[CONTRIBUTION FROM THE BENGAL IMMUNITY RESEARCH LABORATORY OF CALCUTTA]

Effect of Chemical Treatments on the Properties of Activated Charcoal

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The characteristics of activated charcoals are known to vary with the raw materials used, the conditions of activation and the nature of activating agents. Pre-treatment of the raw vegetable material with chemicals, which exert a swelling or solubilizing action, before carbonization has often been found to increase the activity.[1,2,3,4,5] Burrage[1] put forward an explanation based on the selective solvent action of zinc chloride on cellulose in preference to lignin in wood. Kandilarow[3] stressed the importance of the formation of unoriented carbon atoms in the process of activation. But various modifications of the same process of activation are often found to alter the adsorption characteristics of charcoal for different types of adsorbates in different ways.[6,7] Activated charcoal has now multifarious uses in industry and a precise knowledge of the variations in its properties produced by different treatments during the preparation would be of considerable importance. Previous work[5] from this Laboratory has shown that coconut shell and groundnut hull which are easily available in this country, can yield good grades of medicinal charcoals. The same raw materials have been used in the present work for the preparation of activated charcoals under a variety of treatments, including those with zinc chloride, calcium chloride, caustic soda and sulfuric acid, and an attempt has been made to correlate these treatments with the adsorptive powers of the charcoals for different types of substances.

Experimental

Starting Materials.—Coconut shell and groundnut hull were ground to fine powder so as to pass through a 100-mesh sieve.

Zinc chloride was of fused commercial variety, and calcium chloride, caustic soda and sulfuric and hydrochloric acids were all of chemically pure quality.

Assay of Lignin.—Lignin was estimated in the raw materials by a modification of the method of Ost and Wilkening,[8] using 72% sulfuric acid for dissolving the cellulose. Coconut shell was found to contain 32.4% of lignin against only 20.7% in groundnut hull.

Pre-treatment.—The powdered raw material was mixed with an aqueous solution of the activating chemical or mixture of chemicals and digested at the boiling temperature for one or two hours. In all cases, the particles swelled and a dark sticky mass was gradually formed. Groundnut hull swelled more readily than coconut shell. The addition of hydrochloric acid to zinc chloride or calcium chloride reduced the time of digestion considerably.

The chemicals used for pre-treatment, both as actual quantities and as w./w. percentages with respect to the quantities of the powdered raw material, are given in the first columns of the Tables I, II(a) and II(b).

Variations in the treatments or details of any after-treatment of the carbonized char are indicated in the footnotes corresponding to these tables.

Carbonization.—The wet mass was spread on a porcelain basin and dried on a sand-bath prior to carbonization. All the experiments, except one, were carried out with 20 to 40 g. of the raw materials and carbonization was effected by heating the dried mass in 50-ml. covered silica crucibles over a techlu burner to dull red heat (600–800°) for one hour. In one experiment (9) the quantity of shell powder taken was over 2 kg., and in this case the pre-treated mass was carbonized in fire-clay tubes, supported across a coal fired furnace with chimney draft. The maximum temperature of the furnace was 900–1000°.

Washing and Drying.—The carbonized mass was boiled with water containing hydrochloric acid several times till the wash liquid was free from zinc ions and then the mass was heated to dryness on a sand-bath and the heating was continued for a further half an hour to drive off free hydrochloric acid. The charcoal was further washed with hot distilled water until the wash water was free from chloride ions and the *p*H rose to about 6.0. It was finally dried at 250–300° and powdered so as to pass through a 200-mesh sieve.

Two-Stage Carbonization.—Kandilarow[2] suggested a two-stage carbonization process for the preparation of activated charcoal from cellulose in which the raw material is digested with zinc chloride and then carbonized (at 400–450°), but the charcoal so obtained is digested with zinc chloride again and carbonized (at 400–450°) a second time. This procedure was followed in experiment (26) but a portion of the charcoal obtained after the first stage was kept aside (26(a)) for comparison with the final charcoal (26(b)).

