A Preliminary Comparison Between Various Granular Active Carbons for Water Reclamation

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Abstract

The quality of eight commercially available granular active carbons was investigated in laboratory characterization tests and pilot plant scale adsorption columns. Although this was only the first phase of a long-term programme, the results already indicate that the carbons derived from bituminous coal, peat or palm kernel shell charcoal are more suitable for water reclamation.

The data provided may be used as a basis for screening for the most suitable available carbons. The final choice for a particular application should, however, be made only after at least a brief pilot plant scale investigation.

Introduction

Adsorption of dissolved organic substances on the extremely large specific surface area of active carbon has become firmly established as an essential and reliable unit process in water renovation and reclamation. Active carbon treatment, however, constitutes a major cost element in water reclamation and it is therefore of economic importance to select the most suitable carbon on the basis of cost, as well as adsorption capacity and other physical characteristics. The use of powdered active carbon is being rapidly discontinued in favour of granular active carbon, mainly owing to technical problems of regeneration, filtration and poor recovery associated with the powdered form.

Recent years have brought a growing demand for active carbon for water 'polishing', and a rapid increase and improvement in its production. To meet the need for more comparative information on the various granular active carbons commercially available for water reclamation, the National Institute for Water Research (NIWR) embarked upon an extensive evaluation programme.

The first phase of the programme, which is reported in this paper, comprises laboratory characterisation tests and adsorption column studies performed on a pilot plant scale. The next phase will be the thermal regeneration of spent carbons, for which a small-scale furnace has been designed and is being completed.

Regenerability of the carbon is of major economic importance. It is therefore envisaged to continue the pilot plant adsorption studies with the same active carbons for two or more regeneration-adsorption cycles to examine their long-term performance. The effects of pre-ozonation, aeration and prechlorination on the durability and adsorption capacity of the active carbons will form part of future work.

As some of the carbons are apparently not fully exhausted even after months of operation, a detailed comparison cannot be attempted. Preliminary results during this first phase of the programme, however, indicate the superior adsorption capacity of certain carbons.

Active Carbon Products Tested

A description of the eight active carbons tested during the first stage of the programme is given in Table 1.

TABLE 1
DESCRIPTION OF ACTIVE CARBONS TESTED

Carbon No.	Base material	Mesh size (ASTM)	Appearance
3	Bituminous coal	8 x 30	Irregular granules
4	Bituminous coal	12 x 40	Irregular granules
5	Peat	0,8 mm diameter	Cylindrical granules
6	Lignite	12 x 20	Irregular granules
7	Palm kernel shell charcoal	12 x 32	Irregular granules
8	Special coal	8 x 22 (1,6 mm diameter)	Short cylindrical granules
9	Special coal	5 x 18	Irregular granules
10	Coconut shell	10 x 30	Irregular granules

Laboratory Methods

The following characteristics were evaluated during the laboratory tests:

Iodine number, apparent density, particle size distribution, abrasion resistance, hardness, ash content, moisture content, pore size distribution, COD isotherms, and phenol isotherms.

Evaluation was in accordance with the analytical methods and procedures described in *AWWA Standard for Granular Activated Carbon* (American Waterworks Association, 1974). The Ro-tap method was used for the determination of abrasion resistance. Hardness and ash content were determined as described in *Test Methods of the Control Laboratory* (Pittsburg Activated Carbon Company, 1960). Surface areas and pore size distributions were analysed by means of a Micromeritics Model 2100 D Orr surface area-pore volume analyser, using nitrogen gas as the adsorbate (BET method).

The minimum requirements (NIWR, 1978) for the relevant characteristics are shown in Table 2. These values are generally accepted in water reclamation and were used for initial screening of the carbons. The values found by the NIWR, together with those specified by the manufacturers are listed in Tables 3 to 9. The surface areas and pore size distributions are presented in Table 10 and Figure 1, and the chemical oxygen demand (COD) and phenol isotherms in Figures 2 and 3, respectively.

