PREPARATION AND CHARACTERIZATION OF ACTIVATED CARBON FROM TIMBER MILL WASTE AND ITS APPLICATION FOR REMOVAL OF METAL IONS FROM SOLUTIONS

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ABSTRACT

Wood waste of three different species obtained from timber mill were pyrolysed at three different temperatures in a furnace of oxygen-free system. Activated carbon was produced using 10% HCl and steam as activating agents. Temperature and time for the pyrolysis of wood and also the wood species determined the production of carbon and activated carbon. Optimum results for carbon content (19 – 28%) and activated carbon (18 – 27%) were produced at temperatures of 450°C and in 30 minutes. The activating agents used for the process did not affect significantly the production of activated carbon. Optimum adsorption of Cu^{+2}, Cd^{+2} and Pb^{+2} solutions at concentration of 200 ppm each on the carbon and activated carbon were obtained at pH = 4, 5 and 6 respectively. The sorption capacity was found to be in the order of $Pb^{+2}>Cd^{+2}>Cu^{+2}$. Analysis of the sorption data indicated that they were in agreement with the Langmuir and Freundlich equations and showed that there are strong interaction between adsorbent and adsorbate.

INTRODUCTION

Treatment of wastewater in many developing countries is considered as secondary matter and normally is placed at a low priority in their annual budget. One of the major reason is associated with the cost of the importation of water treatment chemicals and other materials.

One solution to these problems is the indigenous production of treatment materials, either by local production of chemicals, or the use of alternative, locally available, treatment materials.

The preparation of low-cost adsorbents for water purification, waste and wastewater treatment has recently been reviewed by Pollard *et al*[1]. A wide range of lignocellulosic agricultural by-products has successfully been converted into activated carbons, including coconut coir[2], jute stick[3], palm-tree cobs[4], rise husk[5] and tamarind nut shells[6-8]. The suitability of these precursors is determined by their local and bulk availability, carbon content and the presence of inherent microstructure within the substrate itself[9]. Viability of their ultimate use may be determined by factors such as the adsorptive capacity, regenerative characteristics and physical form of the subsequent carbon product.

In this study we describe the preparation and characterization of activated carbon from timber mill waste. The examination of preparative requirements and adsorptive characteristics of the activated carbon are the main objective of this study.

MATERIAL AND METHODS

Materials

Wood sawdust was obtained from a timber mill in Padang, Indonesia. Samples were differentiated by the color of the wood powder. Information regarding the samples and some of their properties determined are given in Table 1. These three wood samples were mainly timber processed by the mill. Prior to the carbonization process, the thermogravimetric analysis was carried out with a Perkin-Elmer model TGA7 analyzer heated at 20°C min^{-1} in dry condition, in nitrogen atmosphere from room temperature to 940°C. The information obtained was used to determine the optimum temperature for carbonization.

Table 1. Some Properties of Wood Samples

No.	Name of Wood	Botanical name	Color	Sample Code	Density (g/mL)	Moisture Content (%)
1.	Banio	*Shorea platyclados*	Dark Red	B	0.789	13.6
2.	Meranti	*Shorea leprosula*	Light rown	MR	0.550	12.5
3.	Mersawa	*Anisoptera curtisi*	Yellow	MS	0.563	11.6

Carbonization and Activation

Exactly, 10 g of oven dried wood samples were weighted and placed in a closed porcelain crucible and later carbonized in a muffle furnace out of contact with air at temperature of 350, 450 and 600°C for a series of the carbonization times specified. The carbon produced were activated by activating agents i.e. steam and 10% HCl. Samples were soaked in 10% HCl for 24 hrs, later filtered under vacuum and washed with distilled water. Further activation were carried out in a muffle furnace at temperature similar to carbonization process and for a specified activation times. The activated samples were dried at 105°C and then cooled, weigh to a constant weight. For steam activation, the process was first carried out in autoclave at 120°C and a pressure of 15 psi for two hours. Later, the samples were transferred into muffle furnace and activated with similar process as mentioned earlier.

pH value.

A 5 g portion of sample was placed in a beaker, 50 mL distilled water was added and boiled for 15 min. The contents were left to stand until it cooled down and the sample settled. The supernatant liquid was poured off and its pH was measured with a Griffin pH-meter model 80.

Adsorption Test

Methylene blue adsorption. The measurement was carried out by weighing 0.1 g of carbon or activated carbon, then transferred into a conical flask and added with 15 ml 0.15% methylene blue (w/v). The mixture was shaken for 15 min and later left to settled for another 30 min. The filtrate was diluted 10 times with distilled water and the concentration of methylene blue was determined by uv spectrophotometer at the wavelength 620nm. The amount of methylene blue adsorbed by 1 g of carbon or activated carbon was determined by the difference between the amount adsorbed before and after adsorption.

