

TREATMENT AND UTILISATION OF SPENT COFFEE GROUNDS FOR PREPARING ION EXCHANGE MATERIAL

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SUMMARY

An ion exchange material has been prepared from spent coffee grounds by suitable treatment with sulphuric acid, sodium chloride and alum. The material has been found considerably efficient in removing calcium from 0.1% calcium chloride solution and in removing fluorine from tap water in which known amount of sodium fluoride was dissolved (about 2.5 p.p.m. as fluorine).

1. INTRODUCTION

In a previous communication from this Laboratory (Ramakrishnan *et al.*, 1953) it was shown that an ion exchange material could be prepared from coffee husk by suitable treatment with sulphuric acid, sodium chloride and alum, and that the ion exchange material thus prepared was considerably efficient in removing calcium from calcium chloride solution of known strength and fluorine from tap water to which known amounts of sodium fluoride were added. It was of interest to extend these studies to the treatment and utilisation of spent coffee grounds, *i.e.*, the coffee powder after it has been used for the preparation of the beverage. A considerable quantity of this material could be had, as judged from the available figures for the average consumption of coffee in India. The quantity of coffee consumed in this country during 1947-48 and 1948-49 was 17,078 tons (average), the output of coffee powder being 13,662 tons (*The Wealth of India*, 1951); and this would give rise to about 9,000 tons of spent coffee grounds, reckoning that the waste material from 1 lb. of fresh coffee powder used for the preparation of decoction is about $\frac{2}{3}$ lb. (on air-dry basis).

Some studies have recently been carried out on the possible utilisation of spent coffee grounds, and the results are presented in this paper.

2. ATTEMPTS MADE IN THE PAST TO UTILISE SPENT COFFEE GROUNDS

Coffee grounds from which all the oil, wax and resin have been extracted were used in synthetic resin compositions as filling material (1939). According

to Intonti (1938), the coffee grounds from which 20% of fat was extracted (the remainder containing ash 2.35%, volatile substances 76%) could be used as fuel (4,478 g. cal./g.).

Hammond (1944) considered coffee grounds as a source of energy in the diet of growing chickens. The feeding experiments indicated, however, that coffee grounds exerted a far more deleterious effect on the growth of chicks than could be attributed to a dilution of the diet.

Rode (1944, 1946) outlined three methods of making a water-softening material from spent coffee grounds. In the first method, the waste material was treated with an aqueous solution of sodium hydroxide, sodium carbonate or trisodium phosphate in presence of aluminium. The alkaline solution was sufficiently concentrated as to dissolve the metallic aluminium. The product from which excess solution was drained off had water-softening properties, and after repeated use it was regenerated by a 2% solution of sodium chloride. In the second method, the treatment was with a solution of an alkali metal silicate, such as 10 to 20% sodium silicate, for about 5 hours and then with a solution of caustic soda or soda ash. In the third method (1946), dried coffee particles were soaked in a solution containing 50 g. ferrous sulphate, 50 g. manganous sulphate, 50 c.c. sulphuric acid and 250 c.c. water for 24 hours. The particles were preferably removed, dried and again soaked in the solution for about 24 hours, and again removed and dried. The dried product was roasted for 4-5 hours at 300-350° and cooled. The resulting particles were then soaked in a solution of sodium silicate having a specific gravity of about 1.13, for 12 hours. The coffee particles were then washed with water and dried. This product was found to be a water-softening material of the base exchange type. It weighed 37-40 lb. per cubic foot. 10,000 grains of water-hardening material (calculated as CaCO_3) was removed from hard water by a cubic foot of the dry product. The product could be regenerated by treatment with 2% sodium chloride solution.

3. MATERIAL EMPLOYED IN THE PRESENT STUDIES

Samples of spent coffee grounds were obtained from a section of the Institute Hostel Mess. The moist material as discarded from the Mess was collected for 5 consecutive days and was air-dried. It was found that the moist spent coffee grounds from about 4 lb. of fresh grounds (used for making the beverage for about 150 persons a day) represented 550 g. air-dry material. The air-dry samples for the five days were finally mixed together, and this mixture of spent coffee grounds was used for the experiments described in this paper.

