AJChE 2009, Vol 9, No. 2, 1 – 7

Treatment of Wastewater Containing Wood Waste Pyroligneous Acid Preservative by Activated Carbon in Rubberwood Manufacturing Process

Rizafizah Othaman[a]
Agus Susilo[b]
Hiroaki Habaki[b]
Ryuichi Egashira[b]
[a]*School of Chemical Sciences and Food Technology, Faculty of Science and Technology, Universiti Kebangsaan Malaysia, 43600 UKM Bangi, Selangor, Malaysia*
[b]*Department of International Development Engineering, Graduate School of Science and Engineering, Tokyo Institute of Technology, 12-1, O-okayama-2-chome, Meguro-ku, Tokyo 152-8550, Japan*
E-mail: regashir@ide.titech.ac.jp

In this paper, the feasibility of using the products from thermal treatment of rubberwood waste, i.e., pyroligneous acid as preservative and activated carbon as adsorbent to treat the wastewater containing the preservative was studied. Firstly, the sawdust was thermally treated under various conditions to produce the pyroligneous acid and the activated carbon. Atmosphere and treatment temperature were a significant factor in determining the yield of the products. Secondly, the equilibrium adsorption runs were carried out with the model wastewater containing single, multi solutes, or the pyroligneous acid and with the activated carbon obtained under steam atmosphere. Phenolic compounds were adsorbed at the highest in single solute solutions, and lower in multi solutes solutions. Finally, the feasibility of this process improvement was discussed.

Keywords: adsorption; environmental problems; phenolic compounds; process improvement; thermal treatment; wastewater treatment

INTRODUCTION

In Southeast Asia, rubber tree is widely grown not only for latex but also for wood. Rubberwood (RW) manufacturing especially sawmilling is one of the potential industries in Malaysia, where the logs are processed into timbers and furniture parts. Figure 1 describes the process flow of the sawmilling. The feed logs are cut into timbers. These timbers are preserved and dried, and then molded into products. In the process, only 20% of the logs become products. Some of the wastes are used for heat generation, the other parts are abandoned. At present, the toxic preservative is used. Large quantity of the wood wastes with the harmful preservative is thrown away while the preservative itself is released as wastewater without any treatment, which causes various environmental problems (Ministry of Science, Technology and the Environment 1999).

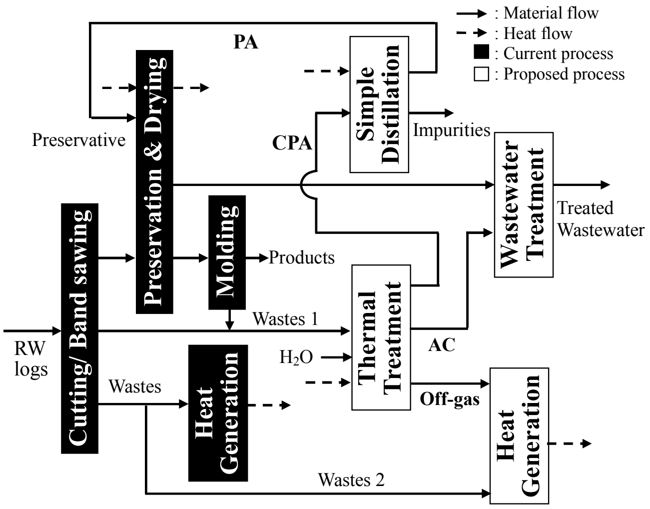

Figure 1. Process Flow of Sawmilling: Current and Proposed Flow

The main aim of this paper is to overcome the environmental problems by utilizing the products of thermal treatment to improve the sawmilling process. Firstly, batch thermal treatments of RW sawdust were conducted under various conditions to obtain, PA and ACs. Secondly, the model wastewater containing single, multi solutes, or the pyroligneous acid was subjected to batch equilibrium adsorptions with the AC prepared by the above treatment. Finally, based on these experimental results, the improvement of the sawmilling process using the thermal treatment products was discussed.

EXPERIMENTAL

Table 1 describes the principal conditions for the thermal treatment. Malaysian rubberwood sawdust was thermally treated under steam (H_2O) or nitrogen (N_2) atmosphere to obtain AC and crude PA (CPA) which was distilled to be PA. The fractional yields of these products were evaluated. The experiment was conducted according to Othaman et al. (2008). Table 2 shows the principal conditions for batch equilibrium adsorption. The feed solutions were single phenolic compound, or mixture of the preservative components according to the composition of PA, or diluted PA solutions. The solutions were analyzed using gas chromatograph.