Adsorption of Methylene Blue.—To 0.03 to 0.04 g. of the charcoal was added 50 ml. of 0.04% solution of methylene blue in a 200-ml. conical flask and boiled under reflux for twenty-five minutes. The suspension was then centrifuged and the clear supernatant liquid matched in a Klett bio-colorimeter with a standard solution of methylene blue of comparable strength.

Adsorption of Iodine.—To 0.05 g. of the charcoal was added 25 ml. of 0.1 *N* iodine solution in a 100-ml. Jena glass bottle, shaken for one hour and centrifuged. An aliquot part of the supernatant liquid was then titrated with 0.1 *N* sodium thiosulfate solution.

Adsorption of Acetic Acid.—0.2 to 0.3 g. of charcoal and 25 ml. of 0.1 *N* acetic acid were taken in a 100-ml. Jena glass bottle, shaken for half an hour and filtered. An aliquot part of the clear filtrate was titrated with 0.1 *N* caustic soda using phenolphthalein as indicator.

Adsorption of Caramel.—A solution of caramel having a total solid content of 2% was used for this experiment; 0.2 g. of the charcoal and 60 ml. of the caramel solution (75 ml. had to be used in one case) were taken in a 250-ml. conical flask and heated on a boiling water-bath under reflux for half an hour. The suspension was filtered and the filtrate matched against standard caramel solutions of comparable strength in a colorimeter. For calculating the adsorption of caramel, the caramel content of the solution has been assumed to be the same as its total solid content.

In all the above adsorption experiments, the results have been expressed as milligrams of the substance adsorbed per gram of charcoal.

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(1) L. J. Burrage, *Trans. Faraday Soc.*, **29**, 445 (1933).

(2) G. G. Kandilarow, *Kolloid-Beihefte*, **48**, 1 (1938).

(3) S. N. Rao and S. N. G. Rao, *J. Indian Chem. Soc., Ind. News Ed.*, **2**, 161 (1939).

(4) L. Ts'ai and K. Ghuang, *Ind. Eng. Chem.*, **34**, 812 (1942).

(5) S. Mukherjee and S. Bhattacharya, *J. Sci. Ind. Res.* (*India*), **4**, 235 (1945).

(6) J. W. Hassler and W. C. McMinn, *Ind. Eng. Chem.*, **37**, 645 (1945).

(7) S. Mukherjee and S. Bhattacharya, *J. Sci. Ind. Res.* (*India*), **6**, 8 (1947).

(8) Ost and Wilkening, *Chem. Z.*, **34**, 461 (1910).

TABLE I

CHARCOAL FROM GROUNDNUT HULL: DETAILS OF TREATMENT

Materials used	Experiment nos.								
	1	2	3	4	5	6	7	8	8(a)
Hull powder, g.	40	25	25	25	25	30	40	25	25
$ZnCl_2$, g.	25	25	35	45	65	15	...	...	..
$ZnCl_2$, % of hull powder	62.5	100	140	180	260	50	...	...	..
$CaCl_2$, g.	..	...	...	...	...	15	40	75	..
$CaCl_2$, % of hull powder	..	...	...	...	...	50	100	300	..
HCl, g.	3.2	4.8	6.4	9.6	12.8	3.21	4.8	9.6	..
HCl, % of hull powder	8	19.2	25.6	38.4	51.2	10.7	12	38.4	..
Water, ml.	70	40	40	30	40	50	70	50	..
Yield of charcoal, % of raw material	32.5	36.0	34.0	32.0	36.0	33.3	32.5	?	?

TABLE II(a)

CHARCOAL FROM COCONUT SHELL: DETAILS OF TREATMENT

Materials used	Experiment nos.										
	9	10[a]	11[b]	12	13	14	15	16	17	18[c]	19
Shell powder, g.	2370	18.5	18.5	37	25	25	25	25	40	40	40
$ZnCl_2$, g.	1580	12.5	12.5	27	30	45	65	65	120	40	..
$ZnCl_2$, % of shell powder	67	67	67	73	120	180	260	260	300		
HCl, g.	175.38	1.11	1.11	3.18	6.4	9.6	...	12.8	6.4	8.1	..
HCl % of shell powder	7.4	6	6	8.6	25.6	38.4	...	51.2	16		
Water, ml.	3160	22.5	22.5	75	30	30	75	40	50	15	..
Yield of charcoal, % of raw material	31.8	32.4	27.0	32,4	34.0	34.0	32.5	36.0	33.75	25.0	30.0

[a] The charcoal, after washing free from zinc salts, was boiled with caustic soda solution (5% strength) and subsequently washed with water till free from chloride and the *p*H of the wash water reached 6.0. [b] The zinc chloride used for digestion was removed by washing before carbonization. [c] The shell powder was carbonized without any activating agent but the charcoal obtained after carbonization was boiled with acidulated zinc chloride solution and finally washed with water.

