Title	CARBONIZATION OF WOOD BY DEHYDRATING AGENT : Part Ⅰ On the Preparation and the Decolorizing Power of the Hydrated Active Charcoal (H-A charcoal) from Wood
Author(s)	HANZAWA, Michio; 半澤, 道郎; SATONAKA, Seiichi et al.
Citation	北海道大學農學部 演習林研究報告, 17(2), 439-463
Issue Date	1955-12
Doc URL	https://hdl.handle.net/2115/20721
Type	departmental bulletin paper
File Information	17(2)_P439-463.pdf

CARBONIZATION OF WOOD BY DEHYDRATING AGENT

Part I

On the Preparation and the Decolorizing Power of the Hydrated Active Charcoal (H-A charcoal) from Wood

By

Michio HANZAWA and Seiichi SATONAKA

脱水剤による木材炭化

半沢道郎
里中聖一

The decolorizing chars are formed by the action of heat and chemical reagents on vegetable substances, however there are very many manufacturing methods.

The methods of manufacturing and preparing decolorizing carbons may be divided into several classes, but the most common method is the carbonization of the organic substances at high temperature such as 700-1200°, and removal of the volatile matters and tarry substances which are formed as by-products, by the most suitable method and resulting in the obtainment of porous active carbon. For the activation air, carbon dioxide, chlorine, over-heated steam, and air and steam are most commonly used.

There are known other methods much different from the above mentioned methods which employ carbnization at high temperature. By another method vegetable materials are carbonized by dehydration with action of concentrated sulphuric acid or phosphoric acid at low temperature, resulting in colloidal and porous active charcoal. The active charcoal which is thus prepared has low degree of carbonization and the carbon content is lower than general active carbon. Hitherto, it has seemed that the carbon of such low-degree carbonization has low decolorizing power activity. But this dehydrated substance is highly effective for decolorization in moistened (hydrated) state.

M. HANZAWA, *Assistant Professor, Doctor* and S. SATONAKA, *Assistant*, both: Institute of Forest Products, Hokkaido University, Sapporo, Japan.

On these active charcoals* there have been few reported investigations (in Germany, Czechoslovakia, Italy, U.S.S.R., and United States).[2] In our country a very interesting study by MIZUNO and KATO[3] has been performed. They obtained a good decolorizing charcoal, which at first, they called "Shitsujun kasseitan" (moistened active charcoal) and after called "Suika kasseitan" (hydrated active charcoal).

MIZUNO and KATO selected raw materials which contain nearly pure carbon (material such as carbohydrates are most preferable), and dehydrated them with concentrated sulphuric acid by heating at 150°, and obtained decolorizing charcoal that had a good activity. However they stated that the presence of lignin in the raw materials should be avoided for the manufacture of hydrated active carbon like a general active carbon because lignin forms tarry substance much more than cellulose, as had been stated by FISCHER and TROPSCH[5]. They also considered that in case of using raw materials for the hydrated active charcoal which differed in reaction mechanism from general active carbon, one should select the materials in which the lignin content is small. They chose mandarin orange peel for the raw material, which is superior to the sawdust of wood, as it has small content of lignin, is easy to gather and is low in cost.

Procedure of preparation of the hydrated active charcoal by MIZUNO and KATO is as follows:

The raw material is dried in air bath by heating at 100°, and ground to size to pass through about 10-mesh. This material (8 g) is placed in a beaker, 70 per cent sulphuric acid (40 g) is added and heated in a water bath at 80° with stirring for an hour. Water vapors are evolved as bubbles and gradually solidified to form a gel, however in such a state further carbonization does not proceed even with additional heating (at 80°). Therefore the gel is ground in a mortar, and is heated at 150° for 8 hours in an oven. During this heating carbonization proceeds with the lapse of time, and the activity of the product is increased. The gel is shrunk and if the heating is too long the activity is decreased in accordance with the shrinkage of the product. The carbonized product is ground again in a mortar and washed with boiling distilled water until the reaction is neutral, filtered in a Buchner's funnel with suction, and stored in sealed jar.

Under these conditions MIZUNO and KATO manufactured hydrated active charcoal from filterpaper, saw dust, lignin (Willstätter lignin) and mandarin orange peel as raw materials. These products were moist and

---

* "Collactivit", "Colloidal C" etc.

in the form of a black powder which the yield and moisture content as shown in following Table:

Yield and moisture content of hydrated active charcoal by Mizuno and Kato.

Raw Material	Moisture (%)	Yield (Oven-dry basis) (%)
Filter paper	85.1	50.5
Saw dust	74.7	50.2
Lignin	71.9	57.7
Mandarin orange peel	75.7	60.4

Elementary analysis, showed that the charcoal made from filter paper contains hydrogen and oxygen atom at the ratio of H_2O 26 per cent, SO_3 3 per cent, while the remainder is carbon.

Mizuno and Kato tested the adsorptive (decolorizing) power and investigated the difference between the sort of raw materials. They compared their material with active carbon that was activated with zinc chloride, and observed the relation between decolorizing power, moisture content and adsorption of electrolyte. They stated that their charcoal is a carbonized product with removal of the water of construction from raw material, and if carbohydrate materials are used the adsorptive power is especially high and characteristic. These charcoals have activity in the moistened state and the activity is decreased by drying. The decolorizing power of these charcoals is of the same order as that of the active carbon which is activated by zinc chloride. They have summarized that their charcoal has a high decolorizing power even if the amount of addition to the colored solution is small, the yield is high, and it has good properties making it suitable for the sugar industry. Later they manufactured the hydrated active charcoal from mandarin orange peel on a large scale and tested it practically at a factory in Taiwan (Formosa)[4]. They persist in the lignin and lignin contained materials are not suitable as the raw material.

Their method has been protected by patent.

The present authors have been considered that from wood it should be possible to obtain an excellent hydrated active charcoal and that the lignin in the material may not be an obstacle to the adsorptive power of the product. Therefore studies were undertaken and carried through on the preparation of the hydrated active charcoal from various wood materials under various conditions; tests were made on the adsorptive (decolorizing) power of the products and compared with that of mandarin orange peel and general active charcoals. Studies also were made on the chemical properties and the mechanism of the adsorption by these hydrated active charcoals, and as one of the practical uses of these charcoal the adsorption and elution of penicillin was investigated.

Raw materials.

(a) Sound woods: Samples were taken for the sound wood raw materials from four species, these were the most common soft and hard woods in Hokkaido[6], viz.,

"Todomatsu" (*Abies Mayriana* MIYABE et KUDO), (Fir).
"Yezomatsu" (*Picea jezoensis* CARR.), (Spruce).
"Shina" (*Tilia japonica* SIMK), (Basswood).
"Nara" (*Quercus crispula* BL.), (Oak).

(b) Decayed woods: Saw dust was taken from decayed wood samples which were being used for the study on the chemical composition of decayed wood in our laboratory.

Brown rotted "karamatsu" ("rakuyosho"), (*Larix Kaempferi* SARG.), (Larch).
Brown rotted "sugi" (*Chamaecyparis obtusa* S. et Z.), (Japanese cypress).
White rotted "yezomatsu" (*Picea jezoensis* CARR.), (Spruce).

(c) Butanol pulp: Prepared from dry saw dust of "shina" (*Tilia japonica* SIMK) (100 g) digested with a mixture of butanol (1 ℓ) water, (1 ℓ) and sodium hydroxide (8 g) at 158°, under a pressue of 132 lb/in^2, in an autoclave. Obtained pulp was washed with water and dried.

(d) Mandarin orange peel: Samples were taken from fruits of medium size.

