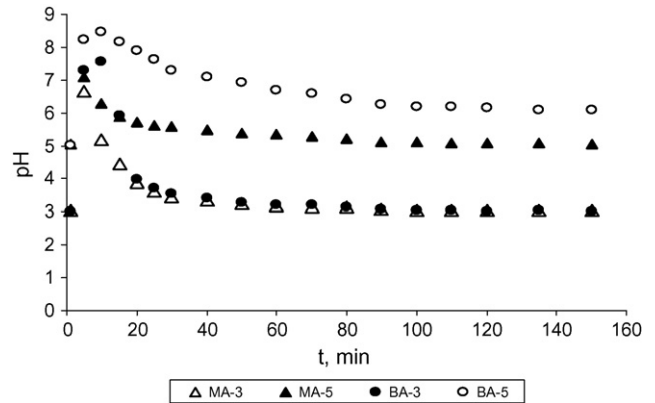


Fig. 2. pH profiles in lead adsorption with complexing agents, 1.0 L/h.

in order to avoid fluctuations in pH values, the activated carbon bed should be pretreated with acidic solution.

#### 3.1.2. Lead with complexing agents

Fig. 2 shows pH profiles for systems containing lead ions and complexing agents, boric and malonic acids. Similarly as in continuous adsorption of single lead, pH increased in the first 15–20 min and then stabilized. However, stabilization of pH was different for the two complexing agents. Thus, the stabilized pH values in the system containing malonic acid were close to the initial solution pH. This is probably associated with the buffering properties of malonic acid,  $pK_1 = 2.85$  and  $pK_2 = 6.1$ . The stabilization pattern and stabilized pH values in the system of lead with boric acid were the same as for single lead. Although, boric acid is known for the buffering properties, its ineffectiveness in the solution with lead is probably explained by its low concentration and high  $pK = 9.24$ .

However, at pH 3 the pH stabilization pattern was the same for both complexing agents.

### 3.2. Continuous adsorption of lead

#### 3.2.1. Single lead

Figs. 3 and 4 show breakthrough curves of lead at pH 3 and 5, and different flow rates, respectively. The comparison of two

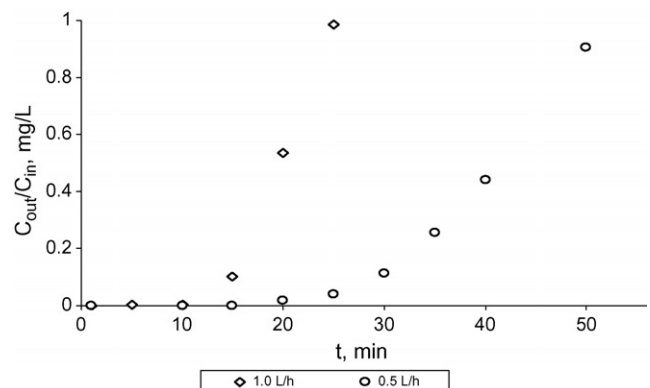


Fig. 3. Continuous adsorption of lead at pH 3.

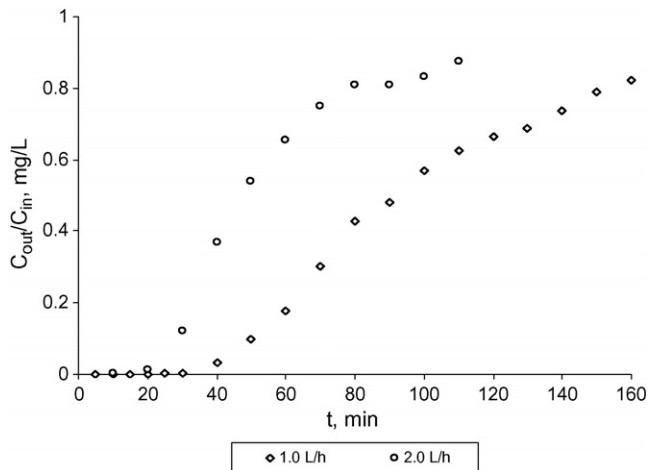


Fig. 4. Continuous adsorption of lead at pH 5.

figures shows that at higher flow rate the breakthrough point is reached earlier, and adsorption of lead is more favourable at higher pH of the solution. The effect of higher pH is associated with lesser competition between protons and lead ions for adsorption sites on the carbon surface. At pH 3, an excess of hydrogen ions can successfully compete with metal ions for binding sites resulting in lower metal uptake [19–23].