TABLE 2
MINIMUM REQUIREMENTS AND RECOMMENDED VALUES FOR GRANULAR ACTIVE CARBON

Paramter	Specification
Minimuym iodine number, mg I_2/g carbon	500
Recommended iodine number, mg I_2/g carbon	>900
Apparent density, g/cm³	0,36
Particle size distribution:	
uniformity coefficient	<2,1
percentage oversized particles*	<15
percentage undersized particles*	< 5
effective size range, mm	0,6 to 1,0
Abrasion resistance, %	>70
Ash content, %	< 8

*Relative to manufacturer's specifications

TABLE 3
IODINE NUMBER (mg I_2/g CARBON)

Carbon	Manufacturer	NIWR
3	900 – 1000	980
4	1000 – 1100	1080
5	1000	1025
6	630 – 670	595
7	>1250	1130
8	850	685
9	1300	1325
10	1100	1245

TABLE 4
APPARENT DENSITY (g/cm³)

Carbon No.	Manufacturer	NIWR
3	0,48 – 0,56	0,50
4	0,44 – 0,54	0,46
5	0,36	0,37
6	0,34 – 0,39	0,41
7	0,46	0,47
8	0,39	0,38
9	0,30	0,29
10	0,45 – 0,55	0,43

TABLE 5
PARTICLE SIZE DISTRIBUTION

Carbon No.	Mesh (ASTM)	% oversize		% undersize		Uniformity coefficient		Effective size (mm)	
		M	NIWR	M	NIWR	M	NIWR	M	NIWR
3	8 x 30	5–15	7	1–5	<1	≤1,9	1,94	0,8–1,1	0,92
4	12 x 40	1–5	6	1–5	2	≤1,9	1,86	0,55–0,65	0,64
5	0,8 mm diam	NA	NA	NA	NA	NA	NA	NA	NA
6	12 x 20	9	4	9	5		1,40		0,92
7	12 x 32	2,2	3	2,5	2		1,29		0,96
8	8 x 22 (1,6 mm diam)		9,5		0		1,50		1,48
9	5 x 18		ND		ND		ND		ND
10	10 x 30		0		3,5		1,64		0,76

NA Not applicable – extruded carbon
ND Not determined
M Manufacturer

TABLE 6
ASH CONTENT (%)

Carbon No.	Manufacturer	NIWR
3	8	5,7
4	8,5	6,9
5	6	6,2
6		11,4
7	5	4,3
8	10	10,0
9	8	5,1
10	3	3,3

TABLE 7
MOISTURE CONTENT (%)

Carbon No.	Manufacturer	NIWR
3	2	0,4
4	2	0,5
5	2	3,4
6	8	7,9
7	4,7	4,4
8	10	8,5
9	5	4,5
10		1,1

TABLE 8
ABRASION RESISTANCE (%)

Carbon No.	Manufacturer	NIWR
3	70 – 80	94,6
4	75 – 80	93,8
5	NA	NA
6		85,2
7		95,9
8	96,4	91,5
9		ND
10		96,7

NA Not applicable – extruded carbon
ND Not determined

TABLE 9
HARDNESS (%)

Carbon No.	Manufacturer	NIWR
3		95
4		96
5	88	ND
6		81
7	95	90
8		93
9		97
10	99	98

TABLE 10
SURFACE AREA AND PORE SIZE DISTRIBUTION

Carbon No.	Surface area (m^2/g)	Volume in pores of indicated diameter (cm^3/g)					
		1—2 nm	2—10 nm	10—50 nm	50—100 nm	over 100 nm	Total over 1 nm
3	895	0,26	0,08	0,09	0,04	0,21	0,68
4	1070	0,29	0,13	0,11	0,04	0,12	0,69
5	1000	0,21	0,20	0,13	0,05	0,29	0,88
6	655	0,09	0,32	0,22	0,04	0,23	0,90
7	1195	0,31	0,21	0,02	0,03	0,19	0,76
8	643	0,10	0,19	0,21	0,05	0,23	0,78
9	1515	0,48	0,23	0,04	0,05	0,36	1,16
10	1210	0,34	0,11	0,05	0,06	0,18	0,74