TABLE IIb

CHARCOAL FROM COCONUT SHELL: DETAILS OF TREATMENT

Materials used	Experiment nos.								
	20	21	22	23	24	25[a]	26(a)[b]	26(b)[c]	
								i	ii
Shell powder, g.	20	40	20	40	40	42	20	20	
$ZnCl_2$, satd. soln., ml.	....	...	....	..	...	..	62.5	62.5	15
$CaCl_2$, g.	20	40	20	..	...	..	..	..	..
$CaCl_2$, % of shell powder	100	100	100	..	...	..	..	..	..
NaOH, g.	....	...	1	..	30	5	..	..	..
NaOH, % of shell powder	....	...	5	..	75	..	..	..	..
H_2SO_4. g.	....	...	....	38	...	..	..	..	..
H_2SO_4, % of shell powder	....	...	....	90	...	..	..	..	..
HCl, g.	....	13	....	..	...	..	..	..	..
HCl, % of shell powder	....	32.5	....	..	...	..	..	..	..
Water, ml.	40	20	50	30	100	50	..	..	..
Yield of charcoal, % of raw material	31.25	30.0	31.25	32.5	10.0	23.8	37.5	37.5	

[a] The shell powder was carbonized without the addition of any activating agent, but the charcoal obtained after carbonization was boiled with caustic soda and finally washed with water. [b] Two stage carbonization experiment: sample collected after the first carbonization. [c] Same experiment as above: final sample.

TABLE III

PROPERTIES OF CHARCOAL FROM GROUNDNUT HULL

Properties	Experiment nos. (*vide* Table I)								
	1	2	3	4	5	6	7	8	8a
Ash content, %	5.95	5.61	5.15	4.58	5.14	4.69	5.70	7.35	10.0
Adsorption of methylene blue, mg./g.	450	291	286	248	250	150	72	105	Nil
Adsorption of iodine, mg./g.	1080	1180	1144	1220	1047	886	590	600	300
Adsorption of acetic acid, mg./g.	78	97	98	97.5	64	101	60	95	68
Adsorption of caramel, mg./g.	380	2430	3820	5830	7330	1010	2440	3300	230
Bulk density, g./ml.	0.60	0.40	0.36	0.27	0.21	0.36	0.21	0.11	...

TABLE IVa

PROPERTIES OF CHARCOAL FROM COCONUT SHELL

Properties	Experiment nos. (*vide* Table IIa)										
	9	10	11	12	13	14	15	16	17	18	19
Ash content, %	1.5	1.5	4.02	0.99	1.66	1.27	1.73	1.66	1.33	5.31	3.5
Adsorption of methylene blue, mg./g.	412	358	85	400	406	370	455	398	468	19	20
Adsorption of iodine, mg./g.	1151	1254	811	1295	1390	1492	1571	1497	1547	700	290
Adsorption of acetic acid, mg./g.	87	93	82	84	108	107	76	83	68	82	31
Adsorption of caramel, mg./g.	509	380	160	860	810	1510	2840	5210	4490	Nil	Nil
Bulk density, g./ml.	....	0.475	....	0.445	0.37	0.32	0.25	0.27	0.23	0.61	...