The results on continuous adsorption of lead on commercial coconut shell activated carbon [24] showed that such parameters as fixed bed thickness, flow rate and initial concentration of lead played significant role in the determination of the breakthrough point. Also pretreatment of the adsorbent resulted in the higher lead removal. However, this study [24] was of much greater scale compared to our study. Although [24], did not specifically examine the effect of pH in continuous adsorption of lead, it was reported that during preliminary runs an increase of the initial pH with following stabilization was observed.

### 3.2.2. Lead with complexing agents

Figs. 5 and 6 show breakthrough adsorption curves of all tested systems: single lead, lead with malonic acid, and lead with boric acid, at pH 5 and 3, respectively. The breakthrough curves for single lead and lead with boric acid at pH 5 are very similar. This indicates that boric acid did not affect the adsorption of lead. However, the effluent concentration of lead in system

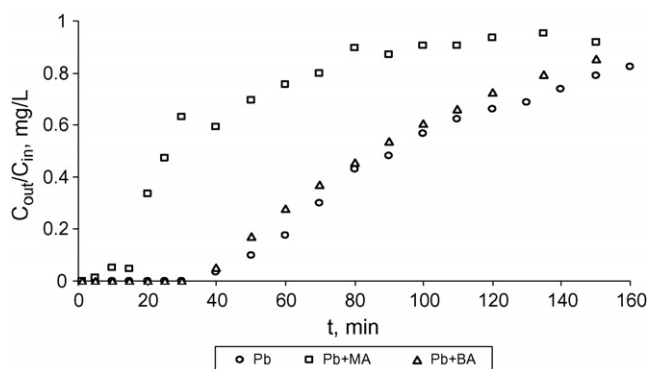


Fig. 5. Comparison lead pH 5, 1.0 L/h.

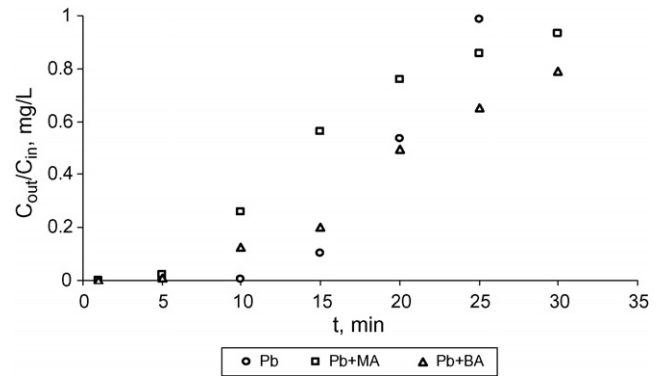


Fig. 6. Flow-through adsorption lead pH 3, 1.0 L/h.

with malonic was noticeably higher and breakthrough point was reached earlier indicating decrease in adsorption of lead relatively to single lead system. Such effect of malonic acid can be associated with carbon pore blockage that lead to the substantial decrease of activated carbon surface area [25,26]. In general, the presence of organic compounds results in slower adsorption due to occupancy of the pores in the region of carbon's macropores [27].

At pH 3, the breakthrough curves for all systems are similar, no effect of complexing agents on adsorption of lead was observed. After about 30 min the effluent concentration of lead exceeded the initial value, which was probably due to commensuration of lead desorption from carbon surface back into solution.

In terms of pH stabilization and breakthrough time, it was observed that at pH 3 the breakthrough of lead coincided with earlier pH stabilization in all three systems studied. Similarly [17], observed that lead breakthrough and drop of effluent's pH occurred simultaneously. However, at pH 5 the breakthrough in the same systems was observed when pH already stabilized.

