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

韓　笑

　東南アジアのゴム木材製材プロセスの改善ために、残材の熱処理生成物である木酢液を木材の防腐剤, 活性炭を防腐剤の排水を処理するための吸着剤として利用する新たなプロセスに対し、使用済み活性炭の処理について検討した。ゴム木材おが屑を熱処理して得られた活性炭及び使用済み活性炭を熱再生して得られた再生活性炭のキャラクタリゼーション及びフェノールとクレゾールを含むモデル排水に対する回分式吸着実験を行った。再生活性炭の吸着性能は未使用活性炭よりも低い吸着性能であった。使用済み活性炭の処理を考慮した製材プロセスのシミュレーション計算を行い, 必要なおが屑の量が実現可能な範囲内にあることを示した。

1. Introduction

In Southeast Asian countries, rubberwood furniture manufacturing is an important industry. The current sawmilling process includes the process shown by black boxes in **Fig.1**. Rubberwood logs are cut, preserved and dried, then molded into products. Two major problems were reported in the existing process; the utilization of toxic preservatives, and large amount of wood residues [2]. The preservatives contain the harmful compounds such as boric acid and mixture of borax pentahydrate and the workers are exposed to these harmful compounds. In addition, the waste water, containing the preservatives, is discharged without any treatment, which causes soil and water pollutions.

To solve these problems, the utilization of the products from thermal treatment of wood residues (WR) was proposed. The proposed process is shown in **Fig.1**. It was suggested that the wood residues were thermally treated to produce pyroligneous acid (PA), activated carbon (AC), and off-gas, and these products were effectively utilized in the process [1][2]. Pyroligneous acid was characterized to contain the components effective for preservations, and it can be used as preservative agent instead of the current purchased preservative agent. However some of the chemical components in pyroligneous acid are necessary to be removed from the wastewater of the preservation. So, the wastewater is treated by the prepared activated carbon to meet the regulation of the wastewater. After treatment of the wastewater, the spent activated carbon (SAC) should be obtained and the treatment of it has not been discussed in previous studies.

In this work, the waste water treatment using activated carbon was studied, in which the treatment of the spent activated carbon was incorporated in the process. The virgin activated carbon (VAC) was obtained by thermal treatment of WR sawdust, and spent activated carbon was prepared by adsorption of phenol with virgin activated carbon. Thermal regeneration of spent activated carbon was carried out to obtain the regenerated activated carbon (RAC). The adsorption of phenol and p-cresol in the aqueous solution by virgin activated carbon and regenerated activated carbon were conducted to measure the change in the adsorption capability. Then the process incorporating the treatment of spent activated carbon was evaluated based on the material and heat balances.
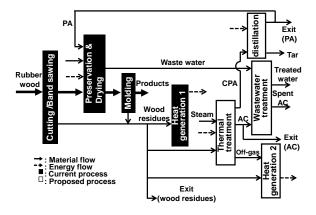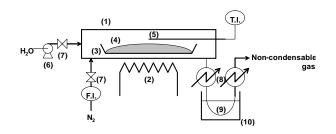

Fig. 1 Current and proposed process of sawmilling: material and heat flows

2. Activated Carbon from Wood Residues
2.1 Experimental

Wood residue, obtained from Malaysia, was thermally treated under steam atmosphere by the thermal treatment equipment, as shown in **Fig. 2** [3], to obtain the virgin activated carbon. Virgin activated carbon was treated by adsorption with phenol

aqueous solution to obtain spent activated carbon. Next, thermal regeneration of spent activated carbon was carried out using the same equipment shown in **Fig. 2** to prepare regenerated activated carbon under N_2 atmosphere. Thermal regeneration was chosen in this study because it was a commonly used regeneration method. **Table 1** and **2** show the principal conditions of thermal treatment and regeneration.

Experiments were also conducted to examine the characterization of the activated carbons. Scanning electron microscope (SEM) was used to observe the appearance of the activated carbon surface. The elemental analysis was conducted to measure the composition of the activated carbons. The specific surface area was measured by a surface area measuring instrument.

