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Study of Gamma Induced Low Temperature Oxidation of Textile Effluents

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May 1973

STUDY OF GAMMA INDUCED LOW TEMPERATURE OXIDATION OF TEXTILE EFFLUENTS

By

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ABSTRACT

Gamma irradiation of textile mill effluents under oxygen pressures up to 1500 psi, with and without activated charcoal present, was studied as a method for removing color and removal of substances contributing to the chemical oxygen demand (COD). Both color and COD reduction are directly related to the radiation dose and pressure of the oxygen over the dye solution samples during irradiation. Color removal was achieved in solutions of dye prepared in the laboratory for process evaluation and for authentic textile mill waste effluents. The study revealed a new method for in-situ reactivation of charcoal by gamma-radiation-induced oxidation of organic compounds adsorbed on charcoal. This discovery permits a large reduction in the gamma source size required for processing textile mill effluents because the water fraction of the effluent does not need to be irradiated to the same degree as the organic material contained in the effluent. A mathematical model for the process, developed late in this study, has not yet been experimentally verified.

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SECTION I

CONCLUSIONS

1. Gamma radiation in combination with oxygen under pressure has been demonstrated to be effective in the removal of color and COD of many dyes and other organic components in textile mill effluents. A large variation exists in the radiation dose required to decolorize and reduce the COD of the various dye compounds which were investigated. In the case of some disperse dyes, the dye compounds became more soluble at low and intermediate doses of gamma radiation, thus causing the concentration of the dye in solution to increase. The radiation-induced oxidation occurs at ambient temperatures and the rate of oxidation is controlled by the radiation dose and availability of oxygen in solution.

2. While the oxidation reaction terminates at carbon dioxide, intermediate products are produced when the radiation dose or oxygen supply is insufficient for complete oxidation. In the case of most of the single dye compounds studied, it was not necessary to completely oxidize the compound to carbon dioxide and water to destroy color.

3. Radiation-induced oxidation appears to be effective in decolorizing refractory dyes that persist through many of the conventional textile mill waste treatment processes.

4. A promising method for applying radiation-induced oxidation to the treatment of textile mill effluents involves adsorbing organic materials from the effluent onto an activated charcoal column located in the irradiator. The study has shown that in situ reactivation of the charcoal can be achieved when the process is operated at 500 to 2000 psi oxygen pressure. Thus, by removing organic from the water as it passes through the irradiator, the organics can be retained for sufficient time to receive a radiation dose adequate for destruction without the necessity of providing this same high dose to the large volume of water from which the organics were adsorbed. This saving in radiation is due to the fact that the residence time of the water in the irradiator is reduced to the level required only for removal of organics by adsorption onto charcoal; therefore, the total radiation dose to the water is greatly reduced when compared to the dose it would receive if the entire mass of water was required to remain in the irradiator until the small organic fraction present received the large dose necessary for destruction of the organic.

5. COD increases were observed when several of the standard dye solutions were irradiated at relatively low total gamma doses. This is believed to be due to the alteration of refractory structures to those more easily oxidized by the COD determination reagents.

6. Pretreatment of effluents that have filterable solids is necessary since charcoal non-adsorbables receive radiation doses too low to be effective in causing oxidation.

7. The color and COD is lowered as the oxygen pressure is increased.

8. Engineering cost estimates for the process have not been made since the research involved only the radiation demands for the process.

Estimates for radiation cost alone were based on a 10% organic loading on the charcoal, a 10^6 R dose to the adsorbed organic, and a 10-minute effluent residence time in the irradiator. Under these conditions the radiation costs only are approximately $0.01 per 1000 gallons of throughput.

SECTION II

RECOMMENDATIONS

1. The data from this study shows that the presence of charcoal increases the rate of oxidation of the organic materials present in aqueous effluents when these are irradiated in the presence of oxygen over the rate observed with radiation in the presence of oxygen alone. This effect needs to be studied to determine the mechanism involved.

2. Other oxidants in combination with gamma radiation should be studied.

3. The mathematical model describing the charcoal adsorption and in situ reactivation should be experimentally tested before it is used as a basis for determination of the theoretical limits of the process.

4. The concept of in situ carbon reactivation at ambient temperature is new and additional studies should be made to fully understand and optimize the process.

5. Since the process should be used in conjunction with low cost primary treatment (coagulants, filtration, etc.) integration of the process with these primary treatments should be evaluated.

6. Additional bench scale test and developmental experiments are recommended to solve problems related to specific plant waste effluents.

SECTION III

INTRODUCTION

Methods used to remove color from textile dye effluents include coagulation with alum, lime and other chemicals, biological processing through activated sludge processing and oxygen, lagoon retention, adsorption on charcoal, incineration, and reverse osmosis. Since oxidation processes for treatment of waste effluents are generally assumed to yield products that are easily assimilated into the natural environment, these processes are desirable for the destruction of the organic constituents that contribute to color in effluents. Aeration in retention lagoons in the presence of ultraviolet light is an effective oxidation process when easily oxidizable compounds are present; however, because of the need for color fast dyes in the textile dyeing operation, many of the dye compounds now used are resistant to oxidation by aeration. Many synthetic fibers require the use of disperse dyes which as a class are more difficult to degrade than many of the dyes used for natural fibers (wool, cotton, flax, etc.).

Gamma radiation has been shown to be effective in the destruction of color in various organic compounds. It also induces oxidation of many organic compounds when a source of oxygen is available. This reaction occurs at ambient temperatures, and compounds that are difficult to oxidize can often be oxidized in the presence of gamma radiation and high pressure oxygen.

Gamma irradiation of dye effluent under oxygen pressures up to 2000 psi was investigated and was shown to be effective in the decolorization of most dye solutions.[1]

The objectives of the work described in this report were (1) to investigate the radiation-induced oxidation of various dye compounds for the destruction of color, (2) to make general identification of oxidation products, (3) to evaluate the process using authentic textile plant effluents, and (4) to estimate the radiation cost of treating effluents by this method.

The high-pressure radiolytic oxidation of a number of dyes selected by class was performed. As the work progressed, it became evident that it would be better to select a small number of standard dyes currently in use by the textile industry in order that the color loss by radiolytic oxidation could be compared with other treatment methods. Hence, the American Association of Textile Chemists and Colorists (AATCC) chose four of the most frequently used dyes for the comparison study.

They were C.I. Direct Blue, C.I. Acid Black 26A, C.I. Disperse Blue 3, and Reactive Red 3.

The individual dyes prepared in water solution with additives as they are used by the textile industry were treated in a batch irradiator at various pressures of oxygen and at different total dose ranges of gamma radiation. The results of this study are given in this report. The efficiency of color removal by gamma-radiation-induced oxidation is compared with other methods in a report by the AATCC.[2] Irradiation of authentic dye effluents were studied with a batch irradiator and two small dynamic irradiation systems.

SECTION IV

EQUIPMENT

Two ^{60}Co gamma irradiators (one containing ∿70,000 Ci ^{60}Co and the other containing ∿50,000 Ci ^{60}Co) were used for this study. These irradiators are water shielded, immersed in an ∿10-ft-deep canal. Figure 1 shows the arrangement of the ^{60}Co around a cavity that could be reached by lowering vessels to be irradiated through the water shield. The gamma dose rate provided by this irradiator was 10^7 R/hr gamma at the center of the source holder. The second irradiator was loaded to provide a dose rate of 5×10^6 R/hr in the center of the cobalt array.

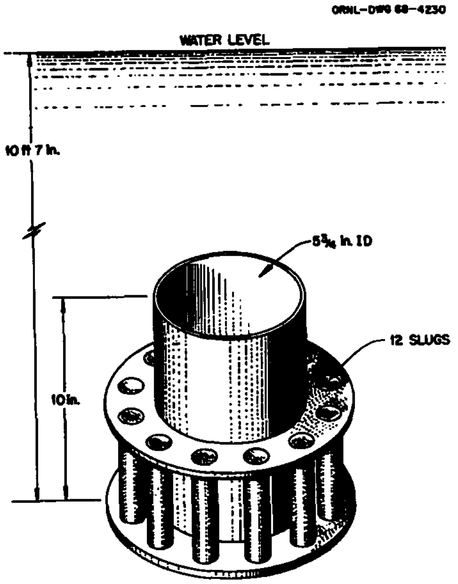

Fig. 1. Cobalt-60 Gamma Irradiator

Samples for single batch irradiation studies were placed in a bottle inside a pressure vessel and pressurized with oxygen (500-1500 psi), and the sealed vessel was lowered into the center of the radiation source for a period of time required to obtain the desired radiation dose.