### 3.3. Modelling on continuous adsorption

In continuous flow-through fixed bed systems the concentration profiles in the liquid and adsorbent phases vary in both space and time. Quantitative modelling approaches are used for optimization and design purposes of such systems, which are usually described in terms of breakthrough adsorption curves [28]. A simple model [14] to predict the breakthrough time in metal removal describes adsorption in a flow-through cell as a change of the metal's concentration over time ( $t$ ):

$$-\left(\frac{dY}{dt}\right) = kXY \quad (1)$$

where  $Y$  is the fraction of metal ions being adsorbed,  $X = (1 - Y)$  is the fraction of metal ions remaining in the bed and  $k$  is the proportionality constant. For metal ion breakthrough at  $X = 0.5$  and the adsorption time  $t$  denoted as  $\tau$  the following formula is used:

$$t = \tau + \frac{1}{k} \ln \left[ \frac{X}{1 - X} \right] \quad (2)$$

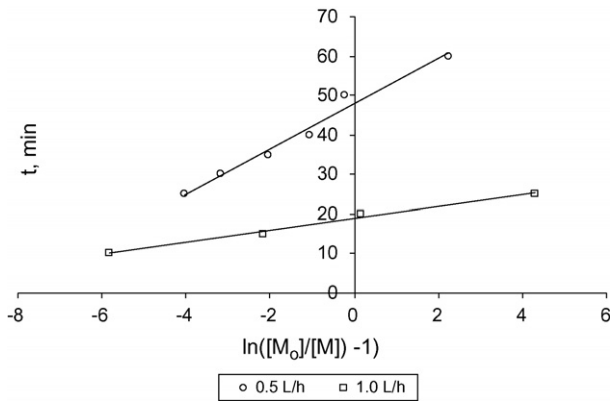
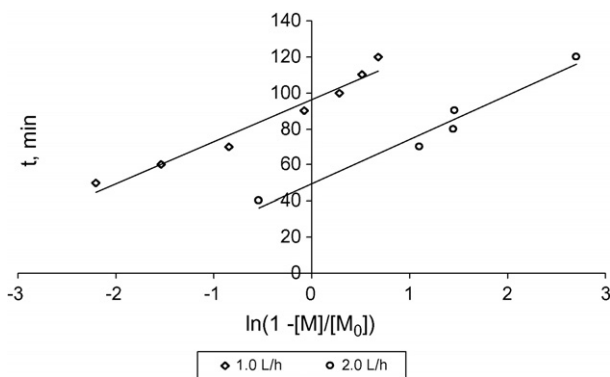
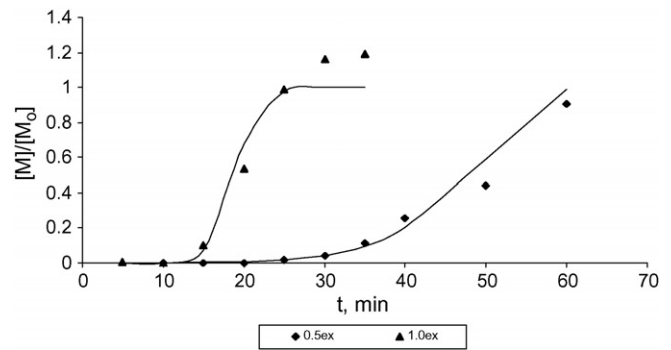
Fig. 7. Adsorption of lead ( $[M_0] = 50 \text{ mg/L}$ ), pH 3.Fig. 8. Adsorption of lead ( $[M_0] = 50 \text{ mg/L}$ ), pH 5.

Fig. 9. Modelling on adsorption of lead, flow rates 0.5 and 1.0 L/h, pH 3.

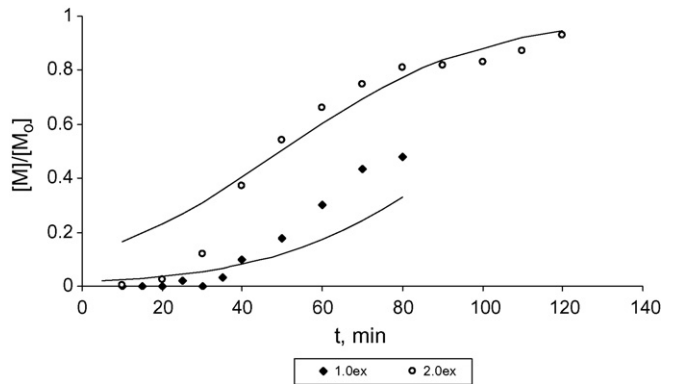


Fig. 10. Modelling on adsorption of lead, flow rates 1.0 and 2.0 L/h, pH 5.

