Wastewater Treatment by Adsorption with Activated Carbon from Wood Residues in Rubberwood Sawmilling Process

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ゴム木材製材プロセスにおける残材由来活性炭を用いた吸着による排水処理

三谷　沙織

　残材の熱処理生成物である木酢液を木材の防腐剤，活性炭を防腐剤の混入した排水を処理するための吸着剤として利用することにより，東南アジア等における本プロセスの改善を計る方法に対して，実用上重要である固定床型吸着装置の適用を試みた。ゴム木材おが屑を熱処理して得られた活性炭によるフェノールを含むモデル排水の吸着実験を攪拌槽，固定床吸着装置を用いて行い，吸着平衡と粒子内有効拡散係数を実測した。活性炭粒子内部の拡散係数が小さく，外部のそれは大きいことが推測された。実験結果に基づくシュミレーション計算より，木酢液は全て同時に得られた活性炭により処理できることが分かった。

1. Introduction

In Southeast Asian countries, rubberwood (RW) furniture manufacturing is an important industry. Sawmilling provides the processed wood for the industry. The current sawmilling process is shown in the black part of Fig. 1. Rubberwood logs are cut, preserved and dried, and molded into products. The problems from the process are to use toxic preservatives and to generate large amount of wood residues. The preservatives contain the harmful compounds such as boric acid and mixture of borax pentahydrate and the workers are exposed to the harmful environment. In addition, the wastewater, containing the preservatives, is discharged without any treatment, which causes soil and water contaminations. The large amount of wood residues with the preservatives are dumped or thrown away in rural sites and burned illegally, causing soil contamination, accidental forest burning and generation of hazardous gases.

To solve these problems in the sawmilling process, we proposed the utilization of the products from thermal treatment of RW residues. The proposed process is shown in Fig. 1, as well. A portion of residues from the cutting and molding process are thermally treated under steam atmosphere to produce the pyroligneous acid (PA), activated carbon (AC) and off-gas. PA is used as preservative, replacing the current purchased preservative because it contains the components useful as preservatives. Table 1 shows the some components in PA which we identified. The concentrations of these toxic components such as phenolic compounds are very low compared with current harmful preservatives, but they need to be removed from the wastewater. So, it is treated by adsorption with the AC. The remaining wood residues and off-gas are used for heat generation. We conducted the thermal treatment of RW sawdust under various conditions, studied the characteristics of the products, and evaluate the feasibility by simple calculation based on these experimental results. These studies showed that the improvement of the process by the proposed method was feasible in terms of material and heat balances [1].

In order to put this method to practical use, more detailed studies of the individual operations in this process should be carried out. For wastewater treatment, it is necessary to study not only adsorption isotherms but also kinetics.

This study aims to design the fixed bed adsorption column for the wastewater treatment in this process. Firstly, thermal treatments of RW sawdust were conducted to obtain the AC. With this AC, the adsorption of phenol, a representative pollutant in PA, from the aqueous solution with stirring vessel and fixed bed column were conducted to measure the adsorption equilibrium and rate parameters.
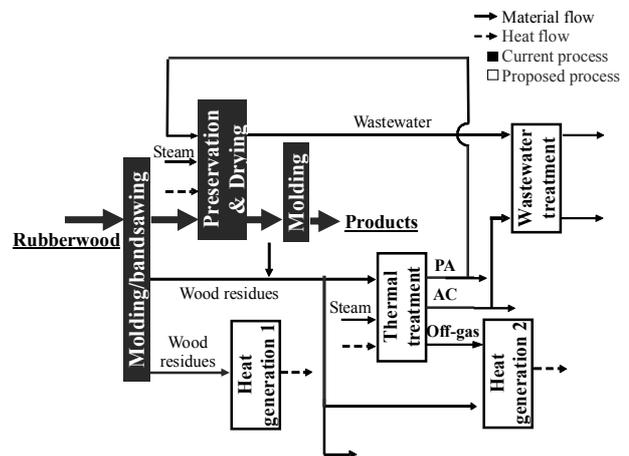
Fig. 1 Current and proposed process of sawmilling: material and heat flows

Table 1 Components in PA

Components	Mass fraction [%]
Water	92
Acetic acid	0.89
Acetone	0.22
Phenolic compounds	0.06
Methanol	0.02

2. Experimental

2.1 Preparation of AC by thermal treatment of RW sawdust

RW sawdust was thermally treated under steam atmosphere in a stainless steel tube heated by an electric furnace to obtain the AC. The experimental equipment is shown in Fig. 2, the same as previous study [1]. The tube was heated from room temperature until the specified treatment temperature, 873K, and the temperature was kept for 1 hour, defined as holding time. Table 2 shows the principal conditions of thermal treatment. The water content in obtained crude PA was measured by Karl Fischer Instruments (758KFD Titrino) from Metrohm company.

