

TREATMENT AND UTILISATION OF COFFEE HUSK FOR PREPARING ION EXCHANGE MATERIAL

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SUMMARY

The characteristics and composition of five types of coffee husk have been studied. An ion exchange material has been prepared from coffee husk by suitable treatment with sulphuric acid, sodium chloride and alum. The ion exchange material thus prepared has been found considerably efficient in removing calcium from 0.1% calcium chloride solution and fluorine from tap water to which sodium fluoride was added (about 2.5 p.p.m. as fluorine).

1. INTRODUCTION

The possibility of utilising the pulpy residue from the coffee bean as cattle feed has been investigated to some extent at the Indian Veterinary Research Institute, Izatnagar (1950). Utilisation of coffee husk for preparing coffee powder (for blending, in place of chicory) has been investigated at the Central Food Technological Research Institute, Mysore (1952). Under certain conditions, *e.g.*, if the husk from certain varieties of coffee is not found fit for the uses just mentioned, the waste material may be treated and utilised in other ways and one of the possibilities is considered in this paper, *viz.*, the preparation of ion exchange material.

Synthetic ion exchangers which resist the action of concentrated acids and alkalies are now being used extensively for a variety of purposes (Kressman, 1952), *e.g.*, purification of water. The cation exchange material can be used, like Permutite, for rendering "hard" waters "soft"; and the material, when its capacity for softening is exhausted, can be regenerated with sodium chloride solution. Underwood and Deatherage (1952) have recently reported the use of an ion exchange resin for the hydrolysis of casein and coffee proteins, and this method is claimed to preclude the customary humin formation which generally takes place in the classical hydrochloric acid hydrolysis.

It is of special interest in this connection to note the observations of Rode (1944) that a product with water-softening properties can be prepared by treating finely ground coffee with an aqueous solution of sodium hydroxide, sodium carbonate, or trisodium phosphate in the presence of aluminium. The alkaline solution must be sufficiently concentrated to dissolve the metallic aluminium. When the reaction is complete, the excess solution is drained off from the product which, after repeated use as a water softener, can be regenerated with a 2% solution of sodium chloride. In an alternative

method, the finely ground coffee is treated with a solution of an alkali metal silicate, such as a 10 to 20 per cent. solution of sodium silicate, for about 5 hours and then with a solution of caustic soda or soda ash.

In view of the above observations, it was of interest to study the possible use of coffee husk in the preparation of ion exchange material. The coffee husk employed in the present studies, the methods of analysis adopted and the experiments carried out are briefly described below.

2. MATERIAL

Five types of coffee husk were obtained from a certain firm in South India through the kind courtesy of Dr. Gilbert J. Fowler to whom the authors' thanks are due. In all the cases the husk material was in various sizes, from almost whole husk to very small bits and in powdery condition. The general appearance and characteristics of the different samples as they were received and after powdering them to pass through 100-mesh sieve, and also the amounts of moisture they held are given in Table I.

TABLE I. *Appearance and Moisture Contents of Different Samples of Coffee Husk*

Samples	Original samples		After powdering and passing through 100-mesh sieve	
	Appearance	Percentage of moisture	Appearance	Percentage of moisture
Type I (P.M.T. husk)	Husks almost uniformly coloured pale white	6.95	Pale white with a greenish tint	12.16*
Type II (cherry husk)	Husks coloured medium brown, dark brown and light brown	11.08	Somewhat dark brown	9.39
Type III (cherry black husk)	Consists largely of black coloured husks and also dark brown husks to some extent	27.06	Very dark brown	17.10
Type IV	.. Consists of brown husks and also of somewhat pale white husks	9.08	Brown	12.00
Type V	.. Resembles P.M.T. husk excepting that it contains a large percentage of finer fraction	8.84	Pale white	10.80

* The moisture content was found to increase slightly on keeping this material. Thus after 11 days the moisture content was 12.5% and after 22 days it was 13.72%.

It may be noted from the table that in the cases of IV and V the moisture contents increased and in the cases of II and III the moisture contents decreased after powdering the materials.