(e) Sulphuric acid: Diluted the concentrated sulphuric acid c. p. grade (ca. 98 per cent) with distilled water.

(f) Water: Used a normal distilled water, not conductivity water.

Both raw materials (a) and (b), were dried at 105° in an oven, and ground with Wiley mill and were sifted through a 17-mesh sieve. Material (c) was only shredded while (d) was dried, ground, and sifted through a 17-mesh sieve.

Method of testing the adsorptive (decolorizing) power and the preparation of testing solutions.

For testing the adsorptive power of the active charcoal, the decolorization of methylene blue and caramel solution was adopted. The procedures for preparation of these solutions were in accordance with the test procedures which are given in the Official Gazette (Kanpo), June 19, 1947[7], but the methylene blue test was somewhat modified for the sake of convenience.

The so-called standard methods of estimation have comparison value only. Adsorption of color by carbon has been shown to be an equlibrium reaction in which materials other than coloring agents take part in the equilibrium.

(A) Methylene blue test.

The preparation of 0.15 per cent methylene blue solution.

"Methylene blue f. Bac. Koch" Dr. G. GRÜBLER & Co. LEIPZIG, was used. It was dried in a desiccator over calcium chloride for several days. Weighed 1.7536 g (amount of the water of crystallization was calculated for $C_{16}H_{18}N_3SCl \cdot 3H_2O$) and dissolved with 1000 g of water. This 0.15 per cent methylene blue solution had a pH value of 2.3.

The preparation of the standard solution for comparison of the degree of decolorization.

For comparison of the color of the decolorized solution by the colorimetric method a series of standard solutions of methylene blue were made from the 0.15 per cent solution above described. First, the 0.15 per cent solution was diluted to 1/1000 of its concentration using a measuring flask, and again this diluted solution was diluted. Ten standard solutions were made which had concentrations of 1/10000, 2/10000, 3/10000, 4/10000, 5/10000, 6/10000, 7/10000, 8/10000, 9/10000, and 10/10000 =1/1000 of the 0.15 per cent solution. Ten glass test-tubes of the same size, thickness of wall and color of the glass were selected; in each of them respectively was placed 9 mℓ, 8 mℓ, 7 mℓ, 6 mℓ, 5 mℓ, 4 mℓ, 3 mℓ, 2 mℓ, 1 mℓ, and 0 mℓ of distilled water. To these test-tubes were added respectively the 1/1000 diluted 0.15 per cent (0.00015%) solutions of methylene blue; the whole volume of the solution in the each test-tube was made up to 10 mℓ. Then tubes were tightly stopped with cork, and for convenience numbered, No. 1, No. 2, No. 3, …… No. 7, No. 8, No. 9, and No. 10 in order of dilute concentration (No. 1 was the most dilute solution). These standard solutions were stored out of day-light; if the color perchance faded new standard solutions were prepared.

Testing procedure.

In the 50 mℓ glass stoppered Erlenmeyer flask or weighing bottle was placed 0.1 g equivalent weight of active charcoal (as the hydrated active charcoal was stored and available in wet state, it was not possible to weighed in moisture-free state directly) and 15 mℓ of 0.15 per cent methylene blue solution was added. Then this mixture was shaken by hand for 5 minutes at room temperature (15–23°), and filtered without suction with Toyo filter paper No. 7. The first few mℓ of filtrate were thrown away in consideration of the adsorption by the filter paper, and the most of the filtrate was taken in the test-tube having the same qualities as the tubes in which standard solution was contained.

Compared the color with the standard solution by the naked eye, and recorded the degree of decoloration by the number of the standard comparing solutions; if it came to between No. 3 and No. 4, the degree of the sample was recorded as No. 3.5 (this number is only for convenience and not mathematical). Commonly 15 mℓ of methylene blue solution were added however, when the color of the decolorized filtrate was more dark than No. 1 of the standard solution, 13 mℓ was added to the active carbon sample, and when it was lighter than No. 1, 20 mℓ was added.

(B) Caramel test.

Preparation of reagents.

Twelve grams of c.p. saccharose (Takeda Pure Chemicals Ltd.) was dissolved with 8 mℓ of distilled water, and 5 mℓ of dilute sulphuric acid (1 mℓ of conc. sulphuric acid (d, 1.84) and 4 mℓ of distilled water) were added. The solution was heated on a water bath for 30 minutes; while it was still hot 2 g of sodium hydroxide were added and mixture was boiled on a wire gauze. After this was cooled (some resinous matter was precipitated) it was neutralized with dilute sodium hydroxide solution (with litmus test paper) and diluted to 120 mℓ with distilled water in a measuring cylinder. Then filtered, and this filtrate was stored with same care as the original solution. The test solution was prepared by means of adding 500 mℓ of distilled water to 40 mℓ of this original solution.

Testing procedure.

In a 100 mℓ glass stoppered Erlenmeyer flask or weighing bottle was placed 0.1 g equivalent weight of the active charcoal, and 40 mℓ of the above described test solution was added. The mixture was shaken for 1.5 minutes at room temperature (13–23°) by hand with the amplitude of 10 cm. and the number of vibrations was 160/min. Then sample was filtered with Toyo filter paper No. 7 without suction. Resultant filtrate was compared with equal amount of the test solution by DUBOSQ's colorimeter, in which the decolorized caramel solution was placed at the depth of 45 in the scale and the depth of the standard solution was varied till the color state became of the same tone with that of the decolorized caramel solution. When the reading of the scale was

Y, the percentage of decoloration may be calculated according to the following equation:

$$\text{Percentage of decolorization} = \left(1 - \frac{Y}{45}\right) \times 100$$

By this percentage of decoloration was shown the power of adsorption of the active charcoal.

Method of determination of ash in the hydrated active charcoal.

The content of ash in the active charcoal was determined by means of micro-analysis[8] with 50 mg of oven dried samples.

Determination of hydrogen ion concentration.

As it is said that pH value exerts considerable influence on the adsorption considerably, the pH value of the wash water at the preparation of the hydrated active charcoal and of the filtrate at the test procedure was measured by means of antimony electrode hydrogen ion concentration (pH) meter.

In order to correct the pH-meter, Clark and Lubs[12] buffer solution was prepared as follows:

Clark and Lubs' Buffer solution (total volume, 200 mℓ) at 20°.

0.2 M NaOH (mℓ)	9.2 M KH_2PO_4 (mℓ)	pH
5.70	50	6.0
29.63	50	7.0
46.80	50	8.0

Katsuta and Okabe[11] have reported that the adsorption of methylene ble is not influenced by pH within the acidic range pH, 2.07~6.95.

Calibration of pH-meter.

With Clark and Lubs' buffer solution the pointed scale of the pH-meter was calibrated as follows:

Solution	Standard pH	pH value expressed by pH-meter	Deviation	Average Deviation
Standard pH sol. Shimazu's	2.04	3.2	+1.16	+1.17 ≒1.2
Clark and Lubs' Buffer solution	6.0	7.1	+1.1	
"	7.0	8.2	+1.2	
"	8.0	9.9	+1.2	

It was known that the value which this pH meter expressed is higher than correct pH, and that the average deviation is about 1.2; then calibration was dependent upon this value.

Experiments on the Preparation of Hydrated Active Charcoal.

To study the suitable conditions for the preparation of the hydrated active charcoal, following factors having influence upon the activities of the products were considered.