2.2 Adsorption with stirring vessel

AC was washed, dried, grounded and sieved before adsorption experiments. The schematic diagram of the vessel is shown in Fig. 3. The experimental conditions are shown in Table 3. A specified amount of AC was mixed with the model wastewater containing phenol in the stirring vessel. The stirring velocity was 500 rpm, which is reported to be high enough for external mass transfer resistance to be negligible under such systems and conditions [2]. The temperature of the material system in vessel was kept at 303 K in an isothermal bath. The samples were intermittently collected until the system reached adsorption equilibrium. The samples were analyzed by gas chromatograph (GC-14B with FID, Shimadzu Co., Ltd.; ULBON HR-20M column I.D. 0.00053 m × 30 m).

2.3 Adsorption with fixed bed

Based on the results of batch adsorption in the stirring vessel, fixed bed adsorption was conducted with the small column which was made of acrylic resin. The column size was 2.1 cm in I.D. and 4 cm in length. Pretreated AC was soaked with deionized water under vacuum condition to remove air in the pores. Then it was packed in the column. The model wastewater containing phenol was supplied to the column in an upward flow direction at a desired flow rate by a delivery pump. Samples were taken from the effluent on the top of the column and phenol concentration was determined by gas chromatograph. Figure 4 shows the

apparatus for fixed bed adsorption. Principal conditions of the experiment are shown in Table 4.

Table 2 Principal conditions for thermal treatment

Feed		RW sawdust
Mass of feed	[g]	25 ± 5
Atmosphere		H_2O
Flow rate	[$m^3 \cdot h^{-1}$]	
< 473K		0.003(N_2)
> 473K		0.0012(N_2)
		0.003(H_2O)
Temperature	[K]	873
Holding time	[h]	1
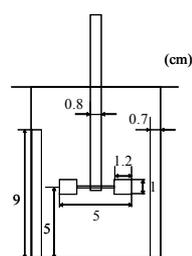
Fig. 3 Schematic diagram of stirring vessel

Table 3 Principal conditions for adsorption with stirring vessel

Feed solution	Phenol solution
Volume of feed solution [m^3]	500×10^{-6}
Concentration of phenol in feed solution, C_0 [$g \cdot m^{-3}$]	100–400
Adsorbent	AC
Particle radius AC, $R_p \times 10^3$ [m]	0.21−0.85, 0.08−0.18
Concentration of adsorbent, C_{AC} [$g \cdot m^{-3}$]	200–2000
Stirring speed [rpm]	500
Sampling size [m^3]	3×10^{-6}
Contacting time [h]	75, 200
Contacting temperature [K]	303
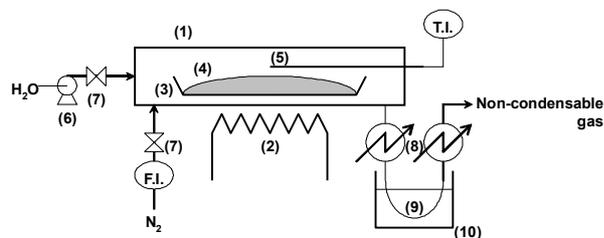
Fig. 2 Schematic diagram of thermal treatment apparatus: (1) tubular reactor; (2) electric tubular furnace; (3) sample holder; (4) feed/solid product; (5) NiCr-Constantan thermocouple; (6) micro-plunger pump; (7) valves; (8) condensers; (9) liquid product trap; (10) iced bath (275~277 K); F.I. flow indicator; T.I. temperature indicator
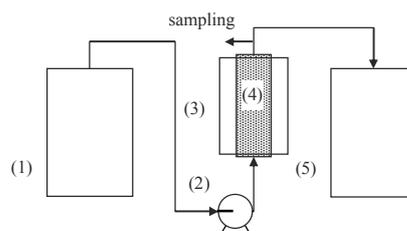
Fig. 4 Schematic diagram of fixed bed apparatus:
(1) Feed tank; (2) Solution delivery pump; (3) Heating water tube; (4) Fixed bed column; (5) Reservoir