Table 1.Principal Conditions for Thermal Treatment of Rubberwood

Feed	RW sawdust
Mass of feed, S_0 [g]	Approx. 30
Atmosphere	N_2, H_2O
Flow rate of atmospheric gas [$m^3 \cdot h^{-1}$]	0.03*
Temperature, T_T [K]	703–1094
Holding time, t_T [h]	0.5, 1

* Only N_2 of 0.03 $m^3 \cdot h^{-1}$ was supplied, before reaching 473 K. The atmospheric gas was supplied, after reaching 473 K. In the case of H_2O atmosphere, N_2 of 0.018 $m^3 \cdot h^{-1}$ was supplied as a tracer as well at over 473 K.

Table 2. Adsorption Experiment Conditions

Feed solution		Single of phenol, guaiacol or cresol solution, mixture of phenol, guaiacol, cresols, acetic acid, methanol and acetone solution, or diluted PA solution.
Volume of solution	[m^3]	25×10^{-6} or 10×10^{-6}
Mass ratio of AC to feed solution	[-]	0.004
Size of AC	[mesh]	36-100
Contacting time	[h]	120
Temperature	[K]	303

RESULTS AND DISCUSSION

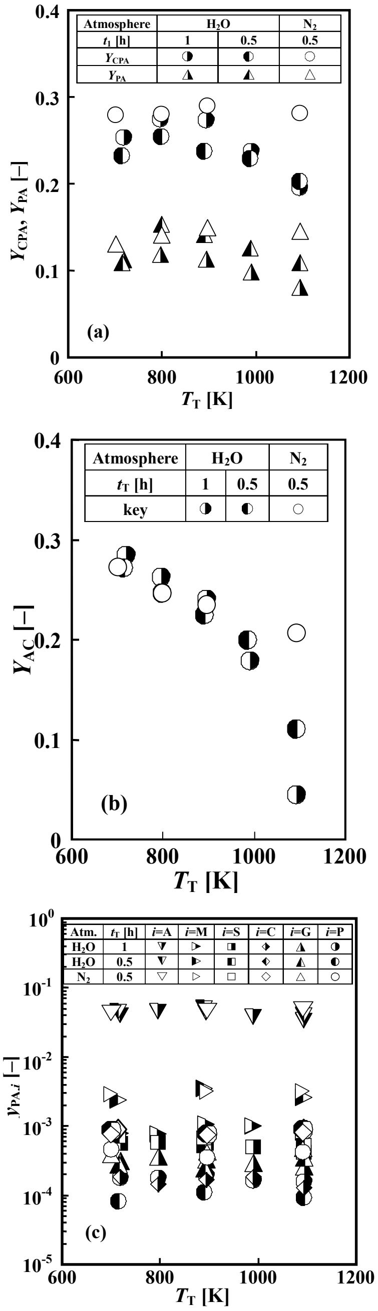

Figure 2. Yields of Products from Thermal Treatment: (a) Crude Pyroligneous Acid and Pyroligneous Acid; (b) Activated Carbon; (c) Preservative Components in PA (A: Acetic acid; M: Methanol; S: Syringol; C: Cresols; G: Guaiacol; P: Phenol)

Figure 2 shows the fractional yields of CPA, Y_{CPA}, PA, Y_{PA}, AC, Y_{AC}, and preservative components in PA, y_{PA}. y_{PA} were calculated from the mass fraction of each component in PA. The yield of CPA changed with temperature slightly and had a maximum over temperature (at 873 K). The same findings were reported by Faghemi *et al.* (2001), that the yield of the liquid products reached a maximum and decreased at temperatures above 873 K due to the secondary reaction of the tar cracking which leads to more production of gases. The yield of CPA was higher in the case of N_2. The yield of AC decreased with treatment temperature (T_T) drastically. Treatment temperature needs to be selected to produce the satisfied amount of AC. In PA, the mass fraction of the acetic acid was the highest, followed by methanol, acetone and phenolic compounds. Those are the studied preservative components in PA. Despite the difference in atmospheres, holding time, and thermal treatment temperature, the yield of each preservative component was constant.