A dynamic irradiator arrangement, shown in Fig. 2, permitted solutions to be pumped from a reservoir by a Lapp pump through a pressure vessel located in the center of the ^{60}Co array shown in Fig. 1. The pressure was controlled by a pressure regulator valve on the exit line from the pressure vessel. Oxygen was injected (by a compressor) into the feed stream between the Lapp pump and the pressure vessel. The flow rate of solution through the irradiator could be adjusted in the Lapp pump from 0.33 to 3 liters/hr. Solution entered the pressure vessel through a nozzle near the bottom of the bomb and was removed near the top through an overflow tube.

The pressure vessel was replaced with a 20-ft-long, 1/8-in.-diam stainless steel pipe, coiled to fit into the inside cavity of the ^{60}Co array, and filled with 130 g of granular (6-14 mesh) activated charcoal.

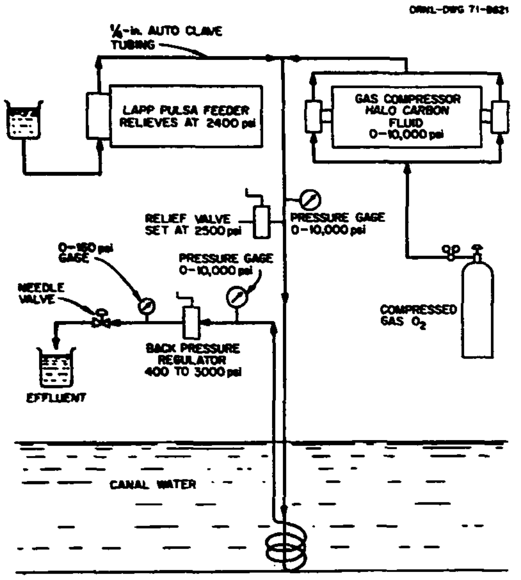

Fig. 2. Schematic of High Pressure Irradiator

A second and larger dynamic irradiator system was fabricated, making it possible to operate at flow rates up to 10 gal/hr. Feed to this irradiator was pumped from a 55-gal reservoir by a piston pump at 500 psi through a 30-ft-long, 1-1/2-in.-diam pipe coiled to form a 20-in.-diam circle (Fig. 3). A ^{60}Co array (Fig. 1) was placed inside this coil to provide an average dose rate of 5×10^6 R/hr to the volume inside the coiled pipe. A bypass valve on the pressure side of the pump was used to recycle part of the pump flow back into the reservoir to provide flow rate control. Oxygen was injected into the stream between the pump and the column. The pressure in the irradiator was adjusted with a throttle valve on the exit end of the column. Thirteen pounds of granular coconut charcoal was placed in the coil.

A Beckman Spectrophotometer Model DB was used for color evaluation of feed and product solutions. The transmissions of filtered solutions were reported directly as percent transmission. The absorbances of solutions which were filtered through 0.80-μ Millipore filter media were used in the calculations of the color intensity [Eq. (1)].

$$\text{Color intensity} = (X + Y + Z)\,D \qquad (1)$$

where X, Y, and Z are the absorbances at the selected wavelengths, and D is the dilution factor.

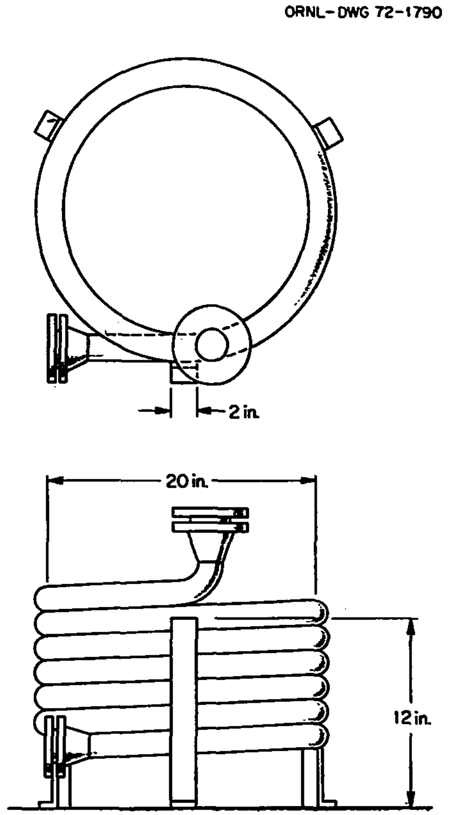

Fig. 3. Continuous Charcoal Irradiator

Equation (2) can be used to calculate the color reduction of a sample.

$$\text{Color reduction} = \frac{A - B}{A} \tag{2}$$

where A is the color intensity on the untreated sample and B is the color intensity on the treated sample.

The chemical oxygen demand (COD) of feed and products was measured by a standard method.[3] An appropriate size sample was diluted to 20 ml and added to 10 ml of standard 0.25 N potassium dichromate and 0.4 g of mercuric sulfate. Thirty milliliters of concentrated H_2SO_4 containing silver sulfate was added to the mixture, and the mixture was refluxed 2 hr. The solution was cooled and the excess potassium dichromate was titrated with standard 0.25 N ferrous ammonium sulfate to a brown end point using ferroin indicator. A blank was run at the same time. The COD can be calculated by Eq. (3).

$$\text{COD (mg/liter)} = \frac{(a - b)\ N_{Fe} \times 8000}{\text{ml of organic sample}} \tag{3}$$

where a = volume of ferrous ammonium sulfate used on sample,
b = volume of ferrous ammonium sulfate used on blank,
N_{Fe} = normality of ferrous ammonium sulfate.

A Beckman Infrared Spectrophotometer IR-18A was used to measure the infrared spectra in samples prepared as KBr pellets.[4]

SECTION V

SINGLE BATCH IRRADIATIONS

(Without Charcoal)

Acid and Chrome Dyes

The high-pressure, radiation-induced oxidation of five acid and chrome dyes was studied. The dyes, their type, and general structures are shown in Table 1, and the composition of solutions prepared from these dyes is shown in Appendix A. Each dye solution except Neolan Yellow BG contained Glaubers salt ($Na_2SO_4 \cdot 10H_2O$) and acetic acid or sulphuric acid at the concentrations used in commercial dyeing of wool. The Neolan Yellow BG solution contained only sulphuric acid. The dye solutions were irradiated under a 1500-psi oxygen atmosphere in a pressure vessel at 10^6 and 5×10^6 R total radiation dose.

Table 1. Acid and Chrome Dyes Used in Single Batch Irradiation Studies of Radiation-Induced Oxidation

Name	Type	Structure
Benzyl Fast Yellow GNC	Weak Acid Dye	Monoazo
Benzyl Blue GL	Weak Acid Dye	Azine
Benzyl Cyanine 6B	Weak Acid Dye	Triphenylmethane
Neolan Yellow BG	Premetalized Acid Dye	Azo
Chrome Fast Flavine A	Chrome Fast Dye	Monoazo

Light transmission measurements and COD determinations of the untreated effluent, the effluent after a 10^6 R gamma dose, and after a 5×10^6 R gamma dose are shown in Tables 2 and 3. In all weak acid dye experiments the odor of acetic acid almost disappeared after a dose of 10^6 R and was completely absent after a 5×10^6 R dose. In all irradiations the color of the solution decreased as the radiation dose increased over the range 10^6 to 5×10^6 R. When the Benzyl Blue GL and Chrome Fast Flavine A solutions were irradiated, some of the dye precipitated from the solution.

The yellow color of the Chrome Fast Flavine A solution changed to orange-olive after a 10^6 R gamma radiation dose and to green after 5×10^6 R.

Table 2. Changes in Light Transmission of Acid and Chrome Dye Solutions After Irradiation Under 1500-psi Oxygen

Dye	Wavelength (mμ)	% Light Transmission After		
		No irradiation	10^6 R	5×10^6 R
Benzyl Fast Yellow GNC	350	41	64.5	65
	396	34	69.5	71
Benzyl Blue GL	450	22	67	83
	600	0	16	65
	700	45	60	90
Benzyl Cyanine 6B	400	54	75	95
	550	0	35	88
	700	41	75	98
Neolan Yellow BG	400	1	1	36
	500	1	6	83
	600	67	69	91
Chrome Fast Flavine A	350	0	2	32
	500	34	38	56
	570	17	17	21

Table 3. Change in the COD of Acid and Chrome Dye Solutions After Irradiation Under 1500-psi Oxygen

Dye	COD (mg/liter) After		
	No Irradiation	10^6 R	5×10^6 R
Benzyl Fast Yellow GNC	1,795	2,052	2,713
Benzyl Blue GL	11,680	4,130	3,800
Benzyl Cyanine 6B	11,900	10,900	10,300
Neolan Yellow BG	920	800	570
Chrome Fast Flavine A	9,300	8,500	8,000

Dye Solutions Used to Compare Various Color Removal Methods

C.I. Direct Blue 106, C.I. Acid Black 26A, C.I. Disperse Blue 3, and Reactive Red 3 dyes, chosen because they are widely used in textile processing, were prepared as standard solutions (see Appendix A for composition). These standard solutions were evaluated by others using various decolorization methods, and the results are reported in the literature.[5] These solutions were irradiated under 1500-psi oxygen to gamma doses of 10^6 and 5×10^6 R. In the case of C.I. Direct Blue 106 dye solution, the solution changed from dark blue to a light blue after a gamma dose of 10^6 R and to water-white after 5×10^6 R exposure. The results are shown in Table 4.