4. METHODS OF ANALYSIS

Calcium was determined by the method given in The Chemists' Year Book (1936). Fluorine was determined by the method proposed by Sanchis (1934). Aluminium was determined by the method suggested by Hatfield (1934).

5. PREPARATION OF THE ION EXCHANGE CARBON

200 g. of the spent coffee grounds was taken in a beaker of one litre capacity and 200 c.c. of concentrated sulphuric acid was added to it gradually; and the contents of the beaker were stirred constantly. This amount of acid was just sufficient to moisten the material completely. It was observed that the maximum yield of granular carbon of suitable size was dependent on the rate of addition of the acid and on the mixing of the acid with the powder. Carbonisation took place almost instantaneously. After about 5 minutes, the reaction proceeded more vigorously giving rise to considerable frothing. The beaker was then cooled and left overnight. The contents were poured into an excess of water, the lumps easily crumbled and filtered on a Buchner funnel. The carbon was washed with water till it was free from acid (using methyl red as indicator), dried and sieved so as to pass through 20 mesh and be retained on 40 mesh. The yield of the carbon was 80 g.

6. EFFICIENCY OF THE CARBON AS A CATION EXCHANGER

For testing the material, 20 g. of the above carbon was taken in a glass percolating column of $\frac{7}{8}$ " diameter, supported over a layer of glass wool. 5% sodium chloride solution was 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 for sodium. The bed was then washed free from excess sodium chloride (as tested by silver nitrate solution). At this stage 0.1% calcium chloride solution was percolated through the bed at the rate of 25 c.c. per minute, and 100 c.c. lots of the effluent were collected successively and analysed for calcium (Table I).

It may be seen from Table I that the efficiency of the carbon increased after repeated use from the 1st cycle to the 4th cycle and remained almost constant afterwards. In the 4th and 5th cycles 20 g. of the carbon removed about 330 mg. of calcium, *i.e.*, 1 lb. of the carbon removed about 19 g. of calcium in terms of calcium carbonate. When the removal of calcium was almost negligible the carbon bed was regenerated by passing 5% sodium chloride solution till the effluent was free from acid and then washing the bed with water till the effluent was free from chloride.

TABLE I
*Efficiency of the Carbon Prepared from the Spent Coffee Grounds in Removing
 Calcium from 0.1% Calcium Chloride Solution*

Lot No.	Amount of calcium									
	1st cycle		2nd cycle		3rd cycle		4th cycle		5th cycle	
	mg. in 100 c.c.		mg. in 100 c.c.		mg. in 250 c.c.*		mg. in 250 c.c.*		mg. in 250 c.c.*	
	In the effluent	Taken up by the carbon	In the effluent	Taken up by the carbon	In the effluent	Taken up by the carbon	In the effluent	Taken up by the carbon	In the effluent	Taken up by the carbon
1	10.6	22.8	1.0	32.2	3.0	80.0	1.5	81.0	1.0	79.0
2	18.4	15.0	1.2	32.0	10.0	73.0	3.0	79.5	2.3	77.7
3	22.2	11.2	1.2	32.0	17.5	65.5	14.0	68.5	2.0	78.0
4	23.6	9.8	2.2	31.0	42.5	40.5	34.5	48.0	13.0	67.0
5	25.6	7.8	4.6	28.6	65.0	18.0	58.5	24.0	60.5	19.5
6	27.0	6.4	8.6	24.6	78.3	4.7	64.5	18.0	74.3	5.7
7	77.5	5.5	78.0	4.5	79.0	1.0
8	81.0	2.0	78.0	4.5	79.3	0.7
9	81.5	1.5	80.5	2.0	80.5	..
10	81.0	2.0	80.5	2.0	80.0	0.0
Blank	33.4	..	33.2	..	83.0	..	82.5	..	80.0	..
Total calcium taken up	..	73.0	180.4	292.7	332.0	328.6				

* As the amount of calcium taken up by the carbon was considerable, 250 c.c. lots were collected instead of 100 c.c. lots. Trials with carbon similarly prepared from coffee husk showed that 20 g. of the carbon removed 119.5 mg. of calcium in the first cycle and 340.5 mg. in the second cycle.