Figure 3 shows the adsorption isotherm of phenol in single solute. Figure 3(a) is the adsorption amount (q) against the mass fraction at equilibrium (x_e) of phenol by AC produced from different thermal treatment atmosphere. The thermal treatments under steam atmosphere gave higher adsorption capacity than that under N_2 atmosphere. This is because AC produced under steam atmosphere exhibited higher surface from the AC produced under N_2 atmosphere which was attributed to the finer pore developed by the reaction of carbon with steam. The surface area from AC produced under steam atmosphere at t_T=1.0 h, T_T=1094 K was compatible with those from manufactured AC as stated by Yoshida (2005) that the BET surface area for activated carbon was around 600-2000 m^3·g-AC^{-1}.

Hereafter, the results of steam treated AC were discussed mainly. Figure 3(b) demonstrates the effects of thermal treatment temperature (T_T) and holding time (t_T) on the adsorption isotherms. The increasing in treatment temperatures increased the adsorption capacities. The adsorption capacity increased with holding time in the thermal treatment only at higher treatment temperature.

Figure 4 shows the adsorption isotherm of phenolic compounds in single and binary solutes solutions. The AC could adsorb the phenolic compounds, and the adsorption amount increased with the treatment temperature. In single solute system, the order of adsorption amount was cresols, guaiacol and phenol. In binary solutes the adsorption amounts of the phenolic compounds were lower than that of single component. In both cases, phenol is adsorbed lower than the co-existing component. The Langmuir model and Jain-Snoeyink model were used to know the adsorption behavior in binary solutes solutions (Jain and Snoeyink 1973). In Figure 5, adsorption amounts calculated from the models, q_{calc}, is compared with that of experiments, q_{exp}. The Langmuir model predicted the adsorption amount slightly better than Jain-Snoeyink model which means that the adsorption might occurs with competition for available sites. This assumption, however, need to be studied further.

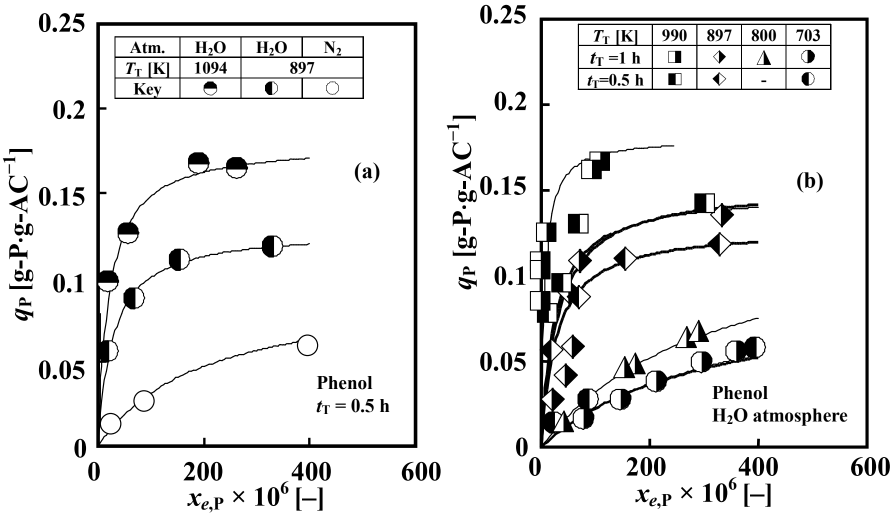

Figure 3. Adsorption Isotherms of Phenolic Compounds: (a) Effect of Thermal Treatment Atmosphere; (b) Effects of Temperature and Holding Time