(I) Wood species, (II) Quantity of acid, (III) Decay of wood, (IV) Concentration of acid, (V) Duration of heating, (VI) Pre-treatment (stirring at room temperature), (VII) Carbonization at lower temperature and increasing the time, (VIII) Pre-treatment (extraction of raw materials with alcohol-benzene), and comparison of charcoal from wood, mandarin orange peel and butanol pulp.

(I) Effect of wood species.

Most popular and much accumlated wood species were selected such as "todo" and "yezomatsu" as softwood and "shina" and "nara" as hardwood, as previously mentioned in the paragraph on the raw materials. Under the same conditions those wood samples were treated and the dehydrated active charcoal was prepared; then the yields and properties were compared.

Referring to MIZUNO and KATO's method, the procedure of preparation were chosen as follows. Each 10 g of oven dried sawdust from four kinds of wood, which passed through a 17-mesh sieve, were placed in ca. 300 mℓ beakers, 50 g of 70 per cent sulphuric acid (quintuple amount of the material), were added and material was stirred with a glass rod in a 80° water bath for one and a half hours. Then sample was transferred into a small mortar and ground, again transferred into the previous beaker and placed in a 150° controlled oven (air-bath) for 8 hours. During the heating, dehydration and carbonization were proceeded and water vapor, SO_2 and other gaseous matters were expelled. Then cooled in a desiccator over calcium chloride and weighed; determined the evaporation percentage during carbonization. Next these products were ground again in a mortar and then filtered on a Buchner's funnel with filter paper by washing with 2000 mℓ of boiling distilled water in several portions.

According to saccharification (hydrolysis) effect, a slight sweet odour was smelled when the first boiling distilled water was added to the charcoal. Some mℓ of the last filtrate was placed in a test-tube and its pH value was determined using pH meter. The wet charcoal was then transferred into a watch glass and weighed, and stored in a glass-stoppered jar. The water contents were determined by usual method with a portion of this product and the yields were calculated on the basis of oven-dry materials. The ash contents were also determined by the usual method.

During pre-heating at 80° in this procedure, the reactions differed by the wood species. "shina" was dissolved most easily, then "nara", next "yezomatsu", while "todomatsu" was hard to dissolve. After one hour "yezo" and "todomatsu" melted completely, "shina" became slightly cohesive, and "nara" was a little more gelatinized. Data resulting from the experiments are recorded in Table 1.

Table 1. Data on preparation of the hydrated active (H-A) charcoals with the most popular wood in Hokkaido.

No. Wood species	Weight after carbon. (g)	Evaporation (%)	pH of last filtr.	Wt. of wet prod. (g)	Moisture (%)	Yield Wt. (g)	Yield (%)	Ash (%)
[I] 1 "todomatsu"	35.7	40.50	3.2	26.6	76.61	6.22	62.22	0.18
[I] 2 "yezomatsu"	41.3	31.17	4.0	26.5	77.33	6.01	60.08	0.17
[I] 3 "shina"	37.9	36.83	3.3	28.3	80.44	5.54	55.35	0.63
[I] 4 "nara"	38.5	35.83	4.4	27.7	78.51	5.95	59.53	0.31

* Weight of the sample was 10 g ; treated with 50 g of 70%-H_2SO_4.

Table 2. and **Fig. 1.** Adsorptive power of H-A charcoals.

No. Wood	Methylene-blue △ 13 mℓ	Methylene-blue pH	Methylene-blue ○ 15 mℓ	Methylene-blue pH	Caramel Reading of scale	Caramel De- × colorization (%)	Caramel pH
[I] 1 "todo"	No. 4.5	2.3	No. 7.5	2.2	12.0	73.33	—
[I] 2 "yezo"	3.0	2.2	6.0	2.3	12.0	73.33	—
[I] 3 "shina"	2.0	2.2	7.0	2.2	11.0	75.56	—
[I] 4 "nara"	1.0>	2.1	1.0>	2.3	9.5	78.89	—

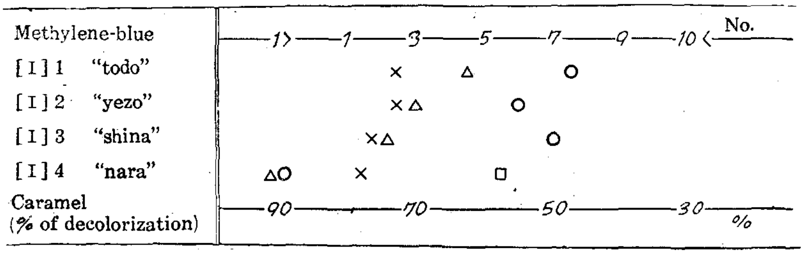

Fig. 1.

△ : Methylene-blue 13 mℓ. ○ : Methylene-blue 15 mℓ. □ : Methylene-blue 20 mℓ. × : Caramel test. From above figures.

Adsorptive powers were tested by means of standard methylene blue test and caramel test as was described above. The results are shown in Table 2 and Fig. 1.

From the results, it is to be seen that ash content of the charcoals made from hard woods was higher than that from softwoods, and the charcoal from "shina" wood had the highest ash content. The activities of the charcoals made from hardwoods were better than those from softwoods, and that from "nara" was the best and that from "todomatsu" was the poorest. The fact that the charcoal made from "nara" (oak) shows the best decolorizing activity agrees with the facts that oak has heavy (dense) and compact tissues and that generally the active carbons made from the materials which have such compact tissues (like coconut, etc.) show high activities.

It seems that the ash contents have not exerted influence upon the adsorptive power in these charcoals.

(II) Quantity of acid.

In order to test the influence of the quantity of acid used upon the activity of the charcoal, the used quantity of 70 per cent sulphuric acid was reduced to quadruple of the weight of the wood sample.

Taking consideration of the results of the above experiment, in this case the time of pre-heating at 80° was also reduced to one hour, and

Table 3. Data on preparation of H-A charcoals with reduced quantity of acid.

No. Wood species	Wt. after carbn. (g)	Evaporation (%)	pH of last filtr.	Wt. of wet prod. (g)	Moist. (%)	Yield		Ash (%)
						Wt. (g)	(%)	
[II] 1 "todomatsu"	36.1	56.80	3.2	27.5	76.13	6.56	65.64	0.10
[II] 2 "yezomatsu"	36.1	47.80	3.4	29.7	79.48	6.09	60.94	0.13
[II] 3 "shina"	32.0	56.00	3.3	29.6	77.60	6.63	66.30	0.71
[II] 4 "nara"	30.3	59.40	3.3	24.7	77.47	5.56	55.65	0.30

Table 4. and Fig. 2. Adsorptive power of H-A charcoal made with reduced quantity of acid.

No. Wood	Methylene-blue				Caramel		
	13 mℓ △	pH	15 mℓ ○	pH	Reading of scale	De- × colorization (%)	pH
[II] 1 "todo"	No. 5	2.2	No. 2.0	2.0	14.0	68.89	—
[II] 2 "yezo"	5.5	2.1	8	2.2	12.5	72.22	—
[II] 3 "shina"	2.5	2.2	6	2.1	12.0	73.33	—
[II] 4 "nara"	1>	2.3	1>	2.3	9.0	80.00	—

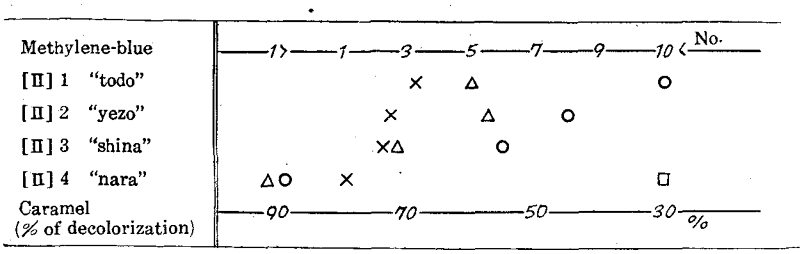

Fig. 2.

the grinding process in a mortar after the pre-heating was ommited. The other conditions were the same as in experiment (I). The results of this varied method preparation are givenin Table 3.