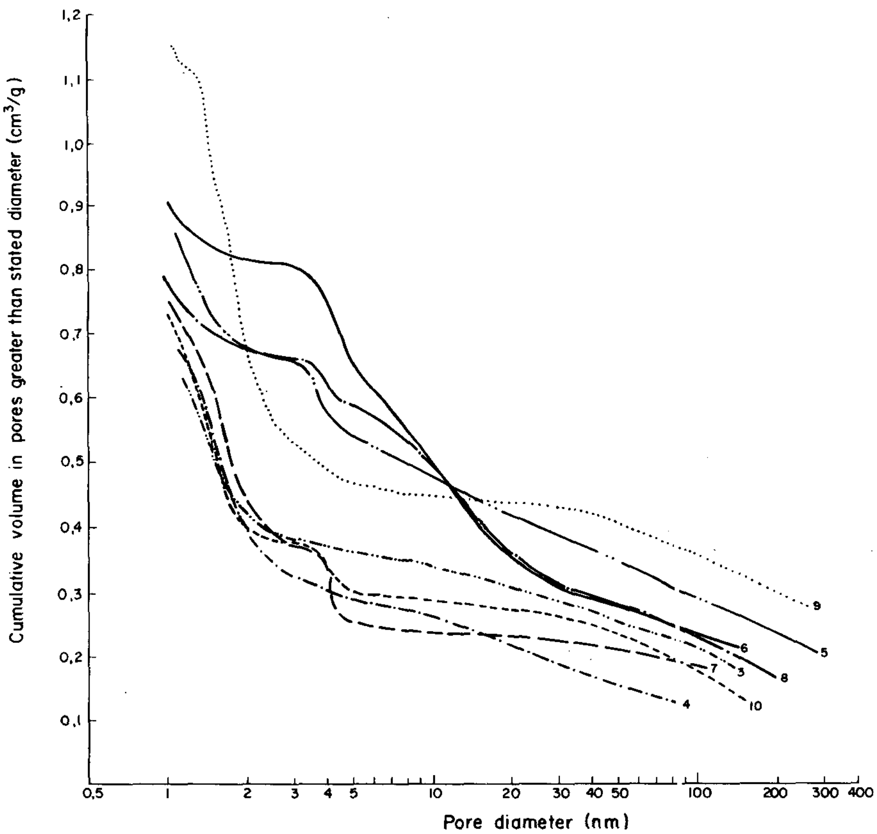


Figure 1
Pore size distributions of active carbons tested

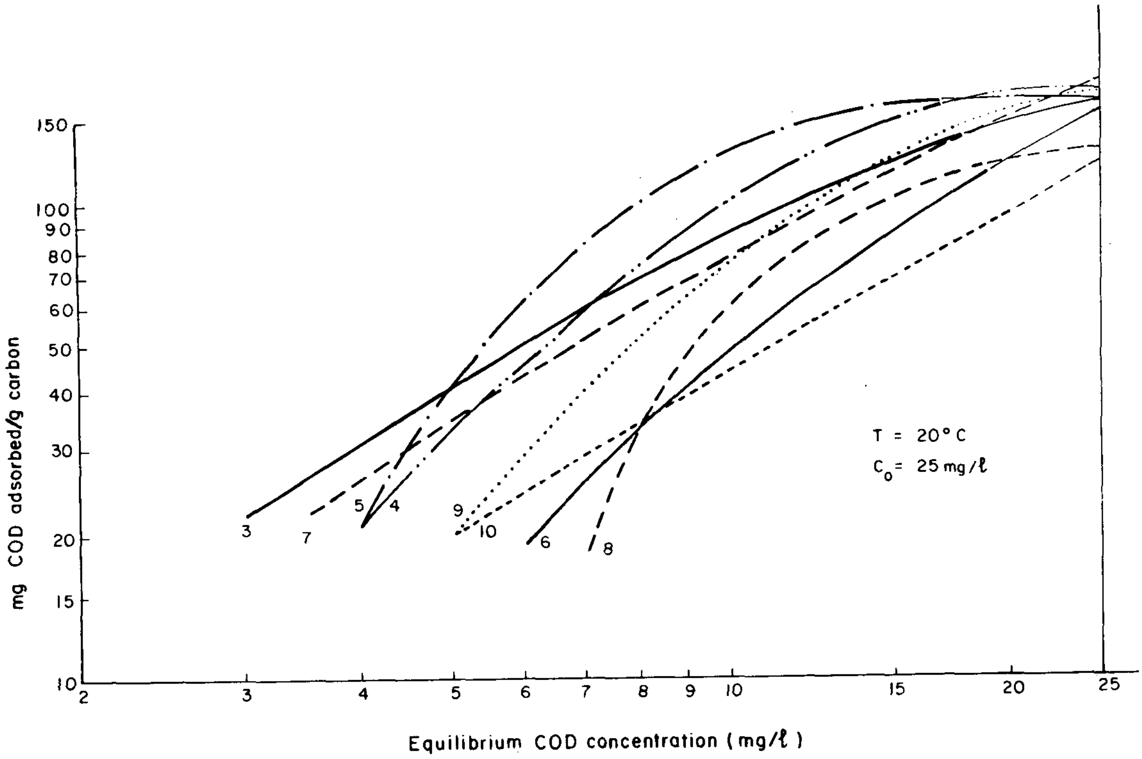


Figure 2
COD isotherms of carbons tested.

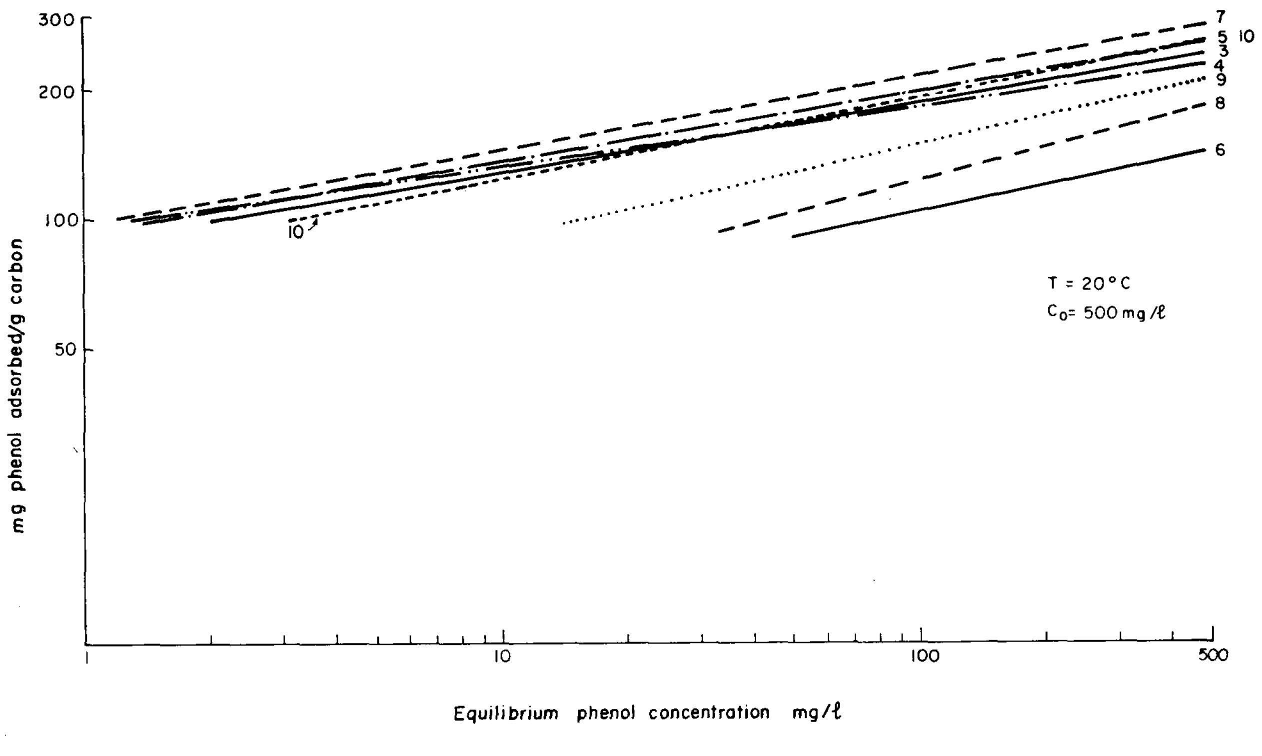


Figure 3
Phenol isotherms of carbons tested.

Adsorption Column Studies

The test facilities consisted of eight identical parallel columns operated in the downflow mode. Design data were based on experience gained from the adsorption system at the Stander water reclamation plant and as described in *Manual for Water Renovation and Reclamation* (NIWR, 1978). To avoid corrosion, PVC was used as construction material for the columns and all the piping.