Table 4. COD and Color Changes in C.I. Direct Blue 106 Dye Solution After Gamma Irradiation Under 1500-psi Oxygen

Oxygen Pressure (psi)	Irradiation Dose (R)	COD (mg/liter)	Absorbances at 480 mμ	580 mμ	680 mμ	Color Intensity	% Color Removal
0	No irradiation	182	0.52	2.44	0.84	3.80	0
1500	10^6	102	0.04	0.13	0.05	0.22	94.4
1500	5×10^6	65	0	0	0	0.0	100

Solutions of C.I. Acid Black 26A changed from a dark purple to colorless after a dose of 10^6 R, and the COD decreased from 104 to 30 mg/liter. The sample that received the 10^6 R dose contained a black precipitate which was removed by filtration before COD measurements. Because this precipitate was removed, the COD of this filtered solution was less than the solution receiving 5×10^6 R exposure, indicating that the precipitate that formed at the 10^6 R dose level was redissolved at the higher dose of 5×10^6 R. The results are shown in Table 5.

Table 5. COD and Color Changes in Direct Black 26A Dye Solution After Irradiation Under 1500-psi Oxygen

Oxygen Pressure (psi)	Irradiation Dose (R)	COD (mg/liter)	Absorbances at 460 mμ	560 mμ	660 mμ	Color Intensity	% Color Removal
0	No irradiation	104	0.128	0.268	0.098	1.48	0
1500	10^6	30[a]	0	0	0	0	100
1500	5×10^6	71	0	0	0	0	100

[a] Black precipitate was filtered from the sample before COD analysis.

C.I. Disperse Blue 3 dye was partially oxidized to a light blue after a dose of 5×10^6 R exposure [a 48% color reduction (Table 6)]. The COD was reduced from 725 to 347 mg/liter at 5×10^6 R.

Table 6. COD and Color Changes in C.I. Disperse Blue 3 Dye Solution After Irradiation Under 1500-psi Oxygen

Oxygen Pressure (psi)	Irradiation Dose (R)	COD (mg/liter)	Absorbances at 430 mμ	Absorbances at 530 mμ	Absorbances at 630 mμ	Color Intensity	% Color Removal
0	No irradiation	752	0.120	0.166	0.232	2.072	0
1500	10^6	555	0.200	0.182	0.212	2.376	-14.7
1500	5×10^6	347	0.33	0.32	0.35	1.000	48.2

The gain in color intensity after a gamma dose of 10^6 R is believed to be due to solid particles of dye that are suspended in solution prior to irradiation and that become solubilized during the irradiation.

The absorbance curves for Disperse Blue 3 dye solution before and after a 10^6 R gamma radiation dose under 1500-psi oxygen are shown in Fig. 4. The peak absorbance at about 600 mμ wavelength was lowered from about 0.247 in the original dye solution to about 0.220 in the irradiated solution. The minimum absorbance in the original dye solution of 0.108 at 460-mμ wavelength was shifted upward in the treated dye solution to 0.160 at 480 mμ. Radiation treatment reduced the height of the color absorbance peak and increased the range of wavelengths over which color absorbance was observed.

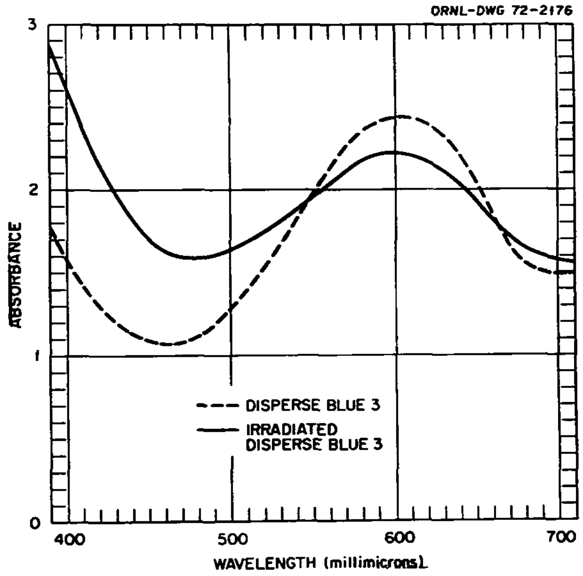

Fig. 4. Spectrophotometric Plot of Absorbance vs Wavelength for Disperse Blue 3 Dye Solution and Irradiated Disperse Blue 3 Dye Solution

It has been observed that ferrous iron can be precipitated from a solution that has been exposed to gamma radiation.[6] To determine whether or not this effect can be utilized to remove dyes from solution during irradiation, $FeSO_4$ at a concentration of 200 and 400 ppm was added to a solution of Disperse Blue 3 dye prior to irradiation. The results of this test are shown in Table 7.

The addition of 0.2 to 0.4 g/liter of $FeSO_4$ to the dye effluent enhanced the decolorization at the 5×10^6 R gamma dose. The 400-ppm addition caused a color reduction of 95% after a 5×10^6 R gamma dose.

Table 7. Effect of $FeSO_4$ Additions on Color Reduction on Gamma Irradiation of Disperse Blue 3 Dye Solution When Irradiated Under 1500-psi Oxygen

Radiation Exposure (R)	$FeSO_4$ Concentration (g/liter)	pH	Absorbances at			Color Intensity	% Color Removal
			430 mμ	530 mμ	630 mμ		
None	0.2	6	0.300	0.368	0.480	1.148	0
10^6	0.2	6	0.712	1.240	1.220	4.172	-263[a]
5×10^6	0.2	6	0.160	0.119	0.089	0.368	68
None	0.4	6	0.368	0.352	0.288	1.008	0
10^6	0.4	6	1.192	0.724	0.680	2.596	-157[a]
5×10^6	0.4	6	0.010	0.014	0.015	0.039	96.6
None	0.4	12	2.200	1.804	2.145	6.149	0
10^6	0.4	12	1.860	1.340	1.640	4.840	21.3
5×10^6	0.4	12	0.592	0.328	0.260	1.180	80.9

[a] Color increase.

The Reactive Red 3 dye solution was decolorized at 10^6 R exposure. The COD was reduced from 123 to 84 mg/liter after a dose of 5×10^6 R. The results are shown in Table 8.

Table 8. COD and Color Changes in Reactive Red 3 Dye Solution After Irradiation Under 1500-psi Oxygen

Oxygen Pressure (psi)	Irradiation Dose (R)	COD (mg/liter)	Absorbances at			Color Intensity	% Color Removal
			420 mμ	520 mμ	620 mμ		
0	No irradiation	123	0.40	2.24	0	2.64	0
1500	10^6	98	0	0	0	0	100
1500	5×10^6	84	0	0	0	0	100

Authentic Textile Mill Dye Effluents

The high-pressure, radiation-induced oxidation of six authentic textile mill effluent samples was studied. Each sample contained a mixture of 50-65 dyes and textile additive chemicals. Each sample was irradiated without charcoal under 1500-psi oxygen pressure in a pressure vessel a radiation doses of 10^6 and 5×10^6 R. The color and odor of the original solution are characterized in Table 9.

Table 9. Color and Odor of Authentic Dye Effluent

Sample Number	Color	Odor
1	Red-brown with red-brown precipitate	Slight odor
2	Green haze with green precipitate	Fish-like odor
3	Blue-green with red-brown precipitate	Sour rancid odor
4	Magenta with magenta precipitate	Fish-like odor
5	Hazy, beige with beige precipitate	Fish-like odor
6	Hazy, grey with grey precipitate	Slight fish-like odor

The results of the radiation-induced oxidation are shown in Tables 10 and 11. The odor of the solutions disappeared or nearly disappeared after a 10^6 R radiation dose. The light transmission increased as the radiation dose increased. The COD increased slightly after a 10^6 R radiation dose, but after a 5×10^6 R radiation dose the COD of four of the six samples decreased.