The results of testing the activities are shown in Table 4 and Fig. 2. Judging from these results, such a small decrease of acid quantity had only a little effect, and "nara" was the best and "todomatsu" was the worst in adsorptive power. To compare the activites of the charcoals, methylene blue test with addition of 20 mℓ of methylene blue solution was tested. It was found that the charcoal made from "nara" with quintuple amount of acid showed better activity than that with quadruple amount of acid, as indicated in Table 5.

Table 5. Comparison of activities in Exp. I and Exp. II.

No. Wood	Methylene-blue	
	20 mℓ □	pH
[I] 4 "nara"	No. 5.5	2.6
[II] 4 "nara"	10.0<	2.4

(III) Effect of decay of wood.

In the decayed wood, depending upon the kind of attacking wood-rot fungi, there are found white rot — attacks lignin in preference to cellulose and allows more cellulose to remain, brown rot — attacks cellulose more rapidly than lignin and allows more lignin to remain, and intermediate rot — attacks both lignin and cellulose to an equal extent[10]. The chemical composition of the wood differs great by the types of rot[10]. In company the activities of hydrate active charcoals that were made from these decayed woods, there is also convenient opportunity to test whether lignin has a bad influence upon the activity. If it is possible to obtain the charcoal that has a good activity, it is interesting in connection with the utilization of decayed wood.

As the raw materials, the authors used (1) brown rotted "hinoki" (Japanese cypress), (2), (3), (4), white rotted "yezomatsu" (Spruce) [order of degree of decay was (2) (3) (4), and order of lignin content was (4) (3) (2)], and (5) brown rotted wood of "karamatsu" (Larch).

The conditions of the preparation of the charcoal were the same as in Experiment (II) with quintuple amount of sulphuric acid. The quantity of woods in this experiment and hereafter used was 5.0 g in dry-weight. The results are given in Tables 6, 7 and in Fig. 3.

Table 6. Data on preparation of H-A charcoals from decayed woods.

No.	Wood species	Wt. after carbon. (g)	Evapo-ration (%)	pH of last filtr.	Wt. of wet prod. (g)	Moist. (%)	Yield		Ash (%)
							Wt. (g)	(%)	
[III] 1	"hinoki" (B)	17.5	41.67	3.8	14.2	72.49	3.91	78.13	0.17
[III] 2	"yezomatsu" (W)	15.5	48.33	3.7	15.3	80.05	3.05	61.05	0.17
[III] 3	"	15.3	49.00	3.6	15.7	81.04	2.98	59.53	0.13
[III] 4	"	13.4	55.33	3.4	14.1	78.90	2.98	59.50	0.29
[III] 5	"karamatsu" (B)	18.7	37.67	3.9	12.7	70.17	3.79	75.77	1.74

Table 7. and **Fig. 3.** Adsorptive power of H-A charcoals from decayed woods.

No.	Wood	Methylene-blue				Caramel		
		13 mℓ △	pH	15 mℓ ○	pH	Reading of scale	Decolor-× ization (%)	pH
[III] 1	Brown rotted "hinoki"	No. 1>	2.6	No. 1>	2.4	24.0	46.67	—
[III] 2	White rotted "yezomatsu"	2	2.6	3.5	2.3	8.5	81.11	—
[III] 3	"	1>	2.4	3.0	2.5	12.0	73.33	—
[III] 4	"	1>	2.5	3.0	2.5	15.5	65.56	—
[III] 5	Brown rotted "karamatsu"	—	—	7	2.8	30.0	33.33	5.2

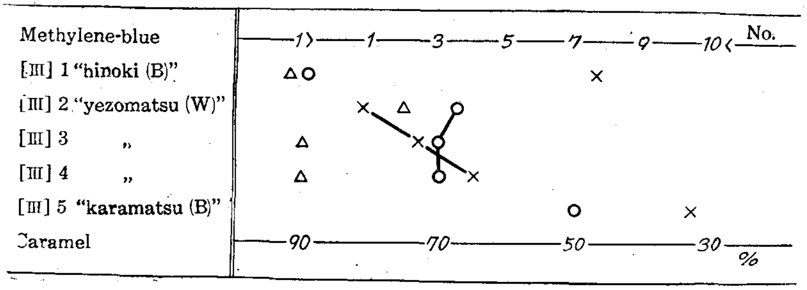

Fig. 3.

The yields of the charcoals made from rotted wood that has much lignin are high. It seems the high lignin content that is a reason why the brown-rotted wood has a high carbon content and is with difficulty dehydrated with sulphuric acid. The high ash content of the charcoal from brown rotted "karamatsu" (larch) seems expectable, because of the high ash content in the wood (1.27 per cent).

However it must be noted that the ash content is rather increased in the charcoal, but dissolves the ash into solution by sulphuric acid in this experiment.

To discuss the results exhibited in Table 7 and Fig. 3, the charcoal made from brown rotted wood of "hinoki" (Japanes cypress) adsorbed methylene blue very well but did not adsorb caramel very well; the charcoal made from brown-rotted wood of "karamatsu" (larch) adsorbed methylene blue a little but not caramel at all. In white rotted woods of "yezomatsu" (spruce), the more the decay progressed, the more methylene blue was adsorbed, however, the less the caramel was adsorbed. By this fact it is found that the result of methylene blue test does not always run parallel with that of caramel test. From the authors' expriments with decayed wood, it appears probable that there are some relations between the adsorptive power of the H-A charcoal made from it and the β-cellulose content of the wood that was used as the raw material[10].

It may also prove that from decayed wood it is possible to obtain hydrated active charcoals which have excellent qualities, and that lignin is not always harmful to the activity of the charcoal produced.

(IV) Comparison with other commercial active carbons.

In order to compare the decolorizing power of the hydrated active charcoal with other commercial active carbons, (S) 1 Merck animal carbon (which has been stored in our laboratory), (S) 2 Ta··· Chemical Ltd. (ditto), (S) 3 and (S) 4 two kind of active carbon A and B (which had been stored at the Pharmaceŭtical Factory of the Hokkaido Dairy Farming Co-operative Co. Ltd. for purification of penicillin) were tested by means of the methylene blue and caramel tests. Moisture and ash content and 0.1 g equivalent weight were given in Table 8.

Table 8. Moisture and ash content of the commercial active carbons.

Sample No.	Mark	Moisture content (%)	Ash content (%)	0.1 g equivalent Wt. (g)
[S] 1	Merck	17.22	1.85	0.1208
[S] 2	Ta	24.33	1.77	0.1322
[S] 3	A	20.42	9.45	0.1257
[S] 4	B	22.32	24.78	0.1287

The ash content of these carbons was rather high, especially the sample (S) 4 was high in that respect.

The results of test are set forth in Table 9 and Fig. 4.

In this experiment, the results of methylene blue test run almost parallel to those of caramel test. (S) 2 sample showed a good activity especially in caramel test, however the other three carbons showed not good results.

Table 9. and **Fig. 4.** Adsorptive power of the commercial active carbons.