For the fraction of metal ions that passes through the adsorption bed,  $X$  equals  $[M]/[M_0]$  with  $[M]$  being the metal concentration in aqueous solution exiting the bed at time  $t$  and  $[M_0]$  being the inlet concentration. According to Eq. (2), a plot of adsorption time  $t$  versus  $\ln([M_0]/[M]) - 1$  yields a straight line with the intercept and slope being  $\tau$  and  $1/\kappa$ , respectively. Once the values of  $\tau$  and  $\kappa$  are determined, the calculation of the capacity of the adsorbent material can be estimated:

$$Q_M = \frac{1}{2} [M_0] F 2\tau = [M_0] F \tau \quad (3)$$

This equation permits to determine adsorption capacity of a given bed  $Q_M$  (mg/g) as a function of initial metal concentration  $[M_0]$  (mg/L), liquid flow rate  $F$  (L/min), and 50% breakthrough time  $\tau$  (min).

Figs. 7 and 8 present linear graphs for continuous adsorption of lead at pH 3 and 5. Figs. 9 and 10 show experimental

and modelled breakthrough curves for adsorption of lead at pH 3 and 5, respectively. Overall, the modelled data are in good agreement with the experimental data for all flow rates tested in the adsorption experiments.

Table 1 shows results on model's parameters values and estimated maximal capacity of the carbon bed to remove metal ions for tested flow rates.

The estimated model parameters values shown in Table 1 showed that  $\tau$  increases with decreasing of the flow rate, and value of  $\kappa$  initially increases with increasing flow rate and starts decreasing when flow rate is greater than 13.33 mL/min. Such observation is in line with the commentary of [14], who described the above trend and pointed that  $\kappa$  value decreases after flow rate is higher than 13.0 mL/min. Authors suggested that adsorption process is likely controlled by diffusion within aqueous stagnant film at flow rates lower than 13.0 mL/min, and by adsorption reaction when flow rate is higher of the latter value.

Table 1  
Parameters used in experiments on adsorption of lead on palm shell activated carbon in a flow-through cell

Flow rate (L/h)	Flow rate (mL/min)	$\tau$ (min)	$k$ (L/min)	$R^2$	$Q$ (Me) (mg/g)
Lead pH 3					
0.5	8.33	47.9	0.18	0.98	22.6
1.0	16.67	18.9	0.66	0.99	17.9
Lead pH 5					
1.0	16.67	96.5	0.04	0.96	90.2
2.0	33.33	49.6	0.04	0.96	92.6

#### 4. Conclusions

Continuous adsorption of lead ions showed that the breakthrough period was shorter at pH 3 than at pH 5. Increase of the flow rate from 0.5 up to 2.0 L/h accelerated the palm shell activated carbon saturation time at both pHs. Presence of malonic and boric acids did not improve adsorption of lead on palm shell activated carbon. Moreover, presence of malonic acids resulted in a shorter breakthrough period at pH 5, compared to single lead system. Modelling results on continuous adsorption allowed estimation of carbon bed capacity to remove metal ions. On the whole, the experimental results demonstrated that untreated granular palm shell activated carbon can be successfully used to remove heavy metal ions from aqueous solution.