Iodine adsorption. The iodine adsorption was determined by weighing 0.25 g of carbon or activated carbon samples, transferred to a conical flask and added with 25 mL 0.05 M iodine solution and the mixture was shaken for 1 min. Exactly 10 mL of filtrate was titrated with 0.05N $Na_2S_2O_3$ and the amount adsorbed was determined based on 1 g of carbon or activated carbon.

Surface area measurement. The surface area of carbon and activated carbon were measured with Accelerated Surface Area and Porosimetry (Model ASAP 2000, Micromeretics Instrument Co., Norcross, Georgea) using nitrogen gas as an adsorbent at 77.4 K. Prior to sorption measurement. The sample was outgas at 150°C to a pressure less than 10^{-5} torr.

Adsorption isotherm. The adsorption capacity of the carbon and activated carbon were measured in term of quantity of copper, cadmium and lead adsorbed from their aqueous solutions. These stock solutions which at the concentration of 1000 ppm were prepared by dissolving $Cu(NO_3)_2$, $Cd(NO_3)_2$, and $Pb(NO_3)_2$ in distilled water respectively. The stock solutions were diluted with distilled water to concentration of 10 to 700 ppm for adsorption studies.

A known quantity of selected carbon and activated carbon samples were shaken with 20 mL of each solutions for 2 hr and let allowed to settle for another 2 hr at 30°C. The mixture was then filtered and the filtrate were analyzed for Cu^{+2}, Cd^{+2} and Pb^{+2} ions by Atomic Absorption Spectrophotometer (Model Alpha4). The amount of metal ions adsorbed on carbon and activated carbon were estimated by considering the initial and final concentrations of the metals in solutions.

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The same experiment was carried out with solutions at concentration of 200 ppm and pH of 1 to 9. The isotherm were then analyzed using the Langmuir and Freundlich models. The Langmuir model assumes that a monolayer of the adsorbate adsorbs to the carbon and activated carbon surface while the Freundlich model is purely empirical.

RESULTS AND DISCUSSIONS

Results obtained from TGA are given in Figure 1 indicating that the formation of carbon is approximately 25% at temperature around 400°C and decreases to about 15% by weight of wood powder as the temperature reached 900°C.

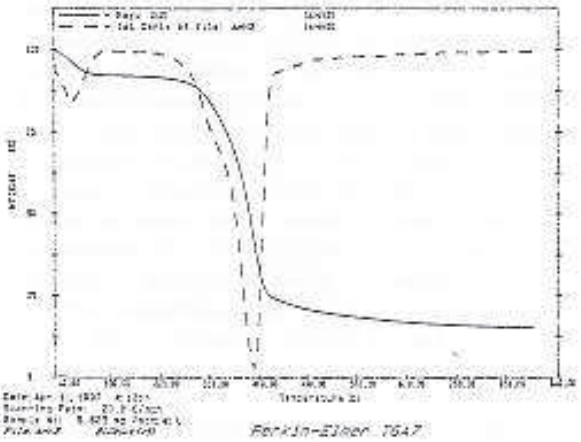

Figure 1. Thermogravimetric curve for wood sample.

Figures 2 - 4 show the effect of temperature on the kinetic of the carbon formation. There are sharp decreases at temperature 450 and 600°C within short period. This indicated that the wood is totally burned to ash at high temperature within a short period although with limited amount of oxygen gas. To obtain optimum carbon product the temperature required should be within the range of 400-500°C and time not more than 30 min[10]. Results also show that different wood species produced significant difference in the amount of carbon.

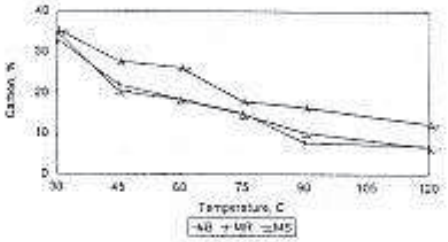

Figure 2. The effect of time on the production of carbon at 350C

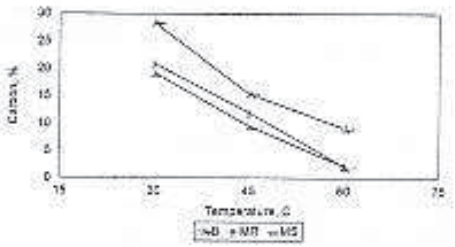

Figure 3. The effect of time on the production of carbon at 450C.