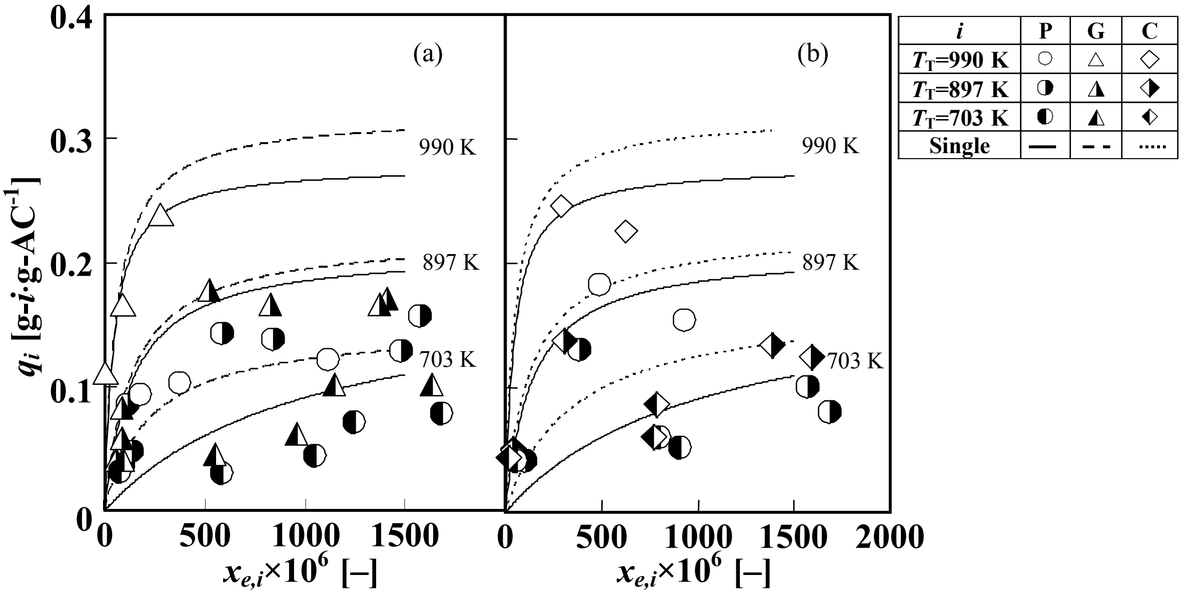

Figure 4. Adsorption Isotherms of Phenolic Compounds in Single and Binary-Component Solutions: (a) Phenol-Guaiacol Solution; (b) Phenol- Cresol Solution

model	Phenol-Guaiacol	Phenol-Cresols
Langmuir	▲	◆
Jain-Snoeyink	△	◇

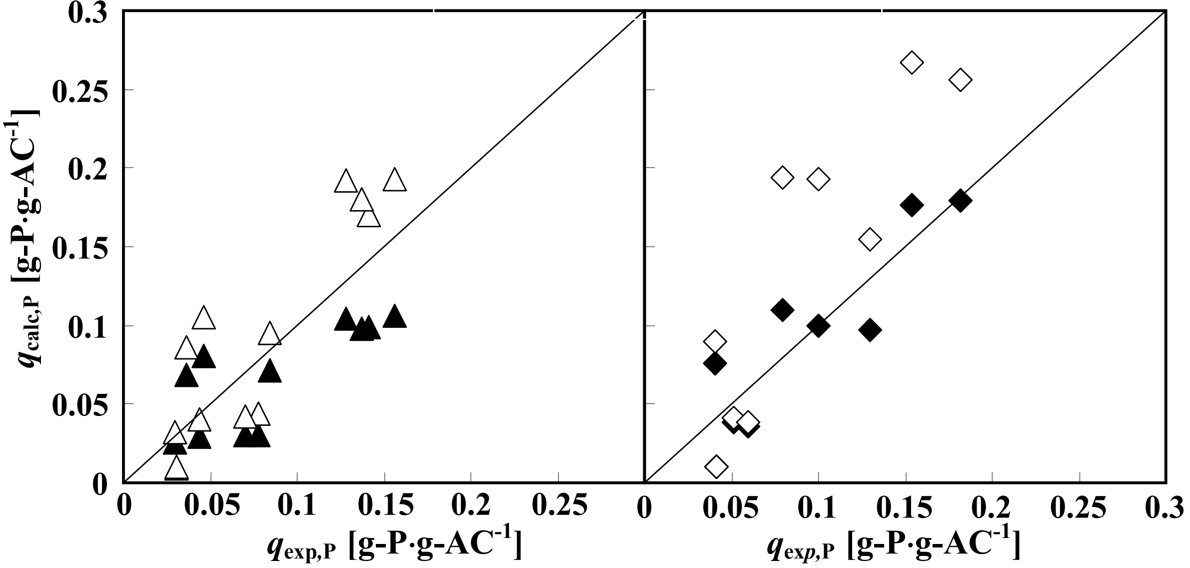

Figure 5. Comparison of Adsorption Amount of Phenol Calculated from The Models Against Experimental Values: (a) Phenol-Guaiacol Solution; (b) Phenol-Cresols Solution