3. METHODS OF ANALYSIS

Phosphoric acid, potassium and calcium were determined by the methods given in *The Chemists' Year Book* (1936). The determination of organic carbon and total nitrogen was carried out according to the method recommended by Bhaskaran, Harihara Iyer, Rajagopalan and Subrahmanyam (1936). Fluorine was determined by the method proposed by Sanchis (1934). Aluminium was determined by the method suggested by Hatfield (1934).

4. COMPOSITION OF COFFEE HUSK

The results of analysis of the five different types of coffee husk (the powdered material) are given in Table II. It may be observed that Type II (cherry husk) and Type III (cherry black husk) contain comparatively high amounts of potash and nitrogen.

5. TREATMENT AND UTILIZATION OF COFFEE HUSK AS A CATION EXCHANGER

In 1934, Liebknecht observed that if certain coals were granulated and treated with hot concentrated sulphuric acid they developed ion exchange properties and, in addition, the product (sulphonated coal) was physically and chemically stable towards acids and to some extent towards alkalis. Based on this observation, the coffee husk was treated with concentrated sulphuric acid thus effecting simultaneously carbonisation and sulphonation of the material in one step. The treatment was carried out as follows.

100 gm. of the coffee husk (Type IV which was available in larger quantity) was taken in a beaker and 200 c.c. of concentrated sulphuric acid added to it with constant stirring. This amount of acid was sufficient just to cover the material completely. Carbonisation took place almost instantaneously. After about five minutes, the reaction proceeded more vigorously giving rise to considerable frothing. The beaker was then cooled in water and left overnight. The contents were poured into an excess of water, the lumps crumbled with fingers and filtered on a Buchner funnel. The carbon was washed with water till free of acidity (using methyl red as indicator), dried and sieved so as to pass through 20-mesh and be retained on 40-mesh.

For testing the material, 20 gm. of the sieved carbon was weighed into a glass tube of 1" diameter in which it was supported on a layer of glasswool spread over a one-holed rubber cork. 5% sodium chloride solution was then passed through it till the effluent showed no acidity to methyl red, thus indicating that all the replaceable hydrogen ions of the carbon were exchanged

TABLE II
Results of Analysis of the Different Samples of Coffee Husk
 (Results expressed as percentages on moisture-free basis)

Samples	Loss on ignition (organic matter)	Residue on ignition (mineral matter)	Acid-insoluble matter (mostly silica)	Organic carbon (C)	Nitrogen (N)	C-N ratio (C/N)	Phosphoric acid (P_2O_5)	Potassium (K_2O)
Type I (P.M.T. husk) ..	99.08	0.92	0.54	40.00	0.72	55.6	Traces	Traces
Type II (cherry husk) ..	90.88	9.12	2.85	35.30	1.92	18.4	0.38	2.56
Type III (cherry black husk) ..	90.92	9.08	1.23	40.60	2.44	16.6	0.42	3.50
Type IV ..	92.96	7.04	1.80	*	*	*	Present in considerable amounts*	
Type V ..	96.44	3.56	1.91	*	*	*	do.*	

* Not determined.

Qualitative tests showed that cherry husk contained comparatively much more iron, and that the calcium contents of the husks examined were negligible.

In view of the considerable amounts of potash and nitrogen in the coffee husks (particularly cherry husk and cherry black husk), some experiments were carried out in order to study the decomposition of the material and the nature of micro-organisms that develop (a) after pre-treating the material with dilute acid and (b) along with domestic sewage. The powdered husks were treated with (a) N/10 sulphuric acid, (b) sewage, and (c) water (at the rate of 1 gm. per 100 c.c., in shallow glass basins). Mixtures of the original husks (Types, I, II and III in the proportion of 1:1:1) were also employed for these experiments. It was of some interest to observe that 72 hours after treatment with the dilute acid certain fungal forms were found to develop, more especially in the basins containing cherry husk and the mixture of the husks. Treatment with sewage considerably facilitated the decomposition of the husks. At the same time, it was observed that the development of the organisms was delayed more perceptibly on the cherry black husk material, e.g., only after a week some of the more sensitive forms of protozoa in sewage became active in the basins containing cherry black husk, while in the other cases the organisms became active earlier. In the "water series" the conditions for the development of the bacteria and smaller forms of protozoa were found promoted, especially on cherry husk and on the mixture of the husks.

for sodium. The bed was then washed free of excess sodium chloride (as tested by silver nitrate solution). At this stage, 0.1% calcium chloride and 100 c.c. lots of the effluent were collected successively and analysed for calcium (Table III).