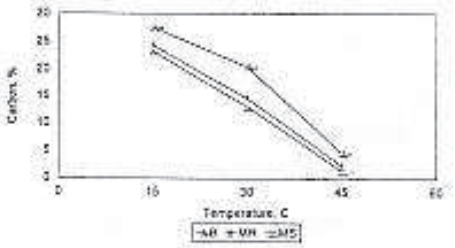

Figure 4. The effect of time on the production of carbon at 600C

Table 2 shows the effect of the temperature, time, wood species and activating agent on the yield of different carbon and activated carbon samples so produced. It can be noticed that as temperature increases and time decreases, the yield for all samples decreases which shows some differences in amount between Banio, Meranti and Mersawa samples. It may be due to the fact that an increase in heating rate during pyrolysis results in higher volatilization and lower yield. If compared with wood density (Table 1), the carbon and activated carbon produced from a higher density wood show a higher yield than a lower density wood. This result is in agreement with the previous studies by Ahmad[11]. The results also show that the yield of activated carbon samples by steam activation are slightly higher than samples that are activated by hydrochloric acid in a range between 2 to 10%.

Table 2. The Influence of Temperature, Time, Wood Species and Activating Agent on the Production of Activated Carbon.

Wood sample	Temp. (°C)	Time (minutes)	Carbon yield (%)	Activated Carbon by (%)	
				10% HCl	Steam
B35	350	45	35	31	33
B45	450	30	28	26	27
B60	600	15	28	26	26
MR35	350	45	33	29	30
MR45	450	30	21	18	20
MR60	600	15	24	21	23
MS35	350	45	35	30	32
MS45	450	30	19	18	18
MS60	600	15	24	22	23

The adsorptive characteristics of carbon and activated carbon samples produced by different temperatures have been determined against iodine, methylene blue and by nitrogen gas adsorption and are given in Table 3 which generally correspond to their micro, meso and total porous structure and correlate with surface area of pore greater than 10 and 15 A° in diameter and total pores respectively (Foster).
Results in Table 3 indicated that in case of iodine and N_2 gas, the activity is generally low at 350°C but increases with an increase in temperature. However, for methylene blue the activity is almost constant. The process of activation does not show much effect on the mesoporous structure of activated product but more pronounced in case of microporous structure and total pores especially at 450 and 600°C. This may be due to the formation of micropores at 500°C and some pores which remain blocked at lower temperature could be available at higher temperature and resulting in an increase in the iodine number[12]. When compared to the commercial sample, the activated carbon prepared are still inferior especially in the value of specific surface area.

Table 3. Adsorption Characteristics of Different Carbon and Activated Carbon

Sample type	Iodine No. (mg/g)	Methylene blue No. (mg/g)	Specific Surface Area (m^2/g)
	Carbon		
B35	140 ± 3	132 ± 3	107
B45	175 ± 2	138 ± 3	596
B60	221 ± 4	140 ± 2	630
MR35	186 ± 5	140 ± 2	113
MR45	227 ± 5	152 ± 5	713
MR60	308 ± 3	145 ± 3	605
MS35	145 ± 2	132 ± 3	-
MS45	239 ± 2	152 ± 5	-
MS60	239 ± 2	142 ± 3	400
	Activated Carbon Produced by 10% HCl Activation		
B35	198 ± 6	142 ± 2	290
B45	279 ± 3	147 ± 3	428
B60	367 ± 3	142 ± 2	589
MR35	227 ± 4	144 ± 2	362
MR45	320 ± 5	142 ± 2	568
MR60	344 ± 2	144 ± 4	636

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MS35	221 ± 3	152 ± 2	334
MS45	290 ± 5	149 ± 3	496
MS60	326 ± 7	152 ± 4	554
	Activated Carbon Produced by Steam Activation		
B35	181 ± 5	144 ± 2	109
B45	250 ± 7	149 ± 3	581
B60	297 ± 6	142 ± 2	637
MR35	239 ± 3	142 ± 2	475
MR45	320 ± 4	140 ± 2	703
MR60	367 ± 6	147 ± 3	634
MS35	221 ± 7	144 ± 2	378
MS45	268 ± 4	152 ± 3	568
MS60	344 ± 3	152 ± 2	567
	Commercial Activated Carbon		
Merck	416 ± 4	216 ± 3	1324

Figure 5 shows the effect of the pH of the copper, cadmium and lead solutions at concentration of 200 ppm on the activated carbon. It indicated that the sorption capacity of metal ions increases steadily until it reached the optimum at the respective pH solutions and later become constant. The optimum sorption capacity are at pH = 4 for Cu^{+2}, pH = 5 for Cd^{+2} and pH = 6 for Pb^{+2}. This behaviour is believed to be due to the precipitation of hydroxide and not because of sorption[13,14].