The internal diameter of every column was 150 mm and the effective length 1,5 m. Each column was packed with 20 ℓ of carbon (packed height, 1,13 m), thus allowing 33 % for bed expansion during backwashing.

A contact time of 20 min, based on empty bed volume, was chosen, for which a volumetric flow rate of 60 ℓ/h was required. The linear liquid velocity through the column, based on empty bed cross section, was therefore 3,4 m/h, which is somewhat lower than the recommended value of 5 m/h. Employing this velocity would lead to a decrease in column diameter from 150 to 120 mm and an increase of the length from 1,5 to 2,35 m, resulting in difficulties in handling the columns and possible occurrence of wall effects, which are known to influence small column operation.

Since the columns were packed with equal volumes of carbon, the mass of individual carbons varied according to their respective apparent or more correctly backwashed, packed densities, as shown in Table 11.

TABLE 11
MASS OF CARBON IN COLUMNS

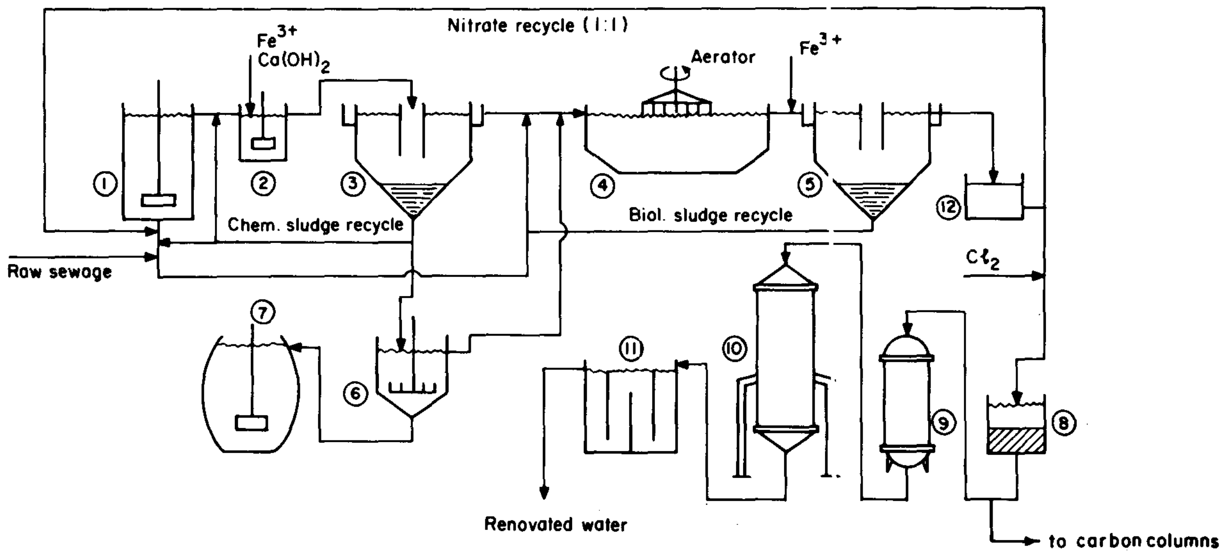
Carbon No.	Approximate mass (kg)
3	9,6
4	8,6
5	7,3
6	8,5
7	9,6
8	8,1
9	5,9
10	7,9

Feed Water

The prechlorinated, filtered biological clarifier overflow from a pilot-scale lime flotation biological (LFB) water reclamation plant was used as feed for all eight carbons tested. A flow diagram of the LFB plant is presented in Figure 4.

The quality of the feed water to the columns varied within the following ranges:

Total organic carbon, mg/ℓ	2 – 6
Chemical oxygen demand, mg/ℓ	15 – 30
pH	7,4 – 8,0
Turbidity, JTU	0,3 – 1,0



(1)	Denitrication reactor	(7)	Anaerobic digester
(2)	Chemical mixing	(8)	Roughing filter
(3)	Chemical clarifier	(9)	Dual media filter
(4)	Nitrification pond	(10)	Active carbon
(5)	Biological clarifier	(11)	Chlorination
(6)	Thickener	(12)	Flow division

Figure 4
Flow diagram of the modified LFB pilot plant (60 m^3/d)