Table 10. The Effect of Irradiation Under 1500-psi Oxygen on the Light Transmission of Six Authentic Textile Mill Effluents

Sample No.	Wavelength (mμ)	% Transmission After		
		No Radiation	10^6 R	5×10^6 R
1	500	65	74	75
	700	80	85	89
2	500	58	67	67
	700	76	81	81
3	390	15	29	47
	420	24	41	52
	700	55	64	72
4	500	39	49	57
	525	37	51	60
	700	70	73	78
5	500	55	62.5	62.5
	700	76.5	82.5	82.5
6	500	70	72	72
	700	83	83.5	84

Table 11. The Effect of Irradiation Under 1500-psi Oxygen on COD of Six Authentic Textile Mill Effluents

Sample No.	COD (mg/liter) After No Radiation	10^6 R	5×10^6 R
1	445	622	347
2	428	711	462
3	1174	1213	860
4	811	808	493
5	706	1180	773
6	1280	1200	822

Azo Dyestuff Manufacturing Waste

An azo dyestuff manufacturing waste mixture was irradiated at doses of 10^6 and 5×10^6 R under 1500-psi oxygen (without charcoal). The phenolic odor was reduced by the radiation process, but some odor remained even after the 5×10^6 R exposure. The brown color of the non-treated solution was so intense that a 10:1 dilution had to be made before it was possible to make light transmission measurements. The light transmission increased and the COD removal (Table 12) were insignificant. No additional experiments were performed to determine the dose required for significant color and COD removal.

Table 12. The Effect of Radiation Under 1500-psi Oxygen on COD and Light Transmission on Azo Dyestuff Manufacturing Waste

Pressure Oxygen (psi)	Radiation Dose (R)	COD (mg/liter)	% Transmission at 450 mμ	550 mμ	650 mμ	Dilution Factor
0	No radiation	21,600	0	17	58	10
1500	10^6	20,900	3	22	61	10
1500	5×10^6	20,100	4	27	65	10

PRODUCTS OF RADIOLYTIC OXIDATION OF STANDARD DYES

Analyses of the irradiated dyes were made to identify the products of the radiation-induced oxidation of the dye. The first dye investigated was Direct Blue 106, having the chemical formula shown in Fig. 5. The pure dye was dissolved in water to simplify separation from other constituents of the dye effluent after the irradiation.

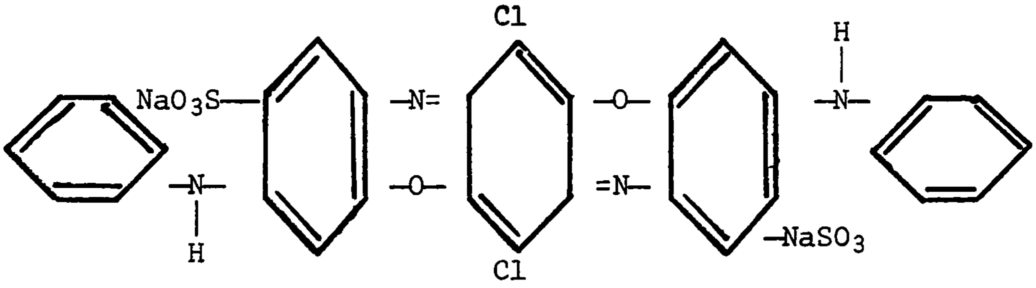

Figure 5. Chemical Formula for Direct Blue 106 Dye

A solution containing 400 mg/liter of dye was prepared for irradiation. About 150 ml of the solution was irradiated without charcoal under 1500-psi oxygen in the pressure vessel to a total dose of 7.5 × 10^6 R. Carbon dioxide was identified in the exhaust gas. The irradiated solution was evaporated to dryness to recover the solids from solution. The final solid content of the irradiated solution contained about 75% of the starting material by weight and was light gray color.

The infrared spectra of the Direct Blue dye prepared for analysis in a KBr pellet was compared with the spectra of the light gray solids obtained from the irradiated sample. The spectra were difficult to interpret due to the large number of groups yielding bands in the 1000-1200 cm^{-1} region of the spectra. Secondary amines were observed in both samples. An aryl peroxide group was observed in the irradiated solid. The band due to the chlorine appears in both samples. It also appears that the CO group was responsible for lines found at 1700 cm^{-1} in the irradiated sample spectra, indicating oxidation of the benzene ring. The SO_3^{2-} bands at 910 and 1000 cm^{-1} did not appear in the irradiated sample, and the band was too wide in the 1000-1200 cm^{-1} region to determine the presence of SO_4^{2-}; however, the SO_4^{2-} group was believed to be present.

The second dye investigated was C.I. Acid Black 26A. Its chemical formula is shown in Fig. 6.

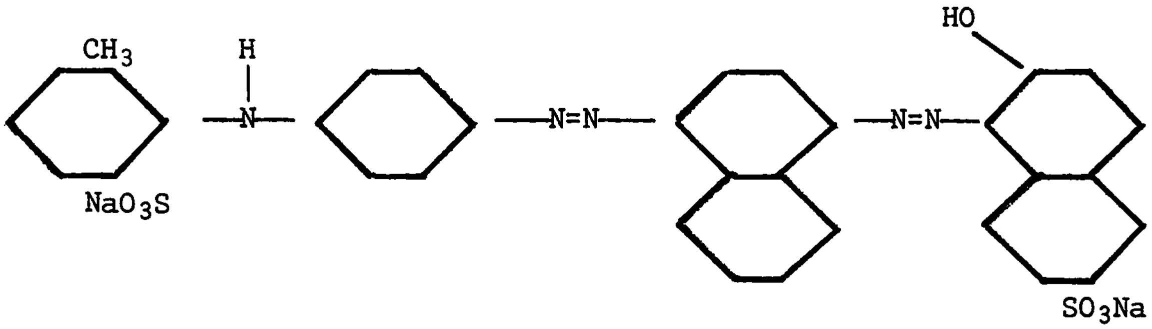

Figure 6. Chemical Formula for C.I. Acid Black 26A Dye

A standard solution containing 268 mg/liter was prepared. About 150 ml of solution was gamma irradiated without charcoal under 1500-psi oxygen to a total dose of 3×10^7 R. The solution was taken slowly to dryness to recover the solids for the analysis. Carbon dioxide was identified in the waste gas. The solid weight yield was approximately the same as present in the feed solution.

The infrared spectra for the unirradiated and the irradiated dye were determined from samples prepared in KBr pellets. Some of the SO_3^{2-} was oxidized to give SO_4^{2-} identified by peaks at 610, 640, and 1130 cm^{-1}. The SO_3^{2-} peaks corresponded to the original dye spectra found at 900 and 980 cm^{-1}. Two broad new peaks at 1440 and 1620 cm^{-1} were found and are due to a COO^- group produced by oxidation of the CH_3 group. The strong broad peak at 3420 cm^{-1} was found in both the original and the irradiated sample and is believed to be due to secondary amine structure. Unfortunately, no identification of the —N=N— group was possible because this group is infrared inactive. This dye compound seems to be quite stable, but when it is oxidized with gamma radiation and oxygen the structure is easily altered from highly colored to colorless.

The third dye investigated was C.I. Disperse Blue 3. Its chemical formula is shown in Fig. 7. A solution containing about 400 mg/liter of dye was used for this work. One hundred fifty milliliters of solution was irradiated under 1500-psi oxygen to a total dose of 3×10^7 R. The exhaust gas contained carbon dioxide. The solution was evaporated to dryness to collect solids for infrared spectra analysis. The final solid content of the irradiated solution was approximately 25% of the original material by weight.

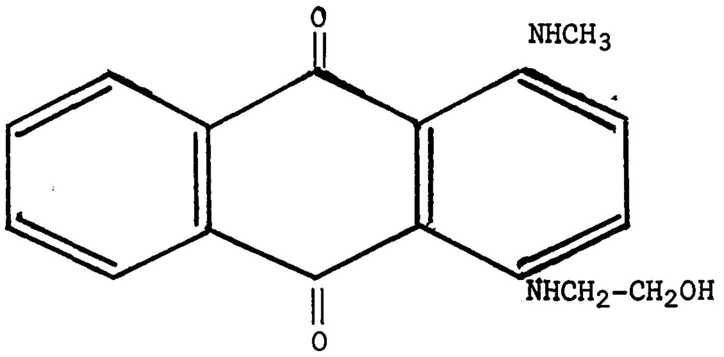

Figure 7. Chemical Formula for C.I. Disperse Blue 3 Dye

The infrared spectra obtained from the non-irradiated blue dye in a KBr pellet was compared with the infrared spectra from the light-gray-colored solid recovered from the irradiated sample. Solids from the irradiated sample were shown to have an anthraquinone structure with some of the secondary amine destroyed or converted to a primary amine. The two C=O groups were identified by the CO bands at 1660 and 1710 cm^{-1}. These CO bands did not appear in the original dye spectra. A proposed H-bond resonance structure shown in Fig. 8 might help to account for the bands shown. This resonance did not appear in the original dye.

