

(Supplementary Documents - Item b)

Effect of Gums on Carbon Treatment of Textile Effluent

The Effect of Polysaccharidic Gums on Activated
Carbon Treatment of Textile Waste Water

by

Christian Roy, B.Sc.A.

Under the Supervision of

Dr. B. Volesky

A thesis submitted to the Faculty of Graduate Studies and
Research in partial fulfillment of the requirements for the
degree of Master of Engineering.

Department of Chemical Engineering

McGill University

Montreal, Quebec

June 1976

ABSTRACT

The activated carbon treatment of wastewater originating from the Celanese Canada Ltd. Carpet plant at Sorel, Quebec, was tested in this study. Typical plant effluent was characterized and prepared. Soluble organics in the synthetic effluent varied between 75 and 185 mg/l TOC. Organic contribution of the dyes alone is in the range of 10% of the total TOC while that of the dyeing process chemicals is as high as 75%; the remaining 15% would be the approximate contribution of the soluble guar gum used as a viscosity adjusting additive in the new continuous dyeing process.

In the first phase of the work, the activated carbon adsorption of the guar gum from its pure solution was examined in laboratory tests. Improved adsorption was observed at low pH values and at elevated adsorption temperatures. Lignite-based carbon out-performed bituminous coal-based carbon. At 30 mg/l TOC of soluble guar gum, low carbon loading in the range of (5-8) mg TOC/g was recorded for various types of carbon at 20°C and neutral pH.

In the second phase of the work, the activated carbon adsorption of typical Celanese dyehouse synthetic wastewater

was examined. Although the presence of non-adsorbable residues in the range of 9-18 mg/l TOC was observed, the adsorption isotherm results indicated that the conventional Celanese effluent is amenable to activated carbon treatment. The changing technology of textile dyeing processes results also in altered composition of liquid effluent being discharged from a dyehouse. Presence of 20 to 100 mg of polysaccharidic guar gum per liter of conventional wastewater mixture had a pronounced effect on the adsorption process. The study revealed that there is an optimum range for the gum concentration in the effluent (estimated at 10-35 mg/l) resulting in a favorable change in the adsorptive behavior. This is reflected in an increase by more than 50% and 100% in the carbon loading at initial concentration and the adsorption intensity (the slope of Freundlich isotherm) respectively.

RESUME

La présente étude porte sur le traitement par carbone activé des eaux usées provenant de l'usine de tapis de Celanese Canada Limitée à Sorel, Québec. Un tableau des eaux résiduelles caractéristiques de cette usine y est brossé. La concentration des polluants organiques présents dans l'échantillon synthétique des eaux résiduelles typiques de l'usine varie entre 75 et 185 mg/l TOC. La contribution des produits chimiques reliés aux procédés de teinture compte à elle seule pour environ 75% du total alors que la contribution organique des colorants n'est que de 10%; le 15% restant serait la contribution approximative de la portion soluble de la gomme de guar utilisée comme agent d'ajustage de viscosité dans le nouveau procédé de teinture à la continue.

En premier lieu, l'efficacité de l'adsorption par carbone activé de la gomme de guar en solution d'eau pure est évaluée. Les tests de laboratoire démontrent une amélioration de l'adsorption à température élevée et à pH acide. Le carbone de lignite s'avéra supérieur au carbone de houille grasse. A une concentration de 30 mg/l TOC de gomme de guar soluble, la

capacité d'adsorption pour différents types de carbone activé à 20°C et pH neutre est assez basse, de l'ordre de 5 à 8 mg TOC/g.

Le seconde partie de l'ouvrage évalue l'efficacité de l'adsorption par carbone activé de différents échantillons synthétiques d'eau résiduaire de la teinturerie de l'usine. Malgré une concentration résiduelle de polluants non adsorbables de 9 à 18 mg/l TOC, les isothermes d'adsorption indiquent que les eaux usées conventionnelles de l'usine peuvent être efficacement traitées par un procédé de carbone activé. Il s'avéra que la présence de 20 à 100 mg de gomme de guar polysaccharidique par litre d'eau résiduaire conventionnelle a un effet très prononcé sur le procédé d'adsorption. L'étude démontre que la concentration optimum de gomme pouvant produire un effet positif sur l'adsorption varie approximativement de 10 à 35 mg/l. Ceci est dénoté en laboratoire par un accroissement d'au moins 50% de la capacité d'adsorption à la concentration initiale et un accroissement de plus de 100% de l'intensité d'adsorption (pente de l'isotherme de Freundlich).

ACKNOWLEDGEMENTS

This work has been done in cooperation with Celanese Canada Limited Carpets Division, Sorel, Quebec, who provided in part the financial assistance. Special thanks are due to Messrs. R. Speak, C. Fontaine, J.A. Juneau, G. Gauthier, H. Plasse and last, but not least, Mr. R. Darsigny.

I would like to express my gratitude to the following people who have aided, either directly or indirectly, in the conception and completion of this work.

Firstly, to my director, Dr. B. Volesky, who stimulated my interest in the field of water pollution control, for his advice, guidance, support, and encouragement throughout all facets of this project.

The guidance of Dr. E. Chornet from Université de Sherbrooke in the field of adsorption by activated carbon is gratefully acknowledged.

Thanks are due to Messrs. C. Ghoche, of Atlas Chemical Industries Canada Limited; B.P. Herner, of Calgon Canada,

P.J. Frekenhorst, of Norit and Actibon Carbons; B.H. Kornegay, of Westvaco Corp., A.W. Markowiak, of Witco Chemical Canada Limited and G. Monteih, of Barnebey-Cheney Limited, for providing the carbon samples required for the experimental part of this work.

The contribution of Mr. G.W. Hines, of Harding Carpets, to the activated carbon process review is appreciated.

I desire also to extend my appreciation to the McGill Engineering Library personnel and to Miss P. Fong for typing this thesis. Sincere gratitude is expressed to the other members of faculty, staff and fellow graduate students for their individual efforts on my behalf.

I also wish to thank my wife and my parents for their continued support and encouragement throughout my education.

TABLE OF CONTENTS

	<u>Page</u>
ABSTRACT	ii
RESUME	iv
ACKNOWLEDGEMENTS	vi
LIST OF FIGURES	xi
LIST OF TABLES	xiii
1. INTRODUCTION	1
1.1 Treatment of Textile Effluent	1
1.2 Activated Carbon Treatment Technology	2
1.3 Activated Carbon Textile Effluent Treatment Process	24
1.4 Pollution Problem at Celanese Canada Ltd., Sorel Carpet Plant	26
1.5 Objectives	27
2. EXPERIMENTAL	29
2.1 Materials	29
2.2 Preparation of Stock Solutions	34
2.2.1 Dye Stock Solution	34
2.2.2 Textile Chemicals Stock Solution	34
2.2.3 Guar Gum Stock Solution	35
2.3 Preparation of Activated Carbon Samples	35
2.4 Laboratory Adsorption Test Procedure	36
3. RESULTS	39
3.1 Characterization of Celanese Dyehouse Wastewater Effluent	39

TABLE OF CONTENTS (continued)

	<u>Page</u>
3.1.1 Introduction	39
3.1.2 Prediction of the Celanese Dyehouse Typical Wastewater Mixtures Composition	40
3.1.3 Description of Typical Mixtures	47
3.2 Study of Adsorption of Jaguar A-40-F Gum	49
3.2.1 Jaguar A-40-F Gum Solution Properties ..	49
3.2.2 Adsorption Kinetics of Jaguar A-40-F ...	52
3.2.3 Effect of pH on Adsorption of Jaguar A-40-F for Various Types of Carbons	52
3.2.4 Effect of Temperature on Adsorption of Jaguar A-40-F for Various Types of Carbons	55
3.2.5 Comparison of Various Types of Activated Carbons for Adsorption of Jaguar A-40-F Gum	57
3.2.6 Effect of Low pH on Hydrodarco 4000 Isotherm for Adsorption of Jaguar A-40-F	62
3.2.7 Effect of Elevated Temperature on Hydrodarco 4000 Isotherm for Adsorption of Jaguar A-40-F	65
3.3 Study of Adsorption of Typical Celanese Dyehouse Wastewater Mixtures	68
3.3.1 Adsorption Kinetics	68
3.3.2 Adsorption Isotherms for Effluents A and B with Hydrodarco 4000	70
3.3.3 Adsorption Isotherms for Effluents C and D with Hydrodarco 4000	73

TABLE OF CONTENTS (continued)

	<u>Page</u>
3.3.4 Adsorption Isotherms for Effluents E and F with Hydrodarco 4000	76
3.3.5 Adsorption Isotherms for Effluent D with Filtrasorb 400 and Norit	79
3.3.6 Adsorption Isotherm for Effluent D with Hydrodarco 4000 Expressed for a COD Parameter	82
4. DISCUSSION	85
4.1 Study of Adsorption of Jaguar A-40-F Gum From its Pure Solution	85
4.2 Study of Adsorption of Typical Celanese Dyehouse Wastewater Mixtures	92
SUMMARY OF RESULTS	100
RECOMMENDATIONS	103
Appendix 1. Physical Properties of Investigated Granular Activated Carbons	105
Appendix 2. Chemical Nature of Jaguar A-40-F Guar Gum	106
Appendix 3. Total Carbon and Inorganic Carbon Calibration Curves	109
Appendix 4. Tabulation of Experimental Results. Study of Adsorption of Jaguar A-40-F Gum ..	117
Appendix 5. Viscosity of the Filtered Jaguar A-40-F Gum Solution	124
Appendix 6. Tabulation of Experimental Results. Study of Adsorption of Typical Celanese Dyehouse Wastewater Mixtures	126
REFERENCES	131

LIST OF FIGURES

<u>Figure</u>		<u>Page</u>
1	Moving bed adsorber. Hollitex Carpet Plant	8
2	Bio-regenerated activated carbon, Masland Plant	10
3	Fixed bed adsorption. Harding Carpets Plant	12
4	Anaerobic-aerobic treatment with activated carbon. Palisades Industries	14
5	Pulsed bed adsorber. Westmill Carpet Plant	17
6	Ozone-carbon treatment. Kanebo Co., Nagahama, Japan	19
7	Fixed bed adsorbers. Weeks Plant	21
8	Activated carbon-activated sludge. Cone Mills	23
9	Effect of filtration on the gum solution (TOC)	51
10	Contact time vs remaining TOC. Pure gum solution. Filtrasorb 400 at 20°C and pH 7.0	53
11	Adsorption isotherms for Jaguar A-40-F. Various types of activated carbons at 20°C and pH 7.0	58
12	Adsorption isotherms for Jaguar A-40-F. Hydrodarco 4000 at 20°C for pH 3.5 and 7.0	63
13	Adsorption isotherms for Jaguar A-40-F. Hydrodarco 4000 for pH 7.0 at 20°C and 65°C	66
14	Adsorption isotherms for effluents A and B. Hydrodarco 4000 at 20°C and pH 7.0	71
15	Adsorption isotherms for effluents C and D. Hydrodarco 4000 at 20°C and pH 7.0	74

LIST OF FIGURES (continued).

<u>Figure</u>		<u>Page</u>
16	Adsorption isotherms for effluents E and F. Hydrodarco 4000 at 20°C and pH 7.0	77
17	Adsorption isotherms for effluent D. Hydrodarco 4000, Filtrasorb 400 and Norit at 20°C and pH 7.0	80
18	Adsorption isotherm for effluent D. Hydrodarco 4000 at 20°C and pH 7.0 expressed for a COD parameter	83
19	Calgon Corp. adsorption isotherm. Celanese gum-free wastewater. Filtrasorb 400 at 68°C and pH 8.0	94

LIST OF TABLES

<u>Table</u>		<u>Page</u>
1	Textile industry effluent treatment. Design features of adsorbers units.	6
2	Granular activated carbons used in this study.	30
3	Dyes used for the typical synthetic waste-water mixtures.	32
4	Textile chemicals used for the typical synthetic wastewater mixtures.	33
5	Volumes of batch and continuous dyeing solutions.	42
6	Dilution factors for dyeing solution constituents.	43
7	Estimation of maximum concentration of typical dyes in dyehouse wastewater.	45
8	Estimation of maximum concentration of typical textile chemicals in dyehouse wastewater.	46
9	Typical synthetic dyehouse effluent mixtures. Celanese Carpets plant, Sorel.	48
10	Effect of pH on adsorption of Jaguar A-40-F gum. Various activated carbons.	54
11	Effect of temperature on adsorption of Jaguar A-40-F gum. Various activated carbons.	56
12	Characteristics of Freundlich isotherms for adsorption of Jaguar A-40-F gum. Various types of activated carbon at 20°C and pH 7.0.	60
13	Characteristics of Langmuir isotherms for adsorption of Jaguar A-40-F gum. Various types of activated carbon at 20°C and pH 7.0.	61
14	Characteristics of Freundlich isotherm for adsorption of Jaguar A-40-F. Hydrodarco 4000 at 20°C and pH 3.5.	64

LIST OF TABLES (continued)

<u>Table</u>		<u>Page</u>
15	Characteristics of Freundlich isotherm for adsorption of Jaguar A-40-F, Hydrodarco 4000 at pH 7.0 and 65°C.	67
16	Remaining wastewater TOC as a function of contact time. Hydrodarco 4000 (carbon dosage 10,000 mg/l) at 20°C and pH 7.0	69
17	Characteristics of Freundlich isotherms for adsorption of effluents A and B. Hydrodarco 4000 at 20°C and pH 7.0.	72
18	Characteristics of Freundlich isotherms for adsorption of effluents C and D. Hydrodarco 4000 at 20°C and pH 7.0.	75
19	Characteristics of Freundlich isotherms for adsorption of effluents E and F. Hydrodarco 4000 at 20°C and pH 7.0.	78
20	Characteristics of Freundlich isotherms for adsorption of effluent D. Filtrasorb 400, Hydrodarco 4000 and Norit at 20°C and pH 7.0.	81
21	Characteristics of Freundlich isotherm for adsorption of effluent D. Hydrodarco 4000 at 20°C and pH 7.0 expressed for a COD parameter.	84

1. INTRODUCTION

1.1 Treatment of Textile Effluent

Textile manufacturing and finishing processes have recently undergone major development resulting in refinements in dyeing and printing techniques which considerably enhance the appearance of fabrics. In dyeing processes, controlling of discrete dye particles in aqueous systems presents a new challenge. In order to control the mobility of these particles special thickening additives have been developed to maintain viscosity of the dyeing solution⁽¹⁾. However, presence of these chemicals in the spent process solution which is ultimately discarded poses a new pollution problem.

Until recently, biological oxidation was predominant in the textile wastewater treatment. Its application to changing dyehouse effluents, however, has recently been widely discussed⁽²⁻⁸⁾. Several advanced techniques have been proposed as alternatives to conventional treatment processes⁽⁹⁻¹⁴⁾. Among these adsorption with activated carbon has attracted particular attention.

1.2 Activated Carbon Treatment Technology

In any applications where relatively small quantities of organic contaminants must be removed from a wastewater stream, activated carbon should be considered as a potential treatment method. The maximum concentration of organic matter in the effluent that can be treated economically by carbon will depend on the particular case. Whenever the concentration of organic compounds exceeds approximately 200 ppm, pretreatment to remove the bulk of the organics prior to carbon treatment should be considered⁽¹⁵⁾.

The adsorptive behavior of activated carbon has been well documented⁽¹⁶⁻¹⁹⁾. Carbon application to wastewater treatment has been discussed in considerable depth by Mantell⁽²⁰⁾, Weber⁽²¹⁾ and Hassler⁽²²⁾.

Studies on dyes removal by carbon have resulted in good understanding of the process and its capabilities⁽²³⁻²⁵⁾. It has been found that activated carbon is effective in removing color from mixed industrial effluents containing dyes^(10,25).

De John compared different types of carbons derived from lignite and coal and their suitability for industrial wastewater treatment⁽²⁶⁾, including textile wastes⁽²⁵⁾.

Porter⁽²⁷⁾ emphasized the necessity of collecting laboratory and pilot plant data prior to wastewater treatment plant design. Process design implies the calculation of contact time and carbon exhaustion rate. Once the two parameters are determined, the regeneration capacity and the carbon contacting

volume are easily derived. The specific column height, diameter and the number of columns, however, can be chosen only after consideration of hydraulic and economic factors. Furthermore, process design for carbon adsorption is complicated by microbial activity and complex adsorption kinetics⁽²⁸⁾. Biological action develops in all carbon columns treating biodegradable effluent in the presence of nutrients and in the absence of toxic compounds. Carbon adsorption kinetics and the mathematical treatment of it are complicated when the column is not operated at steady state as for upflow and down-flow arrangements. The moving bed, however, represents a steady state arrangement.

The simplest possible design approach is based on the assumption of equilibrium between the feed concentration and the exhausted carbon; the only requirement for design is determination of an adsorption isotherm^(29,30). However, the method is limited to systems with no significant biological activity and a highly favourable (irreversible) isotherm⁽²⁸⁾.

Design methods based on pilot plant data include the Short Term Adsorption Wave Method⁽³¹⁾, the Bed Depth Service Time Method⁽³²⁾ and the Operating Line Method⁽³³⁾. The accuracy, restrictions and uses of the above design techniques have been discussed by Benedek⁽²⁸⁾.

It is also possible to design carbon columns for any system without pilot plant work from knowledge of the mass transfer coefficients⁽³⁴⁻³⁷⁾. These mathematical models

represent an effort to optimize the design and to reduce costs and planning time required at both the pilot plant and full-scale levels. They are particularly useful in estimating effect of changes in carbon contacting conditions.

Granular carbon contacting normally occurs in a filter-like equipment, often referred to as columns or adsorbers. The height to diameter ratio for full-scale columns typically ranges from 1.5:1 to 4:1. The preferred material of construction is usually coated carbon steel⁽²⁸⁾.

There are three possible modes of operation for carbon columns⁽³⁸⁾. In the moving bed (or pulsed bed) arrangement, fresh carbon is continuously (occasionally in pulses) fed at the top and exhausted carbon is removed at the bottom; liquid is fed at the bottom. In the downflow arrangement, liquid is fed from the top and the carbon is removed for disposal or regeneration when exhausted. In the upflow arrangement, the liquid is fed at the bottom; columns operate in a packed or fluidized state depending on liquid flowrate.

Dividing the adsorption granular activated carbon operation in either single or multiple column sequence is usually assessed first⁽³⁹⁾. There are two possible methods of arranging the multiple columns: in series and in parallel. According to Hager⁽⁴⁰⁾, the more common column configurations are: single moving bed, downflow in series, downflow in parallel and upflow-expanded in series.

Carbon regeneration technology, which is an important factor in a large-scale operation, has been well evaluated by Smith⁽⁴¹⁾ and Loven⁽⁴²⁾. The techniques differ for granular and powdered activated carbon. Regeneration can be thermal, chemical or biological. Thermal regeneration is performed by means of multiple hearth furnaces, rotary kilns, fluidized bed furnaces and transport reactors. Chemical regeneration includes acid or base extraction, wet oxidation, chemical oxidation and solvent extraction. Biological regeneration can be performed aerobically and anaerobically.

The following paragraphs describe several typical examples of carbon adsorption systems used for the treatment of industrial textile wastewaters.

Moving bed adsorber at Hollitex Carpet plant

Industrial use of activated carbon for treatment and recycle of textile waste effluents was first reported a few years ago at Hollitex Carpet Mill, Southampton, Pennsylvania^(43,44). The Stephen Leedom Carpet Co. plant specializes in tufted carpeting. Rinse water from the dye becks which accounts for approximately 80% of the 500,000 USG/day (1,893 m³/day) total water usage is reclaimed at this plant. A moving bed adsorber has been selected for the wastewater purification. The remaining 100,000 USG/day (379 m³/day) which is concentrated dye solution is segregated from rinse water and discharged into municipal sewer. Color of the influent to the adsorber normally ranges from 100 to 150 APHA while TOC

Table 1
TEXTILE INDUSTRY EFFLUENT TREATMENT*
(DESIGN FEATURES OF ADSORBER UNITS)

PLANT NAME	INSTALLATION DATE	PLANT FLOW RATE [1000 USG/DAY]	RAW WASTE INFLUENT CHARACTERISTICS **	TREATED EFFLUENT CHARACTERISTICS **	RECYCLE	ADSORBER TYPE	TOTAL CARBON CHARGE [1000 LBS]	CARBON REACTIVATION	REFERENCES
HOLLITEX CARPET	1969	500	COLOR: 100-150 APHA TOC: 210-290	COLOR: 5 APHA TOC: 10	YES	MOVING BED	50	MULTIPLE HEARTH FURNACE	RIZZO, 1970 MacCRUM, 1971
MASLAND AND SONS	1971 [Pilot Plant]	50	COD: 305-1450 BOD: 95-700	COD REMOVAL : 75% BOD REMOVAL : 95% COLOR: NONE	NO	TWO FIXED BED SYSTEMS IN PARALLEL	3.6/SYSTEM	AEROBIC REGENERATION	RODMAN ET AL., 1971
HARDING CARPETS	1972	86	TOC: 585 COD: 1800 BOD: 587 COLOR: 8400 UNITS [Hach KH]	TOC: 235 COD: 808 BOD: 198 COLOR: 280 UNITS [Hach KH]	NO	TWO FIXED BED SYSTEMS IN PARALLEL	2.5/SYSTEM	NONE	HINES, 1975
PALISADES INDUSTRIES	1973	75	COD: 1700 - 10500 BOD: 1300 - 7900	COD REMOVAL: 55 - 70% BOD REMOVAL: 65 - 73%	NO	TWO PARALLEL SYSTEMS OF UP- FLOW AND DOWN- FLOW CARBON BEDS	14/SYSTEM	ANAEROBIC AND AEROBIC REGENERATION	POON ET AL., 1973
WESTMILL CARPETS	1973	60	COD: 130 SS: 80 TDS: 800	COD: 10	YES	PULSED BED	2.4	NONE	BURKELL, 1973
KANEBO PLANT	1974	870	COD: 120-170 BOD: 110-160 SS: 8-15	COD: 20-50 BOD: 20-50 SS: 1-2	NO	PULSED BED [Ozone pretreatment]	84	MULTIPLE HEARTH FURNACE	ANONYMOUS, 1974
WEEKS PLANT	1974 [Pilot Plant]	150	TOC: 558 COD: 1883 BOD: 289 SS: 104	TOC: 64 COD: 251 BOD: 42 SS: 12	YES	FIXED BED	N.A.	SUPPLIER	PARDUE ET AL., 1974

* Primary SS removal recommended
** MG/L unless stated otherwise

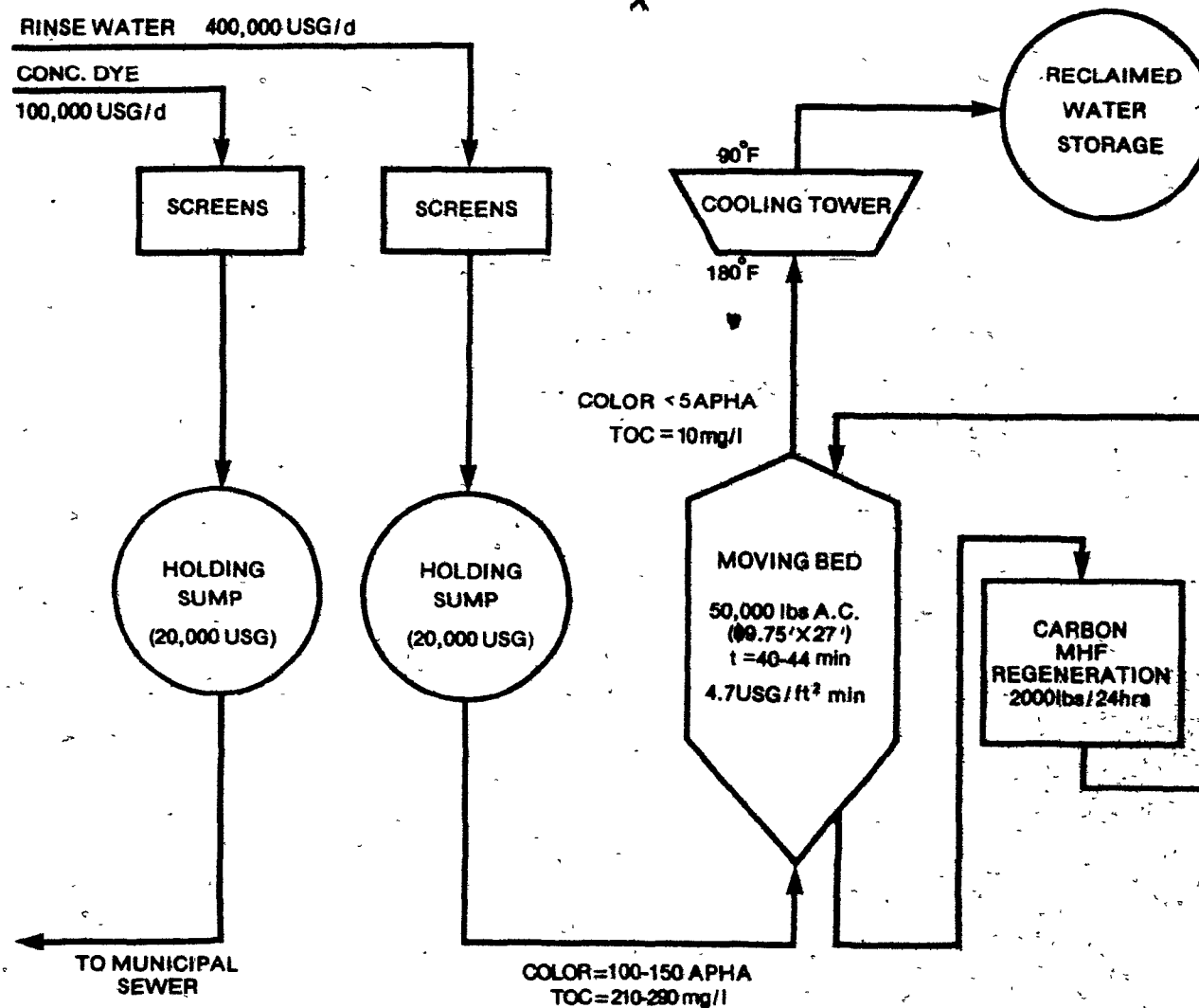
concentration varies from 210 to 290 mg/l. Color of the treated water is less than 5 APHA with approximately 10 mg/l TOC, as shown in Table 1.

The existing plant flow chart is shown in Figure 1. The rinse water prior to its treatment flows through de-linting screens. From two 20,000 USG (76 m^3) holding sumps the wastewater is passed at an upflow flux of $4.7 \text{ USG/ft}^2 \text{ min}$ ($0.19 \text{ m}^3/\text{m}^2 \text{ min}$) through 50,000 lbs (22,680 kg) of granular carbon contained in the 27 ft height x 9.75 ft diameter (8.2 m x 3.0 m) moving bed adsorber. The contact time varies between 40 and 44 minutes. Treated process water then passes through a cooling tower where its temperature is reduced from 180°F (82°C) to 90°F (32°C) before being stored in a tower for reuse. It has been recently reported that carbon used at this plant is exhausted at a rate of 0.55 lb/1000 USG ($66 \text{ kg}/1000 \text{ m}^3$) (45).

Reactivation of spent carbon is accomplished in a six hearth gas fired furnace capable of treating 2000 lbs/24 hours (907 kg/24h). Losses of carbon during the reactivation cycle are reported to be slightly less than 5%. Cost for regeneration is about 9¢/lb (20¢/kg) of carbon reactivated.

