

## Removal of Toluene from Aqueous Solutions Using Oil Palm Shell Based Activated Carbon: Equilibrium and Kinetics Study

Kwong, W. Z.<sup>1</sup>, Tan, I. A. W.<sup>2</sup>, Rosli, N. A.<sup>1</sup> and Lim, L. L. P.<sup>1\*</sup>

<sup>1</sup>Department of Civil Engineering, Faculty of Engineering, Universiti Malaysia Sarawak, 94300 Kota Samarahan, Sarawak, Malaysia

<sup>2</sup>Department of Chemical Engineering and Energy Sustainability, Faculty of Engineering, Universiti Malaysia Sarawak, 94300 Kota Samarahan, Sarawak, Malaysia

### ABSTRACT

This study is an attempt to investigate the adsorption of petroleum hydrocarbon (toluene) from aqueous solutions using granular activated carbon (GAC) synthesized from oil palm shell (OPS) (referred as OPS-based GAC). This study involved a series of batch experiments to determine the adsorption equilibrium and kinetics. The batch experiments were conducted by shaking 200 mL toluene solution containing 0.4 g GAC (initial concentrations of 5, 15, 25 and 30 mg/L) at 180 rpm at 30°C. The OPS-based GAC achieved more than 80% toluene removal in all the experiments. The adsorption capacity of the OPS-based GAC estimated using Freundlich isotherm was 6.039 mg/g (L/mg)<sup>1/n</sup>. The adsorption kinetic study showed that the adsorption of toluene was of chemisorption as the experimental data fitted better to the pseudo-second-order kinetic model than the pseudo-first-order kinetic model.

*Keywords:* Adsorption, equilibrium study, granular activated carbon, kinetics study

### INTRODUCTION

Groundwater pollution caused by the petroleum industry usually occurs due to the leakage from gasoline storage tanks and

pipelines, which is considered as point source pollution (Haest *et al.*, 2010). Groundwater contaminated by petroleum hydrocarbons becomes undrinkable due to the unpleasant taste and odour produced by petroleum hydrocarbons such as methyl tert butyl ether (MTBE) at a concentration as low as 20 µg/L (Khan *et al.*, 2011; Lim & Lynch, 2011). Some petroleum hydrocarbons such as benzene are toxic and carcinogenic (Yu *et al.*, 2011; Caprino & Togna, 1998). In addition, the monoaromatic hydrocarbons

#### Article history:

Received: 21 February 2013

Accepted: 24 April 2013

#### Email addresses:

Kwong, W. Z. ([go\\_go\\_kwong@hotmail.com](mailto:go_go_kwong@hotmail.com)),

Tan, I. A. W. ([awitan@feng.unimas.my](mailto:awitan@feng.unimas.my)),

Rosli, N. A. ([mazalina@feng.unimas.my](mailto:mazalina@feng.unimas.my)),

Lim, L. L. P. ([llpleonard@feng.unimas.my](mailto:llpleonard@feng.unimas.my))

\*Corresponding Author

benzene, toluene, ethylbenzene and xylene (BTEX) can pose a serious threat to human health if consumed (Hameed *et al.*, 2004). Meanwhile, long-term exposure of toluene to human can lead to irreversible and progressive harm to the central nervous system, kidney and liver (ATSDR, 2000). Therefore, there is a need to remediate the groundwater sources contaminated by petroleum hydrocarbons, especially where groundwater is the main drinking water source (Reddy, 2008).

Various groundwater remediation technologies have been developed to remove petroleum hydrocarbons from groundwater such as pump-and-treat, air sparging, and soil vapour extraction. However, the efficiency of these technologies, which typically involve injection or withdrawal operation, is limited by several factors such as soil heterogeneity, strata and hydraulic conductivity (Reddy, 2008). Furthermore, some of these technologies need to be combined with other technologies such as air sparging and soil vapour extraction in order to achieve the desired clean up level, which leads to the increase of the remediation cost. A groundwater remediation approach, which is not affected by soil heterogeneity, is the permeable reactive barrier (PRB). PRB is a trench with subsurface emplacements of reactive materials designed to inhibit migration of a contaminant plume (Craig *et al.*, 2006). Adsorption process is commonly used in PRB to remove contaminants in groundwater (Yu *et al.*, 2011).