TABLE IVb

PROPERTIES OF CHARCOAL FROM COCONUT SHELL

Properties	Experiment nos. (TableIIb)							
	20	21	22	23	24	25	26(a)	26(b)
Ash content, %	3.58	2.96	3.34	5.37	9.95	18.3	1.02	1.46
Adsorption of methylene blue, mg./g.	42	170	74	290	41	5.3	479	384
Adsorption of iodine, mg./g.	562	670	717	768	540	537	1586	1491
Adsorption of acetic acid, mg./g.	76	68	82	82	61	82	89	99
Adsorption of caramel, mg./g.	1820	1820	1820	230	260	Nil	4870	3250
Bulk density, g./ml.	0.23	0.26	0.29	0.75	0.18	0.67	0.24	0.29

Bulk Density.—The charcoal powder was taken in a 10-ml. graduated test-tube and the latter tapped gently so as to have the closest possible packing. Sufficient quantity of charcoal was added to occupy a volume of 10 ml. under the condition and this was subsequently taken out and weighed. The density has been expressed as grams of charcoal per milliliter.

Discussion

The data presented in the above tables show how the characteristics of charcoals vary with the nature of the raw materials and the conditions of preparation. Some general features and correlations are indicated below.

Ash.—The ash yields of groundnut hull charcoals are higher than those of the charcoals from coconut shell and the use of zinc chloride for predigestion produces charcoals leaving the minimum amounts of ash. It has been further observed that with groundnut hull charcoals, there is a regular fall in the ash yields with increasing proportions of zinc chloride used for predigestion. These are in agreement with the authors' previous observations.[5] But relatively high ash yields are obtained when the zinc chloride is removed from the digested material before carbonization (Expt. 11) or when this salt is used only for washing the carbonized mass instead of for predigestion (Expt. 18). These observations show that the ash reducing action of zinc chloride becomes manifest only when the salt remains in contact with the raw material during carbonization. It seems to indicate that zinc chloride reacts with the inorganic matter in the raw material at the temperature of carbonization rendering them into a form in which they are easily removable by washing.

Adsorptive Power and Mode of Activation.—It will be seen from the above tables that, as a rule, predigestion with acidulated zinc chloride produced charcoals possessing the maximum adsorptive powers for methylene blue, caramel and iodine. No significant correlation is found between the adsorption of acetic acid and the conditions of preparation of the charcoals. Charcoals prepared using calcium chloride for predigestion

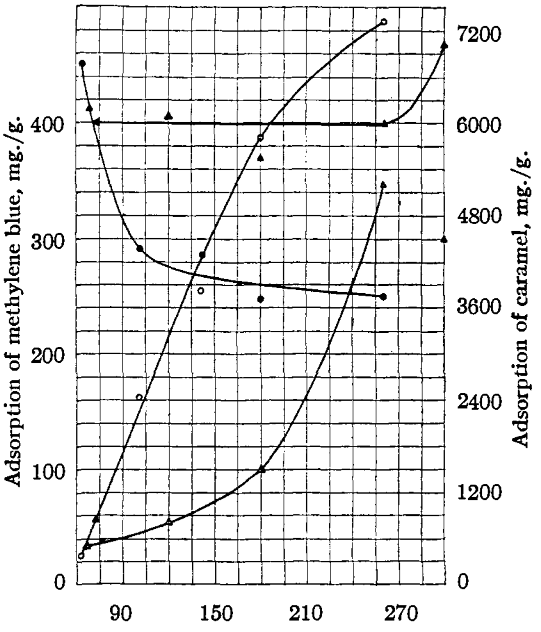

Fig. 1.—Variations of adsorptive powers of charcoal with the proportion of zinc chloride: ●, adsorption of methylene blue on groundnut hull charcoal; ○, adsorption of caramel on groundnut hull charcoal; ▲, adsorption of methylene blue on coconut shell charcoal; △, adsorption of caramel on coconut shell charcoal.

generally show high adsorption of caramel but moderate or low adsorption of methylene blue or iodine. Digestion with sulfuric acid or caustic soda produces charcoals of low adsorptive power.

Variation of the proportion of zinc chloride used for predigestion produces different effects on coconut shell and groundnut hull in respect to the adsorption of methylene blue by the resultant charcoals (*vide* Fig. 1). With groundnut hull charcoal, the adsorption of methylene blue decreases, at first sharply and then slowly, with increase in the proportion of zinc chloride while with coconut shell charcoal a slight increase is observed when very high proportions of zinc chloride are employed. On the other hand, the adsorption of caramel by both groundnut hull and coconut shell charcoals increases continuously with increasing proportions of zinc chloride, the rise being sharper in the former case.