Installed cost of the water reclamation unit was approximately \$350,000. Total operating cost including make-up water and municipal treatment of concentrated dye solution is estimated at 15¢/1000 USG ($4¢/\text{m}^3$).

FIGURE 1
MOVING BED ADSORBER
 Hollitex Carpet Plant



Bio-regenerated activated carbon at Masland plant

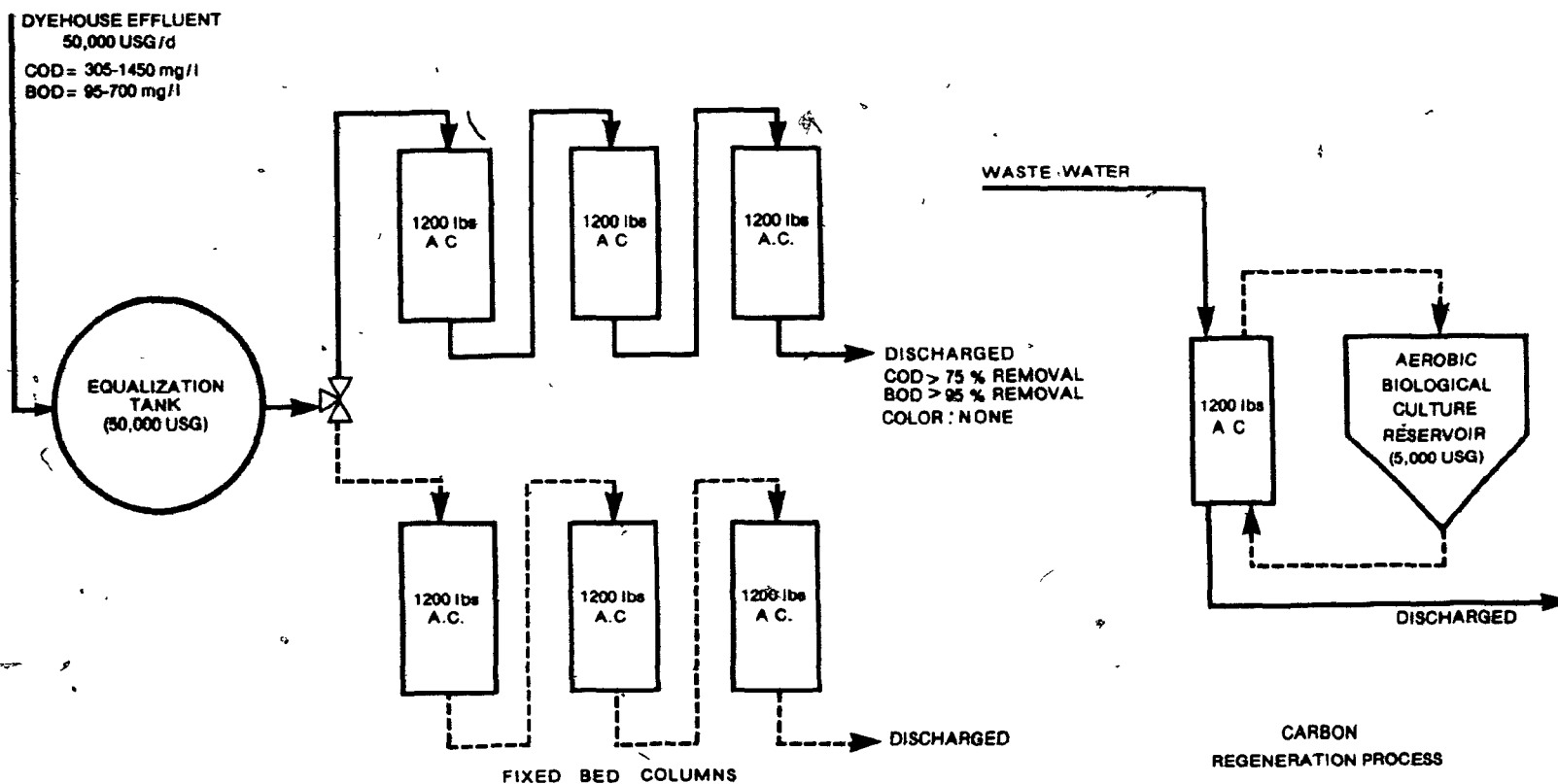
A new textile wastewater treatment process involving biological regeneration of exhausted activated carbon had been in operation at C.H. Masland and Sons plant in Wakefield, R.I. (46). The carpet yarn fabric dyeing facility produces 50,000 USG/day ($189 \text{ m}^3/\text{day}$) of wastewater. Prior to discharge through the small treatment pilot plant unit installed there, mean COD value of the effluent is 700 mg/l, BOD 396 mg/l and suspended solids 27 mg/l; the dyehouse water is heavily colored, with a mean of 2.5 units at 450 nm on the spectrophotometer. The parameter ranges are also presented in Table 1.

Pilot plant data have shown that the process is economically well suited for handling complete treatment of a relatively small volume of textile wastewater up to 75,000 USG/day ($284 \text{ m}^3/\text{day}$). In the case of Masland plant, the textile dye wastes was easily decolorized by a single downflow pass through fixed granular activated carbon beds at an average flux of $12 \text{ USG/ft}^2 \text{ min}$ ($0.49 \text{ m}^3/\text{m}^2 \text{ min}$).

Biological regeneration was accomplished by contacting the columns in an upflow mode at a flux of $10 \text{ USG/ft}^2 \text{ min}$ ($0.41 \text{ m}^3/\text{m}^2 \text{ min}$) with the effluent of a 1200 USG (4.5 m^3) reactor wherein a viable micro-organism seed was maintained. Color removal was virtually complete at the two evaluated fluxes, $8.5 \text{ USG/ft}^2 \text{ min}$ ($0.35 \text{ m}^3/\text{m}^2 \text{ min}$) and $15.6 \text{ USG/ft}^2 \text{ min}$ ($0.64 \text{ m}^3/\text{m}^2 \text{ min}$). COD removal was 85% or higher at the lower flux and only 48% at the higher. Description of the proposed

FIGURE 2

BIO-REGENERATED ACTIVATED CARBON
Masland Plant



full-scale treatment unit is given below. The treatment process flow chart is shown in Figure 2.

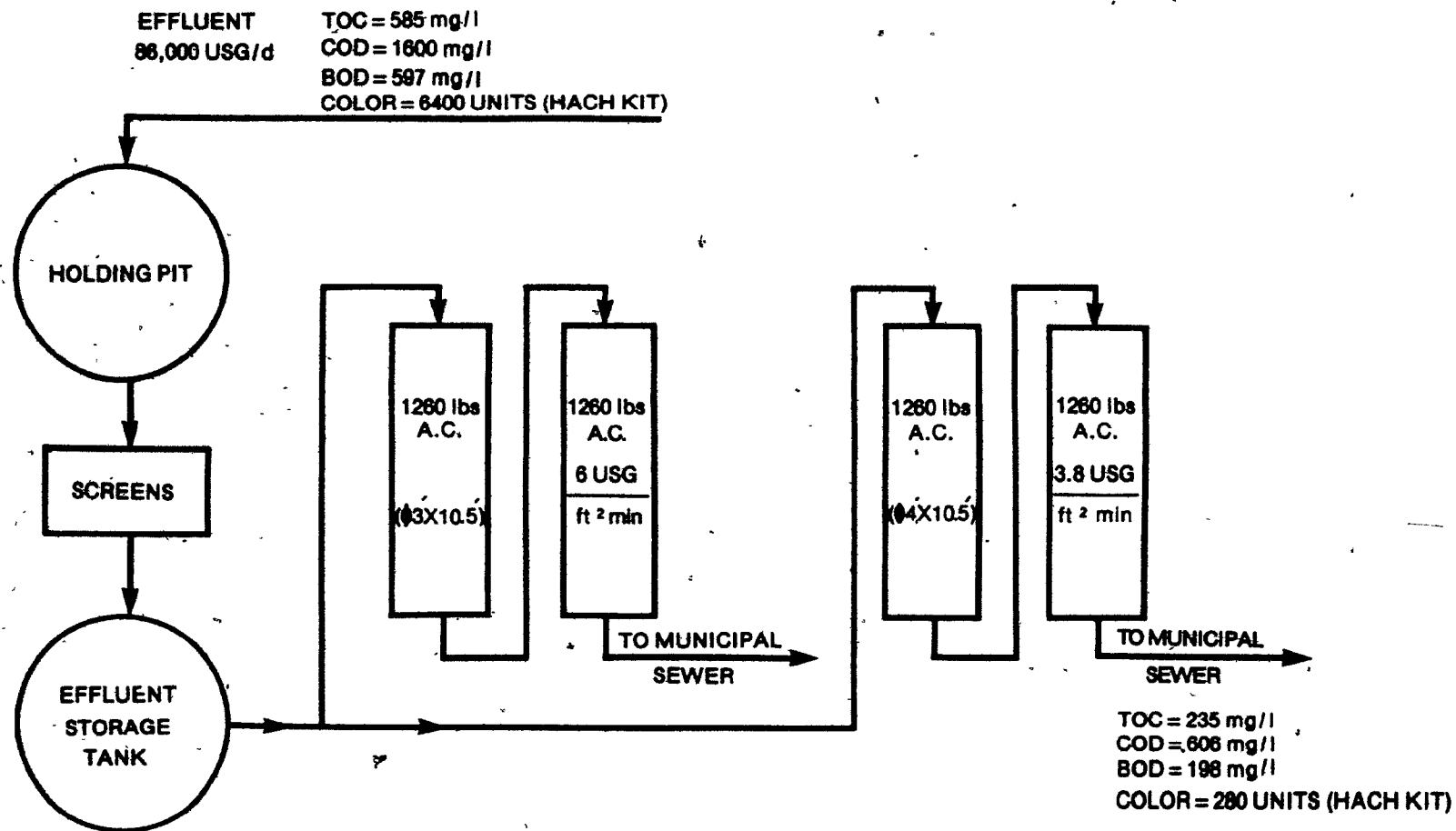
After equalization in a 50,000 USG (189 m^3) tank, the dyehouse effluent passes downflow at an approximate rate of 30-40 USG/min ($0.11\text{-}0.15 \text{ m}^3/\text{min}$) through either one of the two carbon systems each containing three columns in series charged with 1200 lbs (544 kg) of granular carbon per bed. The two systems alternate for treatment and biological regeneration. A regenerant reservoir of 5,000 USG (19 m^3) is suggested. When sufficiently regenerated, the carbon system is switched back on stream, and the other carbon system is subsequently regenerated. The effluent quality of such a system is claimed to be of a tertiary treatment level.

Fixed bed adsorbers at Harding Carpets plant

A wastewater treatment system which consists of two sets of fixed bed adsorbers, each operating with columns in series, has been installed at Harding Carpets, a man-made fibers plant in Collingwood, Ontario. Prime purpose of the treatment system is colour removal from the 86,000 USG/day ($326 \text{ m}^3/\text{day}$) maximum daily wastewater flowrate, a function it is performing well (47).

The existing plant flow chart is shown in Figure 3. Prior to reaching the adsorption system, the waste liquor solution from the dye kettles is discharged into a holding pit, passes through screens and is transferred to a waste storage tank. The first set of adsorbers consists of two downflow fixed bed

FIGURE 3
FIXED BED ADSORPTION
 Harding Carpets Plant



columns connected in series, each holding 1260 lbs (572 kg) of granular carbon; each column is 10.5 ft x 3 ft (3.2 m x 0.9 m). Maximum flux through the columns is 6 USG/ft² min (0.24 m³/m² min). The second set of adsorbers is parallel to the first one and consists of two downflow fixed bed columns connected in series, with a carbon loading similar to the first set of columns; each column is 10.5 ft x 4 ft (3.2 m x 1.2 m). Flux through these columns is 3.8 USG/ft² min (0.15 m³/m² min).

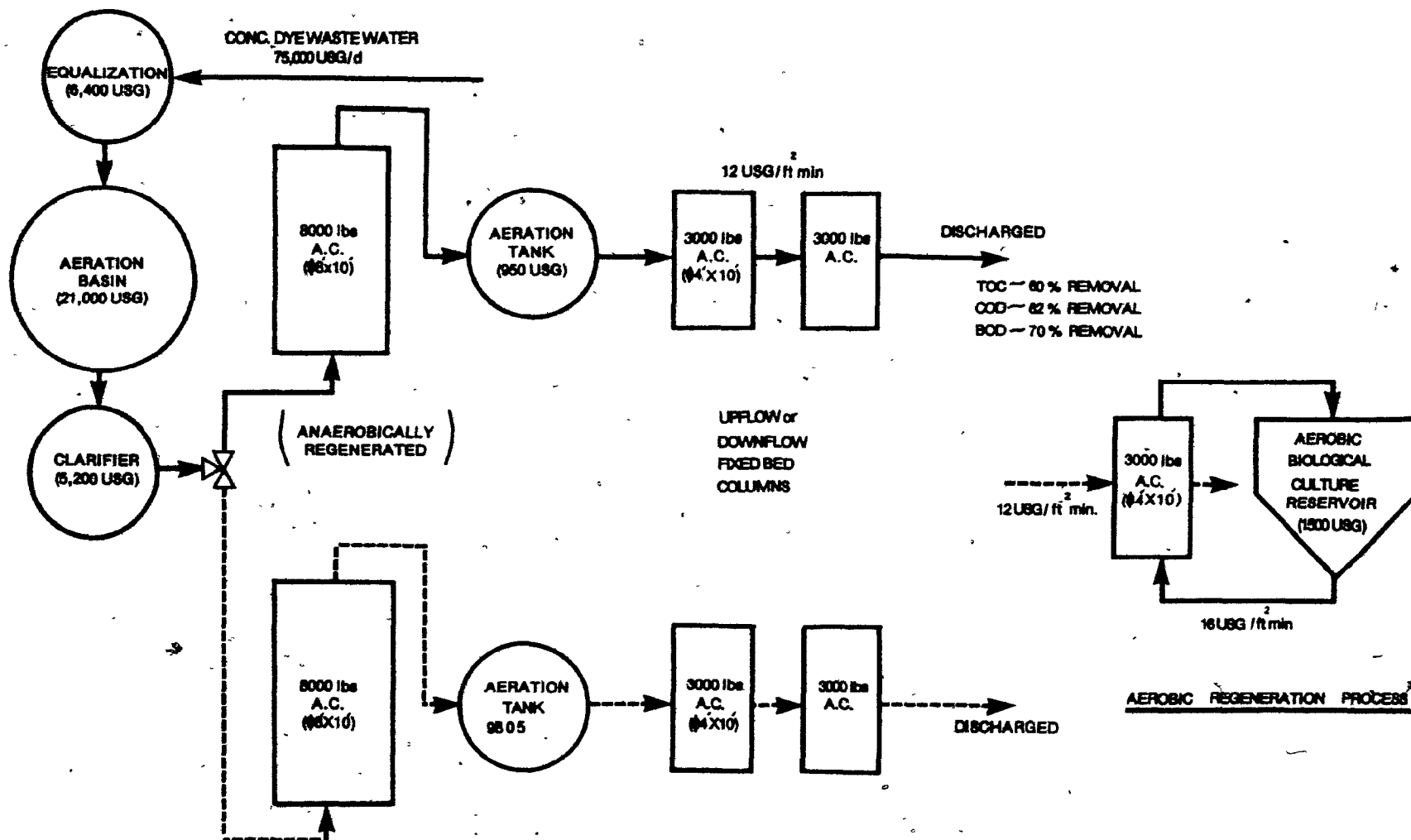
Typical parameters for the raw waste and final treated effluent are summarized in Table 1. Final effluent from the carbon adsorbers is discharged into the municipal sanitary sewer system.

Anaerobic-aerobic treatment with activated carbon at Palisades Industries

A new process for the treatment of high concentration textile dyeing and finishing wastes has been installed at Palisades Industries, a commission dyer and finisher of synthetic and synthetic-cotton blend fabrics at Peace Dale, R.I. (48). Normal flowrate of wastewater from the eight automatic dyeing jigs is estimated to be 75,000 USG/day (284 m³/day).

The existing plant flow chart is shown in Figure 4. The wastewater treatment system consists of three units that are connected in series. Unit 1 is a large basin sectioned by interior walls; key element in that basin is the 21,000 USG (80 m³) aerated equalization pit which serves as a roughing

FIGURE 4
ANAEROBIC—AEROBIC TREATMENT
WITH ACTIVATED CARBON
 Palisades Industries



mechanism to reduce BOD before treatment by activated carbon in Units 2 and 3. Unit 2 comprises two upflow activated carbon reactors receiving the mixed liquor effluent from Unit 1 and serving two functions: (1) Adsorption of soluble organics and color material and (2) Filtration of suspended solids. Each reactor is on stream for a predetermined length of time before it is switched to an anaerobic regeneration cycle, putting the other reactor on stream in the meantime. Each vessel, 8 ft (2.4 m) in diameter, is filled with 8000 lbs (3629 kg) of granular activated carbon. Unit 3 is comprised of four adsorbers each 4 ft (1.2 m) in diameter and filled with 3000 lbs (1361 kg) of granular activated carbon. The four columns are operated as two parallel systems, similar to Unit 2, with two columns in series. To increase flexibility of operation, each pair of columns is piped to operate in either upflow or downflow mode of contact at a flux of $12 \text{ USG/ft}^2 \text{ min}$ ($0.49 \text{ m}^3/\text{m}^2 \text{ min}$). The carbon columns are designed to be regenerated biologically; this is accomplished by contacting the columns at an upflow flux of $16 \text{ USG/ft}^2 \text{ min}$ ($0.65 \text{ m}^3/\text{m}^2 \text{ min}$) with the stream of effluent from a 1500 USG (5.7 m^3) reactor wherein an active aerobic micro-organism culture is maintained. After Unit 3 polishing treatment, effluent is discharged to the river.

Under normal flowrate, the equalization basin can remove approximately 50% of BOD. The total average BOD removal for the entire system currently ranges from 65 to 73%; more data

are also presented in Table 1. Further improvement of the treatment system is possible.

Pulsed bed adsorber at Westmill Carpet plant

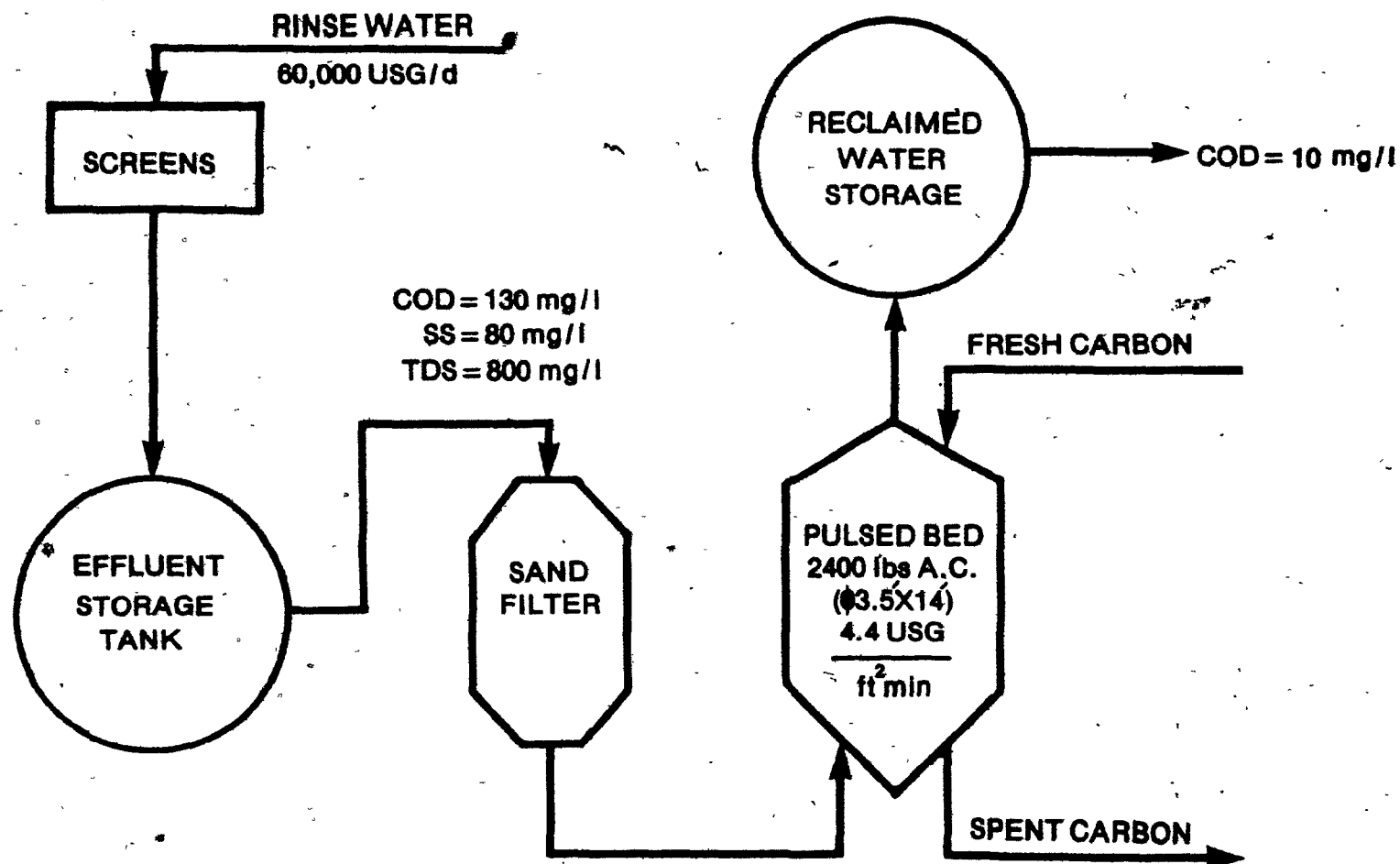
A small pulsed bed column has been installed at Westmill Carpet, a carpet mill in Kelowna, British Columbia, for reuse of rinse waters from dye becks process equipment⁽⁴⁹⁾. Reclaimed water constitutes some 40% of the total water requirement at this plant.

Typical parameters of the dye rinse water are: 130 mg/l COD, 80 mg/l TSS, 800 mg/l TDS, pH is 8 and color is light; water quality of the treated effluent allows satisfactory recycle of process water.

The existing plant flow chart is shown in Figure 5. Treatment system consists of fixed screens to remove the bulk of the loose fiber from the used rinse water and a sand filter for complete removal of fine suspended solids, followed by the activated carbon column. The adsorption system is designed to handle $4.4 \text{ USG/ft}^2 \text{ min}$ ($0.18 \text{ m}^3/\text{m}^2 \text{ min}$) for a total throughput of 60,000 USG/day ($227 \text{ m}^3/\text{day}$). A single pulsed bed column with a carbon loading of 2400 lbs (1089 kg) is employed; the vessel dimension is approximately 14 ft x 3.5 ft (4.3 m x 1.1 m).

Withdrawal and addition of carbon is carried out manually. At the projected carbon use rates, regeneration is not economically justified, and carbon is used on a once-through basis.

FIGURE 5
PULSED BED ADSORBER
Westmill Carpet Plant



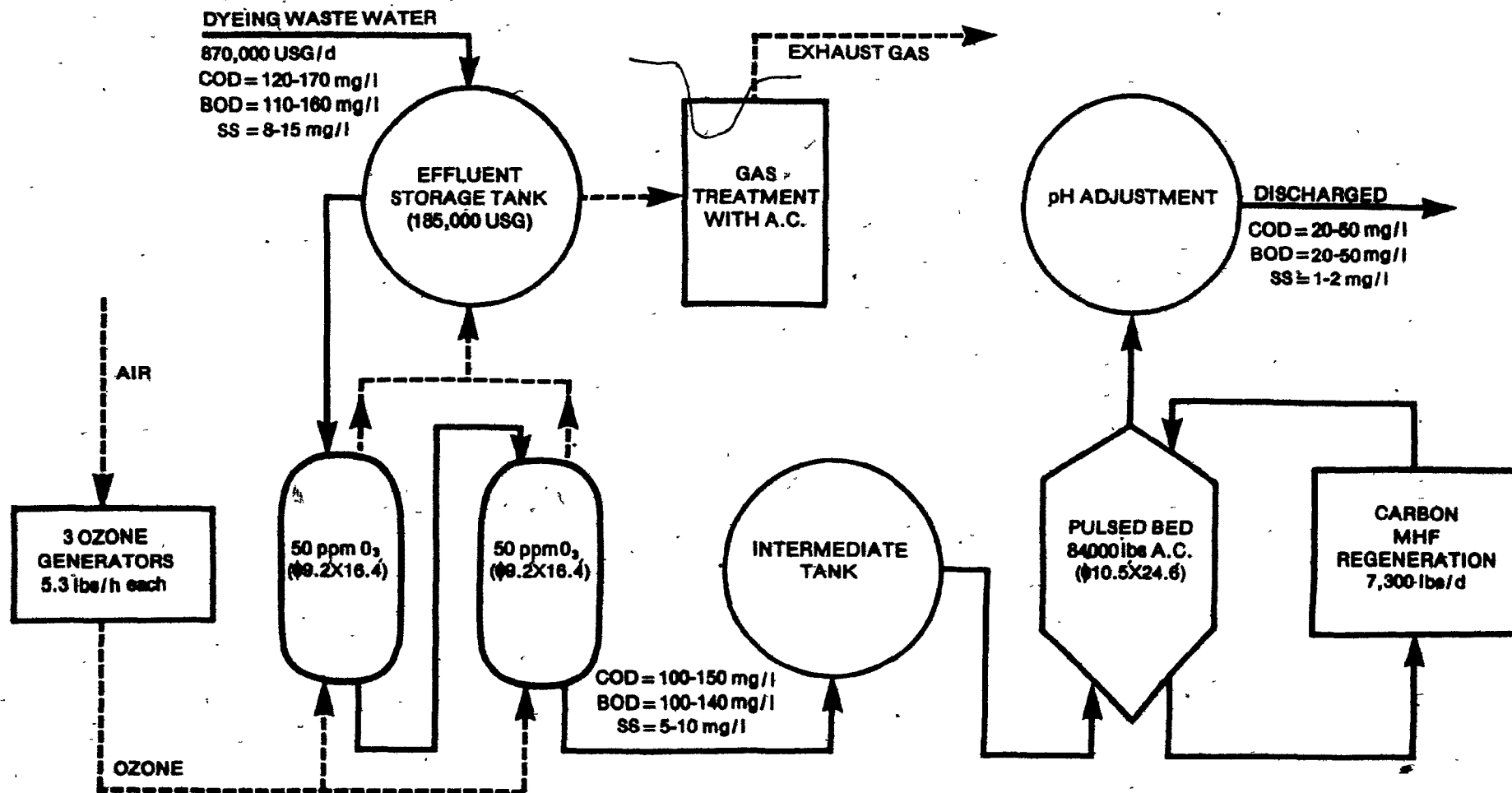
Ozone-carbon treatment system at Kanebo Nagahama plant

A new treatment system combining oxidation by ozone and adsorption by activated carbon has been installed at the Kanebo Nagahama factory, Japan; it consists of two ozone reaction towers followed by a single pulsed bed adsorber. Although the phenomenon of dyes oxidation by ozone is not new⁽⁵⁰⁾, the great importance of the ozone-carbon technique lies in that these two phenomena are combined to produce a synergistic effect in addition to their own individual effects, according to the authors⁽⁵¹⁾.