Adsorption is a physical process involving the attraction of adsorbate molecules to the surface of the adsorbent. This process has been proven to be effective in removing petroleum hydrocarbons from water (Oehm *et al.*, 2007). Granular activated carbon (GAC) synthesized from coconut had been reported to achieve up to 67.05 mg/g MTBE removal, with an initial concentration of 300 mg/L (Khan *et al.*, 2011) and the adsorption capacity of toluene using adsorbent synthesized from discarded rubber tyre showed 7.7535 mg/g at 30°C using the Freundlich isotherm (Hameed *et al.*, 2004).

Adsorption, a passive process, is suitable for removing contaminants from groundwater due to the slow groundwater flow (33 m/year) (Mackay *et al.*, 1986), which implies the slow migration of contaminants and long residence time for contaminated groundwater to flow through PRB. Unlike bioremediation and chemical remediation, the adsorption process does not produce harmful by-products as it mainly immobilizes contaminant molecules from being transported by groundwater. There is a potential for GAC to be synthesized from oil palm shell (OPS) (referred as OPS-based GAC) for groundwater remediation due to the use of cheaper raw material and the low operational cost using an adsorption process. In Malaysia, the production of OPS-based GAC can also reduce significant amount of oil palm wastes to be land filled (Chin, 2011; Pilo, 2011).

Therefore, OPS-based GAC was used to remove toluene from aqueous solutions in a batch experiment in this study. In particular, this study investigated the adsorption performance of toluene onto the OPS-based GAC, encompassing the adsorption equilibrium and kinetic studies.

## MATERIALS AND METHOD

### *Adsorbent*

Commercially available OPS-based GAC was obtained from Bravo Green Sdn. Bhd. located in Kota Samarahan, Sarawak. The size of the OPS-based GAC typically ranges from 1.68 to

3.36 mm (US mesh size of  $6 \times 12$ ). Meanwhile, the BET surface area and pore volume of the OPS-based GAC ranged from 1050 to 1200 m<sup>2</sup>/g and 0.48 cm<sup>3</sup>/g, respectively.

### *Adsorbate*

The adsorbate used in this study was toluene (purity:  $\geq 99.8\%$ , Fisher Chemical, 108-88-3). The initial concentrations of toluene used in this study were 5, 15, 25 and 30 mg/L. The highest toluene concentration was chosen based on the concentration used by Lim and Lynch (2011). The synthesized groundwater was prepared by spiking a predetermined amount of toluene into distilled water.

### *Batch Experiment*

Batch experiment was conducted to study the effects of initial concentration on the adsorption capacity of the OPS-based GAC. The experiments were conducted by adding 0.4 g OPS-based GAC into 200 mL toluene solution of different initial concentrations. The initial concentrations of toluene used were 5, 15, 25 and 30 mg/L. The conical flasks were agitated in an incubated benchtop orbital shaker (Forma) at 180 rpm at  $30 \pm 1^\circ\text{C}$  for 24 hours to obtain a well-mixed solution and to increase the contact frequency between the adsorbent and the adsorbate.

### *Sample Analysis*

The solutions were sampled and analyzed in a 4 mL cuvette using a UV-visible spectrophotometer (Shimadzu UV Mini 1240) at room temperature of  $22 \pm 2^\circ\text{C}$ . Methanol was spiked into the solution to emulsify the petroleum hydrocarbons in water prior to analysis. The methanol is an organic solvent which disperses the petroleum hydrocarbons into little droplets so that it is easily detected using the spectrophotometer.

The amount of adsorption at equilibrium,  $q_e$  (mg/g), was calculated using Equation (1):

$$q_e = \frac{(C_o - C_e)V}{W} \quad (1)$$

where  $C_o$  and  $C_e$  (mg/L) are the liquid-phase concentrations of toluene at initial and equilibrium, respectively.  $V$  is the volume of the solution (L) and  $W$  is the mass of adsorbent used (g).

## **RESULTS AND DISCUSSION**

### *Effect of the Initial Concentration of Toluene on Adsorption Equilibrium*

Figure 1 shows the effects of toluene initial concentrations on the adsorption of toluene by the OPS-based GAC at  $30^\circ\text{C}$ . The OPS-based GAC achieved more than 80% toluene removal in all the batch experiments. The adsorption curves obtained in all the experiments exhibited an increasing trend leading to plateau, indicating that the toluene molecules were adsorbed into the OPS-based GAC until the adsorption equilibrium was achieved. The curve reached a plateau at about 180 minutes after the experiment started for all the initial concentrations. At

the equilibrium point, the adsorption of toluene achieved dynamic equilibrium with the OPS-based GAC. The equilibrium concentration ( $C_e$ ) increased from 0.186 to 3.871 mg/L with the increase of the initial concentration from 5 to 30 mg/L. The amount of toluene adsorbed at the equilibrium time reflected the maximum adsorption capacity of the OPS-based GAC under the specified operating conditions. In this study, the adsorption capacity at equilibrium ( $q_e$ ) increased from 1.193 to 12.171 mg/g with the increase of the initial concentration from 5 to 30 mg/L. This was because the mass transfer driving force would become larger when the initial concentration increased, resulting in a higher adsorption of toluene.