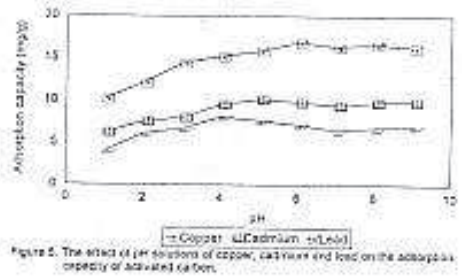

Figure 5. The effect of pH solutions of copper, cadmium and lead on the adsorption capacity of activated carbon.

The influence of various carbon and activated carbon samples on the sorption activity of the metals ion at 200 ppm at their respective pH value is shown in Figures 6 - 8. It indicated that the adsorption capacity of carbon and activated carbon samples prepared from Banio wood species was found to be the highest compared to the other wood species. However, the performance is still not comparable to the commercial activated carbon. It seems that the alteration in temperature for production of carbon and activated carbon do not affect their sorption capacity. The figures also indicated that the sorption of Pb^{+2} was the highest compared to Cd^{+2} and Cu^{+2}, and can be arranged according to their order of ability to adsorbed on carbon and activated carbon as $Pb^{+2}>Cd^{+2}>Cu^{+2}$.

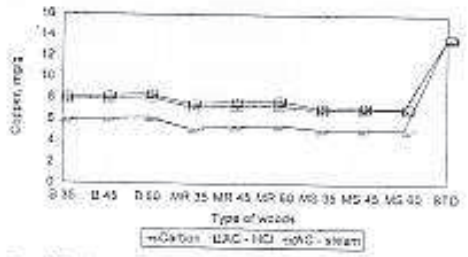

Figure 6. The influence of various carbon and activated carbon on the adsorption activity of the Cu^{+2} (200 ppm) at pH = 4

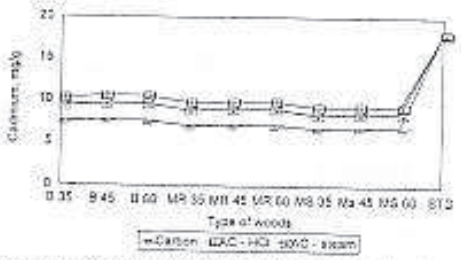

Figure 7. The influence of various carbon and activated carbon on the adsorption activity of Cd^{+2} (200 ppm) at pH = 5

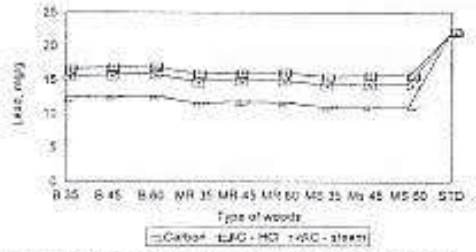

Figure 3. The influence of various carbon and activated carbon on the adsorption activity of Pb^{2+} (200 ppm) at pH = 5.

Data from sorption studies were analyzed using the Langmuir and Freundlich models, the results of which are shown in Table 4 along with the regression coefficient, r^2. From the regression coefficient values indicated that for copper, cadmium and lead adsorbates and also for all type of adsorbents, both models are in agreement to the adsorption data, with the Langmuir model giving a slightly better fit than the Freundlich model. The carbon sample showed lower uptake of all type of adsorbates compared to activated carbon which are in agreement with their adsorption characteristics of methylene blue and iodine numbers and specific surface area that are given in Table 3. Langmuir monolayer coverage constant, Q_m, and Freundlich constant, n, in general show similar trend for sorption in the order as $Pb^{+2}>Cd^{+2}>Cu^{+2}$ as discussed above.

Table 4. Summary of Langmuir and Freundlich Adsorption Isotherm Results.

Adsorbate	Adsorbent	Langmuir			Freundlich		
		Q_m (mg/g)	K_L	r^2	n	K_F	r^2
Copper	Carbon	7.69	0.043	0.998	8.70	3.42	0.987
	Activated $Carbon_{HCl}$	9.79	0.048	0.999	10.06	5.05	0.996
	Activated $Carbon_{H2O}$	9.62	0.053	0.999	8.25	4.43	0.951
Cadmium	Carbon	8.94	0.065	0.999	10.92	4.88	0.994
	Activated $Carbon_{HCl}$	11.46	0.072	0.999	11.86	7.13	0.997
	Activated $Carbon_{H2O}$	12.26	0.078	0.990	9.21	5.79	0.992
Lead	Carbon	14.64	0.076	0.998	13.04	8.81	0.986
	Activated $Carbon_{HCl}$	19.45	0.108	0.999	12.80	11.90	0.994
	Activated $Carbon_{H2O}$	17.73	0.152	0.999	13.40	11.39	0.987

CONCLUSION

This research has shown that a simple production process can produce quite good quality activated carbon from the wood sawdust. The activated carbon has many possible applications, as it is highly microporous with some mesoporosity and shows rapid uptake of pollutants.

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