The existing plant flow chart is shown in Figure 6. From a 185,000 USG (700 m^3) storage tank, the Kanebo's wastewater is pumped at a total rate of 870,000 USG/day ($3,300 \text{ m}^3/\text{day}$) through two ozone reaction towers 16.4 ft x 9.2 ft (5.0 m x 2.8 m) where a maximum of 50 ppm of ozone is maintained. Liquid is then discharged into an intermediate tank and pumped through 84,000 lbs (38,102 kg) of granular activated carbon packed in the 24.6 ft x 10.5 ft (7.5 m x 3.2 m) pulsed bed adsorber. Treated effluent is pH adjusted prior to discharge.

Typical parameters for the raw waste and final treated effluent are summarized in Table 1. Reactivation of spent carbon is performed into a Nicols-Herreshoff vertical gas furnace capable of treating 7,300 lbs/day (3311 kg/day). Total operating costs are estimated at 34¢/1000 gallons (9¢/cubic meter).

FIGURE 6
OZONE—CARBON TREATMENT
 Kanebo Co., Nagahama, Japan



Fixed bed adsorbers at Weeks plant

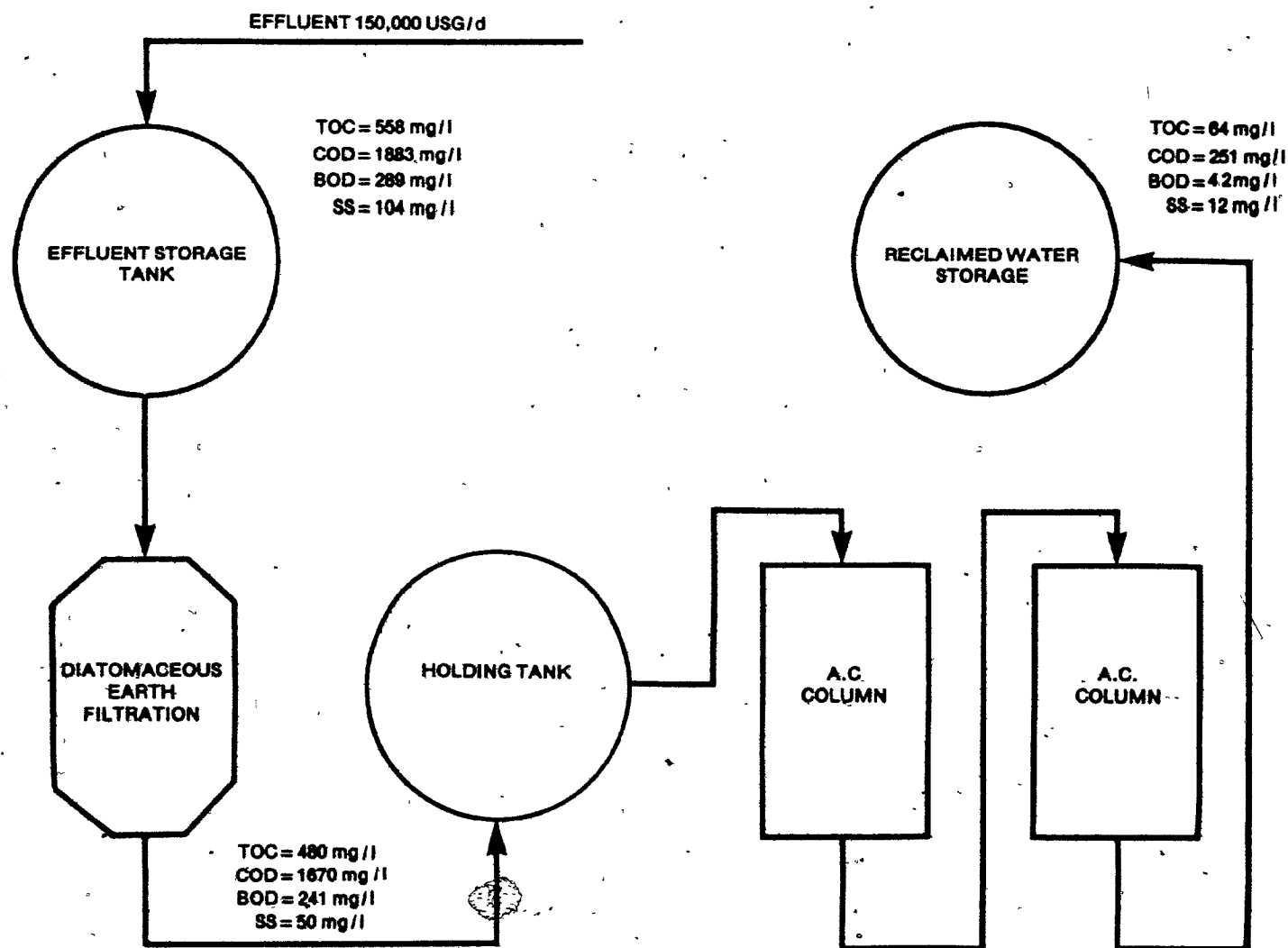
A carbon fixed bed treatment system capable of removing both dispersed and dissolved organic dyes from the dyehouse wastewater effluent has been operated at Weeks plant⁽⁵²⁾.

The Hanes Corporation plant manufactures women's hosiery; it operates 24 hours per day, using 150,000 USG/day ($568 \text{ m}^3/\text{day}$) of water. In addition to disperse dyes which are mixed on a batch basis, the water is comprised of dispersing, softening, finishing agents and stripping compounds. Treated water is recycled to the dyehouse.

The proposed plant flow chart is shown in Figure 7. The pilot plant system consists of a diatomaceous earth filtration unit to remove suspended solids followed by a holding tank; from there, filtered water is pumped downflow at a rate of 3 USG/min ($0.7 \text{ m}^3/\text{h}$) through two carbon adsorbers connected in series. Treated effluent is then recycled to the four small 10-lbs dye machines for the next round of dyeing. Experimental results indicate that the TOC was reduced by approximately 89% overall with complete color removed. Suspended solids were reduced by about 50% across the DE filter. Strict quality control tests conducted after each treatment cycle revealed that the product was equal to that dyed on a normal operation.

Typical parameters for the raw waste and final treated effluent are summarized in Table 1. Reactivation of spent carbon would be performed by the supplier.

FIGURE 7
FIXED BED ADSORBERS
Weeks Plant



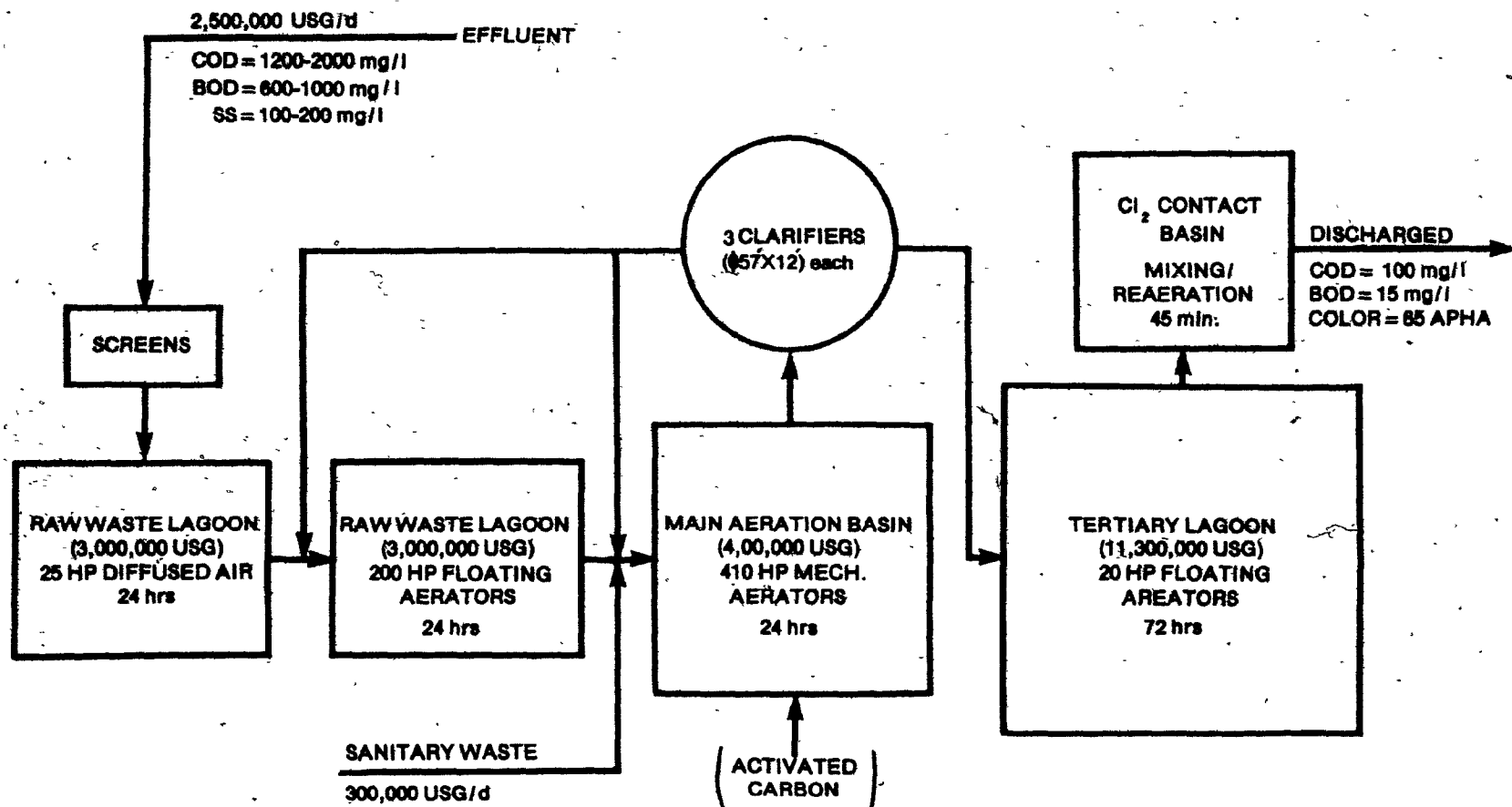
Combination of activated carbon-activated sludge at Cone Mills

An existing secondary treatment plant effluent was subject of further polishing to meet more stringent wastewater standards^(53,13). The Cone Mills Corporation, Greenboro, North Carolina, is a manufacturer of cotton and cotton-synthetic blends. The waste treatment system consists of two 24-hour aerated equalization basins (one of which is equipped for extended activated sludge operation), facilities for adding screened domestic waste if needed, a high-solids 24-hour extended aeration activated sludge basin, clarifiers, a 3-day aerated stabilization basin, post-chlorination, and a 45-minute mixing/reaeration basin. The existing plant flow chart is shown in Figure 8.

It has been observed that an addition of specific amounts of powdered activated carbon to the aeration basin (2000 mg/l) improves the biological treatment efficiency. The exact mechanism responsible for its positive effect is not well understood⁽⁵⁴⁾. In the full-scale testing, the mixed liquor suspended solids level was brought to the 9,000-12,000 mg/l by feeding the powdered carbon along one side of the main reactor basin. Carbon was fed 5 days per week while wasting sludge 5 days per week at a relatively low level. Results over the 1974 year have indicated no major problem due to powdered carbon addition.

The most noticeable change with the previous conventional biological treatment unit has been the great increase in color

FIGURE 8
ACTIVATED CARBON—ACTIVATED SLUDGE
Cone Mills



removal. After carbon addition, this was reduced by 50% to the 60 APHA color units level.

1.3 Activated Carbon Textile Effluent Treatment Process

Several successful applications of activated carbon processes for treatment of textile wastewaters have been described in Section 1.2. Adsorption as a unit process offers many advantages when compared to conventional biological processes: the system requires approximately one-seventh the land required for a biological process⁽⁴³⁾; no secondary sludge is produced; even highly toxic wastes can be easily processed. The adsorption system allows flexibility in design and operation, producing esthetically superior effluent, free of color and odor, at lower capital investment. The degree of treatment is such that it produces effluent suitable for reuse.

Reuse of treated wastewaters is currently performed in both small and large textile plants using carbon adsorption processes. Wastewaters recycle might well become common practice in the not too distant future, for reasons of water supply availability as well as savings^(55,56).

The anaerobic-aerobic bio-oxidation treatment system with activated carbon might well become competitive to the conventional biological treatment process for effluents with high concentrations of biodegradable materials.

While the addition of powdered activated carbon to activated sludge units would tend to increase operating costs,

reduced total expense may be realized through savings on defoamers, coagulants, sludge handling and vacuum filtration chemicals. Higher color removal is expected from this technology.

As a general rule, suppliers of activated carbon provide a table of quality parameters for their products comparable to the one shown in Appendix 1. It has frequently been observed that the products received from various manufacturers do not correspond to the specifications listed in the accompanying data sheet⁽⁶⁶⁾. Often, most of this information is of little value to the individual whose responsibilities include evaluating the economics of several competing activated carbons. An evaluation of each batch of activated carbon in his own system then becomes mandatory for every user.

Several carbon properties should be compared. They may be grouped as primary and secondary properties^(19,67). The primary properties are those most directly concerned with cost and effectiveness of the carbon while secondary properties are less critical. For granular carbon, primary properties include adsorptive capacity, attrition resistance, permeability and extractable solubles contained in carbon. Secondary properties include bulk density, pH of carbon, moisture and ash contents.

According to Mattson⁽⁶⁶⁾, the three parameters of importance for evaluation of granular activated carbons at the laboratory scale level are the adsorptive capacity, the rate of adsorption and the resistance to attrition. The rate of

adsorption determines the contact time and flowrate required to produce a given quality of effluent while the ability of a granular carbon particle to resist mechanical and hydraulic attrition plays an important economic role in selecting the carbon that will result in the lowest operating costs.

Following a lab scale study, most investigators recommend pilot plant studies (58,59,68).

Despite some of its shortcomings, the activated carbon effluent treatment is becoming more widely employed as increasingly stringent environmental regulations are being introduced and enforced. Its potential will further increase if a technological breakthrough is realized which would improve adsorption capacity of activated carbons for low-molecular weight and high-polarity compounds.

1.4 Pollution Problem at Celanese Canada Ltd., Sorel Carpet Plant

In textile industry, several types of continuous dyeing processes are now in use for carpets all of which require thickening additives to control the distribution of the dye. The continuous dyeing process at the Celanese Canada Ltd. Carpet plant located in Sorel, Quebec, uses Syngum D-47-D (Jaguar A-40-F) since its addition results in the required viscosity at a very low concentration. The thickening agent is a highly purified guar gum manufactured by Stein, Hall and Co. Inc.

The spent process solution which is comprised of many dyes, chemicals and gum additives is normally being discarded, this practice posing a serious pollution problem. The mixed dyehouse effluent has to be treated before discharge into the receiving water body in compliance with the new provincial water quality regulations being introduced in Quebec.

The dyehouse effluent treatment procedure which is considered for the Celanese plant is a moving bed adsorption system employing granular activated carbon. Preliminary laboratory and pilot plant studies carried out have indicated satisfactory removal of organic pollutants from conventional dyehouse mixed effluent. An additional study is required, however, which would investigate the effect of gums on the adsorption process. The gums were recently introduced to the effluent originating from a newly installed continuous dyeing process.

The ultimate goal is to recycle 80 to 100% of the treated water back into the dyeing process.

1.5 Objectives

The objectives of the present study are as follows:

1. To characterize the Celanese Sorel dyehouse effluent.
2. To develop information on the adsorption by activated carbon of Jaguar A-40-F gum from its pure solution.
 - a) To determine the adsorptive capacity of various types of activated carbon.
 - b) To determine the effect of pH on adsorption.

c) To determine the effect of temperature on adsorption.

3. To investigate the effect of the gum on the adsorption process treating a typical carpet dyehouse effluent. Different types of activated carbon will be tested.
4. To develop information which could serve as a basis for proper design, sizing and operation of the activated carbon treatment process at the Celanese plant.

2. EXPERIMENTAL

2.1 Materials

Table 2 shows six brands of activated carbon which were examined in connection with this work. All were chosen on the basis of their general applicability in wastewater treatment under an assumption that the samples received from respective manufacturers are representative of the typical activated carbon grade produced on a large scale. However, a new batch of Hydrodarco 4000 was mixed with an equivalent volume of the old Hydrodarco batch for all experiments involving the mixed effluents. The new batch was received from the manufacturer about six months after the first one.

The physical properties of the investigated granular carbons are included in Appendix 1. The data were provided by the carbon manufacturers; a few were taken from literature⁽⁵⁷⁾.

Table 2

GRANULAR ACTIVATED CARBONS USED
IN THIS STUDY

Trade Name	Supplier	Location
Filtrisorb 400	Calgon Canada Ltd.	Bramalea, Ont.
Hydrodarco 4000	Atlas Chemical Industries Canada Ltd.	Brantford, Ont.
Norit	Norit, N.V.	Amsterdam, Netherlands
Nuchar WV-L	Westvaco	Covington, Va.
PC	Barnebey Cheney Ltd.	St. Jean, Que.
Witcarb 718	Witco Chemical Canada Ltd.	Toronto, Ont.

Table 3 shows the dyes selected for preparation of the synthetic wastewater mixtures. The powder dyes were used as supplied by Celanese Sorel plant.

The list of textile chemicals which were used for the synthetic wastewater mixtures is presented in Table 4. All chemicals were used as supplied by the Celanese plant in Sorel. All the samples received were identical with the materials used in the dyehouse.

The guar gum compound was supplied as a cream colored dry powder by the Celanese Sorel plant. The product is manufactured by Stein, Hall and Co. Inc., New York, under the registered trademark of Jaguar A-40-F (Appendix 2). The gum sample was used without further purification.

Table 3

DYES USED FOR THE TYPICAL SYNTHETIC
WASTEWATER MIXTURES

Commercial Name	C.I. Classification	Type
Dispersol Blue BG	Disperse Blue 26	Disperse
Dispersol Yellow AG	Disperse Yellow 3	Disperse
Terasil Pink FG	Disperse Red 55	Disperse
Nylomine Blue AG	Acid Blue 25	Acid
Nylomine Red A2B100	Acid Red 266	Acid
Nylomine Yellow AG	Acid Yellow 135	Acid
Nylosan Yellow CRM	Acid Yellow 219	Acid

Table 4

TEXTILE CHEMICALS USED FOR THE TYPICAL
SYNTHETIC WASTEWATER MIXTURES

Product	Physical State	Use
Acetic Acid (56%)	Liquid	pH Adjuster
Ammonium Sulfate	Crystals	pH Adjuster
Chemcogen 6DL	Liquid	Levelling Agent
Deflavit ZA	Crystals	Stripping Agent
Disperse 1097	Liquid	Compatibilizer
Kalex 50%	Liquid	Sequestering Agent
Levegal FTS	Liquid	Retarding Agent
Progawet Log	Liquid	Wetting Agent
Tesco DDE	Liquid	Anti-foam Agent
Texasist AS	Liquid	Levelling Agent

2.2 Preparation of Stock Solutions

The three groups of products defined in Section 2.1 as Dyes, Textile Chemicals and Gums represent the major pollutants likely to be found in Celanese untreated effluent at Sorel plant. A stock solution for each of these three groups was prepared as described below.

2.2.1 Dye Stock Solution

The dye stock solution was prepared by first adding directly the appropriate amounts of acid dyes to 300 ml of distilled water contained in a 1 l. volumetric flask at 20°C. While continuously stirred with a Thermix stirrer and heater (Model 11-493), the solution was heated to 100°C and the boiling temperature was maintained for about 5 minutes. Following slow cooling to below 60°C, the disperse dyes were added. The stock solution volume was adjusted to one liter with distilled water and stored under refrigeration.

The stock solution, which was 100 times more concentrated than the maximum dyes concentration used in experiments, contained 1930 mg/l of total carbon.

2.2.2 Textile Chemicals Stock Solution

The textile chemicals stock solution was prepared by adding directly the appropriate amounts of chemicals to 100 ml of distilled water contained in a 1 l. volumetric flask. Low heat was applied to help dissolution of crystalline and viscous compounds while stirring at 20°C with the Thermix device. The stock solution volume was then adjusted to 1 l. with distilled water and stored under refrigeration.

The stock solution, which was 100 times more concentrated than the maximum chemicals concentration used in experiments, contained 13,000 mg/l of total carbon.

2.2.3 Guar Gum Stock Solution

The guar gum stock solution was obtained by slowly sprinkling approximately 2 g of Jaguar A-40-F into the vortex of one liter of rapidly agitated distilled water at 20°C. After 45 minutes, the viscous gum solution was vacuum filtered through a 9 cm Whatman filter paper No. 4 using a two-piece Buchner funnel Kimble 54000, the supernatant refiltered through a 9 cm Whatman filter paper No. 5. The resulting clear stock gum solution free of suspended matter was stored in a 1 l. volumetric flask under refrigeration.

The stock solution, which was approximately 24 times more concentrated than the maximum gum concentration used in experiments, contained 708 mg/l of total carbon.

2.3 Preparation of Activated Carbon Samples

The following procedure was repeated for each of the six granular activated carbons under study.

Approximately 100 g of the granular carbon sample was pulverized with a Waring blender and sieved through the No. 325 Tyler mesh size, Canadian Standard Sieve Series (opening in metric: 45 μ m). The carbon powder was dried at 150°C in a forced draft oven for 3 hours. It was subsequently stored in a low humidity room in an enclosed container.

2.4 Laboratory Adsorption Test Procedure

The present study was based on a standard batch adsorption procedure yielding data for adsorption isotherms^(58,59). Stock solutions were used for preparation of synthetic effluent by dilutions and mixing of appropriate components. pH was adjusted when required by additions of either NaOH or HCl. No pH adjustment was necessary for the synthetic mixed effluent with natural pH 6.0 ± 0.3 which was within the acceptable range of pH 5-7.

A 100 ml sample portions were pipeted into 500 ml erlenmeyer flasks. The required amount of carbon powder was manually mixed into the liquid in each sample flask. The flasks were then shaken on a Gallenkamp wrist action shaker for 60 minutes. No carbon was added to a control flask containing the solution only.

Immediately following after the shaking period each solution was vacuum filtered through either a 5.5 cm Whatman filter paper No. 5 placed in a two-piece Buchner funnel Kimble 54000 (used for the pure gum adsorption tests) or a 4.7 cm Gelman filter paper Metrical GN-6, pore size $0.45 \mu\text{m}$, placed in a 250 ml Millipore filter holder (used for all other tests). The Whatman paper was sufficiently wetted with distilled water before filtration. The Gelman paper was thoroughly washed with 300 ml of distilled water before filtration. Approximately 85 ± 15 ml of filtrate was collected from each test.

Approximately 40 ml of each filtrate sample was poured in a clean 50 ml beaker for a TOC analysis. All carbon analyses

in this study were performed with a Beckman Total Organic Carbon Furnace Module (Model 915-A) and a Beckman Non-Dispersive Infrared Analyser (Model 865). A pushbutton operated Hamilton syringe (Model CR-700-200) was used for sample injection. Total Carbon (TC) and Inorganic Carbon (IC) concentration of sample solutions were derived from calibration curves (Appendix 3). Total Organic Carbon (TOC) value was obtained by subtraction of TC and IC values; these measurements were recorded on a 10" Hewlett Packard strip chart recorder (Model 7127A). All recorded peaks fell within the equipment specified repeatability range ($\pm 2\%$ of full scale from 50 to 4000 mg/l).

Most experiments were performed at $20 \pm 1^\circ\text{C}$. For the few cases where a temperature of 65°C was required, a 15.5" x 15.5" x 8.5" Fisher Versa-Bath (Model 131) filled with water controlled at $\pm 0.5^\circ\text{C}$ was used. The water bath and the shaker were set side by side with 250 ml stoppered erlenmeyer flasks submerged in hot water. The flasks containing solutions were heated to 65°C prior to receiving the adsorbent. All other operations of the adsorption procedure remained unchanged.

In the special cases where the contact time was investigated, a 3 l. beaker and a Thermix stirrer (Model 11-493) were used instead of the 500 ml shaker erlenmeyer flasks. One liter of the prepared solution was poured into the beaker which was set on the stirrer. At time zero, the required amount of powder carbon was poured in the liquid stirred at 20°C . At

specific time intervals approximately 30 ml of the black liquor was withdrawn with a 50 ml beaker and filtered according to the established procedure.

All the tests in this study were done in agreement with the Standard Methods for Examination of Water and Wastewater⁽⁹⁰⁾.

3. RESULTS

3.1 Characterization of Celanese Dyehouse Wastewater Effluent

3.1.1 Introduction

Several attempts have been made in the recent few years to quantitatively characterize Celanese dyehouse wastewater at Sorel⁽⁶⁰⁻⁶³⁾. The results, however, do not always agree, the main reason being that the dyehouse effluent composition is dramatically fluctuating, even within short periods of time⁽⁶³⁾.

The industrial effluent under study is comprised of three broad groups of products which in the previous Section were defined as Dyes, Textile Chemicals and Guar Gum. These products originate from the batch (Dye Becks) and/or the continuous (Kuster, Tak type machines) dyeing operations performed at the plant. Dyes used for the two dyeing processes are essentially disperse or acid in nature (Table 3). Out of 100 pounds of dyestuff, about 65 pounds are disperse dyes. In Table 4, all chemicals except Disperse 1097 and Progawet Log are linked to the batch dyeing operation. The great amounts of textile chemicals used are largely responsible for the organic pollution of the dyehouse effluent. Syngum D-47-D (or Jaguar A-40-F)

constitutes the third category of pollutants present in the mixed effluent. It is used as a thickener to control the distribution of the dye for the continuous dyeing process.

3.1.2 Prediction of the Celanese Dyehouse Typical Wastewater Mixtures Composition

For the current study, it was imperative to select a wastewater sample representative of the typical dyehouse effluent. The grab-sampling method was rejected because it is not reproducible and yields samples from which constituents are hardly identifiable. Prediction from the plant dyeing recipes of the range of pollutant concentrations likely to occur in the final dyehouse effluent was considered a more appropriate approach. It was carried out in the following manner:

Five typical batch dyeing recipes were selected: one pale shade (#2105), two medium shades (#2104, #2109) and two deep shades (#2101, #2106). These shades typically represent approximately 90% of the total production; their relative proportion in the dyehouse is 3:5:2 (by weight). The lists of dyes and chemicals involved have been tabulated in Tables 3 and 4.

Based on the same weight of virgin fabric and on the same unit volume of dyeing liquor, the proportion of each component from the five typical recipes was summarized, yielding a composite dyeing liquor which constitutes a typical daily input to the dye beck machines.

The dye components were then segregated from the textile chemicals, with each group being treated differently. Concentration of the dye components in the batch and the continuous dyeing stock pastes are identical. The textile chemicals in the continuous dyeing stock paste are essentially Jaguar A-40-F, Disperse 1097 and Progawet Log. The gum concentration in the stock paste is based on viscosity requirements of the dyeing solution. The initial gum concentration is currently 1 g/l for the Kuster machine while it was estimated to be 5 g/l for the Tak equipment. Concentrations of Jaguar A-40-F, Disperse 1097, Progawet Log and Texasist AS in the stock pastes were each derived from an approximate partial mass balance around the dyehouse where inputs were based on amounts of purchased materials by the Company for the last six months.

Table 5 shows the total daily volumes of batch and continuous stock pastes for the dyeing equipment. Feed volume for the Tak equipment was based on the extrapolated next year production. This was estimated at 10% of the current total production with the continuous dyeing equipment.