The contact time required by the adsorption process to achieve equilibrium was circa 180 mins for all the initial concentrations (see Fig.1). This trend was due to the fact that pores were abundantly available for adsorption in the initial stage, and after some time, these pores became fully occupied. In addition, the faster adsorption rate at the beginning of the adsorption process was due to the adsorption of toluene by the surface of the OPS-based GAC. After some time, the surface reached saturation and the toluene was adsorbed into the interior surface of the OPS-based GAC by pore diffusion (Tan *et al.*, 2008). This phenomenon could be explained by the adsorption process in which the toluene molecules encountered the boundary layer first, diffused from the boundary layer onto the surface of activated carbon and finally diffused into the porous structure of the activated carbon (Faust & Aly, 1983).

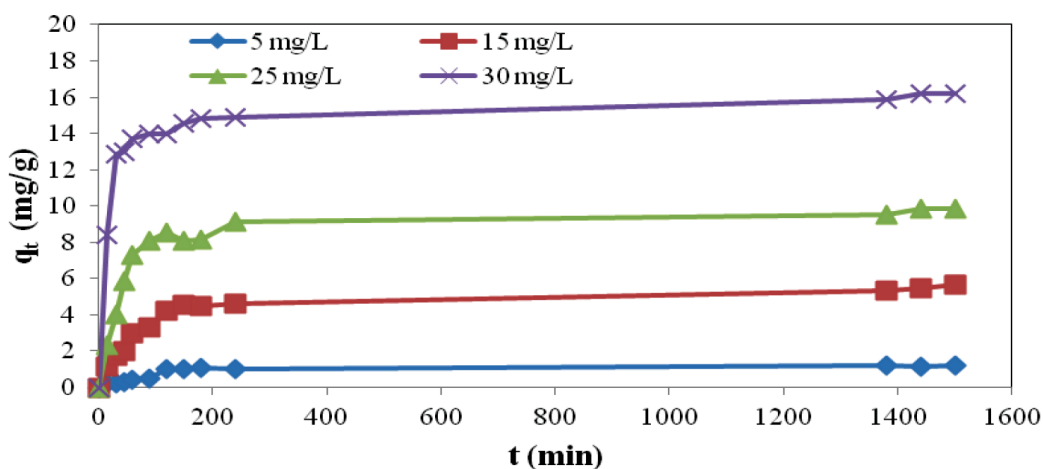


Fig.1: Adsorption of toluene using OPS-based GAC at 30°C at various initial concentrations of 5, 15, 25 and 30 mg/L

#### Adsorption Kinetics Study

The adsorption kinetic study was used to determine the adsorption rate of toluene into activated carbon and the equilibrium time. The two rate equations, namely, pseudo first-order [Equation (2)] (Lagergren, 1898) and pseudo-second-order [Equation (3)] were used to evaluate the adsorption kinetics and the results were compared with the adsorption data (Ho & McKay, 1999).

$$\log (q_e - q_t) = \log q_e - (k_1/2.303)t \quad (2)$$

$$t/q_t = 1/(k_2 q_e^2) + (1/q_e)t \quad (3)$$

where  $q_e$  (mg/g) and  $q_t$  (mg/g) are the amounts of toluene adsorbed into the activated carbon per unit mass of activated carbon when the adsorption equilibrium is achieved and at time,  $t$  (min), respectively. Meanwhile,  $k_1$  ( $\text{min}^{-1}$ ) and  $k_2$  (g/mg/min) are the rate constants of the pseudo-first-order and pseudo-second-order adsorption, respectively.