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

Table 1 Principal conditions for thermal treatment of wood residues

Feed	WR
Mass of feed [g]	30.0 ± 1.0
Atmosphere	N_2, H_2O
Flow rate of atmospheric gas [$m^3 \cdot h^{-1}$]	<473 K 0.003 (N_2) >473K0.0012(N_2), .003(H_2O)
Temperature [K]	873
Holding time [h]	1

Table 2 Principal conditions for thermal treatment of SAC

Feed	SAC
Mass of feed [g]	12.0 ± 1.0
Atmosphere	N_2
Flow rate of atmospheric gas [$m^3 \cdot h^{-1}$]	<473 K 0.003 (N_2)
Temperature [K]	1223
Holding time [h]	0

2.2 Results and Discussion

Thermal treatment of wood residues produced crude pyroligneous acid, virgin activated carbon and off-gas. The colour of crude pyroligneous acid was dark brown and water content was about 80%. It was because it contained a lot of tar components. All wood residues were evenly treated to virgin activated carbon. Virgin activated carbon was black in color and lighter in mass if compared with feed wood residues. Off-gas was non-coloured gas with a bad smell. Mass of obtained virgin activated carbon, crude pyroligneous acid, and off-gas were about 21%, 35% and 44% of the feed sawdust, respectively. Mass of off-gas was derived based on material balance.

From the SEM pictures of virgin activated carbon and regenerated activated carbon, it was found that particle size of the regenerated activated carbon was smaller than that of the virgin activated carbon. The results of elemental analysis were showed in **Table 3**. The content of oxygen could not be measured this time because too much ash content in them. In the case of activated carbon made from plants, it usually had a low content in sulphur and nitrogen [4]. The results of this experiment agreed with this trend. Specific surface area of virgin activated carbon, spent activated carbon and regenerated activated carbon were 582.54, 42.91, 271.19 m^2/g, respectively. After adsorption of phenol, the surface area of virgin activated carbon was obviously reduced. The possible reason was that phenol might occupy the pores of the activated carbon.

Table 3 Element analysis of RW, AC and RAC

Element	[wt%]		
	RW	AC	RAC
C	45.8	87.27	92.5
O	44.77	-	-
H	5.61	1.72	0.39
N	0.19	0.4	0.47
Ash	0.7	3.9	2.7

3. Batch adsorption of Model Wastewater by Activated carbon from Wood Residues
3.1 Experimental

In this study, in order to compare the adsorption performance of virgin activated carbon and regenerated activated carbon, phenol or p-cresol solution was chosen as the model wastewater, because they were typical harmful substances of the pyroligneous acid. Activated carbon was washed, dried, ground and sieved before adsorption experiments to equalize the properties of it. The batch adsorption experiment was conducted using a vessel with magnetic stirrer. Contacting time was decided as 120 hours according to pervious study [3].

After reaching adsorption equilibrium, the sample solutions were analyzed by gas chromatograph (GC-2010 with FID, Shimadzu Co., Ltd.) to determine the concentration of the solution. The experimental conditions are shown in **Table 4**.

Table 4 Principal conditions for adsorption with stirring vessel

Feed solution	Aqueous solution of phenol Aqueous solution of p-cresol
Volume of feed solution [m^3]	250×10^{-6}
Concentration of phenol in feed solution,, C_0 [g·m^{-3}]	540
Adsorbent	AC
Particle radius AC, d$_p$ [µm]	0.15-0.35
Concentration of adsorbent, C_{AC} [g·m^{-3}]	30000
Stirring speed [rpm]	500
Contacting time [h]	120
Contacting temperature [K]	303

3.2 Results and Discussion

The mass balance relation in the adsorption experiments can be expressed as,

$$L_0 C_0 = L_0 C_1 + S_0 q_1$$

L_0, C_0, C_1, S_0, and q_1 are the volume of feed solution [m^3], feed concentration [g/m^3], concentration of the solution after equilibrium [g/m^3], mass of the activated carbon [g], and amount of adsorbate on activated carbon [g/g-activated carbon], respectively. The adsorption amount of each sample was calculated by this equation.

Langmuir equation expressed blow was used to find saturated amount of adsorption:

$$q* = \frac{C_e q * K_L}{1 + C_e K_L}$$

C_e, q,q* ,K_L are concentration of the solution after equilibrium [g/m^3], adsorption amount for 1g adsorbent [g/g-activated carbon], the saturated amount of adsorption for 1g adsorbent, and Langmuir equilibria constant, respectively.

Based on the adsorption results, adsorption isotherms of phenol with virgin activated carbon and regenerated activated carbon are shown in **Fig. 3**, and those of p-cresol are shown in **Fig. 4**. The lines show adsorption isotherm calculated, and the plots show the experimental data. In this study, more than 80% of model harmful substance was adsorbed by virgin activated carbon, and adsorption isotherm could be described by Langmuir equation.