The final mixed dyehouse effluent flowrate fluctuates between 350,000 and 450,000 IG/day ($1,591-2,046 \text{ m}^3/\text{day}$). Table 6 presents the calculated dilution factors.

Table 5

VOLUMES OF BATCH AND CONTINUOUS
DYEING SOLUTIONS

Dyeing Equipment	Volume/Day	
	Minimum (IG)	Maximum (IG)
Dye Becks	4,500	7,500
Kuster	10,000	15,000
Tak	-	2,160

Table 6

DILUTION FACTORS FOR DYEING
SOLUTION CONSTITUENTS

Dyeing Solution Constituent	Dilution Factor	
	Minimum	Maximum
Dyes	14.2	31.0
Textile Chemicals	46.7	100.0
Guar Gum	20.4	45.0

The values in Tables 7 and 8 represent the maximum estimated concentrations of pollutants in the final dyehouse effluent, as calculated from the minimum dilution factors in Table 6 and the recipes. Both Dyes and Textile Chemicals stock solutions were prepared according to Tables 7 and 8. The range of gum concentration in the final effluent, 20-80 mg/l, was estimated in a similar manner.

It was assumed that 90% (by weight) of acid dyes and 80% (by weight) of disperse dyes are being adsorbed on the fabric. It was also assumed that all the textile chemicals (including Jaguar A-40-F) find their way into the dyehouse effluent without losses.

The odorous ammonia compound was not included amongst the textile chemicals in Table 8. The large amounts of ammonia present in the initial stock paste for the dye becks will be considerably reduced with the introduction of new batch dyeing process modifications. Small amounts of mono-sodium phosphate and tetra-sodium phosphate are also present in the batch dyeing stock paste. These were neglected because it is expected that they would not be used in the dyeing process in future. Neither ammonia nor phosphates are being removed by activated carbon⁽⁶⁴⁾.

Table 7

ESTIMATION OF MAXIMUM CONCENTRATION OF
TYPICAL DYES IN DYEHOUSE WASTEWATER

Dye	Concentration (mg/l)
Dispersol Yellow AG	17.7
Terasil Pink FG	8.3
Nylomine Yellow AG	6.6
Dispersol Blue BG	2.1
Nylosan Yellow CRM	1.6
Nylomine Red A2B100	0.7
Nylomine Blue AG	0.5

Table 8

ESTIMATION OF MAXIMUM CONCENTRATION OF TYPICAL
TEXTILE CHEMICALS IN DYEHOUSE WASTEWATER

Chemical	Concentration (mg/l)
Ammonium Sulfate	314.0
Chemcogen 6DL	109.9
Disperse 1097	47.4
Levegal FTS	47.1
Kalex (50%)	38.7
Texasist AS	38.6
Progawet Log	34.2
Tesco DDE	30.7
Deflavit ZA	23.6
Acetic Acid	23.6

3.1.3 Description of Typical Mixtures

Table 9 describes six synthetic wastewater mixtures which represent a wide range of pollutant concentrations likely to be found in the final dyehouse effluent.

Effluents A and B are gum-free mixtures. They represent respectively the highest and the lowest loading of Dyes and Chemicals soluble pollutants in the final dyehouse effluent, based on the current modes of dyeing operations in the plant. All other effluents are simply modifications of the basic effluents A and B.

The amount of gum pollutant present in the effluent is logically expected to be more or less proportional to the mixture total concentration. Indeed, a larger feed volume of continuous dyeing liquor is more heavily gum-loaded when taken as a whole. In face of the final dyehouse effluent composition, this is important since 60 to 70% of the total dyeing production is performed with the continuous dyeing equipment.

Thus, effluents C and D have been prepared by additions of respectively 100 g/l and 65 mg/l of Jaguar gum to the heavily loaded effluent A while effluents E and F have been prepared by additions of 65 mg/l and 20 mg/l of gum to the less concentrated mixture B.

The last three columns in Table 9 show the estimated percent contribution by Dyes, Textile Chemicals and Guar Gum respectively to the average TOC total concentration for each effluent.

Table 9
TYPICAL SYNTHETIC DYEHOUSE EFFLUENT MIXTURES
Celanese Carpets Plant, Sorel

Name of Effluent	Composition	Total Concentration (mg/l TOC)	Estimated Percent Contribution by a Group of Pollutants		
			Dyes (%)	Chemicals (%)	Gum (%)
A	Highest estimated concentration of Dyes and Textile Chemicals in final dyehouse effluent	148±3	13	87	-
B	Lowest estimated concentration of Dyes and Textile Chemicals in final dyehouse effluent	69±2	13	87	-
C	Addition of 100 mg/l of Jaguar A-40-F Gum to effluent A	184±3	10	74	16
D	Addition of 65 mg/l of Jaguar A-40-F Gum to effluent A	171±3	11	78	11
E	Addition of 65 mg/l of Jaguar A-40-F Gum to effluent B	90±2	11	68	21
F	Addition of 20 mg/l of Jaguar A-40-F Gum to effluent B	77±2	12	80	8

In Table 9, the quoted gum concentrations include the non-soluble portion which has to be subsequently filtered (Section 3.2.1).

A few supplementary tests were performed on the typical effluent D. At an initial concentration of 168 mg/l TOC, the Total Suspended Matter content of mixture D was approximately 7 mg/l. The filtrate TOC was 163 mg/l. The low TSM value of the sample is partly due to the presence of disperse dyes. At pH 6, apparent color of the synthetic effluent D corresponds to 0.53 optical density units at $\lambda = 355$ nm. No phosphorus content was detectable in the mixture.

Temperature of the dyehouse final effluent varies normally between 145°F and 160°F (63°C-71°C); average pH is 7.2⁽⁶⁵⁾.

3.2 Study of Adsorption of Jaguar A-40-F Gum

3.2.1 Jaguar A-40-F Gum Solution Properties

Based on plant processes calculations, the gum concentration in Celanese Sorel effluent varies from 20 mg/l to 80 mg/l as shown in Section 3.1. However, increasing the upper limit by a factor of 0.25 makes the estimate safer with regard to further possible increases in the gum requirements at the plant. The corrected new range then becomes 20-100 mg/l and the upper limit 100 mg/l was selected as initial concentration for all adsorption tests performed in Section 3.2.

Some insoluble impurities were observed however in the test solution. The TSM test on a gum solution sample revealed 25 ± 2 mg/l suspended matter. Prior to filtration, the TOC concentration of the gum solution was 40.9 ± 1.0 mg/l while this was reduced to 30.0 mg/l TOC after. The suspended matter repre-

sented approximately 25% of the initial TOC concentration. This ratio was found fairly constant over the entire range of gum concentration under study.

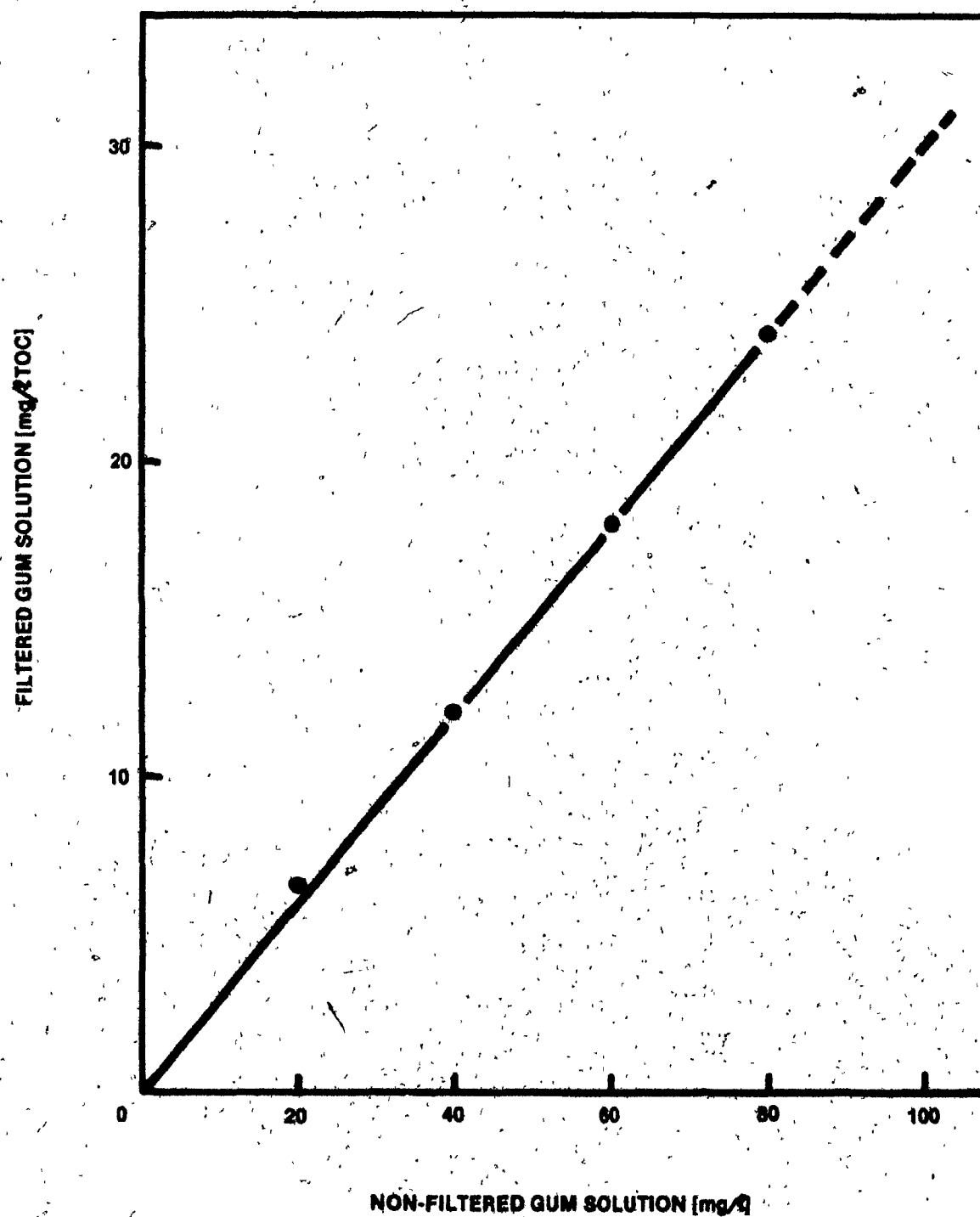
For the lab scale studies, this amount of SM had to be removed prior to adsorption. The relationship between the TOC concentration of the non-filtered gum solution versus the TOC of the corresponding gum solution filtered is shown in Figure 9. The gum concentration range was from 0 mg/l to 100 mg/l. Tabulated data are also presented in Appendix 4.1. The filtration procedure for the four test gum solutions was similar to the stock gum solution filtration procedure (Section 2.2.3). The expected straight line in Figure 9 has been extrapolated after 80 mg/l. A least squares fit yielded a regression coefficient of 0.301 with a standard error of estimate of 0.0.

In Figure 9, the upper limit concentration of the gum non-filtered solution corresponds to a filtered gum solution of 30.0 mg/l TOC which was found equivalent to 77.4 ± 2.0 mg/l COD.

While performing adsorption tests, the initial 30.0 ± 0.6 mg/l TOC filtered gum solution was prepared by diluting the required amount of stock gum solution with distilled water. pH of the solution was approximately 5.3.

Viscosity of the filtered gum solution at 30.0 mg/l TOC was slightly higher than pure water (Appendix 5); hence, this was not a subject of concern for the adsorption tests.

FIGURE 9
EFFECT OF FILTRATION ON THE GUM SOLUTION
[TOC]



3.2.2 Adsorption Kinetics of Jaguar A-40-F

A decrease in the concentration of gum in the solution as a function of the cumulative contact time in presence of Filtrasorb 400 activated carbon is shown in Figure 10. Two carbon dosages of respectively 1,000 mg/l and 6,000 mg/l were employed. Prior to carbon addition, pH of the initial 30.0 mg/l TOC pure gum solution was 7.0; the mixture was continuously stirred at 20°C. The data are tabulated in Appendix 4.2 and 4.3.

From the two curves derived the contact time of 60 minutes was established as sufficiently long to ensure a reasonable approach to equilibrium. Without further investigation, this value was selected for all other gum adsorption tests.

3.2.3 Effect of pH on Adsorption of Jaguar A-40-F for Various Types of Carbons

Table 10 shows the influence of pH on adsorption of gum at 20°C for one carbon dosage of 2,500 mg/l. Jaguar gum solution was initially at 30.0 mg/l TOC. Three different pH values were investigated: 3.0, 7.0 and 10.0. In general, adsorption of gum is higher at pH 3.0; the effect is particularly pronounced for Hydrodarco 4000 and Witcarb 718. Adsorptive capacity of all carbons was lower at pH 10.0.

The carbons have been tabulated by order of decreasing effectiveness at pH 7.0. The order, however, is not the same for the other two pH values. Nevertheless, it appears that Hydrodarco is the best adsorbent of Jaguar gum at any of the three investigated pH.

FIGURE 10
CONTACT TIME vs REMAINING TOC

PURE GUM SOLUTION
FILTRASORB 400 AT 20°C AND pH 7.0

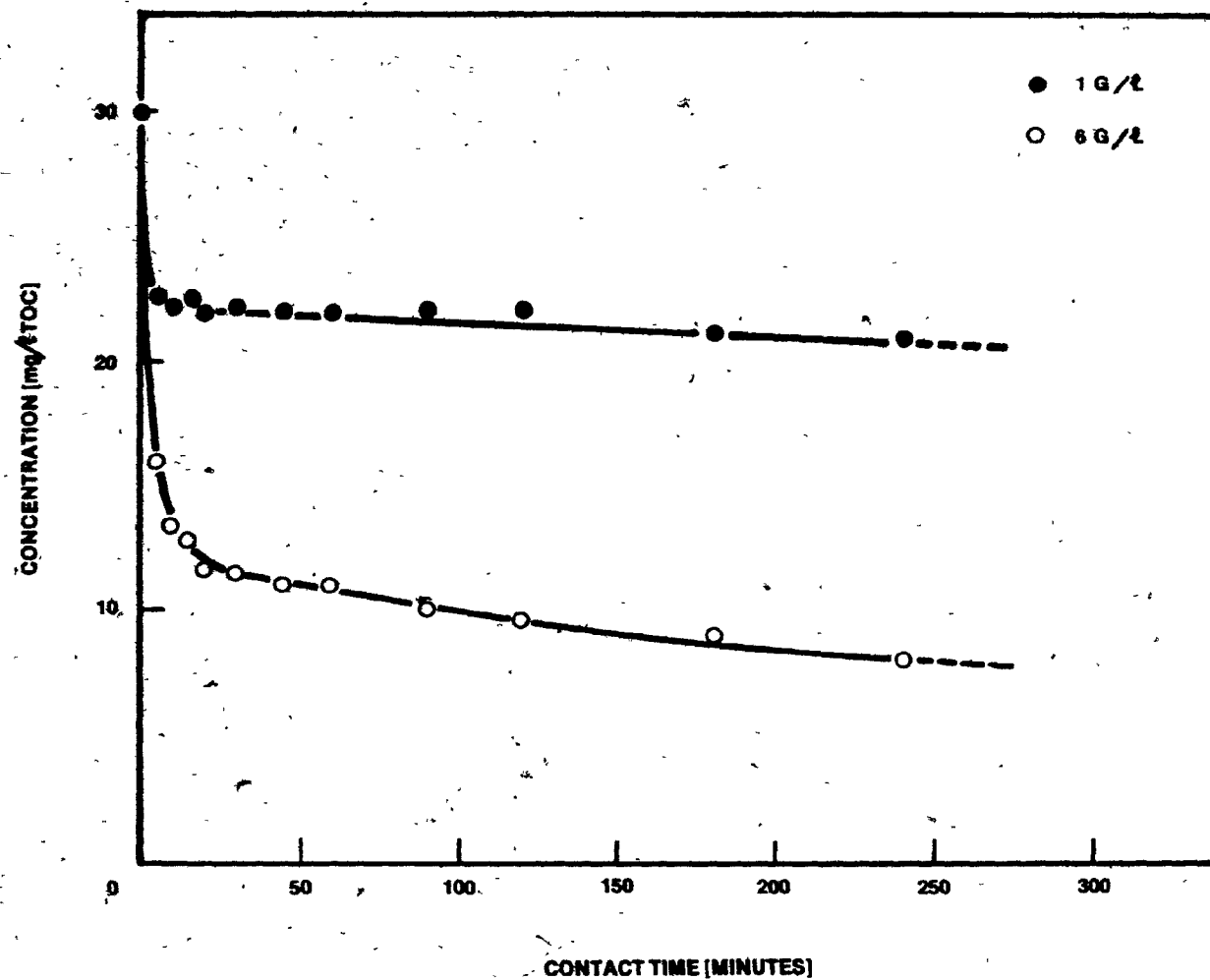


Table 10

EFFECT OF pH ON ADSORPTION OF JAGUAR A-40-F GUM
Various Activated Carbons

Parameters:

Initial TOC Concentration - 30.0 mg/l
Carbon Dosage - 0.250 g/100 ml
Contact Time - 60 minutes
Temperature - 20°C

Type of Carbon	TOC Concentration at Equilibrium (mg/l TOC)		
	pH 3.0	pH 7.0	pH 10.0
Hydrodarco 4000	4.4	13.3	15.7
PC	14.9	16.1	19.6
Norit	17.8	17.1	23.1
Witcarb 718	8.3	17.6	24.0
Nuchar WV-L	15.9	18.5	23.1
Filtrisorb 400	18.3	19.8	24.4

3.2.4 Effect of Temperature on Adsorption of Jaguar A-40-F
for Various Types of Carbons

Table 11 shows the influence of temperature on adsorption of the gum at pH 7.0 for one carbon dosage of 2,500 mg/l of Jaguar gum solution initially at 30.0 mg/l TOC. Temperature for adsorption was 65°C. The results indicated that adsorption of gum is improved at 65°C, as compared to data at 20°C from Table 10. This effect varies with each type of activated carbon used.

Table 11

EFFECT OF TEMPERATURE ON ADSORPTION

OF JAGUAR A-40-F GUM

Various Activated Carbons

Parameters:

Initial TOC Concentration = 30.0 mg/l
Carbon Dosage = 0.250 g/100 ml
Contact Time = 60 minutes
pH = 7.0

Type of Carbon	TOC Concentration at Equilibrium (mg/l TOC)	
	65°C	20°C
Hydrodarco 4000	9.1	13.3
PC	11.0	16.1
Norit	12.8	17.1
Witcarb 718	15.6	17.6
Nuchar WV-L	16.1	18.5
Filtrisorb 400	17.3	19.8

3.2.5 Comparison of Various Types of Activated Carbons for Adsorption of Jaguar A-40-F Gum

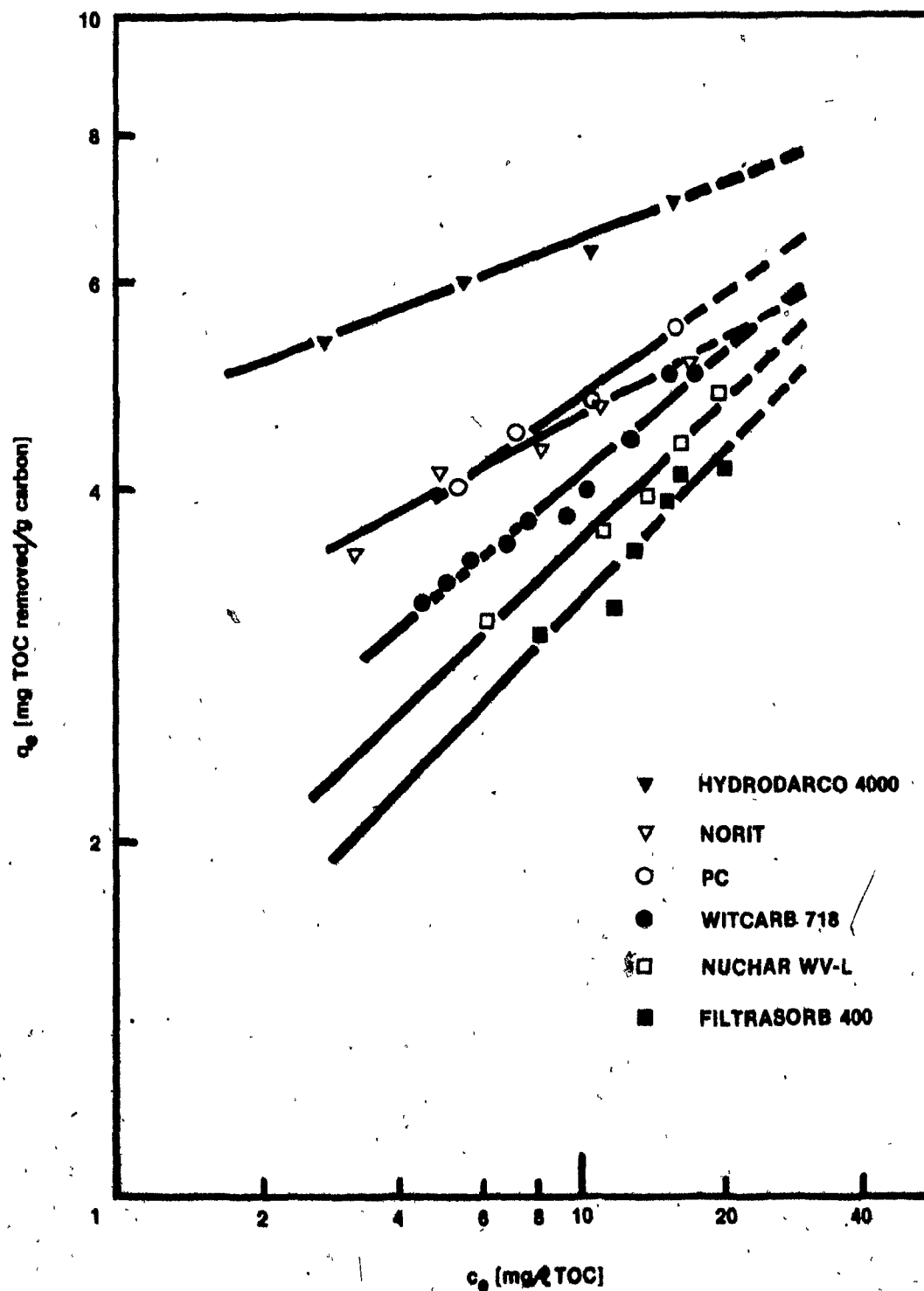
Six adsorption isotherms obtained at 20°C for various types of activated carbon are shown in Figure 11. The adsorption tests were performed with 30.0 mg/l TOC of gum solution (C_0) at neutral pH. The experimental results are shown on a log-log graph paper for easier comparison of adsorptive capacities. Each straight line in Figure 11 represents a least squares fit of the experimental data and is equivalent to the Freundlich empirical equation $q_e = KC_e^{1/n}$ where K and $1/n$ are the intercept and the slope of the linear curve. The loading points (q_e) were calculated from the gum concentration at equilibrium value (C_e) as tabulated in Appendix 4.4.

The isotherms in Figure 11 were extrapolated up to C_0 . However, at the low gum concentration values, a small amount of residual organics remains non adsorbed. This residue was found from the high carbon dosage experiment (Appendix 4.4).

Values of K, $1/n$ and (q_e) with the standard error of estimate for each regression are given in Table 12. The loading values at C_0 were calculated from the corresponding estimated linear regression. The results show that for the range of gum concentration under study, the adsorptive capacity of Hydrodarco 4000 at C_0 is 1.5 times higher than that of Filtrasorb 400.

An attempt to correlate the experimental data with the Langmuir equation $q_e = QbC_e / (1 + bC_e)$ was made. This relation

FIGURE 11
ADSORPTION ISOTHERMS FOR JAGUAR A-40-F
VARIOUS TYPES OF ACTIVATED CARBONS AT 20°C AND pH 7.0



was modified to the equivalent form $C_e/q_e = C_e/Q + 1/Qb$ and C_e/q_e was set as a function of C_e . A linear regression was attempted, yielding the slope $1/Q$ and the intercept $1/Qb$. The constants Q and b for the Langmuir equation are presented in Table 13 along with the standard error of estimate for each type of carbon.

The loadings at C_0 were also calculated from the estimated Langmuir equation fit for each type of carbon. In Tables 12 and 13, the carbons were listed in the order of decreasing $(q_e)_{C_0}$. It is noticeable that the relative positions of carbons are the same in both Tables. Furthermore, in Table 13 the estimated adsorptive capacity of Hydrodarco at C_0 is 1.5 times higher than that of Filtrasorb carbon confirming the results of the Freundlich correlation.

A comparison of the standard errors of estimate of both Freundlich and Langmuir linear regression indicate that adsorption of Jaguar A-40-F gum by activated carbon is better represented by Freundlich fit.

In Table 13, the value of the Langmuir adsorption constant b is a measure of the slope of the adsorption isotherm in the region of low concentration; higher values of b yield steeper slopes. Thus, the larger the slope in this region, the greater the adsorptive capacity of the carbon at the lower gum concentrations. In Table 13, higher values of b are obtained for Hydrodarco 4000 and Norit carbons.

Table 12

CHARACTERISTICS OF FREUNDLICH ISOTHERMS FOR

ADSORPTION OF JAGUAR A-40-F GUM

Various Types of Activated Carbons at 20°C and pH 7.0

Type of Carbon	Intercept K (%/g)	Slope 1/n	$(q_e)_{C_0}$ (mg TOC/g)	Standard Error of Estimate
Hydrodarco 4000	4.59	0.147	7.57	0.009
PC	2.53	0.274	6.43	0.009
Witcarb 718	1.92	0.327	5.85	0.014
Norit	2.84	0.207	5.75	0.014
Nuchar WV-L	1.53	0.372	5.42	0.014
Filtrisorb 400	1.25	0.410	5.04	0.022

Table 13

CHARACTERISTICS OF LANGMUIR ISOTHERMS FOR
ADSORPTION OF JAGUAR A-40-F GUM

Various Types of Activated Carbon at 20°C and pH 7.0

Type of Carbon	Langmuir Adsorption Constant b (l/mg)	Ultimate Monolayer Capacity Q (mg/g)	$(q_e)_{C_0}$ (mg TOC/g)	Standard Error of Estimate
Hydrodarco 4000	2.53	2.23	7.11	0.053
PC	0.90	2.00	5.92	0.067
Witcarb 718	0.67	1.88	5.37	0.116
Norit	1.63	1.69	5.27	0.059
Nuchar WV-L	0.43	1.94	5.13	0.165
Filtrosorb 400	0.37	1.85	4.74	0.190

3.2.6 Effect of Low pH on Hydrodarco 4000 Isotherm for Adsorption of Jaguar A-40-F

The effect of low pH on adsorption of Jaguar A-40-F gum with Hydrodarco 4000 at 20°C is illustrated in Figure 12. At pH 3.5, the adsorptive capacity of Hydrodarco is substantially higher as compared to the isotherm at pH 7.0 from Figure 11. This effect has been demonstrated in Section 3.2.3. Furthermore, Figure 12 shows that the positive effect of low pH on adsorptive capacity is more pronounced as the concentration of gum increases. Experimental data for the isotherm at pH 3.5 are also presented in Appendix 4.5.

Characteristics of the Freundlich correlation at pH 3.5 are shown in Table 14. The loading at C_0 was estimated from the least squares fit extrapolation to 30.0 mg/l TOC.