7. EFFICIENCY OF THE CARBON IN REMOVING FLUORINE FROM WATER

20 g. of the carbon was taken in a glass percolating column of 1" diameter and was treated with 1% sodium carbonate solution till the effluent was alkaline to phenolphthalein, and then the bed was washed with distilled water in order to remove the excess sodium carbonate. The carbon was treated twice with 100 c.c. portions of 1% alum solution, and the effluents were rejected. The carbon was kept overnight in contact with another 100 c.c. of alum solution. The bed was then washed free from soluble aluminium ions as tested with hæmatoxylin. A solution of sodium fluoride in tap water (equivalent to about 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. When the effluent contained toxic amounts of fluorine, the percolation of the sodium fluoride solution was stopped, and the bed was regenerated with alum as indicated above. The observations are given in Table II.

TABLE II

Efficiency of the Carbon Prepared from Spent Coffee Grounds in Removing Fluorine from Tap Water to which Sodium Fluoride was Added

Lot No.	Amount of fluorine in the effluent (in p.p.m.)				
	1st cycle	2nd cycle	3rd cycle	4th cycle	5th cycle
1	0.5	0.4	0.5	0.6	0.3
2	0.9	0.7	0.7	0.5	0.7
3	>1.0	0.5	1.0	0.8	>1.0
4	>1.0	0.9	>1.0	>1.0	>1.0
5	>1.0	>1.0	>1.0	>1.0	>1.0
Blank	2.6	2.4	2.4	2.4	2.2
Volume of water treated to non-toxic levels of fluorine (in litres)	2	4	3	3	2

The amounts of aluminium present in the effluents were negligible.

It may be seen from Table II that 20 g. of the carbon could treat about 2 to 4 litres of water (*i.e.*, 1 lb. of the material could treat about 10 to 20 gallons of water) before toxic amounts of fluorine came through.

8. SOME PRACTICAL ASPECTS

The procedure indicated in the paper for preparing an ion exchange material from spent coffee grounds appears to be simple and economic. The

efficiency of this material in removing calcium from calcium chloride solution, as also in removing fluorine from tap water to which sodium fluoride is added, is considerable. The amount of calcium removed from 0.1% calcium chloride solution by the sulphonated carbon is comparable to the amount of calcium removed from hard water by the patented product of Rode (1946, *loc. cit.*). Calculations show that 1 lb. of the sulphonated carbon can remove 19 g. of calcium (as CaCO_3) while 1 lb. of the product of Rode can remove about 16 g. of calcium (as CaCO_3).

Further work is contemplated in order to study the behaviour of the sulphonated carbon when used for the treatment of natural hard waters and waters containing fluorides. When the efficiency and importance of the new ion exchange material are established under working conditions, a number of practical points would have to be carefully considered. A most important of these would be about the collection, conservation and constant supply of the raw material itself. It might not be possible in actual practice to recover without impurities or foreign material all the spent coffee grounds discarded from various places, *e.g.*, houses and restaurants. But this and other aspects could perhaps be solved through proper agency.

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REFERENCES

1. Ramakrishnan, T., Balasundaram, S., *J. Indian Inst. Sci.*, 1953, 35, 231.
Rajagopalan, R. and Pillai, S. C.
2. .. *The Wealth of India, Industrial Products*, Part II, Council of Scientific and Industrial Research, Delhi, 1951, p. 163, Table 2.
3. .. Extrakto-Chemi, Benda, and Zell. Fr. Patent, 838,499, March 7, 1939; *Chem. Abstracts*, 1939, 33, 7927.
4. Intonti, R. .. *Rend. ist. sanita publica*, 1938, 1, 47; *Chem. Abstracts*, 1939, 33, 5933.
5. Rode, S. D. .. U.S. Patent, 2,346,909, April 18, 1944; *Chem. Abstracts*, 1944, 38, 6028.
6. _____ .. U.S. Patent, 2,391,951, Jan. 1, 1946; *Chem. Abstracts*, 1946, 40, 1256.
7. .. *The Chemists' Year Book*, Sherratt & Hughes, 1936.
8. Sanchis, J. M. .. *Ind. Eng. Chem., Anal. Ed.*, 1934, 6, 134.
9. Hatfield, W. D. .. *Ibid.*, 1934, 16, 233.