If, however, the zinc chloride is removed by washing from the digested mass prior to carbonization the charcoal shows very poor activity (Expt. 11). A similar result is observed when zinc chloride is used for digesting the carbonized char instead of for predigestion of the raw material (Expt. 18). This suggests that activation really takes place during the carbonization of the raw material in contact with zinc chloride.

Experiments 26(a) and (b) show that with coconut shell as the raw material, a single-stage activation is adequate and no advantage is gained by carbonizing a second time.

The effect of the addition of hydrochloric acid to zinc chloride used for predigestion is brought out in Expts. 15 and 16 where it has been shown that for the same proportion of zinc chloride, the addition of hydrochloric acid during predigestion (51.2%) nearly doubles the adsorption of caramel by the charcoal prepared from coconut shell.[4]

It has been mentioned already that predigestion with either zinc chloride or calcium chloride can produce charcoals having high adsorbing power for caramel. The observation has however been made in Expt. 6 with groundnut shell that when a mixture of zinc chloride (50%) and calcium chloride (50%) is used for predigestion, the adsorption of caramel by the resulting charcoal is much lower than when either zinc chloride (100%) or calcium chloride (100%) alone is used for predigestion (*cf.* Expts. 2 and 7). This suggests some sort of antagonism between the two salts (*cf.* Milbauer[9]).

The adsorption of iodine is being found to be the highest for charcoals prepared using zinc chloride for predigestion, and the adsorption by coconut shell charcoal is higher than that by groundnut hull charcoal prepared under similar conditions. Here, also, the removal of zinc chloride before carbonization markedly decreases the adsorption of iodine. With groundnut hull, the adsorption of iodine, as of methylene blue, passes through a maximum with increasing proportions of zinc chloride used for predigestion.

The activation of carbon is generally considered to consist of one or more of the following processes: (1) increasing the active surface area, *e. g.*, by increasing the porosity; (2) removal of any substances, inorganic or organic, which might poison the active centers. (3) Producing fresh active centers, which might consist of unoriented carbon atoms of higher energy potential on the surface or the fixation of other polar atoms or groups on the surface.

The bulk density, which may be taken as a measure of the porosity of the charcoal, shows regular decrease with increasing proportions of zinc chloride or calcium chloride used for predigestion. Correlation of the adsorptive properties with the bulk density however shows that while the adsorption of caramel by charcoal prepared from groundnut hull using zinc chloride for predigestion, increases regularly with decreasing bulk density, the adsorption of methylene blue varies in the reverse manner. This observation indicates a difference in the type of adsorption involved in these two cases.

Burrage[1] offered an explanation of the mechanism of activation of charcoal from vegetable matter based on the differential solvent action of the activating agents on cellulose and lignin. According to him, it is the cellulose or the charcoal formed from it which is being acted upon during activation whereas the lignin or the resultant charcoal is left untouched. This would cause pitting and it is this which activates charcoal. The active points are the carbonized remnants of cellulose (consisting of unoriented carbon atoms) attached to the walls of these activation pores. Over-activation would correspond to that stage where there will be no more cellulose charcoal or cellulose to be pitted and the activation spikes will have been removed by intensive oxidation.

The observations recorded above, namely, that generally zinc chloride has the greatest activating action is in agreement with the above hypothesis since of all the chemicals used in the present investigation, zinc chloride has also the highest solvent action on cellulose, particularly in the presence of hydrochloric acid. Groundnut hull contains a lower proportion (20.7%) of lignin than coconut shell (32.4%) and it may be assumed that the former contains a higher proportion of cellulose than the latter. This finds support in the observation (*vide supra*) that groundnut hull appears to dissolve in zinc chloride more readily than coconut shell. According to Burrage,[1] groundnut hull should therefore be more susceptible to activation as well as to over-activation by treatment with zinc chloride. As a matter of fact, with increase in the proportion of zinc chloride beyond 62.5 per cent. in respect of groundnut hull, the adsorption of methylene blue by the re-

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(9) Milbauer, *Chem. Obzor.*, **7**, 189 (1932); *Chem. Zeitung*, **57**, 581 (1933).

sulting charcoal diminishes steadily, indicating progressive over-activation, *i. e.*, removal of activation centers on which the dye is presumably adsorbed. Simultaneously, there is an increase in the adsorption of caramel.