FIGURE 12
ADSORPTION ISOTHERMS FOR JAGUAR A-40-F

HYDRODARCO 4000 AT 20°C FOR pH 3.5 AND 7.0

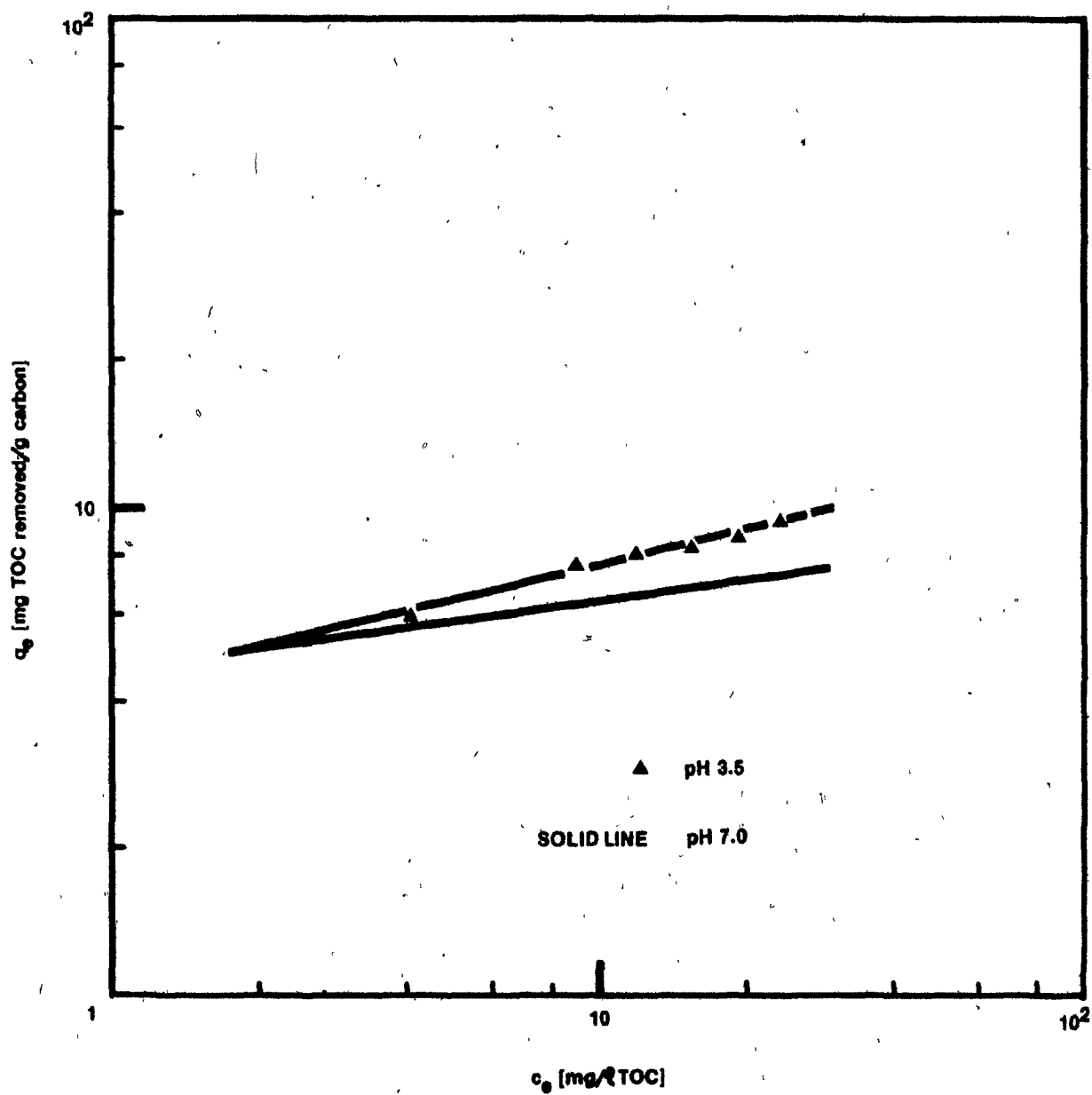


Table 14

CHARACTERISTICS OF FREUNDLICH ISOTHERM FOR

ADSORPTION OF JAGUAR A-40-F

Hydrodarco 4000 at 20°C and pH 3.5

Intercept K (l/g)	Slope 1/n	$(q_e)_{c_o}$ (mg TOC/g)	Standard Error of Estimate
4.38	0.240	9.92	0.011

3.2.7 Effect of Elevated Temperature on Hydrodarco 4000 Isotherm for Adsorption of Jaguar A-40-F

The adsorptive capacity of Hydrodarco carbon is substantially increased at 65°C as compared to its performance at 20°C in Figure 11. This effect has been demonstrated in Section 3.2.4. Figure 13 shows that influence of high temperature on adsorptive capacity is fairly constant over the entire range of gum concentration, with an isotherm slope at 65°C similar to that obtained at 20°C. Experimental data are tabulated in Appendix 4.6.

Characteristics of the Freundlich correlation at 65°C are shown in Table 15. The loading at C_0 was estimated from the least squares fit extrapolation to 30.0 mg/l TOC.

FIGURE 13

ADSORPTION ISOTHERMS FOR JAGUAR A-40-F

HYDRODARCO 4000 FOR pH 7.0 AT 20°C AND 65°C

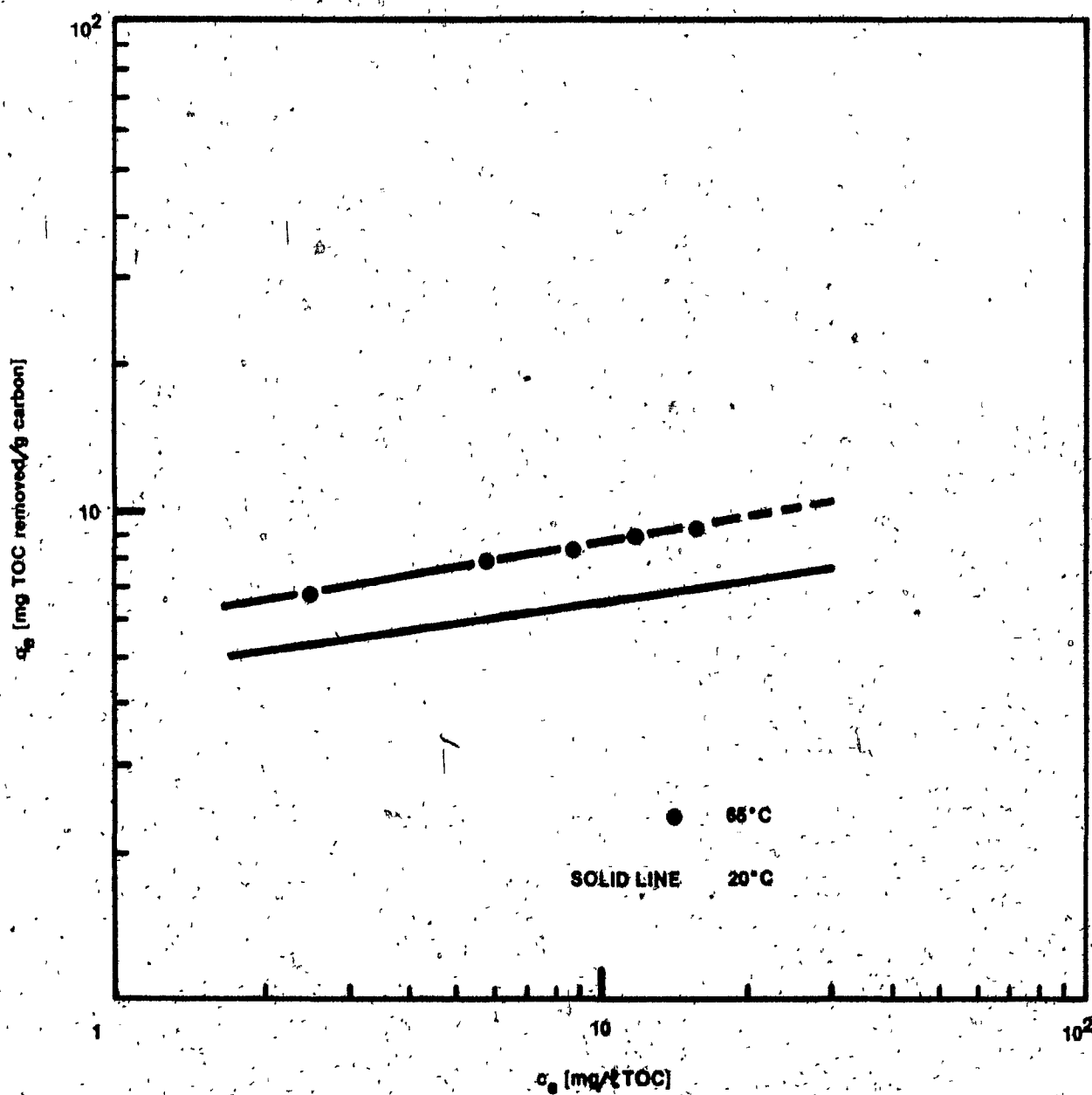


Table 15

CHARACTERISTICS OF FREUNDLICH ISOTHERM FOR

ADSORPTION OF JAGUAR A-40-F

Hydrodarco 4000 at pH 7.0 and 65°C

Intercept K (l/g)	Slope 1/n	$(q_e)_{C_o}$ (mg TOC/g)	Standard Error of Estimate
5.80	0.170	10.33	0.005

3.3 Study of Adsorption of Typical Celanese Dyehouse Wastewater Mixtures

This section is concerned with the activated carbon treatment of typical synthetic wastewater mixtures which are likely to occur at Celanese Sorel dyehouse. The typical effluent compositions mentioned here have been described in Section 3.1.

3.3.1 Adsorption Kinetics

Two different contact times were tested in the experiment designed to establish the time required to reach equilibrium in adsorption. The synthetic mixed effluent was characterized as effluent D (Table 9). The Hydrodarco 4000 carbon dosage used was 10,000 mg/l. Initial pH of the mixture was 7.0; the mixture was continuously stirred at 20°C.

The results summarized in Table 16 show no significant TOC removal after 60 minutes of contact time; this corresponds to the contact time selected in Section 3.2.2 for pure gum solution.

Table 16

REMAINING WASTEWATER TOC AS A
FUNCTION OF CONTACT TIME

Hydrodarco 4000 (Carbon Dosage 10,000 mg/l) *
at 20°C and pH 7.0

Contact Time (minutes)	TOC Concentration (mg/l)
0	* 150.0
60	18.3
120	18.0

* Blank value.

3.3.2 Adsorption Isotherms for Effluents A and B with Hydrodarco 4000

Isotherms characterizing adsorption of effluents A and B with Hydrodarco 4000 at 20°C and pH 7.0 have been developed and results are presented in Figure 14. The artificial effluent mixtures represent two extreme situations which could occur if no gum pollutants were present in the wastewater.

Each isotherm is comprised of two distinct sections. The first section is the straight line well described by the Freundlich least squares fit as shown in Table 17. This section is extrapolated up to the initial mixture concentration. The second section of the isotherm is characterized by a sharp decrease in carbon loading due to the presence of non adsorbed molecules in the mixture. The residual concentration for effluent A is two times that of effluent B. This is also the approximate ratio of the initial TOC concentrations of effluents A and B. Table 17 summarizes the main characteristics of isotherms for effluents A and B. Experimental data are tabulated in Appendix 6.1.

In Section 3.3, no correlation of the data using the Langmuir equation has been possible.

FIGURE 14
ADSORPTION ISOTHERMS FOR EFFLUENTS A AND B
HYDRODARCO 4000 AT 20°C AND pH 7.0

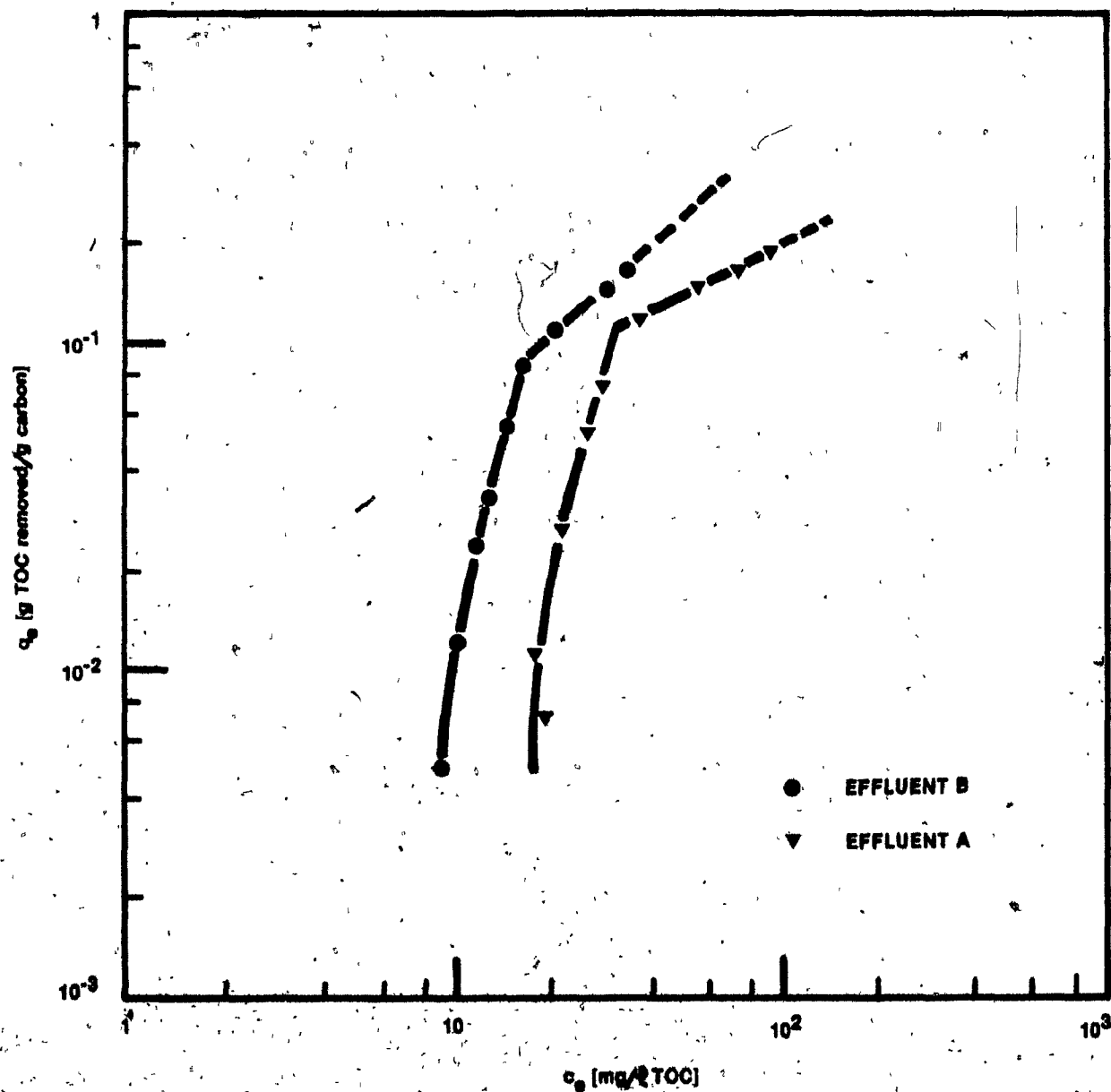


Table 17

CHARACTERISTICS OF FREUNDLICH ISOTHERMS FOR

ADSORPTION OF EFFLUENTS A AND B

Hydrotarco 4000 at 20°C and pH 7.0

Effluent	Initial Concentration C_o (mg/l TOC)	Straight Line Section				Residual Concentration C_R (mg/l TOC)
		Intercept K (l/g, 10^{-3})	Slope 1/n	(q_e) C_o (g TOC/g)	Standard Error of Estimate	
A	148±3	0.0185	0.511	0.23	0.008	18
B	69±2	0.0067	0.908	0.27	0.008	9

3.3.3 Adsorption Isotherms for Effluents C and D with Hydrodarco 4000

Isotherms characterizing adsorption of effluents C and D with Hydrodarco 4000 at 20°C and pH 7.0 are presented in Figure 15. Effluent C represents the highest soluble organic loading likely to occur in the dyehouse wastewater. Effluent D is identical with C in terms of dyes and chemicals except for the soluble gum content which is lower in the former. The results depicted in Figure 15 show a higher carbon loading of Hydrodarco at initial concentration for effluent D and a steeper isotherm slope. Values presented in Table 18 were calculated from least squares regressions of experimental data tabulated in Appendix 6.2.

FIGURE 15 ADSORPTION ISOTHERMS FOR EFFLUENTS C AND D

HYDRODARCO 4000 AT 20°C AND pH 7.0

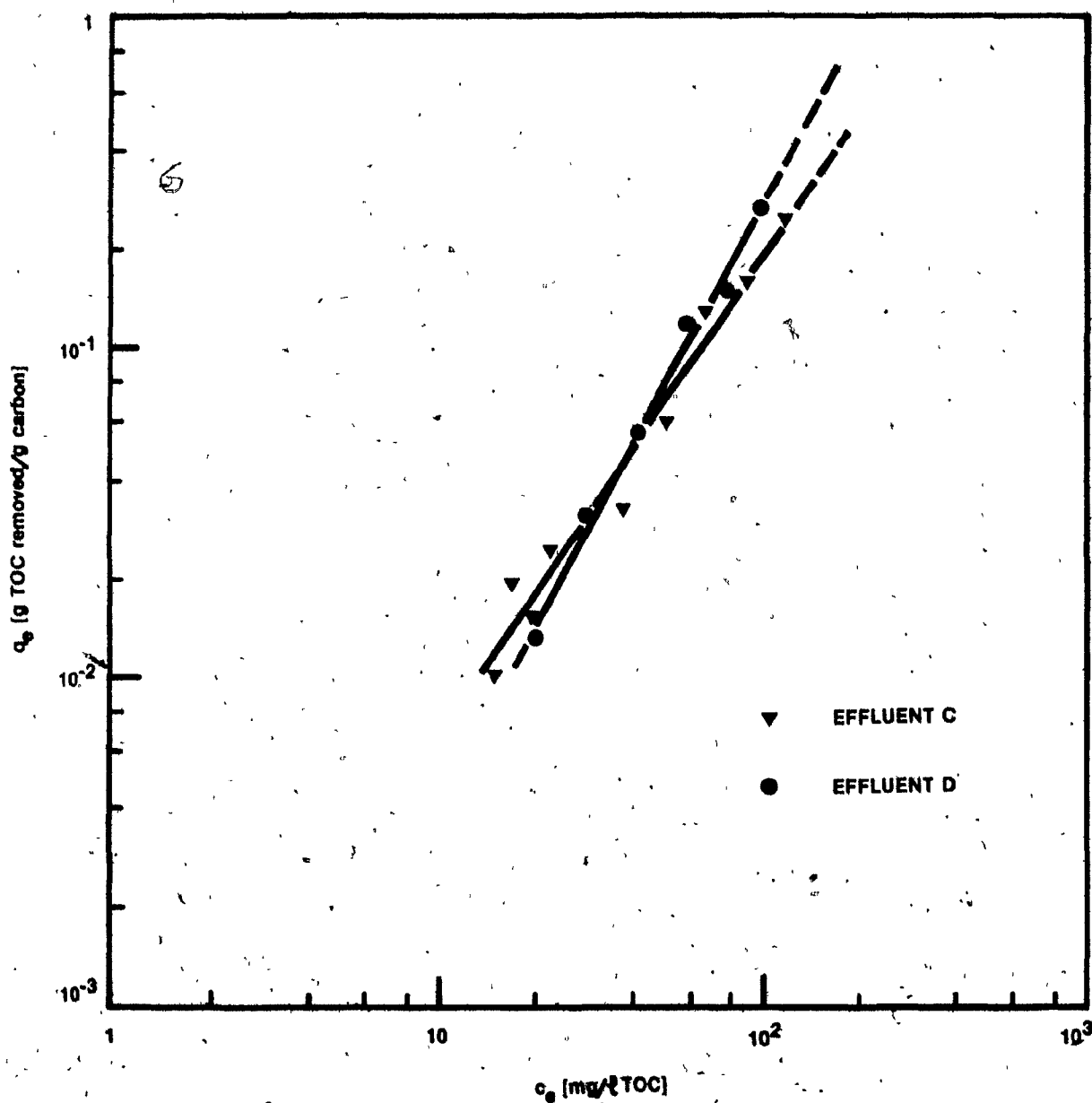


Table 18

CHARACTERISTICS OF FREUNDLICH ISOTHERMS FOR

ADSORPTION OF EFFLUENTS C AND D

Hydrodarco 4000 at 20°C and pH 7.0

Effluent	Initial Concentration C_o (mg/l TOC)	Intercept K ($l/g \cdot 10^{-3}$)	Slope $1/n$	$(q_e) C_o$ (g TOC/g)	Standard Error of Estimate
C	184±3	0.0002	1.46	0.44	0.094
D	171±3	0.00007	1.80	0.69	0.050

3.3.4 Adsorption Isotherms for Effluents E and F with Hydrodarco 4000

Adsorption isotherms for effluents E and F with Hydrodarco 4000 were determined at 20°C and pH 7.0 and are shown in Figure 16. Effluent F represents the lowest soluble organic loading expected in the dyehouse wastewater. Effluent F is identical with effluent E in terms of dyes and chemicals; the gum content, however, is lower in effluent F. The results presented in Figure 16 show a higher carbon loading of Hydrodarco at initial TOC concentration for effluent F and a steeper isotherm slope. Such behavior is similar to what was observed for effluents C and D (Section 3.3.3), at a higher concentration range. Values presented in Table 19 were calculated from least squares regressions of experimental data tabulated in Appendix 6.3.

FIGURE 16

ADSORPTION ISOTHERMS FOR EFFLUENTS E AND F

HYDRODARCO 4000 AT 20°C AND pH 7.0

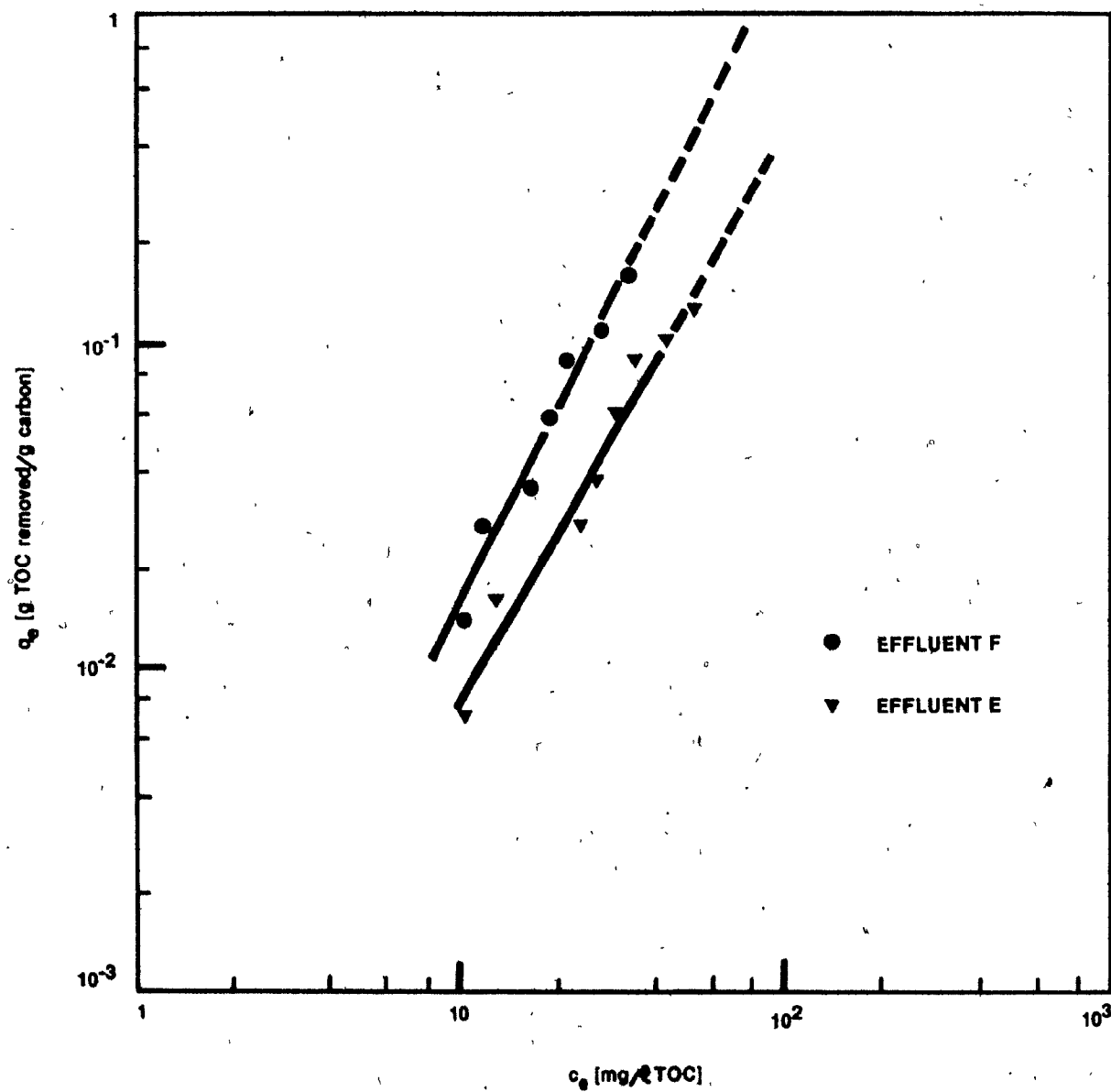


Table 19

CHARACTERISTICS OF FREUNDLICH ISOTHERMS FOR

ADSORPTION OF EFFLUENTS E AND F

Hydrodarco 4000 at 20°C and pH 7.0

Effluent	Initial Concentration C_o (mg/l TOC)	Intercept K (l/g.10 ⁻³)	Slope 1/n	$(q_e) C_o$ (g TOC/g)	Standard Error of Estimate
E	90±2	0.00015	1.74	0.36	0.090
F	77±2	0.00018	1.96	0.88	0.077

3.3.5 Adsorption Isotherms for Effluent D with Filtrasorb 400 and Norit

Comparison of adsorptive efficiencies of three types of activated carbon for the artificial effluent mixture D at 20°C and pH 7.0 is presented in Figure 17. Hydrodarco 4000 isotherm is reproduced from Figure 15. Based on virgin carbon experiments, Filtrasorb 400 exhibited the highest adsorption capacity in the range of TOC concentrations between 40 and 172 mg/l. Its performance, however, is closely followed by Hydrodarco carbon as shown in Table 20. Norit performance is the best below 40 mg/l TOC. The loading values (q_e) in Table 20 were calculated for identical initial TOC concentration of 172 mg/l. A much higher standard error of estimate for Filtrasorb 400 results should be noted here; it will be discussed later. Values presented in Table 20 were calculated from Freundlich least squares regressions of experimental data tabulated in Appendix 6.4.