Sample No.	Methylene-blue						Caramel		
	5 mℓ ●	pH	13 mℓ △	pH	15 mℓ ○	pH	Reading of scale	Decolor-× ization (%)	pH
[S] 1 Merck	No. —	—	No. 10<	—	No. 10<	1.9	30.0	33.33	6.4
[S] 2 Ta	—	—	5	2.3	10	3.2	8.5	81.11	6.1
[S] 3 A	7	5.9	—	—	10<	—	35.0	22.22	6.8
[S] 4 B	1>	4.9	—	—	10<	4.1	27.0	40.00	6.6

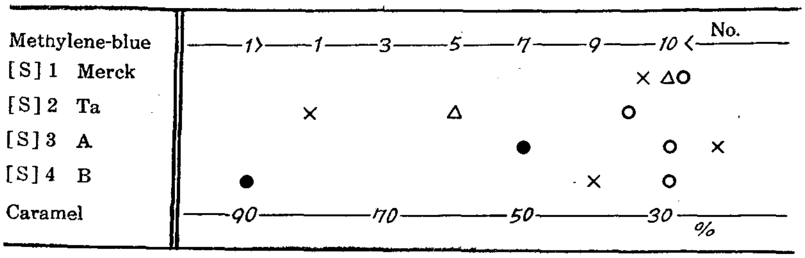

Fig. 4.

(V) Concentration of acid.

In this experiment "nara" (oak) wood was chosen as raw material, from which prepared charcoal had a good adsorptive power. Hydrated active charcoals were prepared under similar conditions to those above described, but only the acid concentrations were varied to 60, 65, 70, 75 and 80 per cent. Five grams of oven-dried wood and 25 g of acid were taken. The data of preparation are given in Table 10 and the results of decolorizing test are shown in Table 11 and Fig. 5.

Table 10. Data on preparation of H-A charcoals from "nara" wood with various concentration of sulphuric acid.

Sample No.	Conc. of H_2SO_4 (%)	Wt. after carbon. (g)	Evaporation (%)	pH of last filtr.	Wt. of wet prod. (g)	Moist. (%)	Yield		Ash (%)
							Wt. (g)	(%)	
[IV] 1	60	13.1	56.33	3.6	10.6	73.63	2.80	55.90	0.29
[IV] 2	65	16.5	46.70	3.8	12.2	75.41	3.00	60.00	0.30
[IV] 3	70	19.5	35.00	3.8	13.3	76.68	3.10	62.03	0.25
[IV] 4	75	20.5	31.67	3.2	15.2	79.55	3.11	62.17	0.30
[IV] 5	80	18.1	39.67	3.8	12.8	76.55	3.00	60.03	0.46

Table 11. and **Fig. 5.** Adsorptive power of H-A charcoals made from "nara" wood with various conc. of H_2SO_4.

Sample No.	Conc. (%)	Methylene-blue						Caramel		
		13 mℓ△	pH	15 mℓ○	pH	20 mℓ□	pH	Reading of scale	De- × colorization (%)	pH
[IV] 1	60	No. 1.5	2.9	No. 2	2.9	No. —	—	24.0	46.67	4.9
[IV] 2	65	1>	2.9	1>	2.9	2.5	2.9	13.5	70.00	5.2
[IV] 3	70	2	3.1	2.5	2.9	10<	2.9	19.0	57.78	5.1
[IV] 4	75	1>	3.3	1.5	2.8	—	—	7.5	83.33	5.0
[IV] 5	80	1>	3.0	3	3.0	—	—	15.0	66.67	5.0

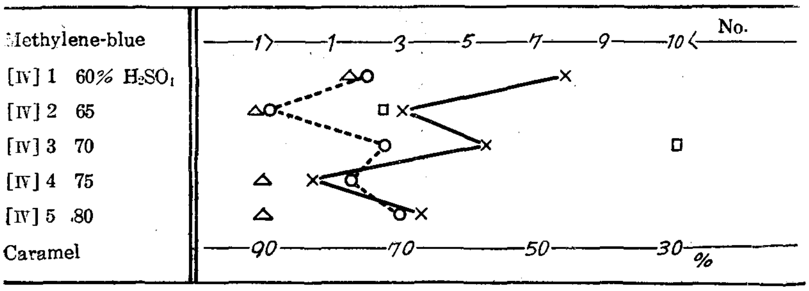

Fig. 5.

According to these results, the charcoals that were made with 65 and 75 per cent of sulphuric acid adsorbed well, and the adsorptive power of the product treated with 70 per cent of sulphuric acid lay between those of 65 and 75 per cent acids. Generally, good activities were obtained with 65~75 per cent of sulphuric acid. It seems that such results are due to the fact that the sulphuric acid of these concentrations has a hydrated form ($H_2SO_4 \cdot H_2O$) which reacts well to the raw material of wood.

(VI) The influences of the length of carbonization time and the stirring at room temperature in pre-treatment.

In order to test the influences of the heating time upon the activity of the charcoals, time periods were varied to 6, 8 and 10 hours on each concentration of the acids of 65, 70 and 75 per cent respectively. In this experiment the pre-treatment was done with stirring at room temperature (ca. 11°) for an hour with and without heating, and the other conditions were the same as those in preceding experiment (V). The results are recorded in Table 12.

The longer the time of heating for dehydration, the greater the amount of losses by evaporation during carbonization (dehydration). But the yield was decreased with the lengthening of the time of heating.

Table 12. Data on preparation of H–A charcoals with various time of heating and conc. of H_2SO_4, pre-treated with and without heating.

Sample No.	Conc. of H_2SO_4 (%)	Time of heat. (hr)	Wt. after carbon. (g)	Evaporation (%)	pH of last filtr.	Wt. of wet prod. (g)	Moisture (%)	Yield Wt. (g)	Yield (%)	Ash (%)
[V] 1	65	6	18.7	37.67	4.2	14.2	78.39	3.07	61.37	0.20
[V] 2		8	14.6	51.33	4.1	11.2	73.70	2.95	58.91	0.19
[V] 3		10	13.2	56.00	4.6	9.6	70.11	2.87	57.39	0.34
[V] 4	70	6	18.2	39.33	4.1	16.0	81.34	2.99	59.71	0.59
[V] 5		8	17.3	42.33	4.7	12.7	79.15	2.63	52.96	0.34
[V] 6		10	13.4	55.33	4.1	9.9	70.79	2.89	57.84	0.25
[V] 7	75	6	21.5	28.33	5.4	16.2	80.54	3.15	63.05	0.20
[V] 8		8	19.9	33.67	4.8	13.4	78.20	2.92	58.45	0.27
[V] 9		10	15.4	48.67	4.7	10.5	73.02	2.83	56.66	0.24
[V] 10*	70	8	12.6	58.00	4.8	8.0	63.85	2.99	59.84	0.54

* Pre-treated without heating (stirring at room temperature).

Also the higher the concentration of the acid, the smaller the amount of losses by evaporation, with small yield at 70 per cent acid, and when material was treated at room temperature in the pre-treatment. The losses by evaporation were much in amount and the moisture contents of the product were low.

The results of decolorization tests are given in Table 13 and Fig. 6.

In the methylene blue test, the charcoals that were carbonized for 8 hours showed good activities in each concentration of acids especially

Table 13. and Fig. 6. Adsorptive power of H–A charcoals made from "nara" wood with various time of heating and concentration of acid and pre-treated with and without heating.