Table 1 summarizes the adsorption coefficients obtained using the pseudo-first-order and pseudo-second-order rate equations. The  $R^2$  values, obtained from the pseudo-first-order and pseudo-second-order kinetics plots, were used to determine the adsorption behaviour (physisorption or chemisorption) of toluene molecules into the OPS-based GAC. The  $R^2$  values were higher for the pseudo-second-order model than that of the pseudo-first-order model for all concentrations of toluene, indicating that the OPS-based GAC adsorption of toluene was of the pseudo-second-order adsorption. This also implied that the adsorption of toluene molecules into the OPS-based GAC was of chemisorption rather than physisorption. Chemical adsorption involves the adherent of toluene to the surface of adsorbent with covalent bonding through sharing or exchanging of electron between adsorbent and adsorbates (Ho & McKay, 1999).

TABLE 1

Pseudo-first-order model, pseudo-second-order model, and correlation coefficients for adsorption of toluene on OPS-based GAC at 30°C

Initial Conc. (mg/L)	$q_e$ exp. (mg/g)	% Removal	Pseudo-first order parameter			Pseudo-second order parameter		
			$q_e$ calc. (mg/g)	$K_1$ ( $\text{min}^{-1}$ )	$R^2$	$q_e$ calc. (mg/g)	$k_2$ (g/mg/min)	$R^2$
5	1.193	92.760	0.603	0.002	0.739	1.239	1.05E-02	0.993
15	5.636	97.400	2.812	0.002	0.773	5.714	3.36E-03	0.998
25	9.850	83.830	3.611	0.001	0.819	10.000	3.51E-03	0.999
30	16.171	90.920	3.579	0.002	0.586	16.393	4.61E-03	1.000

### Adsorption Isotherms

It is important to determine the most appropriate correlation for the equilibrium curve using adsorption isotherms in order to optimize the design of adsorption system. The adsorption isotherms are used to indicate how the adsorption molecules are distributed between liquid phase and solid phase when the adsorption process reaches an equilibrium state. In this study, two well-known adsorption isotherms, namely, the Langmuir (Langmuir, 1916) and Freundlich (Freundlich, 1906) adsorption models were used and compared by judging the correlation coefficient,  $R^2$ , as a criterion (Hussain *et al.*, 2006; Nuithitikul *et al.*, 2010). Equations (4) and (5) represent the linear forms of Langmuir and Freundlich models, respectively:

$$C_e/q_e = 1/(Q_0 K_L) + (1/Q_0) C_e \quad (4)$$

$Q_0$  (mg/g) and  $K_L$  (L/mg) are Langmuir constants in relevant to maximum monolayer adsorption capacity onto a surface with no transmigration of adsorbates onto the surface (Webi & Chakravort, 1974).

$$\text{Log } q_e = \text{log } K_F + (1/n) \text{log } C_e \tag{5}$$

$K_F$  (mg/g(L/mg)<sup>1/n</sup>) and  $n$  are Freundlich constants representing the adsorption capacity on a heterogeneous surfaces and how favourable the adsorption process is, assuming that the stronger binding sites are occupied first and that the binding strength decreases with the increasing degree of site occupation, respectively (Freundlich, 1906; Nuithitikul *et al.*, 2010). The slope of  $1/n$  is used to measure the adsorption intensity or surface heterogeneity ranging between 0 and 1, with the surface becoming more heterogeneous as the value becomes closer to zero (Haghseresht & Lu, 1998). Another essential characteristic of the Langmuir isotherm is a dimensionless equilibrium parameter ( $R_L$ ) (Nuithitikul *et al.*, 2010; Webi & Chakravort, 1974):

$$R_L = 1 / (1 + K_L C_0) \tag{6}$$

where  $K_L$  is the Langmuir constant and  $C_0$  is the initial contaminant concentration (mg/L). The value of  $R_L$  indicates whether the isotherm is unfavourable ( $R_L > 1$ ), linear ( $R_L = 1$ ), favourable ( $0 < R_L < 1$ ) or irreversible ( $R_L = 0$ ) (Nuithitikul *et al.*, 2010).

For the Langmuir isotherm, the correlation coefficient was found to be 0.704, while the value of  $R_L$  was 0.053 at the temperature of 30°C. This indicated that the Langmuir isotherm was favourable for the adsorption of toluene on GAC under the conditions used in this study. Meanwhile, Langmuir constants  $K_L$  and  $Q_0$  were calculated using Equation (4) and their values are shown in Table 2. The maximum monolayer adsorption capacity obtained from the Langmuir isotherm was 16.129 mg/g. The adsorption capacity of the OPS-based GAC was higher than the adsorbent synthesized from montmorillonite (6.71 mg/g) (Nourmoradi *et al.*, 2012).