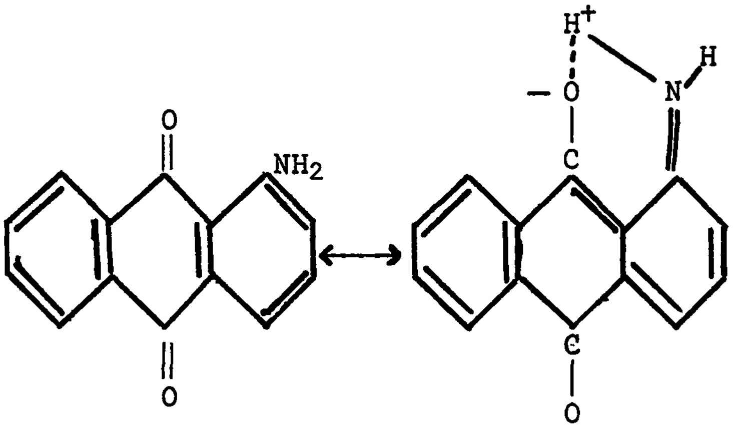

Figure 8. Radiation Oxidation Product of C.I. Disperse Blue 3 Dye

SECTION VII

ADSORPTION ON CHARCOAL

A major bar to the treatment of process effluents with radiation is the necessity for irradiating large quantities of water in order that the small amount of organic present in the effluent can be irradiated. For optimum efficiency the radiation should be totally absorbed in the organic fraction of the effluent that is to be destroyed or altered. One approach to this ideal condition is to separate the organic fraction from the water fraction onto charcoal that is placed in the irradiator; this reduces the radiation dose to the water since the residence time of the water would be limited to that necessary for adsorption of the organic onto the charcoal. Tests were made to determine whether or not the decolorization of dye solutions by gamma-radiation-induced oxidation is increased by the presence of activated charcoal in contact with the solution during irradiation over that expected by gamma irradiation alone plus treatment with charcoal separately.

A standard dye solution (Disperse Blue 3, Appendix A) was used for all tests, and decolorization was determined by light absorbance changes in the 350-, 450-, and 550-mμ wavelengths. To cancel the effect of the physical adsorption of dye from the solution by charcoal, the charcoal was presaturated with dye by adding 100-ml portions of the solution to 10 g of charcoal until the color reduction of the dye solution was less than 5% after the final dye solution portion had been exposed to the charcoal for 16 hr.

This saturated charcoal was then added to 100 ml of the standard dye solution and irradiated under 1000-psi oxygen. The results of this experiment are shown in Table 13. In this test, the presence of charcoal increased the color removal by 72% over that obtained by irradiation alone.

Table 13. The Effect of the Presence of Activated Carbon on Color Removal by Gamma Irradiation

	Std. Dye Solution	100 ml Std. Dye Solution Irr. Without Charcoal	100 ml Std. Dye Solution Irr. With Saturated Charcoal
Irr. Dose (R)	None	10^6	10^6
Irr. Exposure Time (min)	None	72	72
Color Intensity	1.375	0.685	0.187
% Color Removed	None	50	86

The enhanced color removal is believed to be due to the reactivation of charcoal by radiation-induced oxidation of organic material held on adsorptive sites on the charcoal; thus, the increase in color removal is due to the availability of adsorptive sites as this reactivation occurs.

Experiments were conducted to test this hypothesis. In these tests 10 g of charcoal saturated with dye from the standard solution by the saturation method described above was repeatedly irradiated to a dose of 10^6 R gamma in the presence of 100 ml of new standard dye solution under 1000-psi oxygen. The results of this experiment are shown in Table 14.

Table 14. Color Removal from Dye Solutions Irradiated in Contact With Dye Saturated Charcoal

Sample Number	Sample Description and Treatment	Color Intensity (color factor)	% Color Removal[a]
1	100 ml std. dye solution on saturated charcoal 5×10^5 rads of gamma delivered in 36 min	0.440	83
2	100 ml std. feed on charcoal used with sample 1 1×10^6 rads of gamma delivered in 72 min	0.488	81
3	100 ml std. feed on charcoal used with sample 2 1×10^6 rads of gamma delivered in 72 min	0.454	83
4	100 ml std. feed on charcoal used with sample 3 2×10^6 rads of gamma delivered in 144 min	0.204	92

[a] Based on std. solution color intensity of 2.615 obtained after 10^6 R radiation under 1000 psi oxygen without charcoal.

In this test the removal of color from the standard dye solution was nearly constant through four additions of untreated dye solution to the dye-saturated charcoal. Since the color removal to be expected by irradiation of the standard under 1500-psi oxygen at a dose of 10^6 R without charcoal was only 50%, the repeated achievement of 80 to 90% color removal with saturated charcoal present during gamma irradiation to a dose of 10^6 R leads one to conclude that reactivation of the charcoal is achieved, making new sites available for acceptance of dye from solution.

Tests were made to determine the effect of gamma irradiation with oxygen present on the reactivation of dye-saturated charcoal. In these tests 10 g of charcoal saturated with dye solution was irradiated in 100-ml of distilled water under a pressure of 1000-psi oxygen for 72 min to a total gamma dose of 10^6 R. The charcoal was then exposed for 16 hr to another 100-ml of standard dye solution to determine whether or not its adsorptive capacity for dye from the standard dye solution had been restored. The results of this test are shown in Table 15.

Table 15. Reactivation of Charcoal by Gamma Radiation-Induced Oxidation

		Saturated Charcoal (before irradiation under 1000-psi oxygen) Exposed to 100 ml Std. Dye Solution	Saturated Charcoal After Irradiation Under 1000-psi Oxygen With 100-ml Distilled Water (then exposed to 100 ml Std. Dye Solution)
Wt. of charcoal, g	Charcoal Treatment	10	10
Radiation exposure time, min		None	72
Radiation dose, R		None	10^6
Color reduction of std. dye solution after 16 hr shaking with charcoal		5%	91%

Carbon loss during irradiation with oxygen saturated solutions was measured by weighing. No measurable loss was determined after 160 hr of irradiation under oxygen at 1500-psi and at a dose rate of 10^7 R/hr. The irradiated carbon was examined under an electron microscope (Fig. 9) in an attempt to determine physical changes in the carbon structure. Comparison of images of the carbon before and after irradiation with solutions saturated with oxygen under 1500-psi failed to demonstrate any apparent structural change.

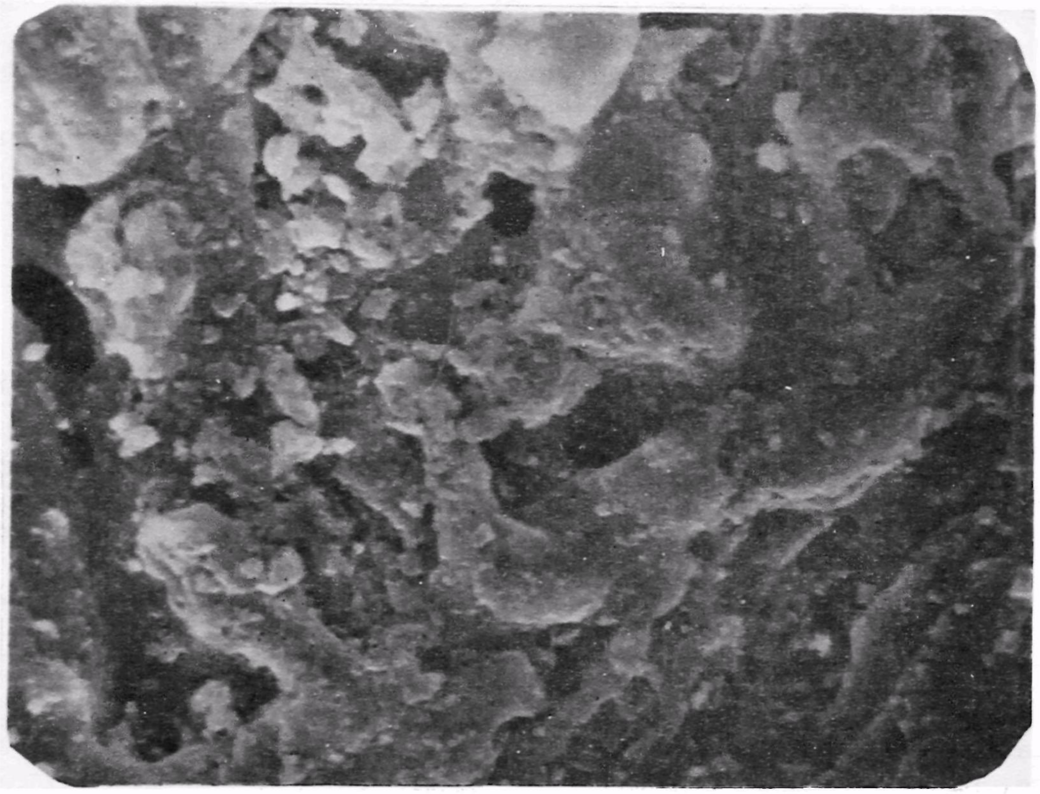

Figure 9. 1900 Magnification of Activated Charcoal After 500 hr of Irradiation at a Flux of 10^7