Table 4 Principal conditions for fixed bed adsorption

Feed solution	Phenol solution
Fluid velocity, $u \times 10$ [m·h^{-1}]	2.6–5.4
Concentration of phenol in feed solution, C_0 [g·m^{-3}]	230–300
Adsorbent	AC
Particle radius of AC, $R_p \times 10^3$ [m]	0.08−0.18
Mass of adsorbent [g]	2.5 ± 0.5
Sampling size [m^3]	3 × 10^{-6}
Contacting temperature [K]	303

Fig. 5 Concentration change in stirring vessel

3 Results and discussion

3.1 Preparation of AC by thermal treatment of RW sawdust

Thermal treatment of RW sawdust produced crude PA, AC and off-gas. The color of crude PA was dark brown and water content was 83 %. It was because it contained a lot of tar components, which we proposed to be removed by distillation. All sawdust was evenly treated to AC. AC was black in color and lighter in mass if compared with feed sawdust. Off-gas was non-colored gas and had a bad smell. Mass of obtained crude PA, AC and off-gas were about 30 %, 20 % and 50 % of the feed sawdust, respectively. Mass of off-gas was derived based on material balance.

3.2 Adsorption with stirring vessel

The basic equation of adsorption rate into the particle is written as Eq. (1)

$$\partial q/\partial t = D_e \cdot (\partial^2 q/\partial r^2 + (2/r)\,(\partial q/\partial r)) \tag{1}$$

with boundary conditions

$r = R_p$; $\rho_s \cdot D_e \cdot \partial q/\partial t = -(V_L/S) \cdot (\partial C/\partial t)$, $q = f(C)$

$r = 0$; $\partial q/\partial r = 0$

and initial conditions $\quad q = 0$ for $0 \leq r \leq R_p$

and $\quad\quad\quad\quad\quad C = C_0$ at $t = 0$

where q is amount adsorbed, D_e is effective intraparticle diffusivity, r is radial position in the particle, ρ_s is particle density, V_L is volume of solution, S is external surface area, C is concentration of phenol in the solution. The measured concentration change allows to estimate the value of D_e.

The time course of the dimensionless concentration, C/C_0, of phenol in the solution are presented in Fig. 5. The concentration decreased over time, which shows that the phenol in the solution could be removed by AC.

C_1/C_0 is shown in table in Fig. 5, where C_1 is the final concentration of phenol. When C_0 was low, C_1/C_0 was low. When the mass fraction of AC in the solution, C_{AC} was low, C_1/C_0 was high.

The adsorption isotherm fitted Henry's type well from C_1 of each run. Theoretical curves by analytical solution of Eq. (1) are also drawn in Fig. 5 [3](dotted lines). D_e was measured by fitting to theoretical curves. However, it was difficult to fit all data with this theoretical curve. Compared with the curve, experimental concentration decreased quickly in early stage and then gradually decreased. Theoretical curves, which are obtained by numerical solution of Eq. (1) with using the different values of D_e for inner part of AC, $D_{e,i}$, and outer part of one, $D_{e,o}$, are also drawn in Fig. 5(solid lines). They fitted the experimental results better than former lines. This suggests that D_e of inner part of AC was smaller than outer part of it and it controlled the overall adsorption rate in later period of time.
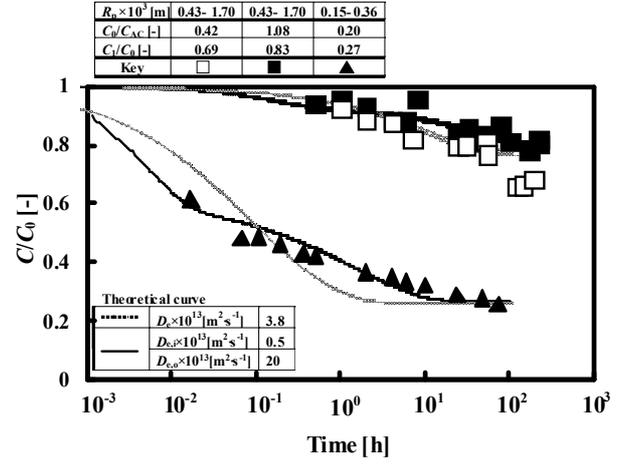
3.3 Adsorption with fixed bed