Sample No.	Conc. of H_2SO_4 (%)	Time of heat (hr)	Methylene-blue 15 mℓ ○	Methylene-blue pH	Caramel Reading of scale	Caramel De- × colorization (%)	Caramel pH
[V] 1	65	6	No. 2	3.1	7.0	84.44	5.4
[V] 2		8	1>	3.2	10.0	77.78	5.2
[V] 3		10	3.5	3.2	21.0	53.33	5.1
[V] 4	70	6	2	3.3	5.0	88.89	5.0
[V] 5		8	1>	3.2	5.0	88.89	5.1
[V] 6		10	6	3.2	12.0	73.33	5.1
[V] 7	75	6	3.5	3.2	5.0	88.89	5.4
[V] 8		8	3	3.2	9.5	78.89	5.4
[V] 9		10	7	3.2	12.5	72.22	5.1
[V] 10*	70	8	6	3.2	18.0	60.00	5.1

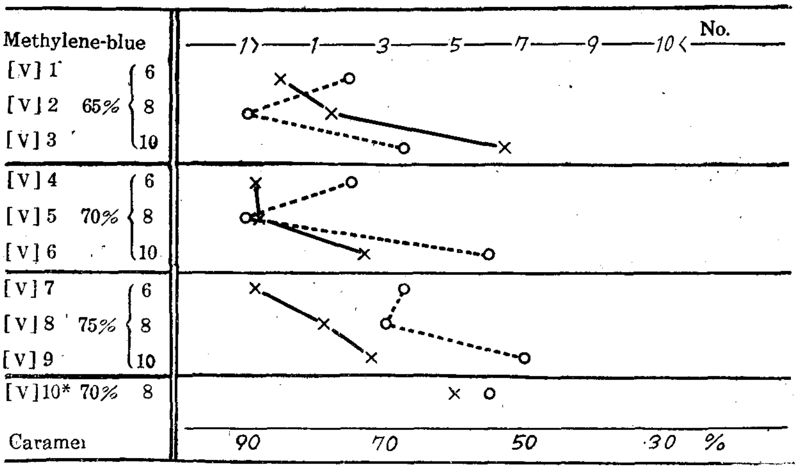

Fig. 6.

65 and 70 per cent. In the caramel test the decolorizing properties were lowered as the time of heating for carbonization was increased. In this experiment the products (V) 4, (V) 5 and (V) 7 showed very high decolorizing power in the caramel test. However, the products which were prepared with 70 per cent sulphuric acid and carbonized for 8 hours showed good results in both test. Therefore, these conditions seem to be optimum conditions to prepare the hydrated active charcoals; but it also seems that the stirring at room temperature in the pre-treatment exerted a bad influence upon the decolorizing preperties of the products.

(VII) Carbonization at comparatively lower temperatures and increase in the time of heating.

The sample ("nara" wood sawdust) was treated at 120°, the time of carbonization was regulated at 8, 9, 10, 11 and 12 hours, and the other conditions were just same as in the preceding experiment. Data of this experiment are given in Table 14.

Table 14. Data on preparation of H-A charcoals from "nara" sawdust carbonized at comparatively lower temperature and increasing time.

Sample No.	Time of heat. (hr)	Wt. after carbon. (g)	Evaporation (%)	pH of last filtr.	Wt. of wet prod. (g)	Moist. (%)	Yield		Ash (%)
							Wt. (g)	(%)	
[VI] 1	8	23.4	22.00	4.85	14.6	79.43	3.00	60.06	0.37
[VI] 2	9	22.5	25.00	4.8	14.5	77.61	3.25	64.93	0.21
[VI] 3	10	21.9	27.00	4.6	15.8	80.02	3.16	63.14	0.27
[VI] 4	11	18.9	37.00	4.95	13.3	76.98	3.06	61.23	0.22
[VI] 5	12	21.4	28.67	4.65	13.2	75.31	3.26	65.18	0.41

* Pre-treatment with stirring at a room temperature.

The results of testing the decolorization power of these charcoals are recorded in Table 15 and Fig. 7.

Table 15. and **Fig. 7.** Adsorptive power of H-A charcoals made from "nara" sawdust carbonized at lower temperature and increasing heating-time.

Sample No.	Time of heat. (hr)	Methylene-blue				Caramel		
		15 mℓ ○	pH	order	state of decolorization	Reading of scale	De- × colorization (%)	pH
[VI] 1	8	No. 10<	3.3	3	considerably dark	11.0	75.56	5.6
[VI] 2	9	10<	3.3	4	a little dark	14.5	67.78	5.6
[IV] 3	10	10<	3.3	2	dark a little	9.0	80.00	5.5
[VI] 4	11	3.5	3.3	1	most light	13.0	71.11	5.5
[VI] 5	12	10<	3.1	5	most dark	16.0	64.40	5.5

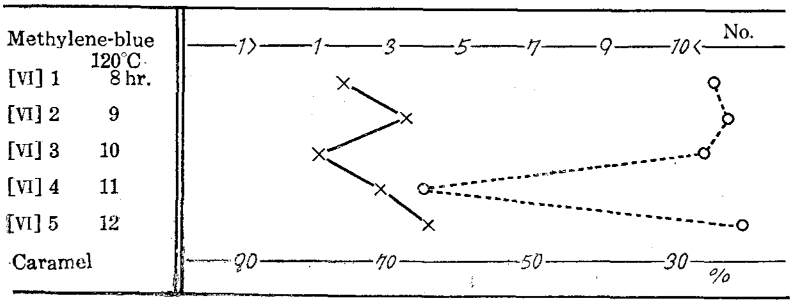

Fig. 7.

In this experiment the decolorizing power in the caramel test of these products was comparably good, but the decolorizing power in the methylene blue test proved weak. It seems that 10 and 11 hours were good for the carbonization, and increasing of time of heating may have more and more adversely effected the activities of the products, the properties of the charcoals that were prepared with heating at 120° were different from those which were prepared at 150°.

(VIII) Influence of extraction of the raw materials with alcohol-benzene and experiments to compare the hydrated active charcoal made from wood with that from mandarin orange peel and butanol pulp.

The following raw materials were used, (1) mandarin orange peel, (2) butanol pulp, (3) "nara" (oak) saw-dust which had been extracted previously with alcohol-benzene (1 : 1) for 8 hours in SOXHLET's extractor, and (4) "nara" sawdust not extracted. Each 5 g of these materials (oven dried) were added with 25 g of 70 per cent sulphuric acid, and heated under stirring in an 80° water bath for an hour (one sample of mandarin orange peel was treated for an additional 30 minutes). The appearances of these reaction mixtures were as follows:

During 7 minutes just after addition of acid: Sample (1) was dissolved almost into a solution, (2) was dissolved gradually and foamed at beginning and colored red, (3) and (4) were almost dissolved but a small insoluble portion remained.

After 10 minutes: (1) became solution, (2) was dissolved completely and foams were disappeared, (3) and (4) became somewhat cohesive.

After 20 minutes: (1) became merely cohesive, (2) had a liquid state, (3) became considerably cohesive, (4) was more cohesive than (3).

After 45 minutes: (1) showed a slightly viscous state, (2) appeared colloidal like a boiled starch solution, (3) and (4) became more cohesive.

After 50 minutes: (1) became jelly-like and had smooth and lustrous surface, (2) became like a jelly but had rough and less lustrous surface, (3) highly cohesive but not lustrous and had rough surface, (4) was more cohesive than (3).

After 1 hour: (1) became cohesive jelly-like, (2) appeared to have rather much moisture, (3) became very cohesive, lumpish a little, and (4) became highly cohesive, lumpish, and did not adhere to the bottom of the beaker.

One of the samples (1) was treated for an additional 30 minutes more in 80° water bath with continued stirring; after 70 minutes from the first addition of acid it became viscous and lumpish a very little; after 80 minutes it was not varied from the last appearance.