SECTION VIII

CONTINUOUS FLOW IRRADIATIONS

Since processing of textile mill effluents for color removal will require continuous flow treatment, studies were made to determine the efficiency of a dynamic irradiator in which charcoal is used to adsorb organic compounds from solution and retain them in the irradiator until oxidation can occur. These studies were made with dye solutions of known concentrations and authentic textile mill effluents.

The capacity of granular (6-14 mesh) activated coconut charcoal for a 0.3% solution of Benzyl Fast Yellow GNC dye was established as 1,700 ml of dye solution for 10 g of charcoal (composition of solution shown in Appendix A). Tests were made (with this solution as a standard mix) to determine the decolorization efficiency of a dynamic irradiator consisting of a simple column fabricated from 1/2-in.-diam pipe bent in the form of a U-tube that could be placed in the center of a ^{60}Co array, as described in the section on equipment. This arrangement provided a 5×10^6 R/hr radiation field. The capacity of the U-shaped column was 35 g of charcoal over a length of approximately 20 in. Tests were made to determine the capacity of the charcoal under flow conditions of 2 liters/hr without irradiation. After 8 liters of solution was passed through the column, a sharp break in decolorization occurred (from approximately 90% color removal to approximately 80%) as determined by percent light transmission in the 420-mμ wavelength. The capacity of the charcoal without radiation for the dye solution was considered to be 7 liters.

The column was then recharged with 35 g of new charcoal and placed in the ^{60}Co irradiator. Benzyl Fast Yellow GNC dye solution was passed through the column at a flow rate of 2.7 liters/hr while 50-psi oxygen was introduced into the feed to the column. The data obtained from this run were normalized to 210 g of charcoal in order that a direct comparison could be made with a second experiment in which this larger quantity of charcoal was used. Table 16 shows the data obtained from this experiment.

Under the conditions of this experiment, only a small gain in decolorization efficiency over charcoal alone was observed, and it was assumed that the flow rate was too great to provide an equilibrium condition of dye adsorption on the charcoal versus dye destruction by radiation-induced oxidation of dye adsorbed on the column.

Table 16. Decolorization Efficiency of Charcoal and Gamma Radiation as a Function of Oxygen Pressure

	Treatment	
	5×10^6 R/hr field 50-psi oxygen	5×10^6 R/hr field 1500-psi oxygen
Weight charcoal, g	35	210
Flow rate, liters/hr	2.7	2.0
Capacity of charcoal, liters of dye solution	7	42
% transmission at 420 mμ of feed solution	10	10
% transmission at 420 mμ of solution after (throughput of liters shown)	88 after 42 liters[a] 82 after 48 liters[a] 72 after 52 liters[a]	97 after 105 liters when experiment was discontinued

[a] Normalized to 210 g charcoal.

A second experiment was performed using the same dye solution in a pressure irradiator consisting of a pressure vessel in which 210 g of charcoal was placed. The pressure of the oxygen feed was increased to 1,500 psi introduced into the feed solution, passing through the irradiator at a rate of 2 liters/hr. Table 16 shows the results of this experiment. Under these conditions, the decolorization efficiency was 97%, and equilibrium for the destruction of dye on the charcoal with dye in feed to the charcoal was achieved.

An irradiation chamber consisting of a 20-ft-long, 1/8-in.-diam stainless steel pipe formed into a 4-in.-diam coil and loaded with 150 g of 6-14 mesh activated coconut charcoal was prepared and used to irradiate a solution containing 0.09 g/liter of Benzyl Cyanine 6B dye. The normal capacity of the charcoal under conditions of no irradiation was determined by flowing the standard Benzyl Cyanine 6B dye solution at a rate of 2 liters/hr through the column. The breakthrough point without irradiation or oxygen present was considered to be 25 liters of this solution per 150 g of charcoal measured by an end point of 82% light transmission at the 550-mμ wavelength (maximum transmission wavelength) compared with a 91% transmission constant obtained over a 24-liter total flow.

Data from this experiment were used to make a comparison of the decolorization efficiency of gamma radiation only versus gamma radiation plus oxygen at 1,500 psi. The results are shown in Table 17.

Table 17. Comparison of Decolorization Efficiency of Gamma Radiation Only Compared With Gamma Irradiation Plus Oxygen at 1,500 psi

	Treatment	
	10^7-R/hr field No Oxygen	10^7-R/hr field 1500-psi Oxygen
Weight of charcoal, g	150	150
Flow rate, liters/hr	2.0	2.0
Capacity charcoal, liters, without irradiation at a flow rate of 2 liters/hr	25	25
% light transmission of feet at 550 mμ	2.5	2.5
% light transmission at 550 mμ after throughput shown, liters	91 after 24 liters 82 after 27 liters	96.5 after 108 liters
COD feed, mg/liter	59	59
COD, mg/liter, after throughput shown	16.8 after 24 liters 19.0 after 27 liters	19.3 after 58 liters 13.0 after 108 liters

In this experiment the decolorization efficiency was 96.5% even after 108 liters of solution was passed through the column; the experiment was discontinued at this point. The COD of the solution was decreased from 59 to 19 at the point where a color breakthrough was considered to have occurred in the solution being irradiated without oxygen. It is not clear why the COD was 19.3 mg/liter after 58 liters and 15 mg/liter after 108 liters. A plausible explanation is variation in analysis.

In this experiment the oxygen supply to the solution being irradiated was stopped to determine the effect of oxygen on the decolorization efficiency. When the oxygen flow was interruped, the transmission in the 550-mμ wavelength decreased from >95% to <80% after one column volume of flow. Decolorization was restored when the oxygen flow was restored.

Direct Blue 106 dye solution (composition in Appendix A) was processed through the 20-ft-long, 1/8-in.-diam irradiator containing 130 g of charcoal. The effluent was sampled only after equilibrium was reached, as determined visually for various flow rates. Table 18 shows the results of this experiment. The method for measuring color was changed from one of transmission to absorbance since several absorbance wavelengths could be summed to provide a color factor based upon a wider color range.

Table 18. The Effect of Flow Rate on Color Removal of Direct Blue 106 Dye Solution in a Continuous Flow System Under 1500-psi Oxygen in a 10^7 R/hr Gamma Flux

Flow Rate (liter/hr)	Dilution Factor	Absorbances at 480 mμ	Absorbances at 580 mμ	Absorbances at 680 mμ	Color Factor	% Color Removal
0 (control std. solution)	4	0.13	0.61	0.21	3.80	0
1.25	3	0.08	0.11	0.80	0.81	79
0.50	3	0.08	0.08	0.06	0.66	83
0.35	3	0.07	0.07	0.04	0.54	86

A larger dynamic irradiator was fabricated from a 30-ft-long, 1-1/2-in.-diam pipe. The pipe was coiled to form a 20-in.-diam spiral which was placed around a ^{60}Co source array. The average gamma radiation flux in the irradiator coil was determined to be 5 × 10^5 R/hr by Fricke solution dosimetry. This column was loaded with 11 lb of granular activated coconut charcoal, and the charcoal fines were washed from the column. The maximum operating pressure for this system was 500 psi.