TABLE 12
TOTAL COD AND TOC REMOVAL PER m³, TON AND R1000 WORTH OF CARBON

Carbon No.	Cost R/kg*	kg COD removed per			kg TOC removed per			Ratio COD/TOC removed
		m^3	ton	R1000*	m^3	ton	R1000*	
3	1,89	82,1	171,1	90,5	26,1	54,4	28,8	3,1
4	2,06	81,1	188,7	91,6	31,8	73,8	35,8	2,6
5	1,90	75,1	205,7	108,3	24,3	66,5	35,0	3,1
6	3,00	62,4	146,7	48,9	18,5	43,5	14,5	3,4
7	1,57**	77,7	161,9	103,1**	24,4	50,8	32,4**	3,2
8	1,99	55,3	136,4	68,6	17,2	42,5	21,3	3,2
9	1,83	66,0	223,7	122,2	19,3	65,3	35,7	3,4
10	1,85	61,2	155,0	83,8	16,6	42,0	22,7	3,7

* Prices as in August 1979, excluding transport cost
**1978

Performance of the Carbon Columns

COD and total organic carbon (TOC) were monitored continuously for both the inflow and outflow of all eight columns. A total of 275,6 m³ of feed were passed through each column. On average, this feed water contained 22,34 mg COD and 3,63 mg TOC per ℓ respectively. In other words every column, containing 20 ℓ of carbon, was loaded with organic material equivalent to about 6,2 kg COD and 1,0 kg TOC. The net running time was 191 days.

The capabilities of the carbons to adsorb these substances under the conditions of the experiment were expressed as cumulative removal against the cumulative load (both in kg COD/TOC per m³ of carbon) and are shown in Figures 5 and 6. These curves are in fact a modified form of integrated conventional breakthrough curves.

As mentioned previously, the columns were packed with equal volumes, but unequal masses of carbon. Since the columns are designed on a volumetric basis, and the carbons usually sold by mass, it is useful to compare the capacities of the carbons on the basis of both mass and volume. The mass of COD and TOC substances adsorbed per volume, mass and cost unit of the respective carbons are compared in Table 12.

The columns were backwashed weekly and small samples of carbons were taken at the same time to determine their respective iodine numbers (shown in Table 13).

TABLE 13
IODINE NUMBERS DURING THE TEST
(mg I_2/g CARBON)

m³ of feed passed per column	Carbon No.							
	3	4	5	6	7	8	9	10
0	980	1080	1025	595	1130	685	1325	1245
27,8	709	653	636	464	699	582	1026	741
55,9	800	840	810	425	640	560	1048	1000
108,3	627	691	559	435	590	526	963	782
165,2	617	630	494	405	544	471	905	824
217,2	603	627	523	427	558	492	880	801
265,7	598	606	510	412	549	481	864	773

Discussion and Conclusion

In general, there was very little difference between the values claimed for the various carbon characteristics and those found during laboratory testing by the NIWR.

The pore size distribution curves (Table 10 and Figure 1) may be somewhat misleading in the assessment of the carbons as they are based on carbon mass. For instance, the cumulative volume in pores greater than 1 nm varied between 0,68 and 1,16 cm³/g carbon, which, considering the respective apparent densities, means a much closer range of between 0,30 and 0,37 cm³/cm³ carbon. The shape and the position of the curves are basically determined by the raw material and are geometrically quantitative rather than physically qualitative characteristics. Carbon No. 9 has the largest surface area, biggest micropore and total pore volume, but its volumetric adsorption capacity is far from the best. The pore size distribution curves are valuable tools for measuring the degree of restoration of the original structure during thermal regeneration.

The reason for the COD isotherms being non-linear in the log-log plot is that they describe a multi-component system (similar to the feed water to the pilot plant columns), while phenol isotherms were obtained using a synthetic phenol solution. The values corresponding to the isotherms extrapolated to C_o = 25 (original concentration) in Figure 2 represent the amount of COD adsorbed per g of carbon when the carbon is in equilibrium with the influent concentration to the columns, and is the *ultimate capacity of the carbon*.