TABLE 2  
Langmuir and Freundlich isotherm model constants and correlation coefficient for adsorption of toluene onto GAC at 30°C

Langmuir Isotherm				Freundlich Isotherm		
$Q_0$ (mg/g)	$K_L$ (L/mg)	$R^2$	$R_L$	$1/n$	$K_F$ (mg/g(L/mg) <sup>1/n</sup> )	$R^2$
16.129	0.756	0.704	0.053	0.618	6.039	0.743

For the Freundlich isotherm, the correlation coefficient was 0.743. The slope of  $1/n$  obtained was 0.618, indicating that the adsorption of the toluene onto the GAC surface was homogeneous since it was closer to one. The correlation coefficient,  $R^2$ , for the Freundlich isotherm model was higher than that of the Langmuir model, which showed that the Freundlich model was more favourable for the adsorption of toluene onto OPS-based GAC under the specified condition. The adsorption capacity of the OPS-based GAC obtained using the Freundlich model was 6.039 mg/g(L/mg)<sup>1/n</sup>. This result was comparable with that of discarded

rubber tyre-based adsorbent, with the  $K_F$  value of  $7.7535 \text{ mg/g(L/mg)}^{1/n}$  (Hameed *et al.*, 2004). The adsorption capacity of the GAC for toluene was compared with other adsorbents reported in the literature as shown in Table 3.

TABLE 3  
A comparison of the adsorption capacity of toluene on various adsorbents

Adsorbents	Adsorption capacity	References
OPS-based GAC <sup>a</sup>	16.129 mg/g	This work
OPS-based GAC <sup>b</sup>	$6.039 \text{ mg/g(L/mg)}^{1/n}$	This work
Montmorillonite modified with nonionic surfactant <sup>a</sup>	6.71 mg/g	Nourmoradi <i>et al.</i> (2012)
Discarded rubber tyre-based adsorbent <sup>b</sup>	$7.7535 \text{ mg/g(L/mg)}^{1/n}$	Hameed <i>et al.</i> (2004)
Bentonite <sup>c</sup>	66 mg/g	Amari <i>et al.</i> (2010)
Manganese-embedded PAN-based activated carbon nanofibers <sup>c</sup>	400 mg/g	Oh <i>et al.</i> (2008)

<sup>a</sup>Langmuir isotherm model

<sup>b</sup>Freundlich isotherm model

<sup>c</sup>Experimental data

## CONCLUSION

This study showed that OPS-based GAC was successfully used in removing toluene from aqueous solutions. In more specific, all the adsorption achieved more than 80% toluene removal. The equilibrium data were best described by Freundlich isotherm with adsorption capacity of  $6.039 \text{ mg/g(L/mg)}^{1/n}$ . The adsorption capacity obtained from the Langmuir isotherm was 16.129 mg/g, while the adsorption kinetics was found to follow closely the pseudo-second-order kinetic model. This study also highlighted the potential of the activated carbon for groundwater remediation which would be used for the removal of petroleum hydrocarbons in its intended application in future study.

## ACKNOWLEDGEMENTS

We would like to thank Universiti Malaysia Sarawak and Osaka Gas for funding this research through the Small Grant Scheme (grant no. 02(S84)/820/2011(18)) and Osaka Gas Foundation in Cultural Exchange (OGFICE) Research Grant Scheme, respectively, as well as Bravo Green Sdn. Bhd. for providing the OPS-based GAC.

## REFERENCES

- Amari, A., Chlendi, M., Gannouni, A., & Bellagi A. (2010). Optimised activation of bentonite for toluene adsorption. *Applied Clay Science*, 47(3-4), 457-461.
- ATSDR. (2000). *Public Health Statement: Toluene*. Atlanta: Agency for Toxic Substances and Disease Registry Division of Toxicology and Environmental Medicine.