The saturated amount of adsorption is shown in **Table 5**. Adsorption amount of phenol and p-cresol were almost the same. The adsorption amount of regenerated activated carbon was about 10% of virgin activated carbon.

From the results mentioned above, we propose to treat spent activated carbon as energy source, because the efficiency of regenerating it is not very good.
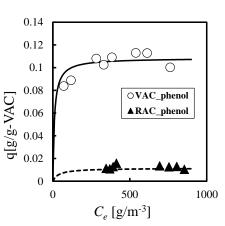

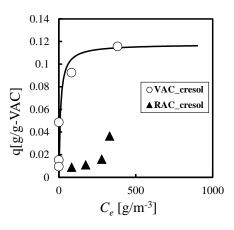**Fig.3** Adsorption isotherm for phenol by VAC and RAC

Fig. 4 Adsorption isotherm for p-cresol by VAC and RAC

Table 5 Saturated amount of adsorption

	VAC	RAC
q*$_{phe}$[g/g-AC]	0.10838	0.01147
q*$_{cre}$[g/g-AC]	0.12423	-

4. Improvement of Rubberwood Sawmilling Process
4.1 Overview of the process

In this study, the simulation calculation was based on the assumption that all the spent activated carbon is used as energy source in heat generation2 process. In heat generation2, off-gas and spent activated carbon will be used preferentially, then wood residues will be used. The rest of wood residues will get out of the system. Residue ratio $\alpha_{wr,Th}$ means the ratio of wood residues using for thermal treatment to total wood residues. Possible range of $\alpha_{wr,Th}$ was calculated from material balance and heat balance of the proposed process.

4.2 Calculation

In this study, toxic component in wastewater was assumed to be only phenolic components. The concentration of phenolic components in waste water was considered, because adsorption of unfavorable substance in wastewater was affected by not only activated carbon adsorption performance, but also the concentration of the substance. Since previous study reported that there were 2.7% of phenolic components existed in pyroligneous acid [1]. The concentration of that in wastewater could be calculated as 499ppm. The standard concentration of wastewater in Malaysia is 1ppm [1]. By using the data mentioned above, activated carbon amount in wastewater treatment process could be calculated.

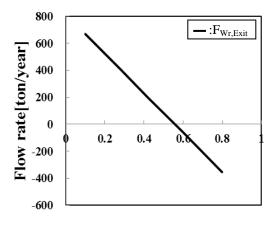Flow rate of feed rubberwood was supposed to be 1000 ton of a year.

The yield and other characteristics of products were based on experimental results of this study and previous study [3].

4.3 Results and Discussion

$F_{Wr,Exit}$ means the flow rate of wood residues which get out of the system, and the change of it is shown in **Fig.6**. In this figure, if $F_{Wr,Exit}$ become minus, it means the necessary heat for the whole process can't be covered by using the products from thermal treatment of wood residues. Maximum residue ratio could be calculated from this figure as 0.53. In this case, no wood residue is left, 749 ton/year excess amount of pyroligneous acid and 102 ton/year excess amount of activated carbon could be obtained.

If excess amount of pyroligneous acid is 0, namely, the amount of pyroligneous acid produced equal to the amount of pyroligneous acid required. In this case, activated carbon produced couldn't cover the requirement.

If excess amount of activated carbon is 0, namely, the amount of activated carbon produced equal to the amount of activated carbon required. In this case, 32 ton/year excess pyroligneous acid could be obtained, and 772 ton/year wood residues will be left. Minimum residue ratio could be calculated as 0.044 in this case.

Fig. 6 Flow rate change of exited wood residues

5. Conclusion

Model harmful substance could be removed by activated carbon made from wood residues.

The adsorption isotherm results showed that the adsorption amount of regenerated activated carbon was about 1/10 of that of virgin activated carbon. Therefore, it is concluded that regenerated activated carbon didn't have sufficient adsorption capacity compare to virgin activated carbon. So spent activated carbon was proposed to be used as energy source.

Based on the experimental data obtained from this study, the possible range of residue ratio$\alpha_{wr,Th}$ was calculated. In some cases, excess amount of pyroligneous acid and activated carbon could be obtained. The process was proposed to solve the environment problems in rubberwood sawmilling process.

References
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