Solution	T_T [K]	AA	M	A	Phenolic compounds
Multi-components	897	▼	▶	◀	●
Multi-components	703	▽	▷	◁	○
PA	897	⧩	▶	◀	◐
PA	703	⧨	▷	◁	◑

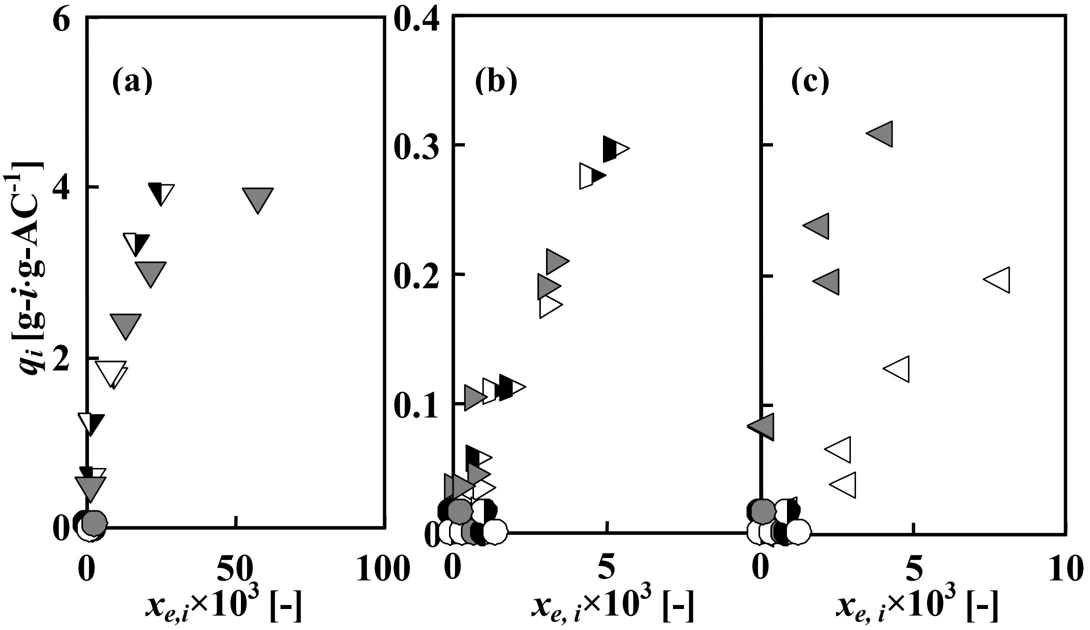

Figure 6. Adsorption Isotherms of: (a) Acetic Acid; (b) Methanol; (c) Acetone

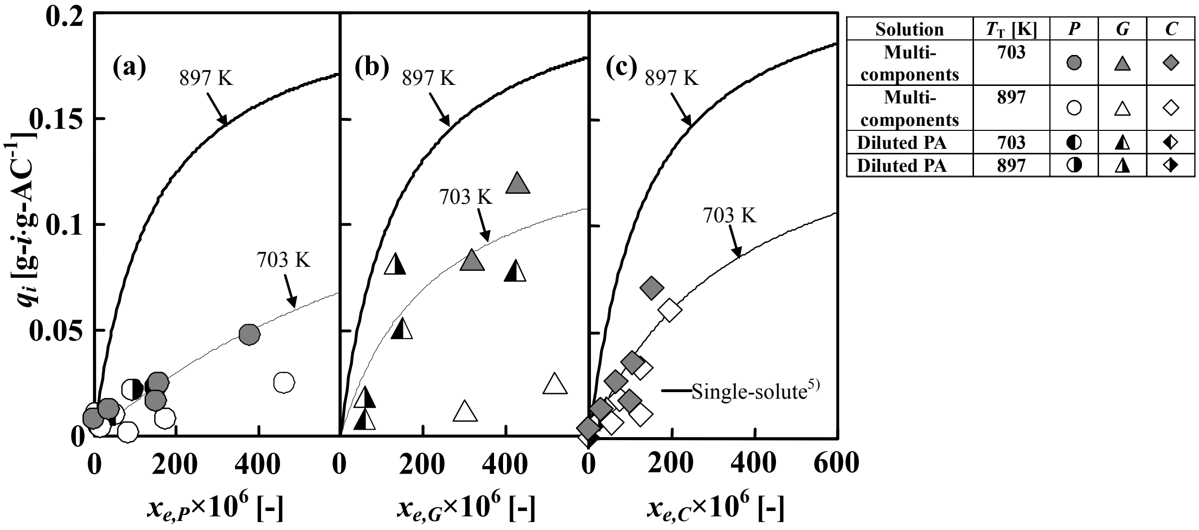

Figure 7. Adsorption Isotherms of: (a) Phenol; (b) Guaiacol; (c) Cresols

Figure 6 demonstrates the adsorption isotherms of the studied components in multi solutes and PA solutions. The rubberwood AC could adsorb the preservative components in all runs. The adsorption amounts of acetic acid, methanol and acetone, the major components were higher than those of phenolic compounds. Since phenolic compounds are the targeted components to be removed, the adsorption isotherms are shown in Figure 7. The adsorption amount of each phenolic compound in multi solutes and PA solutions was lower than in single solute solution. The other components, existing in both multi solutes and PA solutions, filled the available adsorption sites competitively, and thus lowered the adsorption amounts of the phenolic compounds. The adsorption amount increased as the treatment temperature to produce the AC increased.

The saturated amount of single phenolic compound adsorbed on the yielded AC was significantly higher than the overall yield of the compound in PA, especially for steam treated AC, indicate the feasibility to use the PA and AC within the manufacturing process (Lim et al. 2004, Othaman et al. 2007, Othaman et al. 2008). Figure 1 depicts the proposed process improvement as well. Wood wastes from the process are thermally treated under H_2O atmosphere to produce CPA, AC, and off-gas. The CPA is distilled into pure PA. The utilization of the PA as preservative for timbers can replace the current purchased toxic preservative. The components contained in PA, especially phenolic compounds, should not released to external water resources either, so that these components are removed from wastewater by the AC as adsorbent. The off-gas with addition of wastes is used as energy and heat sources for these additional operations (Othaman *et al.*, 2008). The proposed method will hopefully improve the RW manufacturing process and at the same time overcome the respected problems occurred due to wastes.