This difference in the types of adsorption of methylene blue and caramel on charcoal is also found in the charcoals prepared using neutral, acidulated and alkaline calcium chloride solutions for predigestion (Expts. 20, 21 and 22). No significant difference is observed in the adsorption of caramel but the adsorption of methylene blue is considerably higher when acidulated calcium chloride is employed. The above observations tend to indicate the development of different types of active centers during activation.

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Summary

Charcoal has been prepared from groundnut hull and coconut shell using zinc chloride, calcium chloride, sulfuric acid and caustic soda for predigestion of the raw material and subsequent carbonization at 600–800°, and studies have been made of the adsorptive powers of the resultant charcoals for methylene blue, caramel, iodine and acetic acid and of their ash contents and bulk density.

Predigestion with acidulated zinc chloride generally produces the most active charcoals. Increase in the proportion of zinc chloride is accompanied with lowering of ash content and of bulk density and increase of the absorption of methylene blue, iodine and caramel, but with groundnut shell charcoal there is a reduction in the adsorption of methylene blue.

Predigestion with calcium chloride, sulfuric acid and caustic soda generally fail to produce charcoals of high adsorptive power with the exception that charcoals prepared using calcium chloride show fairly high adsorption of caramel.

Zinc chloride is not effective as an activating agent unless it is present in the raw material during carbonization.

The mechanism of activation has been discussed in relation to the solvent power of the activating agent on the vegetable matter used for the preparation of charcoal.

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[CONTRIBUTION FROM THE UNIVERSITY OF MANITOBA, WINNIPEG, CANADA]

The System Iron–Tin: Liquidus Only

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This work originated in an observation by the Consolidated Mining and Smelting Company of Canada, Trail, B. C., that the iron content of the tin metal recovered from their Sullivan ore was always much lower than the accepted value for the amount of iron in the iron–tin eutectic. This metal is filtered at about 353°; in experimental work it has been filtered at as low as 250°, but in no case did the filtrate contain more than 0.01% iron. Interpolation of existing data indicates a much higher iron content than this in the eutectic, although, since there has been no direct determination, it is difficult to quote a figure. Difference of opinion also exists as to whether the equilibrium diagram does or does not exhibit a miscibility gap in the liquid state. Unquestionably there is a long horizontal, or almost horizontal, portion, on the liquidus curve, which indicates the existence of such a gap, but the observation is only conclusive if the apparent horizontal portion is actually completely horizontal, *i. e.*, if there is no fall of temperature whatever over this region of concentration; a slight fall of temperature would defeat this argument. We therefore decided to investigate the liquidus curve over a range of concentration from pure tin to a point beyond the hypothetical gap, say 50% iron. The last portion of the liquidus, up to pure iron, presents little interest and is well known from the results of thermal analysis. We have succeeded in determining the iron content of the eutectic and in showing, beyond all reasonable doubt, that a miscibility gap exists.

Previous Work

It is only necessary to discuss the existing literature in so far as it refers to the liquidus. The most important literature references are given in Jänecke's "Kurzgefasstes Handbuch aller Legierungen,"[1] where, however, the liquidus is very incorrectly drawn. The only figures actually determining the form of the liquidus, and based on thermal analysis, are those of Isaac and Tammann.[2]

Our problem had three parts: the determination of the eutectic composition and temperature, the investigation of the liquidus curve from the eutectic temperature to the temperature of the gap, and the investigation of the limits of the gap.

The eutectic temperature and composition were determined by adding powdered iron to tin and observing the depression in the freezing point of tin.

Thermal analysis lacks sensitivity, at least in its crude form, as a method of determining a liquidus when the slope is steep. As a method of

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(1) Spamer, Leipzig, 1937, pp. 217 and 220.

(2) Isaac and Tammann, *Z. anorg. Chem.*, 53, 281 (1907).