Table 19. COD and Color Removal From Direct Blue 106 Dye Solution by Radiation-Induced Oxidation in a 5 × 10^5 R/hr Radiation Flux Under 500-psi Oxygen

Sample No.	Amt. Through Irradiator (gal)	Time From Start of Run (hr)	Flow Rate (gal/hr)	Color Factor[a]	% Color Removal	COD (mg/liter)
Original	(control)	-	-	3.80	-	182
4	7	2	3	0.137	96.4	12
7	8.5	2.5	3	0.055	98.7	ND[b]
11	12.5	4.5	2	0.132	96.5	ND
15	16.5	6.5	2	0.153	96.0	12
18	18	8	1	0.110	97.1	12
21	21	9.5	2	0.154	96.0	15
24	22.5	11	1.5	0.141	93.3	14
29	25.75	13.5	1.5	0.218	94.3	ND
32	28	15	1.5	0.318	91.5	ND
37	31.25	17.5	1.5	0.274	92.8	ND
42	34.5	20	1.5	0.245	93.5	ND
47	37.75	22.5	1.5	0.245	93.5	ND
52	41	25	1.5	0.293	92.3	ND
58R	48.75	28.5	4	0.459	88.0	ND
62R	53.75	30.5	3	0.145	96.2	ND

[a] Calculated from light absorbance measurements over the 480-, 580-, and 680-mμ wavelengths.

[b] Not determined.

Fifty-five gallons of Direct Blue 106 dye solution was prepared for tests with this irradiator. The normal capacity of the charcoal without irradiation for dye from this solution was determined to be equivalent to 32 gal of solution per 11 lb of charcoal. The solution was passed through the irradiator at 500-psi oxygen pressure with variations in the flow rate from 1 to 4 gal/hr. COD determinations were made on six different samples, but they were discontinued after the COD values appeared to have reached an equilibrium. Table 19 shows the results of this experiment.

Authentic Textile Mill Effluents

Four samples of authentic textile mill effluents (~1 gal each) were provided by the American Association of Textile Chemists and Colorists (AATCC) members. These samples were processed through a small pressure vessel equipped with an inlet and outlet for dynamic operation.

Approximately 3 liters of each sample was pumped through the pressure irradiator without charcoal at 1.6 liters/hr under 1500 psi; the radiation dose to the solution at this flow rate was 10^6 R. The results are shown in Table 20.

Table 20. COD and Color Changes in Authentic Textile Mill Effluent at a Dose of 10^6 R Gamma Under 1500-psi Oxygen

	COD (mg/liter)		% Transmission		
Sample No.	Original	Treated	Original	Treated	Wavelength (mμ)
1	445	742	65	60	500
			80	76	700
2	428	631	58	59	500
			76	74	700
3	1174	1220	15	17	390
			24	30	420
			55	59	700
4	811	811	39	43	500
			37	44	525
			70	72	700

Samples 3 and 4, the most highly colored of the as-received effluent, were slightly decolorized by the treatment. The increase in COD in all samples following treatment has been observed in other irradiated samples and may be due to a partial decomposition of refractory materials that do not contribute to COD prior to irradiation.

A 40-gal batch of total plant effluent from a silk screen print textile mill and a 55-gal batch of total plant effluent from a weaving, dyeing, and finishing plant were supplied by the AATCC. The effluents were typical for silk screen print mills and for synthetic fabric mills.

Both of the authentic effluents were collected over a 1-hr period from a process stream that feeds themmill effluent treatment plant. The silk screen plant effluent contained disperse dye in the form of printing inks dispersed in organic solvents such as varsol, pine oil, terpentine, and binder resins to form an emulsion. The dyeing and finishing plant effluent consisted of detergents, disperse dyes and dye additives. Both plants incorporated their sanitary sewage into the feed. One plant produces a total of 3.5 × 10^6 gal/day, with approximately 4000 people contributing to the sanitary sewage input.

Both effluents were filtered through a sintered polyethylene filter to remove large particulates prior to treatment in the irradiator; however, all solid materials were not removed. These effluents were processed in the 1-1/2-in.-diam column, charcoal-loaded irradiator. Both effluents were quite turbid when introduced into the irradiator. When the silk screen mill effluent was treated with charcoal alone, only 51% of the color was removed by a combination of charcoal adsorption and Millipore filtration, based upon light absorbance as measured in the 350-, 450-, and 550-mμ wavelengths. After the effluent was processed through the irradiator under 500-psi oxygen, 82% color removal was achieved. Results are shown in Table 21.

Table 21. Color and COD Removal From Silk Screen Textile Plant Effluent by Gamma Radiation at a Dose Rate of 5 × 10^5 R/hr With Charcoal and 500-psi Oxygen

Sample No.	Amount Through Irradiator (gal)	Time From Start of Run (hr)	Flow Rate (gal/hr)	Color Factor	% Color Removal	COD (mg/liter)
Feed: Filtered through sintered polyethylene	-	-	-	1.555		1065
10	10	5.5	2	0.159	90	
18	18	10.5	2	0.489	69	
22	23	12.5	2	0.300	81	262
25	28	14.5	2	0.174	89	
30	33	17.0	2	0.332	79	293[a]
37	38	20.0	2	0.188	88	

[a] COD after removal of solids with clay was determined to be 92 mg/liter.

The color intensity determined by light absorbance is sensitive to the presence of any solids present in the sample. These solids are not removed when the effluent is passed through 0.80-μ Millipore filter membranes. The solids material is white and, while it does not contribute to color as such, it does disperse and attenuate light, as shown in Table 22. Also the COD was reduced from 293 to 92 mg/liter after solids removal.

Table 22. The Effect on Light Absorbance of Solids Removal

Sample No.	Color Factor Before Removal of Solids	% Color Removal from Original	Color Factor After Solids Removal	% Color Removal from Original
22	0.300	81	0.089	99.4
25	0.174	89	0.059	99.6
30	0.332	79	0.029	99.9
37	0.188	88	0.032	99.8

It is apparent from these experiments that color due to dissolved material is effectively removed from the effluent by irradiation in the presence of charcoal under 500-psi oxygen. Also, the solids that persist through the irradiation process can be easily removed by the addition of a flocculating agent producing a marked decrease in the light attenuation used in the measurement of color.

The charcoal column does not remove the solids. Samples that had been processed through the irradiator to a 82% color removal (includes solids) were not further depreciated in color value by exposure to 20 hr to an excess of new granular charcoal.

The silk screen textile effluent is especially difficult to treat due to the disperse dyes present and the organic materials used in the printing inks. The effluent as received had a very strong solvent odor — varsol/pine oil combination — which was completely removed in the radiation processing.

Effluent from the dyeing and finishing plant was processed in the same way as the silk screen plant effluent. The feed solution appeared pink in color and contained small solids that could not be removed by filtration through a polyethylene sintered filter (filter pore size is greater than 500 μ). Data from this run are shown in Table 23.

The problem of solids in the product was very severe with this effluent; however, the solids in the product coagulated within 6 hr after removal from the irradiator from samples 1 through 14 and less slowly thereafter as the run progressed. This can be seen in the effect on the color factor shown in Table 23. As was observed with the silk screen effluent, when the solids in the product were removed by the addition of a flocculating agent, the color removal (absorbance) reached 99% (Table 24).

Table 23. Dyeing and Finishing Plant Effluent Color and COD Reduction by Gamma Radiation at a Dose Rate of 5×10^5 R/hr with Granular Charcoal and 500-psi Oxygen

Sample No.	Amount Through Irradiator (gal)	Time From Start of Run (hr)	Flow Rate (gal/hr)	Color Factor	% Color Removal from Original	COD (mg/liter)
Feed	-	-	-	2.255	-	1894[a] 1710[b]
4	3	1	3	0.018	99.5	46
9	10.5	3	3	0.049	98.0	116
14	15.5	6	3	0.145	95.6	123
19	18.0	8.5	1	0.210	91.0	200
28	31.5	13.0	3	0.253	88.8	ND[c]
35	42.0	16.5	3	0.185	92.0	154
43R[d]	54.0	20.5	3	0.575	74.5	160

[a] Before Millipore filtration.
[b] After Millipore filtration.
[c] Not determined.
[d] Sample treated with chlorine prior to irradiation.

Table 24. Dyeing and Finishing Plant Effluent. The Effect on Color Absorbance Factor of Removal of Solids From Sample

Sample No.	Color Intensity Before Removal of Solids	% Color Removal from Original	Color Intensity After Removal of Solids	% Color Removal from Original	COD
28	0.253	88.8	0.077	99.7	77
30	0.365	84.0	0.017	99.9	77
39	0.488	78.6	0.018	99.9	ND[a]
47R	0.550	76	0.031	99.8	58

[a] Not determined.

The dyeing and finishing plant effluent was examined for coliform bacteria; the results are shown in Table 25.