From the column adsorption studies it can be concluded that active carbons prepared from bituminous coal, peat or palm kernel shell charcoal (carbons Nos. 3, 4, 5 and 7) are more suitable for water reclamation with respect to volumetric adsorption capacity. This was not unexpected as the COD iso-

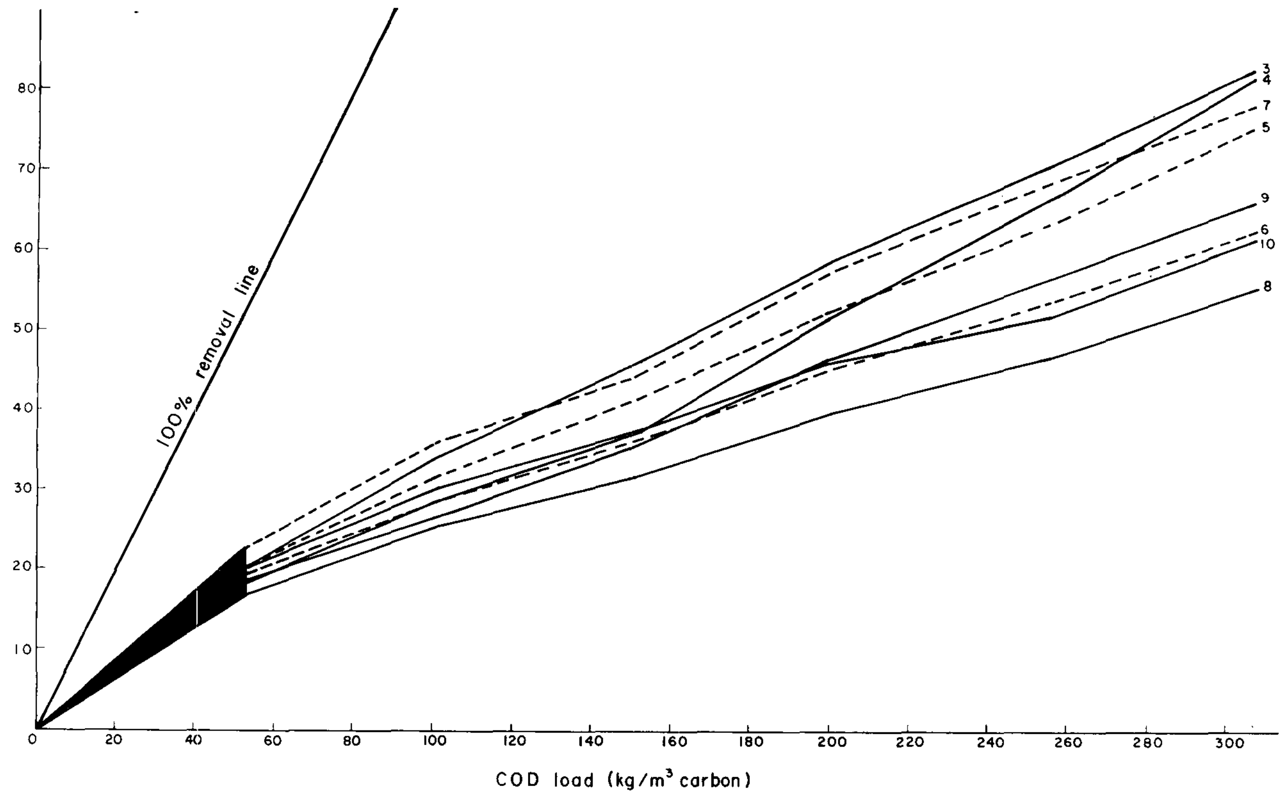


Figure 5
COD removal

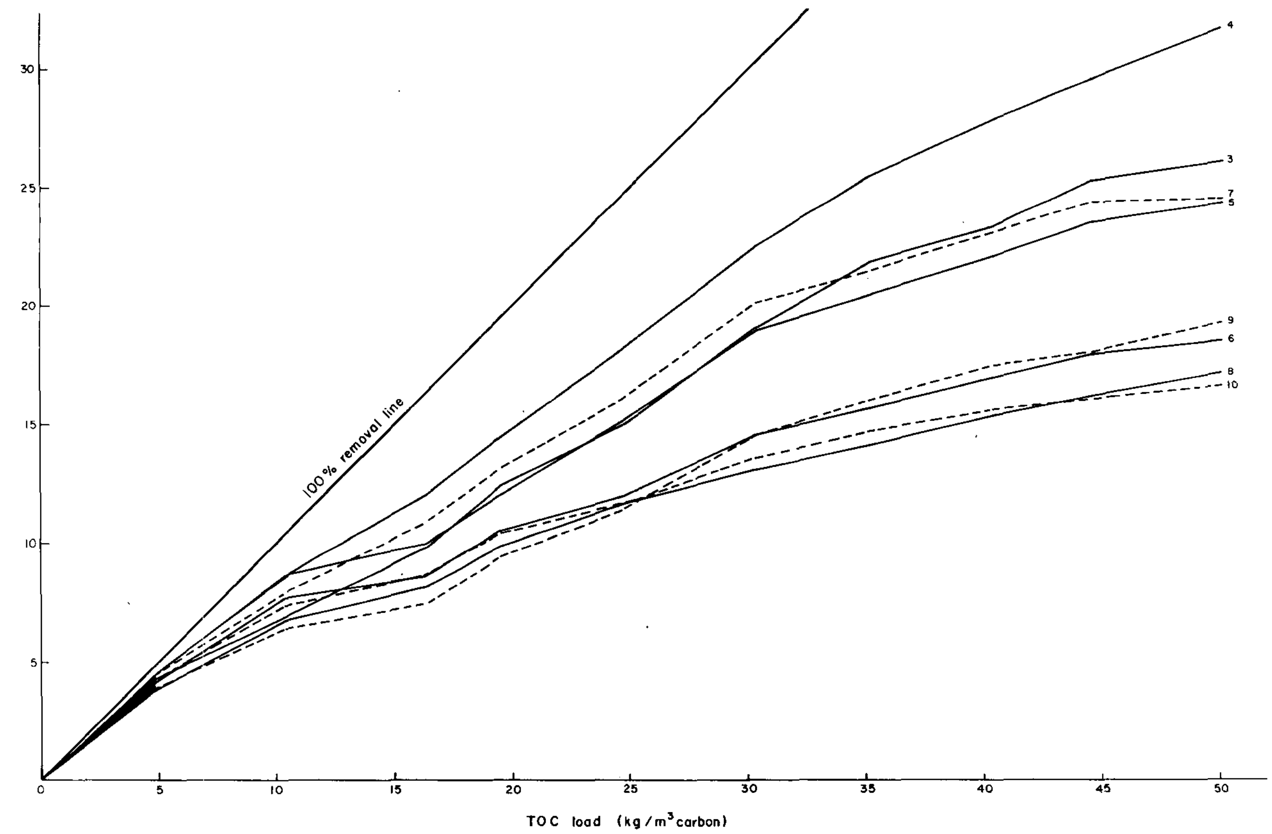


Figure 6
Total organic carbon removal

therms already indicated a similar order of capacities (with the exception of carbon No. 9, which is higher due to its lower apparent density). The TOC removal followed the same pattern.

On a mass basis, carbon No. 9 performed the best, again partly owing to its low apparent density. In practice an appreciably higher capital investment would be required to effect the same effluent quality as with carbons Nos. 3, 4 or 5, for example.

Carbons Nos. 9 and 5 (the extruded type) appear to be the most economical (subject to their mechanical properties after a few regeneration cycles).

Comparison on a mass (and therefore a cost) basis is rather complex as factors such as hydraulic resistance, contact time and column capacities are functions of specific volume. It would seem that, for the designer, the volume of carbon as column packed would be the best basis for comparison. Ideally the carbon should be sold per volume of backwashed, column packed material.

The iodine number is not decisive as it also includes the micropores, some of which are of little value for this particular application. However, it still remains a useful parameter for assessing the relative state of exhaustion (compare Table 13 and Figures 5 and 6).

The relatively low removal efficiencies are due to the carbons having been tested under single stage contacting conditions. In practice, two columns, one with partly exhausted and one with fresh or regenerated carbon connected in series, are employed, resulting in higher efficiencies. More comprehensive data will be available after the second phase of the programme, which will include regeneration.

It should be borne in mind that the final choice of carbon for a particular application cannot be based on laboratory evaluation alone. A brief pilot-plant investigation (at least) should also be conducted.

Acknowledgement

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