Material balance equation in fixed bed is written as Eq. (2)

$$u \cdot \partial C/\partial z + \rho_b \cdot \partial q_{ave}/\partial \theta = 0 \tag{2}$$

with boundary conditions

$r = R_p$; $\rho_b \cdot \partial q_{ave}/\partial \theta = k_f a_v \cdot (C - C_s)$,

$\quad\quad \rho_b \cdot \partial q_{ave}/\partial \theta = D_e \cdot a_v \cdot \rho_p \cdot (\partial q/\partial r)$, $q = f(C)$

$r = 0$; $\partial q/\partial r = 0$

and initial conditions $\quad q = 0$ for $0 \leq r \leq R_p$

and $\quad\quad\quad\quad\quad C = C_0$ for $t = 0, z = 0$

where, u is flow rate, C is bulk concentration of phenol in the bed, z is axial location in the column, ρ_b is bed density, q_{ave} is average amount adsorbed, θ is time, ρ_p is particle density, $k_f a_v$ is fluid phase mass transfer coefficient, and C_s is concentration at interface. Eq. (1) and (2) can be solved numerically to obtain the breakthrough curve.

Fixed bed adsorption runs were conducted under three different conditions. u and C_0 were varied. The breakthrough curve was measured for each run shown in Fig. 6. Breakthrough concentration, C_B, was fixed 10% of C_0.

From the results, effluence concentration of phenol, C, was 0 at first. This is because whole phenolic compound was adsorbed by AC which was packed in the column during the solution flowing in the column. Then, C/C_0 gradually increased with time. Breakthrough time, t_B, showed increasing tendency with decreasing u.

The shapes of the curves spread widely at high concentration field. Probably, the intraparticle mass transfer might dominate in this adsorption. Some researchers reported that for rate control in the mobile

phase, the wave "fronts" has a sharp tail; for rate control in the stationary phase, the wave "tails" has a sharp front [4].

Theoretical breakthrough curves were estimated by same method as before. Similarly to stirring vessel, model of smaller $D_{e,i}$ than $D_{e,o}$, which are shown by solid lines in Fig. 6, fitted better to experimental results better than model of uniform D_e values in the particle, which are shown by dotted lines. Appropriate values of $D_{e,i}$ was small compared with that of stirring vessel. Possible reason was difference of adsorption operation. For example, channeling might occur in the column. If so, flow rate became inconstant and it caused earlier increase of concentration. But decisive reason was not clear.

Then, simulation calculation for industrial adsorption column operation was conducted. Figure 7 shows the process flow for simulation calculation. The yield and other characteristics of products were based on experimental results. Toxic component in wastewater was assumed to be only phenol and the concentration was 1500 ppm, which is sum of phenolic compounds in obtained PA. C_B was fixed 1 ppm, which is the permissible level in Malaysia. Simulation was done to meet following conditions, which all of PA is treated by t_B within unit of time and excess amount of AC is discharged. Then, relations were obtained as follows to satisfy these conditions.

$$u \cdot t_B \cdot \xi / L \geq 1, \; 1 \geq t_B$$

In this equation, ξ is yield and density parameter obtained by experiment and L is column length. Table 5 shows the example of simulation calculation. All of PA could be treated by AC and excess amount of AC could be treated.

4. Conclusion

AC which posses the adsorption ability of phenol was sufficiently obtained by thermal treatment of RW sawdust.

In adsorption with stirring vessel, it was found that mass transfer rate of inner part of AC particle was much smaller than outer part.

In adsorption with fixed bed, mass transfer rate in inner part of AC particle was small similarly to stirring vessel. Based on the results, simulation calculation showed that all of PA obtained by thermal treatment could be treated by AC.

Therefore, it is concluded that application of fixed bed operation for wastewater treatment in proposed sawmilling process will be feasible.