Then each mixture was heated at 150° for 8 hours, and cooled in a desiccator over calcium chloride and weighed.

In respect to the appearances of the charcoals after carbonization, the charcoal made from mandarin orange peel that was pre-heated for one and a half hours was porous and the most lustrous, and that which was pre-heated for an hour was porous with small pores and less lustrous than the former; the charcoal made from butanol pulp had many small pores and was moderatly lustrous. The charcoals made from "nara" sawdust appeared lumpish, but not lustrous and appeared like a dried mud.

These carbonized substances were treated by ordinary procedure, and following data were obtained as shown in Table 16.

The charcoal which was prepared from butanol pulp had a little more of ash content and low yield.

The results of the test for the adsorptive power are shown in Table 17 and Fig. 8.

For the charcoal made from mandarin orange peel, the longer

Table 16. Data on preparation of H-A charcoals from mandarin orange peel, butanol pulp, and extracted and unextracted "nara" sawdust.

No.	Raw material	Wt. after carbon. (g)	Evaporation (%)	pH of last filtr.	Wt. of wet prod. (g)	Moist. (%)	Yield Wt. (g)	Yield (%)	Ash (%)
[VII] 1	Orange peel*	17.3	42.33	4.8	11.0	76.72	2.56	51.22	0.38
[VII] 2	Orange peel**	19.6	34.67	4.5	13.3	79.82	2.68	53.68	0.37
[VII] 3	Butanol pulp	20.2	32.67	5.1	13.9	82.45	2.44	48.79	1.47
[VII] 4	"nara sawdust***"	18.3	39.00	5.1	12.8	76.60	3.00	59.90	0.36
[VII] 5	" ****	15.8	47.33	4.9	10.0	73.42	2.66	53.16	0.29

* Pre-heated for 1 hour.
** Pre-heated for 1.5 hours.
*** Extracted with alcohol-benzene.
**** Unextracted.

Table 17. and Fig. 8. Adsorptive power of the H-A charcoals from mandarin orange peel, butanol pulp, and extracted and unextracted "nara" sawdust.

Sample No.	Wood	Methylene-blue 15 mℓ ○	Methylene-blue pH	Caramel Reading of scale	Caramel Decolor- × ization (%)	Caramel pH
[VII] 1	mandarin orange peel (1 hr)	No. 3	3.3	16.0	64.44	5.4
[VII] 2	" (1.5 hr)	6	3.3	15.0	66.67	5.5
[VII] 3	Butanol pulp	1>	3.3	11.0	75.56	5.3
[VII] 4	"nara" (Alcohol-Benzene)	2	3.3	12.0	73.33	5.4
[VII] 5	"	3	3.3	17.0	62.22	5.3

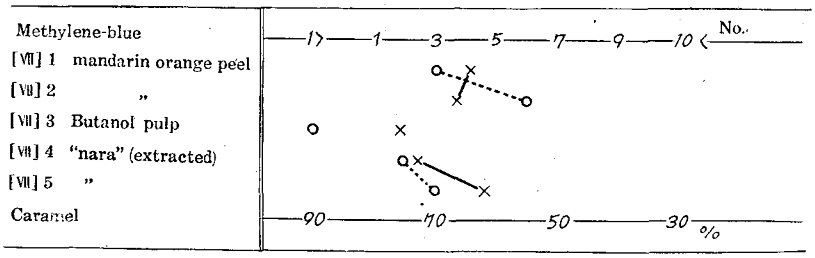

Fig. 8.

pre-treatment had somewhat favorable influence on the adsorption of methylene blue, but on the adsorption of caramel the influence was somewhat unfavorable. The charcoal made from mandarin orange peel was always not so excellent as that made from "nara" (oak) sawdust, in this experiment (VII). The adsorptive power of both these charcoals showed similar degree, however in the other experiments the charcoals made from "nara" sawdust were better than those from mandarin orange peel in respect to the adsorptive power. The charcoal that was made from butanol pulp decolorized well both methylene blue and caramel. The influences an extraction of the raw materials with alcohol-benzene on the activities of the products were not very remarkable, however it seemed to exert some beneficial effect upon the activities. The extraction of such components as essential oil and resinous matter did not much influence the activity in the case of "nara" wood. But it may be necessary to study further the cases of the wood which contains much essential oil and resin.

Recovery of sulphuric acid.

The concentration of sulphuric acid that is used in the preparation of the hydrated active charcoal is high. Following the dehydration and carbonization reaction the acid is washed with boiling distilled water, and the initial washing water contains a considerable amount of sulphuric acid which may be recovered. Therefore experiments on acid recovery were made in the preparation of the hydrated active charcoal with "nara" (oak) sawdust.

Twenty grams of dried sawdust (passed through 17-mesh sieve) was placed in a small beaker, added with 100 g of 70 per cent sulphuric acid, and stirred in a water bath at 80° for an hour. The mixture was placed in a 150° drying oven for 8 hours. Then the reaction mixture

Table 18. Recovery of sulphuric acid.

No.	Volume of washing		Conc. of filtrate	Weight of H_2SO_4 in filtrate	Percentage* of recovery	
	Each filtrate (mℓ)	Cumulative sum (mℓ)	(N)	(g)	In each portion (%)	Cumulative sum (%)
1	80	80	5.3314	20.8990	29.86	29.86
2	208	288	2.3516	23.9670	34.24	64.10
3	267	555	0.9211	12.0508	17.22	81.32
4	175	730	0.6393	5.4818	7.83	89.15
5	186	916	0.2864	2.6102	3.73	92.88
6	197	1113	0.1209	1.1671	1.07	94.55
7	168	1281	0.0561	0.4620	0.66	95.21
8	178	1459	0.0255	0.2221	0.32	95.53
9	222	1681	0.0188	0.1285	0.18	95.71
10	338	2019	0.0053	0.0875	0.12	95.83
Total	2019			67.0758	95.83	

* Percentage of recovery was calculated on the basis of 70 g sulphuric acid contained in 100 g of 70%-H_2SO_4.

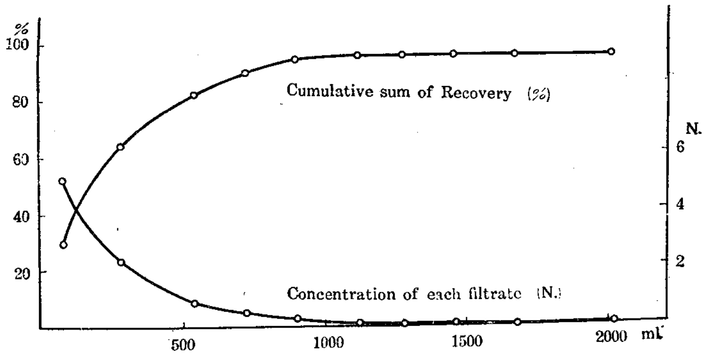

Fig. 9.

was ground in a mortar, and washed with total ca. 2000 mℓ of boiling distilled water divided into ten portions. At one time approximately 200 mℓ of boiling distilled water were added to the charcoal in the mortar, stirred and allowed to stand for a short time, then filtered under suction. The filtrate was collected in a measuring cylinder and then titrated with the standard sodium hydroxide solution. First to fourth washing portions were titrated with 0.122N–NaOH, and the other 6 portions were titrated with 0.0122N–NaOH using a micro-burette. Each portion was titrated three times and the mean values were taken, and then from the average of those data percentages of recovery were calculated. The results are recorded in Table 18 and Fig. 9.