CONCLUSIONS

Enough amounts of pyroligneous acid and activated carbon were produced from thermal treatment. The proposed method is feasible since the produced activated carbon has convincing performance for PA adsorption in wastewater.

REFERENCES

Faghemi, L., Khezami L. and Capart R. (2001). Pyrolysis Products from Different Biomasses: Application to the Thermal Cracking of Tar, *Appl. Energy, 69*, 293.

Jain, S.J., and Snoeyink, V. L. (1973). Adsorption from Bisolute Systems on Active Carbon, *J. of Water Pollution Control Fed.* , *45*, 2463.

Lim, K.G., and Egashira, R. (2004, April 2). Characterization of Products from Thermal Treatment of Rubberwood (In Japanese), Osaka, Japan. SCEJ 69th Meeting, Osaka University, Osaka City, Japan.

Ministry of Science, Technology and the Environment. (1999). *1999 Annual Report*, Ministry of Science, Technology and the Environment, Kuala Lumpur, Malaysia.

Othaman, R., Lim, K.G., Konishi, S., Sato, M., Shi, N., and Egashira, R. (2008). Thermal Treatment of Wood Residues and Effective Utilization of Its Products to Improve Rubberwood Manufacturing Process, *J. of Chem. Engng. of Japan*, *41(12)*,1149.

Othaman, R., Lim, K.G., Konishi, S., Sato, M., Shanshan, Q., Shi, N., and Egashira, R. (2007, May 15). Thermal Treatment of Rubberwood Residue for Its Effectual Use, Phoenix, USA. 26th Annual International Conference on Incineration and Thermal Treatment Technologies (IT3) Meeting, The Sheraton Crescent Hotel, Arizona, USA.

Othaman, R., K.G. Lim, S. Konishi, R.Egashira and H. Habaki. (2008, October 17). Utilization of Thermal Treatment Products from Wood Residues to Improve Rubberwood Manufacturing Process, Tokyo, Japan. International Workshop on Process Intensification 2008, Tokyo Institute of Technology, Tokyo, Japan.

Yoshida, H. (2005). *Handbook on Porous Adsorbent*. Fuji Technosystem, Tokyo, Japan.