TABLE III. *Efficiency of the Coffee Husk-Carbon in Removing Calcium from Calcium Chloride Solution*

Lot No.	Calcium in the effluent (mg. in 100 c.c.)	Calcium taken up (mg. in 100 c.c.)
1	0	36.4
2	2.4	34.0
3	9.6	26.8
4	17.8	18.6
5	36.0	0.4
Blank (Calcium chloride solution)	36.4	..

It may be seen from Table III that 20 gm. of the coffee husk-carbon took up 116.2 mg. of calcium. It is possible that the capacity of cation exchange of this material may improve after it has been "conditioned" through a number of cycles.

6. UTILISATION OF COFFEE HUSK-CARBON FOR REMOVING FLUORINE FROM WATER

The occurrence of excess of fluorides in drinking water, which produces the disease of fluorosis in men and cattle, has been reported from all parts of the world. In India fluorides have been reported to occur in parts of the Madras Presidency (Shortt, Pandit and Raghavachari, 1937; Raghavachari and Venkataramanan, 1940), in Travancore (Pillai, 1938), in the Punjab (Wilson, 1939; Khan and Wig, 1945) and in Hyderabad-Deccan (Davar, 1945). One of the methods suggested for removing the fluorine is by the use of an alum-treated anion exchanger (Myers and Herr, 1945). The removal is also effected by a similarly treated cation exchange resin (Venkataramanan, Krishnaswamy and Ramakrishnan, 1951). It was therefore of interest to study the use of the cation exchange material prepared from coffee husk in removing fluorine from water.

20 gm. of the sulphonated coffee husk-carbon was converted into the sodium form by treating the material with 1% sodium carbonate solution

till the effluent was alkaline to phenolphthalein, and then washing the bed with distilled water in order to remove the excess sodium carbonate. The washed material was taken in a glass tube of 1" diameter and was further treated with 100 c.c. of 1% alum solution twice and the effluents were rejected; and then 100 c.c. of the alum solution was kept in contact with the carbon overnight. The bed was then washed free of soluble aluminium ions as tested with hæmatoxylin, and a solution of sodium fluoride in tapwater (equivalent to 2.5 p.p.m. fluorine) was percolated through the bed at the rate of 25 c.c. per minute. One litre lots of the effluents were collected successively and tested for fluorine and aluminium. The alkalinity and total solids of these lots were also determined. When the residual fluorine reached the toxic limit (1.0 p.p.m.), the percolation of sodium fluoride was stopped and the carbon regenerated with alum solution as indicated above. Four such cycles were completed, and the results are presented in Table IV.

TABLE IV. *Efficiency of the Coffee Husk-Carbon in Removing Fluorine from Water*

(Results expressed as parts per million)

Lot No.	Fluorine				Aluminium IV	Total solids IV	Alkalinity as CaCO ₃ IV
	Cycle I	II	III	IV			
1	0.2	0.2	0.2	0.1	0.075	175	16
2	0.8	0.5	0.2	0.2	0.075	186	16
3	1.1	0.7	0.3	0.2
4	..	1.0	0.4	0.4
5	0.4	0.5
6	0.6	0.6
7	0.8	0.8
8	1.0	1.0
Blank (Sodium fluoride solution)	2.4	2.4	2.4	2.4	Nil	224	96

Trials with different batches of the carbon (20 gm.) showed that the volume of water that could thus be treated varied from 4 to 8 litres.

It may be seen from Table IV that after the first two cycles, 20 gm. of the carbon dealt with 4-8 litres of water (*i.e.*, one pound of the material could treat about 20-40 gallons of water) containing 2.4 p.p.m. of fluorine before the toxic amount came through. The total solids and alkalinity of the water were also reduced in the exchange process.

The sulphonated carbon can thus be utilised for removing fluorine from water in the endemic fluorosis areas. The material may be applied either in small units for use by individual households or, on a larger scale, in a centrally situated water purification plant from where the treated water can be distributed to the community. In the latter case, two beds will have to be provided, so that one can always be in use while the other is regenerated. Arrangements will have also to be made for backwashing the beds periodically.

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