According to these data about 96 per cent of the sulphuric acid may be recovered from the washing of about 2000 mℓ portion with boiling distilled water. However, the washing of 555～730 mℓ recovered about 81～89 per cent which was a suitable amount for practical application.

Summary

In this report were recorded some solution on the preparation and the adsorptive power of hydrated active charcoal (H-A charcoal) that was made from wood by dehydration and carbonization with sulphuric acid at low temperature.

(1) The hydrated active charcoals were made from the sawdust of the wood of "todomatsu" (Fir, *Abies Mayriana* M. et K.), "yezomatsu" (Spruce, *Picea jezoensis* CARR), "shina" (Basswood, *Tilia japonica* SIMK), and "nara" (Oak, *Quercus crispula* BL.) which were most common and much cut and stocked woods in Hokkaido. The decolorizing activity of those charcoals was studied. Under the following conditions of preparation the decolorizing properties of the charcoals are caused to differ by species of wood from which they were derived.

Oven dried sawdust samples were stirred with quintuple amount of 70 per cent sulphuric acid in 80° water bath for an hour and a half, and heated at 150° for 8 hours, then ground in a mortar and washed with boiling distilled water. The adsorptive power of these charcoals was tested with 0.15 per cent methylene blue solution and caramel solution. The order of the adsorptive activity was "nara", "shina", "yezomatsu" and "todomatsu"; therefore it may be said that hardwood is superior to softwood for the preparation of hydrated active charcoal.

(2) In order to investigate the condition under which preparation of the charcoals was made, a series of experiments was carried out on various factors that seem to influence the activities of the products. First, the quantity of acid was examined; it was found better to use acid of the amount of 5 times the weight of the wood than to use 4 times the weight. The order of the adsorptive power of the charcoal was also the same as found in previous experiment. Ash content of the charcoals made from softwoods was ca. 0.1–0.2 per cent, that from "shina" wood was ca. 0.65 per cent, and that from "nara" wood was ca. 0.3 per cent.

(3) To investigate the influences of decay of wood upon the adsorptive power, charcoal was made from five rotted woods, namely, brown rotted "hinoki" (Japanese cypress, *Chamaecyparis obtusa* S. et Z.), three of white rotted "yezomatsu" at different stage of rot, and brown rotted "karamatsu" (Larch, *Larix Kaempferi* SARG). The yield of charcoal made from brown rotted wood was high, because such wood has high content of lignin. The charcoal made from "hinoki" decolorized methylene blue very well but not caramel, while charcoal made from "karamatsu" decolorized neither methylene blue nor caramel. In white rotted "yezomatsu", the more the rot had advanced the more methylene blue was decolorized, however, the less caramel was decolorized. The charcoal that was made from brown rotted "karamatsu" had much ash content because the wood itself had much ash content.

(4) Four commercial active carbons (not hydrated active charcoal) were compared under identical conditions. The decolorizing power of these samples was rather inferior to that of the hydrated active charcoals made from wood, except one sample.

(5) Various concentrations of sulphuric acid, such as 60, 65, 70, 75 and 80 per cent, were examined for their effect in the preparation of "nara" H–A charcoal. The charcoals prepared with 65 and 75 per cent acid decolorized well, especially the former class in the methylene blue test and the latter class in caramel test.

(6) The point of greatest activity was investigated as effected by duration of carbonization process and various acid concentrations. The

period of carbonization was varied from 6 to 8 to 10 hours for each acid concentration of 65, 70 and 75 per cent. The charcoal prepared with 70 per cent sulphuric acid and 8 hours carbonization showed excellent activity both in the methylene blue and in the caramel test.

(7) Stirring, in pre-treatment, at room temperature in stead of at 80° for 1 or 1.5 hours, influenced the activity adversely.

(8) Lowering the carbonization (dehydration) temperature to 120°, and varying the time of heating between 8, 9, 10, 11 and 12 hours, the maximum decolorizing power point for caramel test was found in charcoal carbonized by 10 hour treatment. However, for methylene blue test that carbonized by 11 hours of heating had a maximum activity. It appeared probable that by making the heating time too long the decolorizing activity was deteriorated.

(9) Pre-treatment of raw materials by extraction with alcohol-benzene mixture, appeared to exert some good influences upon the products.

(10) Charcoal made from butanol pulp showed considerably good activity, but the ash content should be noted.

(11) Charcoal made from mandarin orange peel had a better decolorizing power than that from "nara" (oak) sawdust, however, it was worse than that from extractive-free "nara" sawdust.

(12) In the acid recovering experiment, about 96 per cent of acid could be recovered by washing with hot water of about 20 times the amount of the acid that was used.

From these results it is obviously possible to obtain the hydrated active charcoal, which has an excellent decolorizing activity, from wood, especially from hardwood. The optimum conditions for the preparation are as follows: Dry sawdust is treated with 5 times quantity of 65～75 per cent sulphuric acid, and stirred at 80° for an hour, then this is heated at 150° for 8 hours in an oven. After carbonization (dehydration) is properly carried out, the product is washed well with boiling water and stored in a sealed jar in moistened state.

Acknowledgment

The authors wish to express their sincere appreciation to Prof. G. FUKUYAMA and Prof. G. OKUDA for their kind advices.

Literature Referenced

1) MANTELL, C. L.: "Industrial Carbon", Chapter IX, D. Van Nostrand Co. Inc., New York (1946).

2) VELDKAMP, C.: Deutsch. Zuckerind., **62**, 499 (1937).
SAUDERA, K.: Z. Zuckerind. Cech. Rep. **61**, 185 (1937).
SMIRNOV, V. A., DOBUSH, O. A. and MYMRIKOVA, V. N.: J. Applied Chem. (U.S.S.R) **19**, 651–8 (1946); C. A. **41**, 4290 (1947).

VANZETTI, B. L.: Chemicae industria (Italy) **25**, 137–44 (1943); C. A., **39**, 176 (1945).
RAYMOND, G. DAVIS: U. S. P. 2,245,579, June 17 (1941); C. A., **35**, 6096 (1941).
BRRODERICK, S. J. and BOGARD, D.: U. S. Bur. Mines. Rept. Investigations, 3559, 17 pp. (1941); C. A., **35**, 3416, 5610 (1941).

3) MIZUNO, S. and KATO, Y.: Jour. Soc. Chem. Ind. (Japan), **46**, 961 (1943).
4) KATO, Y.: Nippon Kagaku Sōran, Complete Abstracts of Japanese Chemical Literatures, Vol. 13, No. 12, 762 (1939).
5) FISCHER, F. and TROPSCH, H.: Ber., **56B**, 2418 (1923).
6) Ringyo Kaisetsu Henshu-shitsu, Hokkaido Shinrin Tōkei Zuhyo (Statistical Diagrams of Hokkaido Forest), 12 (1948).
7) Kanpo (Official Gazette) (Japan), 18, June (1947).
8) OCHIAI, E. and TSUDA, K.: "Yuki Biryo Shoryo Bunseki Ho," (Organic Micro- and Semimicro-analysis). 63 (1937).
9) PREGL, F.: "Quantitative Organic Micro-analysis", 163 (1930).
10) FUKUYAMA, G., HANZAWA, M. and KAWASE, K.: Research Bulletin of the College Experimental Forests, College of Agriculture, Hokkaido University, Vol. XVI, II. 243–280 (1953).
11) KATSUTA, Y. and OKABE, S.: Bulletin of Sanitary Experimental Station (Japan), **40**, 171 (1932).
12) KASHIMOTO, K.: "Kagaku Jikken Gaku" (Experimental Chemistry), Experimental Methods of Micro-organism and Enzyme, 135. (1944).