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#### References

- [1] D.W. Grosse, Innovative Practices for Treating Waste Streams Containing Heavy Metals: A Waste Minimization Approach, Technomic Pub, USA, 1990.
- [2] Malaysia Environmental Quality Report 2002, Ministry of Science, Technology and the Environment of Malaysia (ISSN 0127-6433), 2002.
- [3] J. Guo, A.C. Lua, Preparation and characterization of adsorbents from oil palm fruit solid wastes, *J. Oil Palm Res.* 12-1 (2000) 64–70.
- [4] J. Guo, A.C. Lua, Adsorption of sulphur dioxide onto activated carbons prepared from oil palm shells impregnated with potassium hydroxide, *J. Chem. Technol. Biotechnol.* 75 (2000) 971–976.
- [5] G. Guo, The effect of local hydrodynamics on mass transfer in disordered porous media, Ph.D. Dissertation, Louisiana State University, USA, 2002.
- [6] J. Guo, A.C. Lua, Textural and chemical properties of adsorbent prepared from palm shell by phosphoric acid activation, *Mater. Chem. Phys.* 80 (2003) 114–119.
- [7] M.Z. Hussein, R.S.H. Tarmizi, Z. Zainal, R. Ibrahim, M. Badri, Preparation and characterization of active carbons from oil palm shells, *Carbon* 34 (11) (1996) 1447–1454.
- [8] W.M.A. Wan Daud, W.S. Wan Ali, M.Z. Sulaiman, Effect of activation temperature on pore development in activated carbon produced from palm shell, *J. Chem. Technol. Biotechnol.* 78 (2002) 1–5.
- [9] W.M.A. Wan Daud, W.S. Wan Ali, Comparison on pore development of activated carbon produced from palm shell and coconut shell, *Bioresour. Technol.* 93 (2004) 63–69.
- [10] N. Abu Bakar, Adsorption studies of phenols in aqueous solution using activated carbon prepared from several part of oil palm tree, M.Sc. Thesis, University Putra Malaysia, 1999.
- [11] F. Othman, M.R. Salim, R. Ahmad, MOPAS for metal removal, in: Proceedings of the 20th WEDC Conference, Colombo, Sri Lanka, 1994, pp. 292–294.
- [12] M.R. Salim, F. Othman, Md. Imtiaj Ali, J. Patterson, T. Hardy, Application of locally available materials for the treatment of organic polluted water, *J. Water Sci. Technol.* 46 (2002) 339–346.
- [13] G. Issabayeva, M.K. Aroua, N.M.N. Sulaiman, Removal of lead from aqueous solutions on palm shell activated carbon, *Bioresour. Technol.* 97 (18) (2006) 2350–2355.
- [14] Y.-H. Wang, S.-H. Lin, R.-S. Juang, Removal of heavy metals ions from aqueous solutions using various low-cost adsorbents, *J. Hazard. Mater. B* 102 (2003) 291–302.
- [15] G. Issabayeva, M.K. Aroua, M.N. Sulaiman, Electrodeposition of copper and lead on palm shell activated carbon in a flow-through electrolytic cell, *Desalination* 194 (1–3) (2006) 192–201.
- [16] J.P. Chen, X. Wang, Removing copper, zinc and lead ions by granular activated carbon in pretreated fixed-bed columns, *Sep. Purif. Technol.* 19 (2000) 157–167.
- [17] S.V. Dimitrova, Use of granular slag columns for lead removal, *Water Res.* 36 (2002) 4001–4008.
- [18] K. Yamashita, T. Ikenata, K. Tate, K. Nakahara, Method of removing dissolved heavy metals from aqueous waste liquids, US Patent 4,377,483 (1983).
- [19] C. Ravat, J. Dumonceau, F. Monteil-Rivera, Acid/base and Cu(II) binding properties of natural organic matter extracted from wheat bran: modelling by the surface complexation model, *Water Res.* 34 (4) (2000) 1327–1339.
- [20] J.P. Chen, L. Hong, S. Wu, L. Wang, Elucidation of interactions between metal ions and Ca-alginate based ion exchange resin by spectroscopic analysis and modelling simulation, *Langmuir* 18 (24) (2002) 9413–9421.
- [21] J.P. Chen, M.S. Lin, Equilibrium and kinetics metal ion adsorption onto a commercial H-type granular activated carbon: experimental and modelling studies, *Water Res.* 2 (35) (2001) 2385–2394.
- [22] M.O. Corapcioglu, C.P. Huang, The adsorption of heavy metals onto hydrous activated carbon, *Water Res.* 21 (1987) 1031–1044.
- [23] K.H. Chu, M.A. Hashim, Adsorption and desorption characteristics of zinc on ash particles derived from oil palm waste, *J. Chem. Technol. Biotechnol.* 77 (2002) 685–693.
- [24] J. Goel, K. Kadirvelu, C. Rajagopal, V.K. Garh, Removal of lead (II) by adsorption using treated granular activated carbon: batch and column studies, *J. Hazard. Mater. B* 125 (2005) 211–220.
- [25] J.P. Chen, S. Wu, K.-H. Chong, Surface modification of a granular activated carbon by citric acid for enhancement of copper adsorption, *Carbon* 41 (2003) 1979–1986.
- [26] M.A. Ferrero-Garsia, J. Rivera-Utrilla, I. Bautista-Toledo, C. Moreno-Castilla, Adsorption of humic substances on activated carbon from aqueous solutions and their effect on the removal of Cr(III) ions, *Langmuir* 14 (1998) 1880–1886.
- [27] F.W. Petersen, J.S.J. van Deventer, The influence of pH, dissolved oxygen and organics on the adsorption of metal cyanides on activated carbon, *Chem. Eng. Sci.* 46 (1991) 3053–3065.
- [28] K.H. Chu, Improved fixed bed models for metal biosorption, *J. Chem. Eng. Jpn.* 97 (2004) 233–239.