FIGURE 17

ADSORPTION ISOTHERMS FOR EFFLUENT D

HYDRODARCO 4000, FILTRASORB 400 AND NORIT AT 20°C AND pH 7.0

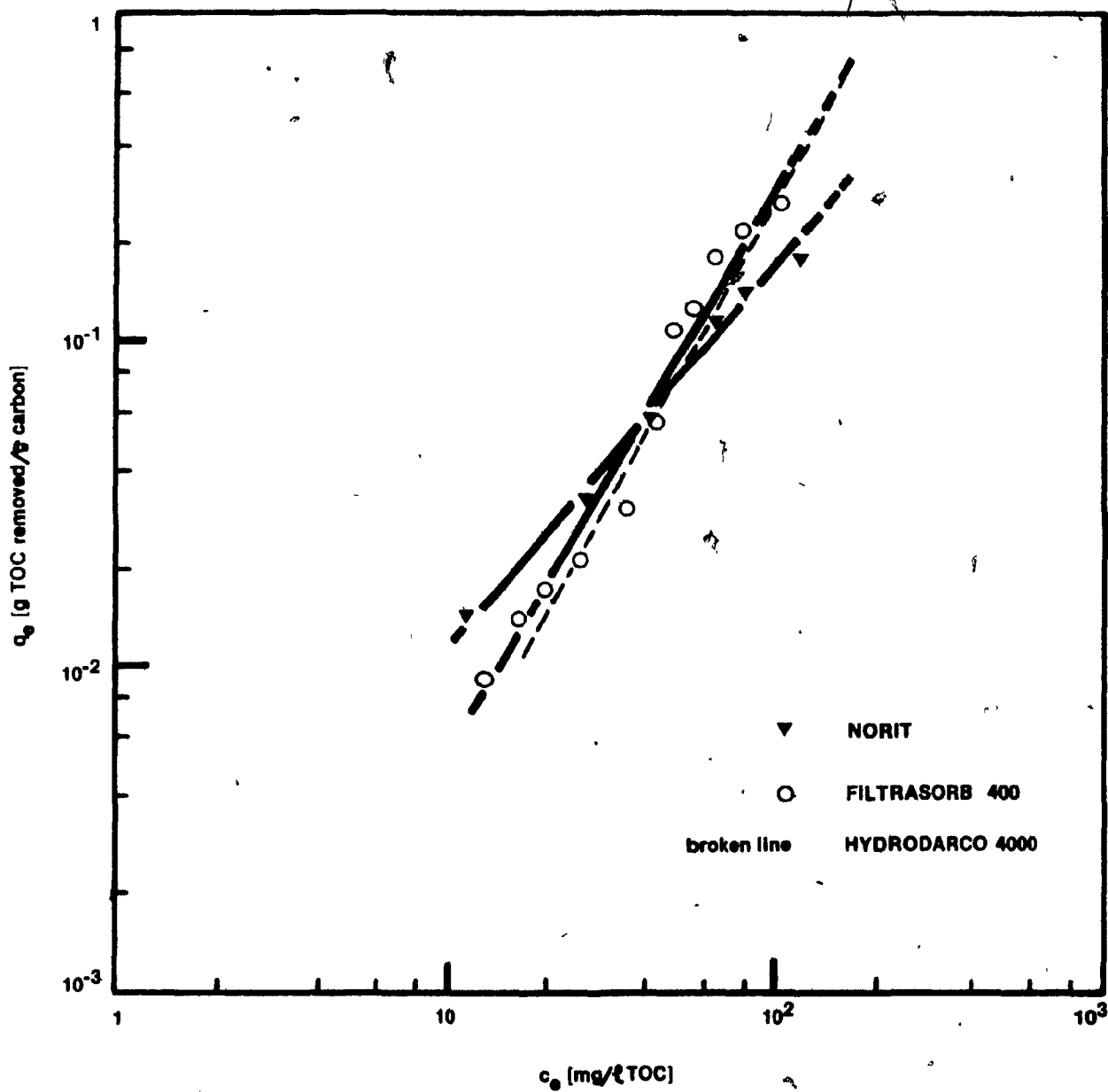


Table 20

CHARACTERISTICS OF FREUNDLICH ISOTHERMS FOR

ADSORPTION OF EFFLUENT D

Filtrisorb 400, Hydrodarco 4000 and Norit at 20°C and pH 7.0

Type of Carbon	Intercept K ($\text{l/g} \cdot 10^{-3}$)	Slope 1/n	* (q _e) C _o (g TOC/g)	Standard Error of Estimate
Filtrisorb 400	0.00009	1.75	0.72	0.105
Hydrodarco 4000	0.00007	1.80	0.69	0.050
Norit	0.0008	1.16	0.30	0.053

* C_o - 172 mg/l TOC

3.3.6 Adsorption Isotherm for Effluent D with Hydrodarco 4000 Expressed for a COD Parameter

The adsorption isotherm for effluent D treated with Hydrodarco 4000 at 20°C and pH 7.0 expressed for a COD parameter confirms the previous results based on the TOC parameter. The results are presented in Figure 18.

Table 21 shows the characteristics of the Freundlich isotherm obtained in this experiment. High carbon loading of Hydrodarco at C_0 , 1.15 g COD removed/g carbon should be noted. Values presented in the Table were calculated from a least squares regression of experimental data presented in Appendix 6.5.

FIGURE 18
ADSORPTION ISOTHERM FOR EFFLUENT D
HYDRODARCO 4000 AT 20°C AND pH 7.0 EXPRESSED FOR A COD PARAMETER

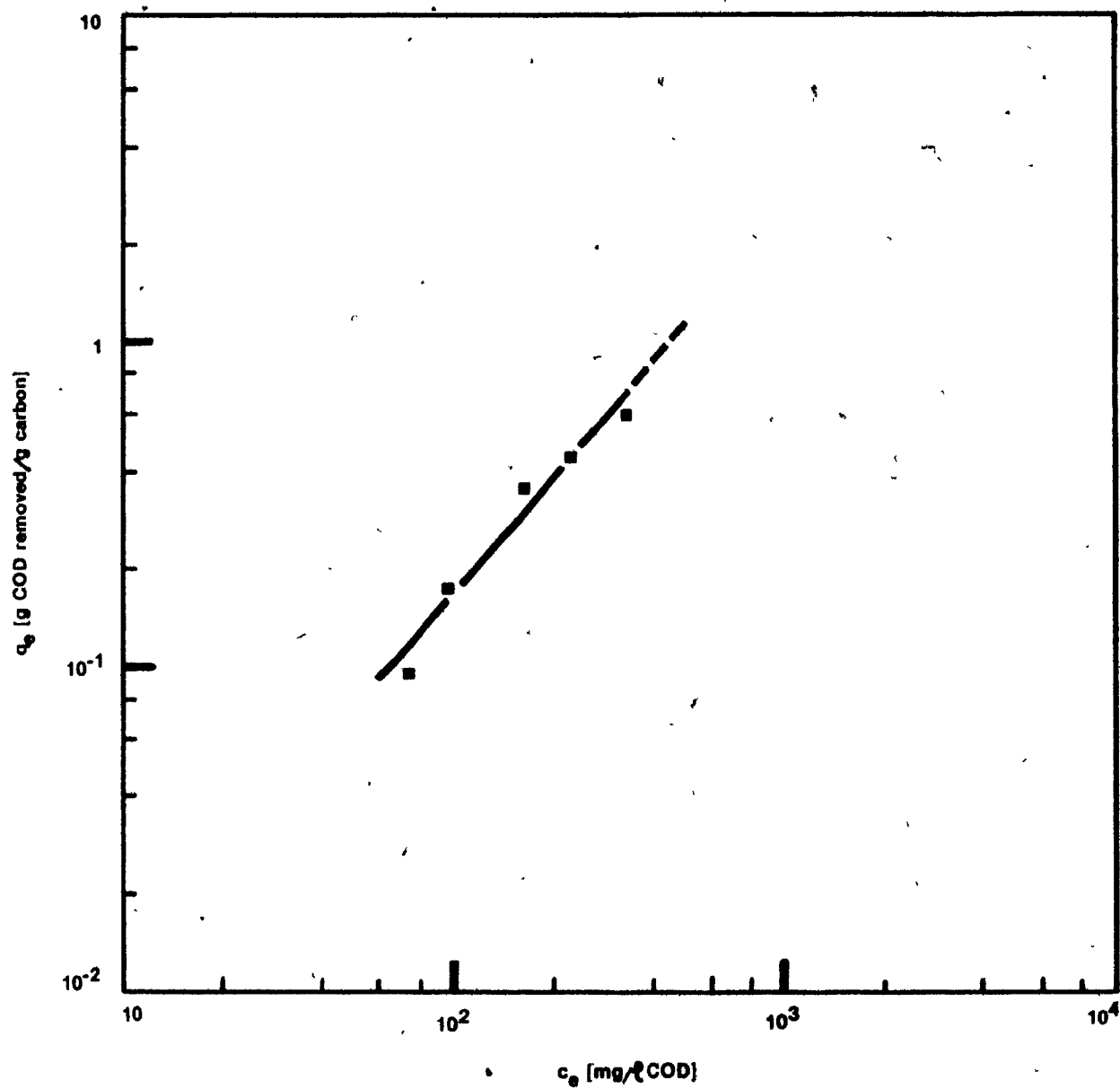


Table 21

CHARACTERISTICS OF FREUNDLICH ISOTHERMS FOR

ADSORPTION OF EFFLUENT D

Hydrodarco 4000 at 20°C and pH 7.0 expressed for a COD Parameter

Initial Concentration C_o (mg/l COD)	Intercept K^a (l/g.10 ⁻³)	Slope 1/n	$(q_e)_{C_o}$ (g COD/g)	Standard Error of Estimate
500	0.0006	1.21	1.15	0.079

4. DISCUSSION

4.1 Study of Adsorption of Jaguar A-40-F Gum From Its Pure Solution

Establishment of the contact time required to reach adsorption equilibrium was required for the adsorption isotherm batch tests. The resulting value of one hour is in agreement with usual contact periods for batch adsorption experiments^(58,69). It should be clearly understood, however, that the contact time selected for this study is a laboratory parameter and does not represent the residential contact time in the carbon column of the full-scale treatment plant.

In general, the remaining TOC concentration decrease is rapid within the first ten minutes of adsorption, followed by a progressively slower trend as the curve asymptotically approaches zero residue. That contact time is usually chosen for regular use, beyond which there is insignificant further reduction in adsorbate concentration⁽⁷⁰⁾. The results obtained here with Filtrasorb 400 at both high and low carbon dosages were considered sufficiently close to the normal kinetic behavior and no further investigations were necessary.

The effect of viscosity on penetration of the liquid into the capillary structure of the carbon and the effect of

viscosity on retarding motion of the particles during stirring, are also factors affecting contact time necessary to reach equilibrium. Another factor affecting contact time is the suspended matter other than activated carbon in the liquid. An appreciable amount of it would reduce the mean free path of the carbon particle and thereby increases the necessary contact time.

In this study, influence of these two factors was reduced to minimum with the viscosity of the gum solution similar to that of pure water (Appendix 5) while insoluble fiber and cellulose present in the guar gum aqueous solution was removed prior to the adsorption tests by filtration (Section 3.2.1).

Since pH and temperature are two factors which also affect adsorption, experimental approach was taken to establish their effect.

In general, adsorption of typical organic pollutants from water improves with decreasing pH. According to Weber⁽⁷¹⁾, this may result from neutralization of negative charges at the surface of the carbon with increasing hydrogen ion concentration, thereby reducing hindrance to diffusion and making available more of the active surface of the carbon. This effect can be expected to vary for different carbons, because the charges at the surface of the carbon depend on the composition of the raw materials used for carbon manufacturing and on the technique of activation.

The increased adsorption at lower pH values is well illustrated in Figure 12 for the studied non-ionic galactomannan guar gum adsorbate. This effect varies for different carbons as shown in Table 10. In Figure 12, intercepts (K) for both isotherms are quite similar while the slopes (1/n) differ appreciably. According to Weber⁽⁷²⁾, the intercept is roughly an indicator of sorption capacity and the slope of adsorption intensity.

The negative effect of alkaline pH on adsorption has also been demonstrated in this study (Table 10). Helbig⁽⁷⁰⁾ pointed out that the impression that carbons adsorb better in acid than in alkaline solutions probably arises from the fact that above pH 9.5-10.0, many adsorbable substances are susceptible to hydrolysis, with consequent simplification of physical and chemical structure and therefore lower adsorbability.

In a recent study⁽⁷³⁾, Wang et al investigated the effect of pH on activated carbon adsorption of different types of organic compounds in single component systems. Results are reported on organic acids and bases, anionic and cationic surface-active agents, non-ionic organic compounds and polymers. These authors concluded that pH adjustment has little or no effect on carbon adsorption of non-ionic organic compounds, provided that the chemical nature of the adsorbate is not changed by the added acid or base. An obvious extrapolation of this conclusion in this work would be a statement that the

chemical nature of the gum adsorbate underwent some pH-dependent modification. This, however, would have to be further substantiated.

Results presented herein (Figure 13) with regard to the effect of temperature on adsorption of the dissolved gum by Hydrodarco 4000 at pH 7.0 indicates the similarity of slopes for both isotherms while the intercepts differ appreciably.

According to Helbig⁽⁷⁰⁾, it is usually advantageous to treat effluents at as high a temperature as the nature of the liquid permits. However, the extent of adsorption should generally increase with decreasing temperature, as adsorption reactions are normally exothermic⁽⁷⁴⁾. This is apparently a contradiction to theoretical considerations but actually, the governing factor appears to be viscosity. As this is reduced at higher temperatures, penetration of the liquid into the submicroscopic capillary structure of the carbon is improved, with proportionate effect on development of effective interface and rate of adsorption.

According to Hassler⁽⁷⁵⁾, the influence of temperature is not the same for all types of carbon. This is indicated by the results presented in Table 11.

The Freundlich equation is commonly used for a comparison of powdered carbons in water treatment. Parameters for the Freundlich fit have been determined (Table 12) with a fairly small error of estimate. Results from the full-scale plant operation, however, could be more difficult to analyze.

The capacity of an adsorbent is partially governed by the availability of its surface to the adsorbate molecules. In order to characterize an adsorbent, information must be available on its physical structure, that is its surface area, pore size distribution and the chemical nature of the surface.

Abram⁽¹⁹⁾ pointed out that the total surface area and total volume give some measure of the potential capacity of the carbon. However, the true capacity will depend on the distribution of area or volume with pore size, and the distribution of molecular size to be adsorbed.

The results presented in Figure 11 indicate that the lignite-based Hydrodarco 4000 carbon out-performs the bituminous coal-based Nuchar WV-L and Filtrasorb 400 carbons which have a greater total surface area. However, the coal carbons have more surface area in the micropore range while the lignite carbon has more surface area in the transitional pore size.

De John⁽²⁶⁾ compared adsorption data from studies on industrial waste streams where the pollutants were predominantly large molecules (oil refineries, textile and dye plants, pulp and paper mills). In each case, the lignite carbon out-performed the bituminous-coal carbon on an equivalent volume basis.

According to the author, the nature of these pollutants (high molecular weight organics and color bodies) is such that

they are adsorbed in the transitional pores. Because lignite carbon has more surface area in this range, it should be expected to perform better. Indeed, it has been reported that adsorbing color bodies and high molecular weight organics require pores ranging in size from 20 to 500 Å⁰(26).

This could explain the behavior illustrated in Figure 11 where adsorption of the high molecular weight galactomannan gum is better accomplished with Hydrodarco 4000 type of carbon as compared to coal-based carbons. Data on pore size distribution for other types of carbons reported in Figure 11 were not available.

On the other hand, it has been suggested^(17,24) that surface functional groups of the carbon play some role in determining its adsorptive capacity. This phenomenon, however, is not well understood yet and it has not been possible to establish the relative importance of this effect upon results reported in this study.

It has also been reported⁽⁷⁶⁾ that molecular structure of the adsorbate affects its adsorbability. Carbon loadings at initial concentration (Figure 11) are fairly low, in the range (5-7.5) mg TOC/g. This might be explained by the high molecular weight effect. As molecular weight increases, solubility decreases and, therefore, adsorption increases for relatively low molecular weight substances. The Lundelius rule states that in general an inverse relationship can be anticipated between the extent of adsorption of a solute and

its solubility in the solvent from which adsorption occurs. This is well illustrated by the recent data of Guisti et al⁽⁷⁷⁾. On the other hand, Benedek et al⁽⁷⁸⁾ pointed out that as molecular weight increases to the extent that some pores become unavailable, adsorption loading may become lower. The high molecular weight gum adsorbate (> 200,000) used in this work probably falls in the latter category.

In Figure 11, isotherms have been determined for virgin batches of activated carbons. Upon regeneration, however, the internal pore structure of the carbon is altered. Surface area in the micropore range is drastically reduced while transitional pore surface area is increased slightly⁽²⁶⁾.

The significance of this change in pore size distribution is that the adsorptive performance of a regenerated carbon can change significantly⁽⁷⁹⁾. The degree of change will depend on the nature of the organics to be adsorbed. When the solution contains predominantly large molecules (as the gum adsorbate in Figure 11), the system scale-up design can be based on the virgin carbon data, because the performance of the regenerated carbon will be at least as good as that of the virgin carbon⁽²⁵⁾.

Adsorption data plotted as q_e/M vs C_e on logarithmic paper will in practically all cases yield a straight line over a considerable range of concentrations. However, the line will curve at both ends at extremes of concentration, i.e. K and $1/n$ are no longer constant⁽⁷⁰⁾. The right-hand portion of the lines in Figure 11 have been extrapolated up to the initial

gum concentration. The organic residuals characterized by the left-hand (lower concentrations) portion of the isotherms are due to different amounts of extractable impurities present in the carbons^(67,70). It has been reported⁽⁸⁰⁾ that very little, if any, impurities are washed off by distilled water from activated carbon during a 48-hour shaking period. Other authors⁽⁶⁶⁾ report the use of concentrated HCl to remove inorganic ash from carbon. Although they could have slightly improved the accuracy of the results, these supplementary procedures were not applied in the selected experimental method used in this study.

4.2 Study of Adsorption of Typical Celanese Dyehouse Wastewater Mixtures

The sharp break in carbon loading at the low-concentration end of the isotherms in Figure 14 is known as the "apparent end point"⁽⁷⁰⁾; greater dosages of carbon below this point affect no significant further decrease in organics. In Figure 14, the residuals vary linearly from approximately 9 to 18 mg/l TOC with the bulk of organics present in the mixtures.

According to Helbig⁽⁷⁰⁾, the end point for a particular liquid having this characteristic is not necessarily the same for all carbons; furthermore, an end point will not necessarily be found to exist for all carbons tested on that liquid.

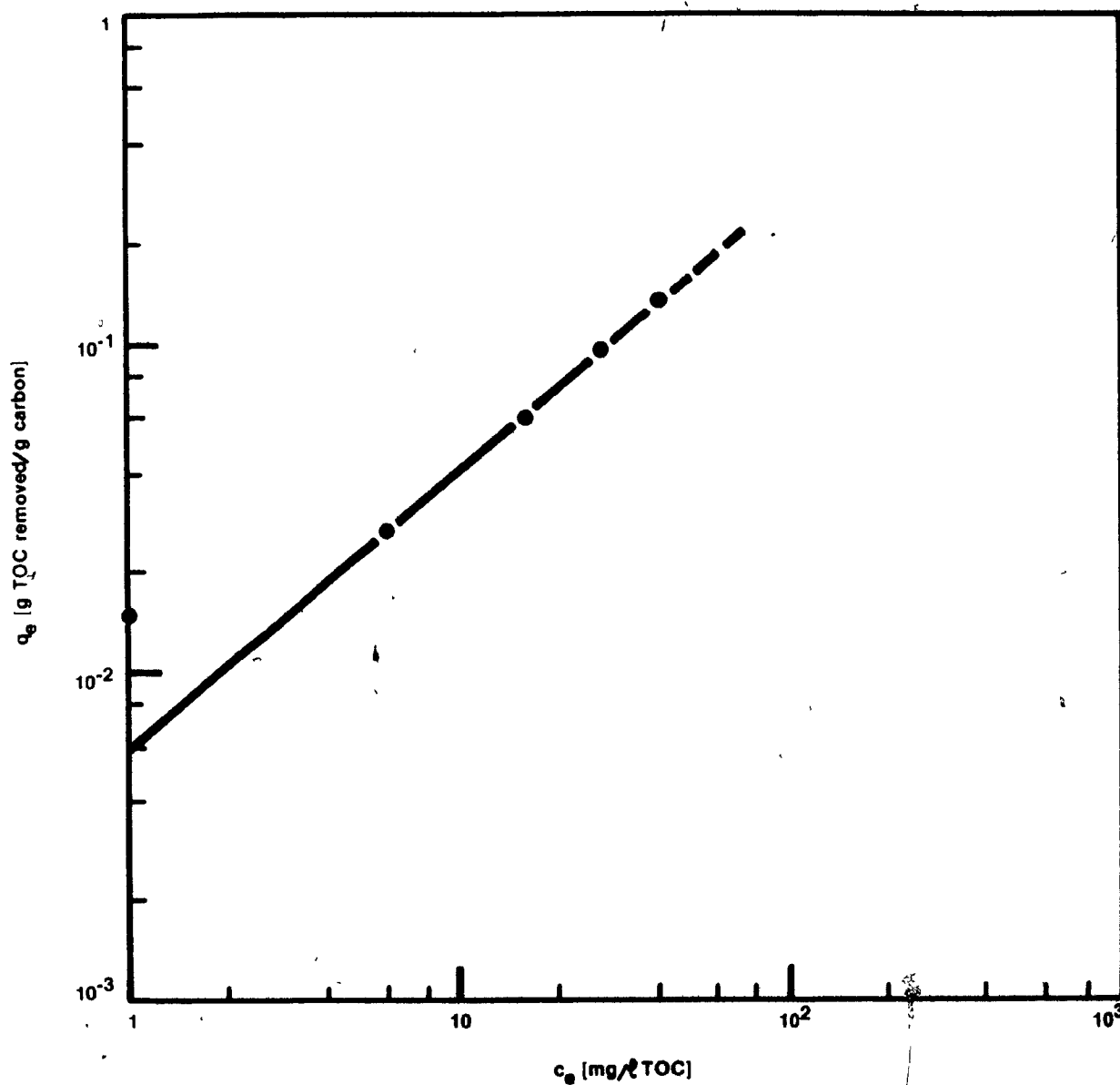
Benedek^(28,78) studied the magnitude of the non-adsorbable or residual fraction of various wastewaters and found many of

them to be below 10 mg/l TOC. Although this is quite small, nature of the non-adsorbable compounds is important as industrial recycling of effluents is desirable and probable. More work will have to be done on elucidation of the exact nature of non-adsorbable compounds. Residuals are generally believed to consist of highly water soluble or polar organics, although a direct proof of this assumption has not been presented yet. It appears that amino acids and small ionized organic salts may form part of the residue, just as high molecular weight or colloidal organics frequently reported in sewage⁽⁷⁸⁾. DeWalle et al⁽⁸¹⁾ reported that the high molecular weight (above 50,000) humic carbohydrate-like material is poorly adsorbed in carbon columns.

For the present work, analysis of results from Figures 11, 14, 15 and 16 demonstrates that the high molecular weight gum pollutant does not form part of the residue. With no visible color present in the high carbon dosage treated samples, it is likely that the residual TOC concentration detected is due to at least one of the chemicals listed in Table 8.

Figure 19 shows the adsorption isotherm of Celanese dye-house gum-free wastewater determined by Calgon Corp.⁽⁶³⁾. Filtrasorb 400 carbon was used at 68°C and pH 8.0. Effluent samples were collected and analysed prior to introduction of gum thickening agents in the dyeing process. The Calgon blank sample of 74 mg/l TOC taken as initial concentration in Figure 19 is slightly higher than the minimum predicted dyehouse

FIGURE 19
CALGON CORP. ADSORPTION ISOTHERM
CELANESE GUM-FREE WASTEWATER
FILTRASORB 400 AT 68°C AND pH 8.0



wastewater initial concentration (69 ± 2 mg/l TOC) in Figure 14, effluent B. For the Calgon isotherm, the slope is 0.841 and K is 5.8 l/g; in Figure 14, slope of the Hydrodarco 4000 isotherm was 0.908 and K was 6.7 l/g.

The major difference between the two isotherms appears to be the amount of non-adsorbable compounds remaining in solution. At the same 10,000 mg/l carbon dosage, isotherm B in Figure 14 exhibits a residual concentration of 9 mg/l TOC while Calgon reported a negligible value lower than 1 mg/l TOC.

The latter result is interesting in light of other investigations which all report a small amount of residual in their treated waste⁽⁷⁸⁾. Furthermore, Figure 17 also shows the presence of residuals for Filtrasorb 400 carbon when tested on a current typical Celanese dyehouse wastewater mixture at 20°C. The substantial difference in treated sample temperatures could explain the discrepancy in amounts of residuals, but further investigations conducted at 68°C with Filtrasorb 400 carbon failed to confirm this hypothesis. It is more reasonable to assume that the complex mixture prepared for experiments reported in Figure 14 included some non-adsorbable compounds which were not present in the effluent grab samples serving as a basis for development of the Calgon isotherm (Figure 19).

Nevertheless, the high carbon loading at initial concentration, in the range of 0.25 g TOC/g, exhibited in either case demonstrates that the conventional dyehouse waste is amenable to activated carbon treatment⁽⁵⁹⁾.

The results obtained in this work show that addition of small amounts of natural guar gum change drastically the adsorptive behavior of conventional effluent mixture. In comparison with Figure 14, the isotherms from Figures 15 and 16 exhibit no abrupt break in carbon loading, the slope is increased by more than 100% and the carbon loading at initial concentration is increased by at least 50%. The effect of (20-100) mg/l gum addition on a typical conventional carpet textile waste treatment was tested. The study revealed that there is an optimum range for the gum concentration in the effluent (10-35 mg/l) resulting in a favorable change in the adsorptive behavior.

Other investigators also observed a synergistic effect of adsorption between some organic compounds. DiGiano et al⁽²⁴⁾ obtained equilibrium adsorption isotherms for several dye mixtures of Foron Blue ER and a dye carrier and reported that the presence of the dye carrier significantly altered the adsorptive behavior of the disperse dye. At a lower carrier concentration, 100 mg/l, competitive effects caused a decrease in the adsorptive capacity of the dye. As the carrier concentration was increased, however, synergistic effects between the dye and the carrier resulted in an increase in adsorptive capacity. At the highest carrier concentration used, 400 mg/l, the adsorption of the dye approached that of the much more adsorbable basic dyes.

As explanation to that phenomenon, it was hypothesized that a thin film is formed by the carrier at the carbon surface which significantly affects adsorption of the dye. The immediate effect of this film is to suppress the electrical double layer surrounding the carbon surface, thereby reducing the repulsive forces between the dye and the carbon surface. Furthermore, because the dye is more soluble in the carrier than in the aqueous phase, a concentration gradient is established between the outer region of the carrier film and the carbon surface. Molecular diffusion of the dye within the carrier film allows the dye to freely migrate to an active site on the carbon surface.

In this study, however, adsorption of the disperse dyes alone was extremely slow, with contact times of four to five weeks required to attain equilibrium. Even after this long contact time, true equilibrium may not have been attained. With the addition of the dye carrier, the contact times required to attain equilibrium decreased to about one week. The effect of the dye carrier may, therefore, be to increase the rate of adsorption rather than increasing the actual capacity for adsorption. With this increase in the rate of adsorption, true equilibrium is attained in a much shorter time period.

Other instances are reported of solutes that are able to enhance the adsorption of certain other specific solutes⁽⁸²⁾. The phenomenon of cooperative action of adsorbates has been termed co-adsorption by Hassler⁽⁸²⁾.