Nomenclature
C_0: feed concentration [g·m^{-3}], R_p: particle radius [m], C_{AC}: concentration of AC [g·m^{-3}], u: velocity of the fluid [m·h^{-1}], D_e: effective intraparticle diffusivity [m^2·s^{-1}], q: amount adsorbed [g·(g-AC)$^{-1}$], t: time [s], r: radial position within a particle [m], ρ_s: particle density [g·m^{-3}], V_L: volume of solution [m^3], S: external surface area [m^2], C: concentration in the fluid phase [g·m^{-3}], C_1: final concentration [g·m^{-3}], $D_{e,o}$: effective intraparticle diffusivity of outer part in AC [m^2·s^{-1}], $D_{e,i}$: effective intraparticle diffusivity of inner part in AC [m^2·s^{-1}], z: axial location in the column [m], ρ_b: bed density [g·m^{-3}], q_{ave}: average amount adsorbed [g·(g-AC)$^{-1}$], θ: adjusted time [s]($= t-\varepsilon\cdot z/u$), ρ_p: particle density [g·m^{-3}], $k_f a_v$:

fluid phase mass transfer coefficient [s^{-1}], C_s: concentration at interface [g·m^{-3}], a_v: specific surface area [m^2], C_B: breakthrough concentration [g·m^{-3}], t_B: breakthrough time [h], ξ: yield and density parameter [-]($\xi = \rho_{PA} Y_{AC} / \rho_b Y_{PA}$), L: column length [m], R: mass of RW residues [kg·h^{-1}], Y_{PA}: yield of PA [-], Y_{AC}: yield of AC [-], $M_{AC,Column}$: amount of AC for column [kg], $M_{AC,Exit}$: excess amount of AC [kg]

References
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[2] Suzuki Motoyuki, et.al. *J.Chem. Eng. Japan*, Vol. 8, No. 1, pp. 79-81 (1975A)
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$u \times 10$ [m·h^{-1}]	5.4	2.6	2.9	Theoretical curve	
C_0 [g·m^{-3}]	270	300	230	$D_{e,i} \times 10^{16}$ [m^2·s^{-1}]	6.0
t_B [h]	0.5	4.0	6.5	$D_{e,o} \times 10^{12}$ [m^2·s^{-1}]	2.0
Key	▲	△	△	$D_e \times 10^{12}$ [m^2·s^{-1}]	2.0
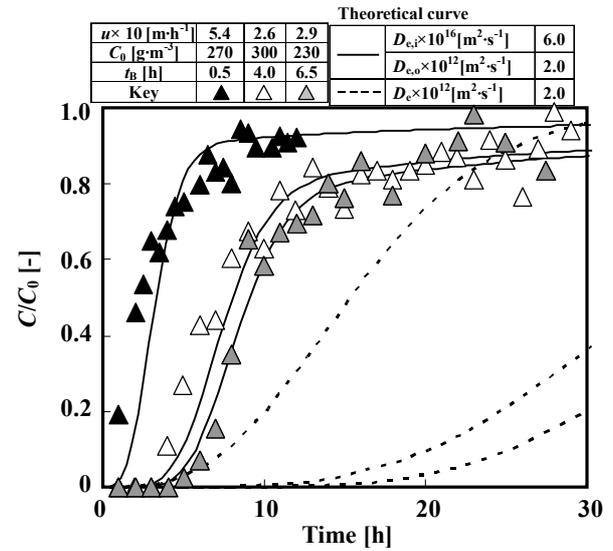
Fig. 6 Breakthrough curves of phenol
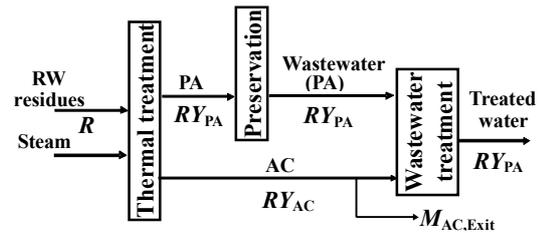
Fig. 7 Process flow for simulation calculation

Table 5 Example of simulation calculation

Mass of RW residues, R [kg·h^{-1}]	10000
Mass of obtained PA, RY_{PA} [kg·h^{-1}]	14000
Mass of obtained AC, RY_{AC} [kg·h^{-1}]	2080
Volumetric flow rate of waste water to column [kg·h^{-1}]	14
Column length, L [m]	3.0
Fluid velocity, u [m·h^{-1}]	98
Breakthrough time, t_B [h]	1.0
Amount of AC for column, $M_{AC,Column}$ [kg]	90
Excess amount of AC, $M_{AC,Exit}$ [kg]	1990