- Caprino, L., & Togna, G.I. (1998). Potential health effects of gasoline and its constituents: A review of current literature (1990-1997) on toxicological data. *Environmental Health Perspectives*, 106(3), 115-125.
- Chin, J. (2011). *Sarawak's share in Malaysia oil palm*. The Borneo Post, Kuching.
- Craig, J. R., Rabideau, A. J., & Suribhatla, R. (2006). Analytical expressions for the hydraulic design of continuous permeable reactive barriers. *Advances in Water Resources*, 29(1), 99-111.
- Faust, D. S., & Aly, M. O. (1983). *Chemistry of Wastewater Treatment*. Butterworths: Boston.
- Freundlich, H. M. F. (1906). Over the adsorption in solution. *Journal of Physical Chemistry*, 385-470.
- Haest, P. J., Lookman, R., Keer, I. V., Patyn, J., Bronders, J., Joris, M., Bellon, J., & De Smedt, F. (2010). Containment of groundwater pollution (methyl tertiary butyl ether and benzene) to protect a drinking-water production site in Belgium. *Hydrogeology Journal*, 18(8), 1917-1925.
- Haghseresht, F., & Lu, G.Q. (1998). Adsorption characteristics of phenolic compounds onto coal-reject-derived adsorbents. *Energy Fuels*, 12(6), 1100-1107.
- Hameed, B. H., Mohamed, A. R., & Chong, H. Y. (2004). Adsorption of toluene using low cost adsorbent. *Jurnal Teknologi*, 40(F), 17-26.
- Ho, Y. S., & McKay, G. (1999). Pseudo-second order model for sorption processes. *Process of Biochemistry*, 34(5), 451-465.
- Khan, M. A., Lee, S.-H., Kang, S., Paeng, K.-J., Lee, G., Oh, S.-E., & Jeon, B.-H. (2011). Adsorption studies for the removal of methyl tert-butyl ether on various commercially available GACs from an aqueous medium. *Separation Science and Technology*, 46(7), 1121-1130.
- Lagergren, S. (1898). Zur Theorie der Sogenannten Adsorption Geloster Stoffe. *Veternskapsakad Handlingar*, 24(4), 1-39.
- Langmuir, I. (1916). The constitution and fundamental properties of solids and liquids. Part I: Solids. *Journal of the American Chemical Society*, 38(11), 2221-2295.
- Lim, L. L. P., & Lynch, R. J. (2011). Feasibility study of a photocatalytic reactor for in situ groundwater remediation of organic compounds. *Journal of Hazardous Materials*, 194, 100-108.
- Mackay, D. M., Freyberg, D. L., Roberts, P. V., & Cherry, J. A. (1986). A natural gradient experiment on solute transport in a sand aquifer: Approach and overview of plume movement. *Water Resources Research*, 22(13), 2017-2029.
- Nourmoradi, H., Nikaeen, M., & Khiadani (Hajian), M. (2012). Removal of benzene, toluene, ethylbenzene and xylene (BTEX) from aqueous solutions by montmorillonite modified with nonionic surfactant: Equilibrium, kinetic and thermodynamic study. *Chemical Engineering Journal*, 191, 341-348.
- Nuithitikul, K., Srikhun, S., & Hirunpraditkoon, S. (2010). 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*, 41(5), 591-598.
- Oehm, C., Stefan, C., Werner, P., & Fischer, A. (2007). Adsorption and abiotic degradation of methyl tert-butyl ether (MTBE). In D. Barcelo (Ed.), *The Handbook of Environmental Chemistry* (pp. 191-212). New York: Springer-Verlag Berlin Heidelberg.
- Oh, G.-Y., Ju, Y.-W., Jung, H.-R., & Lee, W.-J. (2008). Preparation of the novel manganese-embedded PAN-based activated carbon nanofibers by electrospinning and their toluene adsorption. *Journal of Analytical and Applied Pyrolysis*, 81(2), 211-217.



- Pilo, W. (2011). *Sarawak Needs More Palm Oil Mills to Stem Loss*. The Borneo Post, Kuching.
- Reddy, K. R. (2008). Physical and chemical groundwater remediation technologies. In C. J. G. Darnault, *Overexploitation and Contamination of Shared Groundwater Resources* (pp. 257-274). Chicago: Springer Science + Business Media BV.
- Tan, I. A. W., Ahmad, A. L., & Hameed, B. H. (2008). Enhancement of basic dye adsorption uptake from aqueous solutions using chemically modified oil palm shell activated carbon. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 318 (1-3), 88-96.
- Webi, T. W., & Chakravort, R. K. (1974). Pore and solid diffusion models for fixed-bed adsorbers. *AIChE Journal*, 20(2), 228-238.
- Yu, F., Ma, J., & Wu, Y. (2011). Adsorption of toluene, ethylbenzene and xylene isomers on multi-walled carbon nanotubes oxidized by different concentration of NaOCl. *Frontiers of Environmental Science and Engineering in China*, 6(3), 320-329.