The performances of Hydrodarco 4000, Filtrasorb 400 and Norit carbons for adsorption of contaminants from the complex dyehouse mixture are compared in Figure 17. In comparison to the lignite and the coal-based carbon, Norit, a peat-based carbon, exhibits a different adsorption behavior. With a less steep isotherm slope, the latter performs better than its competitors only at the low concentration level.

It has been reported⁽⁸³⁾ that in the marketed activated carbons major differences actually can exist within the same batch because of little control over the raw materials, additives and activation conditions. This may lead to some scatter of experimental data obtained from laboratory studies carried out with different batches of the same carbon. This may have been the reason for the relatively more scattered data points involving Filtrasorb 400 carbon in this work.

Isotherms reported in Figures 14 to 18 were based on virgin batches of activated carbon. According to De John⁽²⁵⁾, data developed on virgin coal-based carbon may lead to undersized adsorption treatment unit, if the water stream contains predominantly small molecules. Reasons for that were mentioned in the previous Section. It follows that the adsorptive capacity of Filtrasorb 400 may appear to be lower than Hydrodarco carbon if experiments were performed with regenerated carbon.

Dyehouse effluent mixtures which have been prepared for the laboratory adsorption tests contain many chemicals which are unlikely to be present all at the same time in the 20,000 IG

(91 m³) equalization tank prior to the full-scale adsorption unit. Furthermore, the synthetic effluent was prepared assuming a maximum daily production. The effluent concentration calculations were based on a total mass balance around the dyehouse, without taking into account any losses of materials by process evaporation, binding on fibers or any sort of output except the regular effluent channel. The scale-up procedures based on the parameters derived from the isotherms for this synthetic effluent are expected to produce a rather conservative design. Indeed, better performance is expected from the full-scale plant provided an appropriate removal of suspended matter is accomplished prior to the adsorption treatment.

SUMMARY OF RESULTS

The following summarizes the results obtained in the present work:

(A) Characterization of Celanese Dyehouse Wastewater Effluent, Sorel Plant

- The Celanese industrial effluent is comprised of three groups of pollutants which were defined as Dyes, Textile Chemicals and Guar Gum.
- ◆ Based on plant dyeing recipes, the range of concentrations of 7 acid and disperse dyes and 11 textile chemicals (including the guar gum) likely to occur in the dyehouse effluent was predicted and typical effluent mixtures were evaluated in terms of TOC content.
- The TOC concentration of the dyehouse effluent varies between approximately 75 and 185 mg/l (suspended matter content in the synthetic mixtures was lower than 10 mg/l). Contribution of the Dyes alone is in the range of 10% of the total concentration while that of the Textile Chemicals is as high as 75%. The remaining 15% is the contribution of the soluble Guar Gum thickener.

(B) Study of Adsorption of Jaguar A-40-F Gum from its Pure Solution

- The Guar Gum thickening agent (Jaguar A-40-F or Syngum D-47-D) used in the continuous dyeing process is a polysaccharidic galactomannan; it is a non-ionic, high molecular weight (220,000-250,000) organic compound.
- Adsorption of the gum increased at acid pH. The effect varies with the type of carbon and at pH 3 it was particularly positive for Hydrodarco 4000 and Witcarb 718 activated carbon.
- There is a negative effect of alkaline pH on adsorption of the gum from its pure solution dependent upon the type of carbon.
- Positive effect of elevated temperature from 20°C to 65°C on adsorption of the gum was observed.
- The lignite-based Hydrodarco 4000 carbon out-performs the bituminous coal-based Nuchar WV-L and Filtrasorb 400 carbons for adsorption of the guar gum from its pure solution. This may be the result of higher surface area of the lignite carbon in the transitional pores.
- Either Freundlich or Langmuir equations fit satisfactorily the gum adsorption data points. However, it is better represented by the former.
- Low carbon loadings in the range of (5-8) mg TOC/g for adsorption of guar gum from its pure solution at 30 mg/l TOC soluble gum concentration may be the result of the very high molecular weight of the adsorbate.

(C) Study of Adsorption of Typical Celanese Dyehouse Wastewater Mixtures

- The high carbon loading at initial wastewater concentration, in the range of 0.25 g TOC/g, exhibited by the typical adsorption isotherms demonstrates that the conventional Celanese wastewater is amenable to activated carbon treatment.
- (9-18) mg/l TOC residual after the treatment of conventional Celanese dyehouse effluent varied linearly with the bulk of organics present in the wastewater. Addition of the gum to the conventional waste did not alter appreciably the residue TOC concentration. It appears that the residue originated from one or several of the Textile Chemicals present in the complex effluent mixture.
- Addition of small amounts of polysaccharidic guar gum altered drastically the conventional dyehouse effluent adsorptive behavior. It appears that there is an optimum range for the gum concentration in the effluent (10-35 mg/l) resulting in a favorable change in the adsorptive behavior. The effect of the gum addition on typical conventional carpet textile waste was verified for the range of gum concentration between 20 mg/l and 100 mg/l.
- Based on virgin batches of activated carbon, Hydrodarco 4000 and Filtrasorb 400 carbons perform in a similar way

and are the best at high TOC concentrations. The Norit peat-based carbon performs better than its competitors at low TOC concentrations.

- Results presented in this section have been derived for higher than average effluent loadings. Better performance is expected from the full-scale plant provided an appropriate removal of suspended matter is accomplished prior to the adsorption treatment.

RECOMMENDATIONS

- Information derived from the batch test procedure can serve as a basis for design of the activated carbon effluent treatment system for the Celanese plant at Sorel. The study demonstrated that carbon accomplishes effective purification of typical wastewater effluent. Further investigation with a carbon pilot plant is suggested, however, which would evaluate hydraulic factors of the current industrial plant effluent stream and confirm the results of the laboratory scale study.
- As a complement to the pilot plant unit, an application of an adsorption process model such as the general-purpose computer simulation program developed by Weber⁽³⁷⁾ is also strongly suggested which would help to estimate the effect of changes in contacting conditions on the adsorption efficiency.

- Effect of reactivation of carbon on the adsorption efficiency should be established prior to scaling-up the treatment unit.
- Presence and accumulation of the non-adsorbable organic residuals, ammonia and phosphates in the carbon-treated effluent should be closely examined with regards to the contemplated water reclamation.

Appendix 1. Physical Properties of Investigated Granular Activated Carbons

Property	Units	Filtrisorb 400	Hydrodarco 4000	Norit	Nuchar WV-L	PC	Witcarb 718
Raw Material		Bituminous Coal	Lignite	Peat	Bituminous Coal	Coconut Shell	Petroleum Hydrocarbons
Total Surface Area	m ² /g	1050-1200	600-700	650-850	1000	800-1100	1150
Average Pore Diameter	A°		60	30-40	45	20	
Apparent Density	lb/ft ³	25	22	17	30	31	32
Iodine Number, min		1050	550		950		1050
Moisture, max	%	2	9	8	2	5	1
Ash, max	%		18	6	7.5	10	.5
Mesh Size (U.S.S.)		12 x 40	12 x 40	8 x 20	8 x 30	12 x 30	18 x 40

Appendix 2. Chemical Nature of Jaguar A-40-F Guar Gum

Jaguar A-40-F (or Syngum D-47-D) is a highly purified guar gum manufactured by Stein, Hall and Co. Inc., N.Y. (84,85). It is a readily dispersible, non-ionic, high viscosity thickener formulated for continuous dyeing and printing of tufted carpet. It is compatible with acid, premetalized acid, dispersed, direct basic and nickel chelating dispersed dyes.

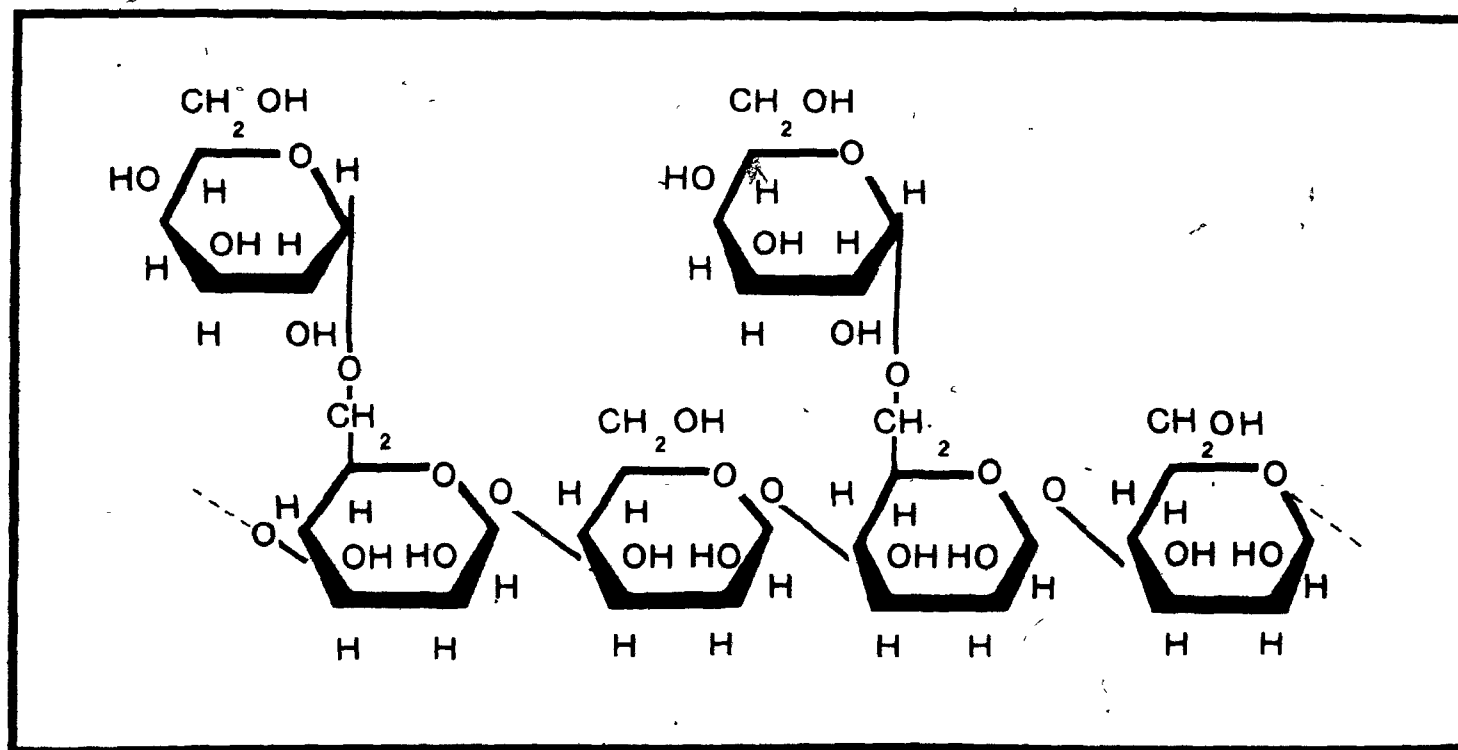
Guar gum is the principal component of the seed of the guar plant, Cyamopsis tetragonolobus or C. psoraloides. In nature, guar gum resides in the endosperm of the seed and is used as food by the embryo plant.

The purified guar gum, chemically classified as a galactomannan, is a high molecular weight (220,000-250,000) homogeneous carbohydrate polymer or polysaccharide made up of many D-mannose and D-galactose units (> 1000) linked together in the ratio of 2 moles:1 mole, as shown in the accompanying illustration.

The chemical structure of the guar gum molecule shown in Figure A-1 has been thoroughly studied. It was shown chromatographically that the cleavage fragments of the methylated gum contain small amounts of two unknown methylated sugars and consequently, it is possible that a small percentage of additional branching is present in the molecule⁽⁸⁶⁾.

The guar molecule is essentially a straight chain mannan branched at regular intervals with single membered galactose

FIGURE A-1
**GENERAL STRUCTURE OF THE
 GUAR GUM MOLECULE**



units on alternate mannose units. The mannose units are linked to each other by means of beta (1, 4) glycosidic linkages. The galactose branching is by alpha (1, 6) linkage. The cis-hydroxyl groups of the gum molecule make it an effective hydrogen bonding agent in solution. The long, straight chain nature of this molecule, combined with its regular side branching, is unique among the natural colloids.

Guar gum solutions are slightly cloudy due to the presence of a small amount of insoluble fiber and cellulose⁽⁸⁷⁾. Solutions are also thixotropic and the viscosity is relatively unaffected by the presence of electrolytes. It is relatively stable over the range of pH 4-10.5 and exhibits a slight buffering action.

Appendix 3. Total Carbon and Inorganic Carbon Calibration Curves

The total carbon stock solution was prepared by dissolution of 2.125 g of Reagent Grade anhydrous potassium biphthalate ($\text{KHC}_8\text{H}_4\text{O}_4$) in distilled water; the solution was diluted to 1 liter in a volumetric flask. This stock solution contains 1000 mg/l organic carbon. Stock solutions of other concentrations can be prepared by dilution of appropriate weight of potassium biphthalate.

The inorganic carbon stock solution was prepared by dissolving 4.404 g of anhydrous sodium carbonate (Na_2CO_3) and 3.497 g of anhydrous sodium bicarbonate (NaHCO_3) in distilled water; the solution was diluted to 1 liter in a volumetric flask. This solution contains 1000 mg/l inorganic carbon.

The TC stock solutions concentrations were corrected for distilled water contamination. This was done by adding to the known TC stock solutions concentrations the average TC concentration (1.5 mg/l) of distilled water. The IC concentration in distilled water was sufficiently low (< 0.5 mg/l) to neglect it.

In Figures A-2, A-3 and A-4, the full scale corresponds to 100 units scale on the chart recorder. Figure A-2 shows the TC calibration curves for 36.5 mg/l TC stock solution at 93% and 97% of full scale. The line at 95% of full scale was intrapolated between the two other curves. Figure A-3 shows

the TC calibration curves for 201.5 mg/l TC stock solution at 92% and 96% of full scale. The line at 94% full scale was intrapolated between the two other curves. Figure A-4 shows the IC calibration curves for 10 mg/l IC stock solution at 94% and 88% of full scale. The line at 91% full scale was intrapolated between the two other curves. In these figures, each near-full scale calibration curve was obtained by adjusting the gain value of the analyser (with the injected sample volume kept constant); a clock-wise rotation of the gain control increases the near-full scale values.

Data for Figures A-2 to A-4 are also presented in Tables A-1 to A-3.

Preparation of stock solutions was based on Beckman instructions manual for Model 915A Total Organic Carbon Analyser⁽⁸⁸⁾.



FIGURE A-2 **TC CALIBRATION CURVES OF [0-36.5 mg/l TC]** **STOCK SOLUTIONS**

BECKMAN MODEL 915A TOC ANALYSER
 RANGE 1,100 μ SAMPLES

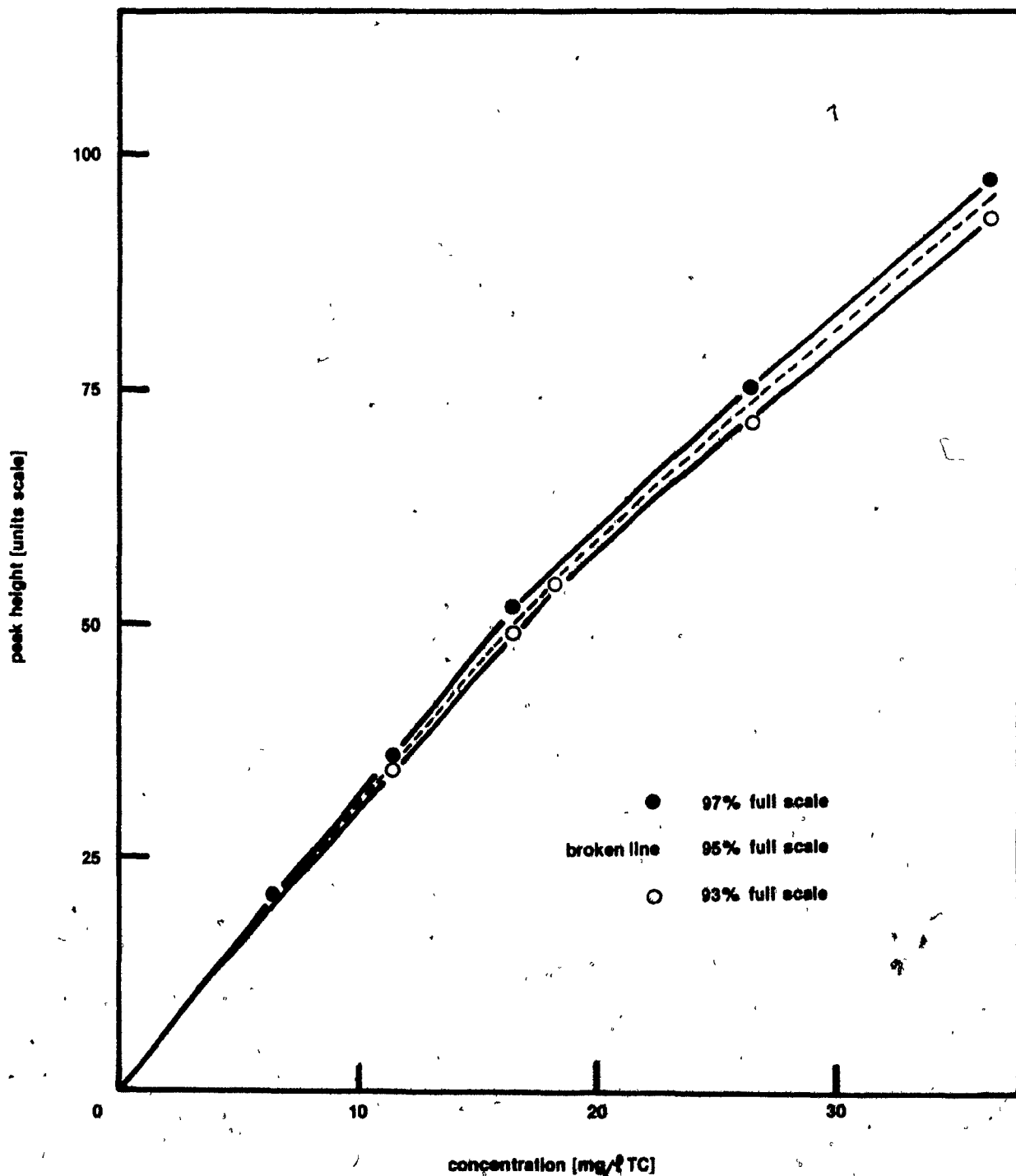


FIGURE A-3
TC CALIBRATION CURVES OF [0-201.5 mg/ℓTC]
STOCK SOLUTIONS

BECKMAN MODEL 915A TOC ANALYSER
RANGE 1, 20 μℓ SAMPLES

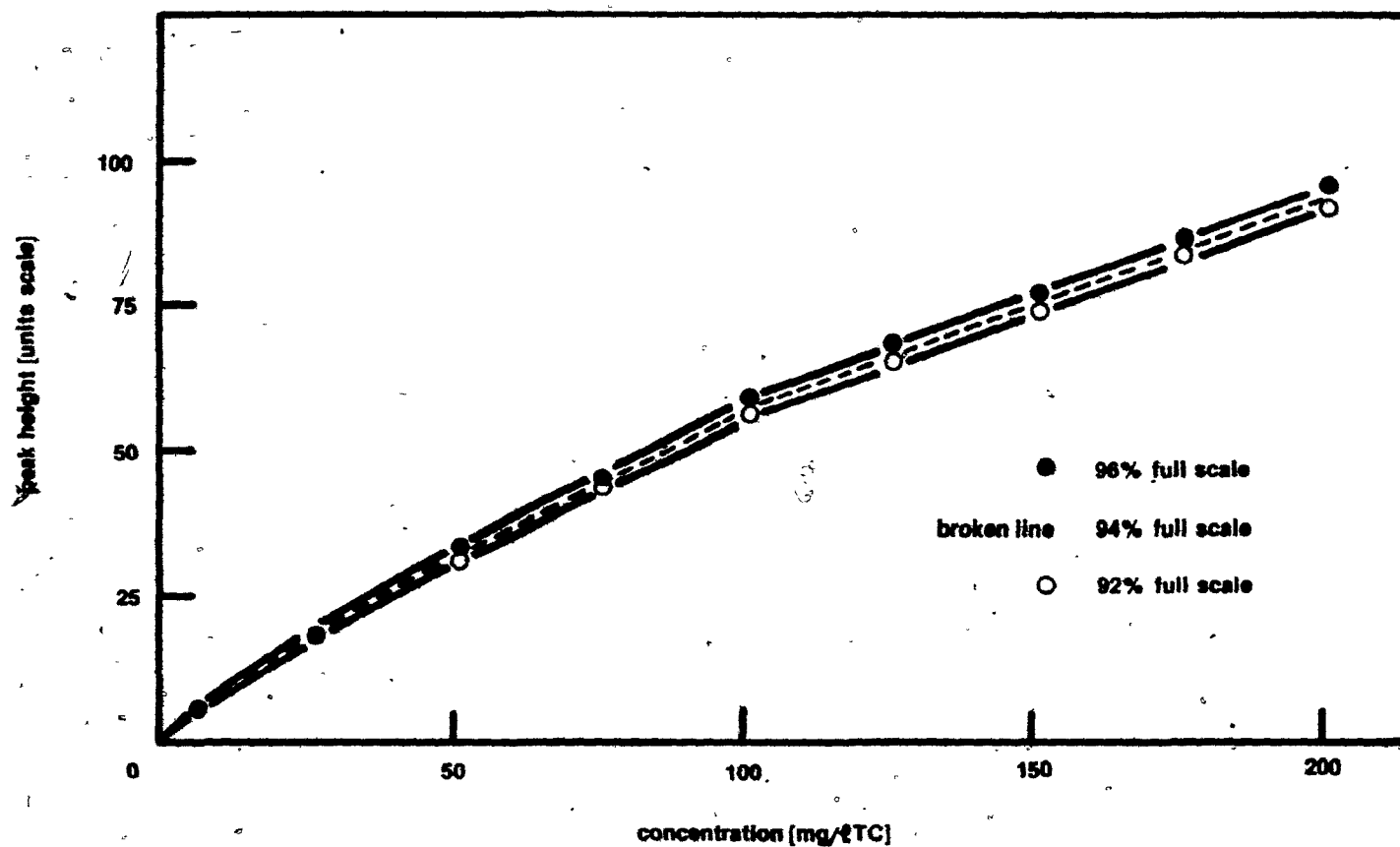


FIGURE A-4

IC CALIBRATION CURVES OF [0-10.0 mg/l IC]

STOCK SOLUTIONS

BECKMAN MODEL 915A TOC ANALYSER
RANGE 2,100 μ l SAMPLES

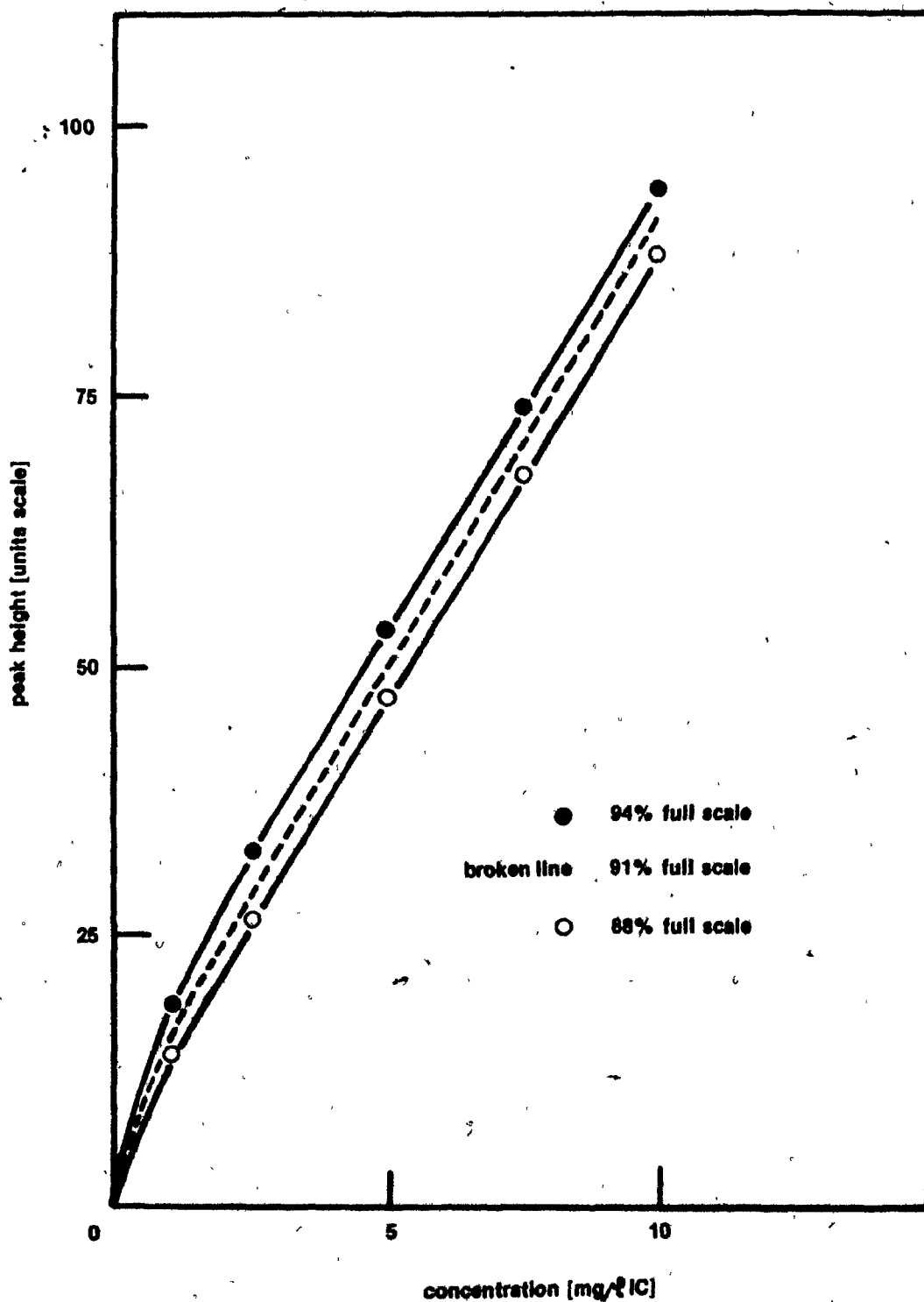


Table A-1. Data for TC Calibration Curves for
(0-36.5 mg/l TC) Stock Solutions

Stock Solution Concentration (mg/l TC)	Peak Height (units scale)
36.5	97.0
26.5	75.4
16.5	51.8
11.5	36.0
6.5	21.0
36.5	93.0
26.5	71.4
18.3	54.2
16.5	49.0
11.5	34.4
6.5	21.0

Table A-2. Data for TC Calibration Curves for
(0-201.5 mg/l TC) Stock Solutions

Stock Solution Concentration (mg/l TC)	Peak Height (units scale)
201.5	96.0
176.5	87.0
151.5	77.0
126.5	68.5
101.5	59.0
76.5	45.0
51.5	33.0
26.5	18.0
6.5	5.5
201.5	92.0
176.5	84.0
151.5	73.5
126.5	65.5
101.5	56.0
76.5	43.5
51.5	31.0
26.5	17.5
6.5	6.0

Table A-3. Data for IC Calibration Curves for
(0-10.0 mg/l IC) Stock Solutions

Stock Solution Concentration (mg/l IC)	Peak Height (units scale)
10.0	94.0
7.5	73.8
5.0	53.4
2.5	32.8
1.0	18.5
10.0	88.0
7.5	67.6
5.0	47.0
2.5	26.6
1.0	13.8

Appendix 4. TABULATION OF EXPERIMENTAL RESULTS -
Study of Adsorption of Jaguar A-40-F Gum

4.1. Concentration of the Gum Solution and Concentration
of the Corresponding Filtered Gum Solution

Raw Solution (mg/l)	Filtered Solution (mg/l TOC)
20	6.5
40	12.0
60	18.0
80	24.0

4.2. Remaining Gum Solution Concentration as a Function of Contact Time for Filtrasorb 400 (Carbon Dosage 1 g/l) at 20°C and pH 7.0

Contact Time (minutes)	Concentration (mg/l TOC)
0	30.0
5	22.5
10	22.2
15	22.4
20	21.9
30	22.1
45	21.9
60	21.9
90	22.1
120	22.1
180	21.2
240	20.9

4.3. Remaining Gum Solution Concentration as a Function of Contact Time for Filtrasorb 400 (Carbon Dosage 6 g/l) at 20°C and pH 7.0

Contact Time (minutes)	Concentration (mg/l TOC)
0	30.0
5	15.9
10	13.4
15	12.8
20	11.7
30	11.6
45	11.2
60	11.1
90	10.0
120	9.7
180	9.1
240	8.1

4.4. Adsorption of Jaguar A-40-F Gum at 20°C and pH 7.0 on Various Types of Activated Carbon

Type of Carbon	Carbon Dosage M (mg/l)	Concentration at Equilibrium C_e (mg/l TOC)	Change in Concentration ΔC (mg/l TOC)	Loading $q_e = \Delta C/M$ (mg TOC/g)
Hydrodarco 4000	Blank	29.4	-	-
	2000	15.5	13.9	6.95
	3000	10.4	19.0	6.33
	4000	5.5	23.9	5.98
	5000	2.8	26.6	5.32
	10000	1.7		
Norit	Blank	29.6	-	-
	2500	16.9	12.7	5.08
	4000	10.9	18.7	4.68
	5000	8.1	21.5	4.30
	6000	4.9	24.7	4.12
	7500	3.2	26.4	3.52
	10000	2.8		
PC	Blank	29.4	-	-
	2500	15.8	13.6	5.44
	4000	10.5	18.9	4.73
	5000	7.2	22.2	4.44
	6000	5.4	24.0	4.00
	10000	4.9		

Witcarb 718	Blank	30.0	-	-
	2500	17.6	12.4	4.96
	3000	15.2	14.8	4.93
	4000	12.5	17.5	4.38
	5000	10.2	19.8	3.96
	5500	9.3	20.7	3.76
	6000	7.6	22.4	3.73
	6500	6.8	23.2	3.57
	7000	5.7	24.3	3.47
	7500	5.1	24.9	3.32
	8000	4.5	25.5	3.19
	10000	3.4		
Nuchar WV-L	Blank	29.4	-	-
	2000	19.8	9.6	4.80
	3000	16.3	13.1	4.37
	4000	13.7	15.7	3.93
	5000	11.1	18.3	3.66
	7500	6.2	23.2	3.09
	10000	2.6		
Filtrisorb 400	Blank	30.5	-	-
	2500	20.1	10.4	4.16
	3500	16.2	14.3	4.09
	4000	15.0	15.5	3.88
	5000	12.8	17.7	3.54
	6000	11.6	18.9	3.15
	7500	8.0	22.5	3.00
	10000	2.9		

4.5. Adsorption of Jaguar A-40-F Gum at 20°C and pH 3.5
on Hydrodarco 4000

Carbon Dosage M (mg/l)	Concentration at Equilibrium C_e (mg/l TOC)	Change in Concentration ΔC (mg/l TOC)	Loading $q_e = \Delta C/M$ (mg TOC/g)
Blank	28.2	-	-
500	23.5	4.7	9.40
1000	19.5	8.7	8.70
1500	15.6	12.6	8.40
2000	12.0	16.2	8.10
2500	9.0	19.2	7.68
4000	4.1	24.1	6.03

4.6. Adsorption of Jaguar A-40-F Gum, at 65°C and pH 7.0
on Hydrodarco 4000

Carbon Dosage M (mg/l)	Concentration at Equilibrium C_e (mg/l TOC)	Change in Concentration ΔC (mg/l TOC)	Loading $q_e = \Delta C/M$ (mg TOC/g)
Blank	29.5	-	-
1500	15.7	13.8	9.20
2000	11.7	17.8	8.90
2500	8.8	20.7	8.28
3000	5.8	23.7	7.90
4000	2.5	27.0	6.75

Appendix 5. Viscosity of the Filtered Jaguar A-40-F Gum Solution

A Cannon-Fenske type capillary of viscometer size No. 50 (Range 0.8-3.2 centistokes) with a precision of $\pm 0.2\%$ was used for the kinematic viscosity estimation of the filtered Jaguar A-40-F gum solution. Concentration of the 10 ml gum sample solution used in the experiment was 30 mg/l TOC.

The calibration data were obtained with a 10 ml distilled water sample at 10°C , 25°C and 40°C . The simplified empirical relation⁽⁸⁹⁾ used to compute the gum solution kinematic viscosity was:

$$\nu = Ct + B/t$$

where ν is the kinematic viscosity (centistokes) and t is the efflux time (seconds). Constants C and B were evaluated from the least squares fit of the calibration points.

The final expression $\nu = 0.0027t - 2.1841/t$ (Standard error of estimate = 0.0) was then used to calculate the gum sample kinematic viscosity at three different temperatures (T). Experimental results are the following:

Temperature ($^{\circ}\text{C}$)	Efflux Time (seconds)	Calculated Kinematic Viscosity (centistokes)
10	559.8	1.4796
25	380.2	1.0017
40	279.0	0.7316

This set of data was plotted with the logarithm of the kinematic viscosity (centistokes) as a function of the reciprocal absolute temperature ($^{\circ}\text{K}^{-1}$). Based on a least squares regression (Standard error of estimate = 0.006), the resulting linear relation between the gum solution kinematic viscosity and temperature (Range 10-40 $^{\circ}\text{C}$) was:

$$\log v = \frac{900.4778}{T} - 3.0109$$

From this equation, the estimated gum sample kinematic viscosity is 1.147 centistoke at 20 $^{\circ}\text{C}$; at 65 $^{\circ}\text{C}$, the extrapolated value is 0.451 centistoke.

In terms of absolute viscosity, assuming the density of the diluted gum solution being identical to that of pure water, this is 1.145 centipoise at 20 $^{\circ}\text{C}$ and 0.442 centipoise at 65 $^{\circ}\text{C}$.

Appendix 6. TABULATION OF EXPERIMENTAL RESULTS - Study of Adsorption of Typical Celanese Dyehouse Wastewater Mixtures

6.1. Adsorption of Effluents A and B at 20°C and pH 7.0 with Hydrodarco 4000

Effluent	Carbon Dosage M (mg/l)	Concentration at Equilibrium C_e (mg/l TOC)	Change in Concentration ΔC (mg/l TOC)	Loading $q_e = \Delta C/M$ (g TOC/g)
A	Blank	131.2	-	-
	200	93.6	37.6	0.188
	350	73.4	57.8	0.165
	500	56.5	74.7	0.149
	800	37.5	93.7	0.117
	1400	28.4	102.8	0.073
	2000	25.7	105.5	0.053
	4000	21.8	109.4	0.027
	10000	18.1	113.1	0.011
	15000	19.4	111.8	0.007
B	Blank	58.7	-	-
	150	34.1	24.6	0.164
	200	29.7	29.0	0.145
	350	20.9	37.8	0.108
	500	16.5	42.2	0.084
	800	14.5	44.2	0.055
	1400	12.6	46.1	0.033
	2000	11.5	47.2	0.024
	4000	10.0	48.7	0.012
	10000	9.1	49.6	0.005

6.2. Adsorption of Effluents C and D at 20°C and pH 7.0 with Hydrodarco 4000

Effluent	Carbon Dosage M (mg/l)	Concentration at Equilibrium C_e (mg/l TOC)	Change in Concentration ΔC (mg/l TOC)	Loading $q_e = \Delta C/M$ (g TOC/g)
C	Blank	167.3	-	-
	200	119.3	48.0	0.240
	500	89.3	78.0	0.156
	800	67.4	99.9	0.125
	2000	51.5	115.8	0.058
	4000	37.7	129.6	0.032
	6000	22.4	144.9	0.024
	8000	17.3	150.0	0.019
	10000	19.7	147.6	0.015
	15000	15.3	152.0	0.010
D	Blank	151.8	-	-
	200	99.9	51.9	0.260
	500	78.1	73.7	0.147
	800	59.1	92.7	0.116
	2000	42.1	109.7	0.055
	4000	29.1	122.7	0.031
	10000	20.0	131.8	0.013
	16000	18.9		
	20000	17.7		

6.3. Adsorption of Effluents E and F at 20°C and pH 7.0 with Hydrodarco 4000

Effluent	Carbon Dosage M (mg/l)	Concentration at Equilibrium C_e (mg/l TOC)	Change in Concentration ΔC (mg/l TOC)	Loading $q_e = \Delta C/M$ (g TOC/g)
E	Blank	78.0	-	-
	200	52.2	25.8	0.129
	350	43.1	34.9	0.100
	500	34.3	43.7	0.087
	800	29.9	48.1	0.060
	1400	26.2	51.8	0.037
	2000	23.3	54.7	0.027
	4000	12.8	65.2	0.016
	10000	10.1	67.9	0.007
F	Blank	64.9	-	-
	200	33.2	31.7	0.159
	350	27.3	37.6	0.107
	500	21.2	43.7	0.087
	800	18.5	46.4	0.058
	1400	15.9	49.0	0.035
	2000	11.7	53.2	0.027
	4000	10.2	54.7	0.014
	10000	8.2		

6.4. Adsorption of Effluent D at 20°C and pH 7.0 with Filtrasorb 4000 and Norit

Type of Carbon	Carbon Dosage M (mg/l)	Concentration at Equilibrium C_e (mg/l TOC)	Change in Concentration ΔC (mg/l TOC)	Loading $q_e = \Delta C/M$ (g TOC/g)
Filtrasorb 400	Blank	154.9	-	-
	200	103.7	51.2	0.256
	350	80.8	74.1	0.212
	500	65.9	89.0	0.178
	800	56.8	98.1	0.123
	1000	50.2	104.7	0.105
	2000	45.0	109.9	0.055
	4000	35.7	119.2	0.030
	6000	26.0	128.9	0.021
	8000	19.8	135.1	0.017
	10000	16.7	138.2	0.014
	15000	12.9	142.0	0.009
Norit	Blank	155.0	-	-
	200	119.5	35.5	0.178
	500	81.7	73.3	0.147
	800	66.5	88.5	0.111
	2000	43.0	112.0	0.056
	4000	26.9	128.1	0.032
	10000	11.5	143.5	0.014

6.5. Adsorption of Effluent D at 20°C and pH 7.0 with Hydrodarco 4000 expressed in COD

Carbon Dosage M (mg/l)	Concentration at Equilibrium C_e (mg/l COD)	Change in Concentration ΔC (mg/l COD)	Loading $q_e = \Delta C/M$ (g COD/g)
Blank	444	-	-
200	324	120	0.600
500	224	220	0.440
800	160	284	0.355
2000	96	348	0.174
4000	72	372	0.093
10000	60		

REFERENCES

1. Cooney, J.A. 1975. Thickeners for carpet printing. Am. Dyest. Rep. 64, (6), 20-22.
2. Flege, R.K. 1968. Determination, evaluation and abatement of color in textile plant effluents. Georgia Institute of Technology, Water Resources Center, Atlanta, Georgia. WRC-0868.
3. Newlin, K.D. 1971. The economic feasibility of treating textile wastes in municipal systems. J. Water Pollut. Control Fed. 43: 2195-2199.
4. Porter, J.J. 1971. Textile waste treatment: practices, needed research, and federal legislation. Presented at The American Association of Textile Chemists and Colorists Symposium, The Textile Industry and the Environment, Atlanta, Georgia, March 31-April 1, 1971.
5. Masselli, J.W., N.W. Masselli, and M.G. Burford. 1973. Textile waste treatment: past, present and future. Presented at The American Association of Textile Chemists and Colorists Symposium, The Textile Industry and the Environment, Washington, D.C., May 22-24, 1973.
6. Alspaugh, T.A. 1973. Treating dye wastewater. Text. Chem. Color. 5: 255-260.
7. Purvis, M.R. 1974. Aerobic treatment of textile wastes. Am. Dyest. Rep. 63, (8), 19, 22, 24, 26.
8. Shelley, M.L., C.W. Randall, and P.H. King. 1976. Evaluation of chemical-biological and chemical-physical treatment for textile dyeing and finishing waste. J. Water Pollut. Control Fed. 48: 753-761.
9. Mytelka, A.I., and R. Manganelli. 1968. Energy-induced changes in an azo dyestuff waste. J. Water Pollut. Control Fed. 40: 260-268.
10. Trimmer, T.H., et al. 1971. Removal of color from textile dye wastes. Text. Chem. Color. 3: 239-247.
11. Institute of Textile Technology, and Hydrosience Inc. 1973. Recommendations and comments for the establishment of best practicable wastewater control technology currently available for the textile industry. American Textile Manufacturers Institute Inc., Charlotte, North Carolina.

12. Leslie, M.E. 1974. Peat: new medium for treating dye-house effluent. Am. Dyest. Rep. 63, (8), 15, 16, 18.
13. Hodges, J.L., and T.A. Alspaugh. 1975. Advanced waste treatment: the use of carbon, alum, and adsorptive resins for treating textile wastes. Presented at The American Association of Textile Chemists and Colorists Symposium, Face-to-Face with Environmental Problems, Charlotte, North Carolina, May 28-29, 1975.
14. Brandon, C.A., and J.J. Porter. 1975. Hyperfiltration as applied to textile wastewater. Presented at The American Society of Mechanical Engineers, National Textile Engineering Conference, Clemson, South Carolina, October, 1975.
15. Ross, R.D., ed. 1968. Industrial waste disposal. Reinhold Book Corp., New York. p. 144.
16. Smisek, M., and S. Cerny, ed. 1970. Active carbon: manufacture, properties and applications. American Elsevier Publishing Co., New York.
17. Mattson, J.S., and H.B. Mark, ed. 1971. Activated carbon: surface chemistry and adsorption from solution. Marcel Dekker Inc., New York.
18. Porter, J.J. 1972. Concepts for carbon adsorption in waste treatment. Text. Chem. Color. 4: 29-35.
19. Abram, J.C. 1973. The characteristics of activated carbon. Presented at the Water Research Association Conference, University of Reading, England, April 3-5, 1973.
20. Mantell, C.L., ed. 1968. Carbon and graphite handbook. Interscience Publishers, New York.
21. Weber, W.J. Jr., et al., ed. 1972. Physicochemical processes for water quality control. Wiley - Interscience, New York.
22. Hassler, J.W., ed. 1974. Purification with activated carbon: industrial, commercial, environmental. Chemical Publishing Co., Inc., New York.
23. Porter, J.J. 1973. Stability and removal of commercial dyes from process wastewater. Pollut. Eng. 5, (10), 27-30.

24. DiGiano, F.A., W.H. Frye, and A.S. Natter. 1975. Factors affecting removal of textile dyes by carbon adsorption. *Am. Dyest. Rep.* 64, (8), 15-18, 20.
25. De John, P.B., and R.A. Hutchins. 1975. Treatment of dye wastes with granular activated carbon. Presented at The American Association of Textile Chemists and Colorists, National Technical Conference, Chicago, Illinois, October 15-17, 1975.
26. De John, P.B. 1974. Factors to consider when selecting granular activated carbon for wastewater treatment. Proceedings of the 29th Industrial Waste Conference, Purdue University, Lafayette, Indiana, May 7-9, 1974.
27. Porter, J.J. 1972. Treatment of textile waste with activated carbon. *Am. Dyest. Rep.* 61, (8), 24-27.
28. Benedek, A. 1974. Carbon evaluation and process design. Environment Canada, Environmental Protection Service (Water). Technology Transfer Seminar, Proceedings of the Physical-Chemical Treatment Activated Carbon Adsorption in Pollution Control, Ottawa, Ontario, October 24, 1974.
29. Fornwalt, H.J., and R.A. Hutchins. 1966. Purifying liquids with activated carbon. *Chem. Eng.* 73, (8), 179-184.
30. Eckenfelder, W.W., and D.L. Ford, ed. 1970. Water pollution control; experimental procedures for process design. Pemberton Press.
31. Lukchis, G.M. 1973. Adsorption systems. Part I: design by mass transfer-zone concept. *Chem. Eng.* 80, (13), 111-116.
32. Hutchins, R.A. 1973. New method simplifies design of activated-carbon systems. *Chem. Eng.* 80, (19), 133-138.
33. Erskine, D.B., and W.G. Schuliger. 1971. Graphical method to determine the performance of activated carbon processes for liquids. *AIChE Symposium Series, Water - 1971*. 68, (124), 185-190.
34. Allen, J.B., R.S. Joyce, and R.H. Kasch. 1967. Process design calculations for adsorption from liquids in fixed beds of granular activated carbon. *J. Water Pollut. Control Fed.* 39: 217-229.

35. Keinath, T.M., and W.J. Weber, Jr. 1968. A predictive model for the design of fluid-bed adsorbers. J. Water Pollut. Control Fed. 40: 741-765.
36. Cookson, J.T. Jr. 1970. Design of activated carbon adsorption beds. J. Water Pollut. Control Fed. 42: 2124-2134.
37. Weber, W.J. Jr., and J.C. Crittenden. 1975. MADAM I: a numeric method for design of adsorption systems. J. Water Pollut. Control Fed. 47: 924-940.
38. Swindell-Dressler Co. 1971. Process design manual for carbon adsorption. U.S. Environmental Protection Agency, Technology Transfer. Program #17020 GNR. October, 1971.
39. Fornwalt, H.J., and R.A. Hutchins. 1966. Purifying liquids with activated carbon. Chem. Eng. 73, (9), 155-160.
40. Hager, D.G. 1973. Industrial wastewater treatment by granular activated carbon. Am. Dyest. Rep. 62, (11), 69, 70, 72-74.
41. Smith, S.B. 1974. Techniques of activated carbon regeneration. Environment Canada, Environmental Protection Service (Water). Technology Transfer Seminar, Proceedings of the Physical-Chemical Treatment Activated Carbon Adsorption in Pollution Control, Ottawa, Ontario, October 24, 1974.
42. Loven, A.W. 1974. Activated carbon regeneration perspectives. AIChE Symposium Series, Water - 1974: I. Industrial Wastewater Treatment. 70, (144), 285-295.
43. Rizzo, J.L. 1970. Adsorption/filtration: a new unit process for the treatment of industrial wastewaters. Chemical Engineering Progress Symposium Series (AIChE), Water - 1970. 67, (107), 466-470.
44. MacCrum, J.M. 1971. Adsorption ... a solution to textile dye wastes. Presented at The American Association of Textile Chemists and Colorists Symposium, The Textile Industry and the Environment, Atlanta, Georgia, March 31-April 1, 1971.
45. Anonymous. 1975. Activated carbon for water reclamation. Text. Ind. 139, (10), 130.

46. Rodman, C.A., and E.L. Shunney. 1971. Bio-regenerated activated carbon treatment of textile dye wastewaters. U.S. Environmental Protection Agency, Water Quality Office. Project #12090 DWM. January, 1971.
47. Hines, G.W. 1975. Collingwood plant dyehouse effluent activated carbon treatment system. Unpublished.
48. Poon, C.P.C., and P.P. Virgadamo. 1973. Anaerobic-aerobic treatment of textile waste with activated carbon. U.S. Environmental Protection Agency, Office of Research and Monitoring. Project #12090 EQO. May, 1973.
49. Burkell, J.E. 1973. An application of activated carbon to the treatment of a textile dyeing wastewater. Environment Canada, Environmental Protection Service, Technology Development Branch (Water). Technology Transfer Seminar, Proceedings of the Physicochemical Treatment/Activated Carbon Adsorption in Water Pollution Control, Vancouver, British Columbia, September 9, 1973.
50. Snider, E.H., and J.J. Porter. 1974. Ozone destruction of selected dyes in wastewater. Am. Dyest. Rep. 63, (8), 36, 38, 41, 44, 46, 48, 58, 60.
51. Anonymous. 1974. Ozone-carbon dye-waste treatment. Text. Ind. 138, (10), 43, 45.
52. Pardue, E.E., M.M. Stark, and B.M. Lalli. 1974. Reclaiming dye wastewater for reuse with activated carbon. Presented at The American Association of Textile Chemists and Colorists, National Technical Conference, Braniff Place, New Orleans, October 9-11, 1974.
53. Snyder, A.J., and T.A. Alspaugh. 1974. Catalysed bio-oxidation and tertiary treatment of integrated textile wastewaters. U.S. Environmental Protection Agency, Office of Research and Development. Project #12090 HLO. June, 1974.
54. Adams, A.L. 1976. Carbon adsorption aids activated sludge treatment at dyeing and finishing plants. Am. Dyest. Rep. 65, (4), 32, 34, 36, 38.
55. Porter, J.J. 1973. Reusing treated wastewater: will it work in the plant? Am. Dyest. Rep. 62, (4), 79, 80, 82.
56. Burke, D.J., and C.M. Palesh. 1974. Wastewater recycle for dyehouses. Am. Dyest. Rep. 63, (10), 60, 63, 65.

57. Perry, R.H., and C.H. Chilton, ed. 1973. Chemical Engineers' Handbook. McGraw-Hill Book Co., New York.
58. Anonymous. 1966. The laboratory evaluation of granular activated carbons for liquid phase applications. Pittsburgh Activated Carbon Co. March, 1966.
59. Anonymous. 1972. Adsorption isotherm of granular carbon for wastewater. ICI America Inc., Pollution Control Venture Department. May, 1972.
60. Anonymous. 1971. Progress report. Phase I: waste water survey Chemcell Limited, Sorel. Pollutech Pollution Advisory Services Limited, Oakville, Ontario. Project #512. October 4, 1971.
61. Anonymous. 1972. Waste water treatability studies for Celanese, Sorel, Quebec. Pollutech Pollution Advisory Services Limited, Oakville, Ontario. Project #512. October 16, 1972.
62. Anonymous. 1973. Report on waste water disposal for Celanese Canada Ltd., Sorel, Quebec. Waste Consulting Services Ltd., Thornhill, Ontario. Job #W71-405. June 15, 1973.
63. Barre, L. 1973. Feasibility report Filtrasorb granular carbon treatment for Celanese Canada Limited. Calgon Canada, Bramalea, Ontario. October 31, 1973.
64. Hassler, J.W., ed. 1974. Purification with activated carbon: industrial, commercial, environmental. Chemical Publishing Co., Inc., New York. p. 133.
65. Bobrow, S., J. Simon, and T. Levan. 1974. Rapport sur l'ingénierie préliminaire de l'usine d'épuration des eaux résiduelles à Sorel. Surveyer, Nenniger and Chênevert Inc., Montreal, Quebec. SNC #36-54-0000. November 14, 1974.
66. Mattson, J.S., and F.W. Kennedy. 1971. Evaluation criteria for granular activated carbons. J. Water Pollut. Control Fed. 43: 2210-2217.
67. Rinehart, T., et al. 1970. A symposium on activated carbon. ICI America Inc. June, 1970.
68. Bradley, K.C. 1975. Design of an activated carbon waste water treatment system for a multi-product organic chemical plant. 25th Canadian Chemical Engineering Conference, Montreal, Québec, November 2-5, 1975.

69. Hassler, J.W., ed. 1974. Purification with activated carbon: industrial, commercial, environmental. Chemical Publishing Co., Inc., New York, p. 309.
70. Helbig, W.A., ed. 1946. Adsorption from solution by activated carbon. In Colloid Chemistry, 6: 814-839. Reinhold Publishing Corp., New York.
71. Weber, W.J. Jr., et al., ed. 1972. Physicochemical processes for water quality control. Wiley - Interscience, New York. p. 234.
72. Id, p. 210.
73. Wang, L.K.P., R.P. Leonard, D.W. Goupil, and M.H.S. Wang. 1972. Effect of pH adjustment upon activated carbon adsorption of dissolved organics from industrial effluents. Proceedings of the 27th Industrial Waste Conference, Purdue University, Lafayette, Indiana, May 2-4, 1972.
74. Weber, W.J. Jr., et al., ed. 1972. Physicochemical processes for water quality control. Wiley - Interscience, New York. p. 236.
75. Hassler, J.W., ed. 1974. Purification with activated carbon: industrial, commercial, environmental. Chemical Publishing Co., Inc., New York, p. 33.
76. Id, p. 16.
77. Guisti, D.M., R.A. Conway, and C.T. Lawson. 1974. Activated carbon adsorption of petrochemicals. J. Water Pollut. Control Fed. 46: 947-965.
78. Benedek, A. 1973. Fundamentals of physicochemical treatment. Environment Canada, Environmental Protection Service, Technology Development Branch (Water). Technology Transfer Seminar, Proceedings of the Physicochemical Treatment Activated Carbon Adsorption in Water Pollution Control, Vancouver, British Columbia, September 9, 1973.
79. Wallace, R.N., and D.E. Burns. 1976. Factors affecting powdered carbon treatment of a municipal wastewater. J. Water Pollut. Control Fed. 48: 511-519.
80. Ho, K.W.A., and A. Benedek. 1972. The oxidation of activated carbon in the TOC and COD tests. Wastewater Research Group, Department of Chemical Engineering, McMaster University, Hamilton, Ontario. Report #72-101-1. 1972.

81. DeWalle, F.B., and E.S.K. Chian. 1974. Removal of organic matter by activated carbon columns. Proceedings of the American Society of Civil Engineers, Journal of the Environmental Engineering Division. 100: 1089-1104.
82. Hassler, J.W., ed. 1974. Purification with activated carbon: industrial, commercial, environmental. Chemical Publishing Co., Inc., New York. p. 18.
83. Mattson, J.S., and H.B. Mark, ed. 1971. Activated carbon: surface chemistry and adsorption from solution. Marcel Dekker Inc., New York. p. 38.
84. Anonymous. 1972. Syngum D-47-D. Textile Department, Stein, Hall and Co., Inc., New York. Technical Bulletin 72, Section II. August, 1972.
85. Anonymous. Jaguar guar gum and guar derivatives. Stein, Hall and Co., Inc., New York.
86. Smith, F., and R. Montgomery, ed. 1959. The chemistry of plant gums and mucilages and some related polysaccharides. American Chemical Society Monograph Series No. 141. Reinhold Publishing Corp., New York.
87. Furia, T.E., ed. 1972. Handbook of food additives. The CRC Press, Cleveland, Ohio. p. 319.
88. Anonymous. 1974. Model 915A total organic carbon analyser. Beckman Instruments, Inc., Fullerton, California. Beckman Instructions 015-082355. January, 1974.
89. Hardy, R.C. 1962. NBS viscometer calibrating liquids and capillary tube viscometers. National Bureau of Standards Monograph 55, U.S. Department of Commerce. December 26, 1962.
90. Taras, J.M., et al., ed. 1971. Standard methods for the examination of water and wastewater. 13th edition. American Public Health Association, Washington.