Table 25. Reduction in Bacteria Count by Irradiation Processes on Dyeing and Finishing Plant Effluent

Sample No.	Flow Rate (gal/hr)	Colonies Coliform Bacterial per 100-ml Sample
Feed	-	1,000
1	3	90
2	2	22

Two additional 55-gal batches of authentic textile mill effluent were processed through the 500-psi charcoal irradiator. One effluent consisted of detergent, dyes, and dye additives, along with some sanitary sewage input and was representative of the mill effluent as it was received by the mill's activated sludge treatment plant. The other was the product from the activated sludge treatment plant. Both effluents were filtered through a sintered polyethylene filter prior to the irradiation treatment to remove the large particles from the waste. Both effluents were turbid after the filtrations.

The color of effluent samples taken during the irradiation was determined by measuring the light absorbances at 350-, 450-, and 550-mμ wavelengths after the samples were filtered through a 0.80-μ Millipore membrane filter. Color factors were calculated from these results. Data obtained from these runs are shown in Table 26.

As the run progressed, the quantity of solid material in the product increased. Since these solids contribute to the color as measured by adsorbance, a flocculating agent was added to the effluent sample to remove them, and the sample was filtered through a 0.80-μ Millipore membrane. The color factor and percent color removal from samples after this step are shown in Table 26. After 18 gallons had been treated, the color removal was constant at 88 to 89%.

About 12 gallons of the treated dye effluent was recycled for a second pass through the irradiator. Before this second pass treatment, 200 ppm of chlorine was added. The second irradiation treatment before solids removal lowered the color intensity of the effluent by about 35%, and after solids removal by 86-90%. The addition of 200 ppm of chlorine did not appreciably aid in color removal.

The activated sludge plant product was prepared for irradiation by treating with agricultural lime (ground limestone) to raise the pH of the solution from 6.7 to approximately 7.5 and was then refiltered to remove large particles. Thirteen pounds of new (10-30 mesh) coconut charcoal was loaded into the pressure vessel for this treatment. This

Table 26. Color Removal From Dyeing and Finishing Plant Effluent by Gamma Radiation at a 5×10^5 R/hr Dose Rate With Granular Coconut Charcoal and 500-psi Oxygen

	Amount Through Irradiator	Flow Rate	Before Solids Removal[a]		After Solids Removal[a]	
Sample No.	(gal)	(gal/hr)	Color Factor	% Color Removal	Color Factor	% Color Removal
Original			3.030			
4	4.5	3	0.336	88.9	0.270	91.1
8	8.5	2	0.360	88.1	ND[b]	ND[b]
12	11.5	1.5	0.296	90.2	0.243	92.0
15	13.0	1.0	0.264	91.3	0.241	92.0
18	17.5	3	0.595	80.4	0.329	89.1
21	22	3	0.675	77.7	0.336	88.9
25	28	3	0.864	71.5	0.324	89.3
29	34	3	1.381	54.4	0.363	88.0
31	36	2	1.440	52.5	0.328	89.2
35	40	2	1.600	47.2	0.326	89.3
40	45	2	1.905	37.3	0.358	88.2
43	48	2	1.955	35.5	0.361	88.1
Recycle Feed	200 ppm Cl_2 added before second pass through irradiator					
51R	8	2	0.881	33.5	0.189	85.7
55R	12	2	0.821	38.1	0.138	89.6

[a] Sample filtered through a 0.80-μ Millipore membrane filter before absorbance measurements.

[b] Not determined.

change in charcoal mesh size was made in an attempt to increase the adsorption rate of dye onto the charcoal which would permit a greater flow rate through the irradiator. The color absorbances at 350-, 450-, and 550-mμ wavelengths were measured after filtration through an 0.80-μ Millipore membrane filter and were used to calculate the color factor shown in Table 27. There was a continuous increase in the color factor before solids removal from sample 1 through sample 29 (during which 43.5 gallons of effluent was processed). This was due to an increased quantity of solids in the sample. After 36 gallons of effluent had been processed to coagulate these solids, 200 ppm of potassium aluminum sulfate was added to the activated sludge plant product in the column feed reservoir. Another 200 ppm addition was made after 43 gallons had been processed. Sample 31 represents a total of 400 ppm addition of potassium aluminum sulfate and has lower color factor than the four preceding samples reported.

The column effluent samples contained a greater quantity of solids as the run progressed. These solids, which contributed to the measured color intensity, were removed by the addition of a flocculating agent before the Millipore filtration. The color removal and color intensity after the solids removal are also shown in Table 27. The addition of the first 200 ppm of $AlK(SO_4)_2 \cdot 12H_2O$ increased the color removal from 81 to 87%. The 400 ppm of $AlK(SO_4)_2 \cdot 12H_2O$ further increased the color removal to the 92-95% range. Hence, the $AlK(SO_4)_2 \cdot 12H_2O$ addition to the effluent before the treatment enhanced the color removal.

Table 27. Color Removal From the Product of an Activated Sludge Treatment Plant by Gamma Radiation (5×10^5 R/hr) at 500-psi Oxygen With Granular Coconut Charcoal

Sample No.	Amount Through Irradiator (gal)	Flow Rate (gal/hr)	Before Solids Removal		After Solids Removal	
			Color Factor	% Color Removal	Color Factor	% Color Removal
Original			1.975			
6	9	3	0.512	74.1	0.402	79.6
10	15	3	0.477	75.8	0.388	80.3
14	21	3	0.731	63.0	0.312	84.1
18	27	3	0.990	49.9	0.388	80.4
22	33	3	1.080	45.3	0.365	81.5
26[a]	39	3	1.047	47.0	0.248	87.4
29	43.5	3	1.084	40.1	0.157	92.1
31[b]	46.5	3	0.815	58.7	0.108	94.5

[a] 200 ppm $AlK(SO_4)_2 \cdot 12H_2O$.

[b] 200 ppm more $AlK(SO_4)_2 \cdot 12H_2O$.

SECTION IX

ACKNOWLEDGMENTS

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SECTION X

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SECTION XI

GLOSSARY

Radiation-induced oxidation - Oxidation processes initiated by gamma radiation usually at room temperatures.

Authentic effluents - Effluents produced by a process during routine production operations.

In situ carbon reactivation - Reactivation of activated charcoal by destruction of adsorbed material at the same time the charcoal is exposed to adsorbable materials from a solution passing through the column.

Batch irradiator - A vessel placed in a gamma radiation field in which single batches of a material may be irradiated.

Dynamic irradiator - A vessel placed in a gamma field equipped with flow through capability in which materials may be continuously flowed and exposed to gamma radiation.

Rad (R) - A measure of radiation adsorbed and equals 100 ergs/g.

Radiation dose - A general term denoting the quantity of radiation or energy adsorbed in a specified mass.

Dose rate - The adsorbed dose per unit of time.

SECTION XII

APPENDICES

APPENDIX A

Composition of Acid, Chrome Dye Solutions

Benzyl Fast Yellow GNC

0.3% dye
10% Glaubers salt
2% of 28% acetic acid

Benzyl Blue GL

0.05% dye
10% Glaubers salt
2% of 28% acetic acid

Benzyl Cyanine 6B

0.18% dye
10% Glaubers salt
2% of 28% acetic acid

Neolan Yellow BG

0.3% dye
4% of concentrated sulfuric acid

Chrome Fast Flavine A

0.4% dye
5% Glaubers salt
3% of 28% acetic acid

APPENDIX B

Composition of Four Standard Dye Solutions

C.I. DIRECT BLUE 106

Preparation:

1. Dissolve dyestuff in one liter of boiling water.
2. Add dye solution to remainder of the warm water.
3. Add in the following sequence:

   Intravon G, TSPP, sodium sulfate

	For 1 Gallon
Dyestuff, g	0.50
Tetra sodium pyro phosphate, g	5.04
Sodium sulfate, g	0.25
Intravon G (wetting agent), g	0.50
Warm tap water, 5 gal	1 3.79 liters

NOTE 1:

Based upon a 2000^+ pound solution (approximately 267 gallons) 100 pounds of cloth treatment theoretical batch. Ref. Intracolor Ex 5.0.1 (1/1/68). Cloth ratio 20/1.

C.I. ACID BLACK 26A

Preparation:

1. Dissolve dyestuff in one liter of boiling water.
2. Add dye solution and other chemicals to the remainder of the warm water (not over 120°F). In making the one-gallon solution, be sure to cool the dye solution before adding other ingredients.
3. Adjust pH to 5.5 - 6.0 with acetic acid.

	For 1 Gallon
Dyestuff, g	0.34
Sodium sulfate, g	21.04
Ammonium sulfate, g	2.10
Intravon G (alkylaryl sulfate wetting agent, g	0.084
Warm tap water, gal	1 3.79 liters
Acetic acid (50%)	To adjust final pH to 5.5 - 6.0

NOTE 1:

Based upon a 2000^+ pound solution (approximately 267 gallons) 100 pounds of cloth treatment theoretical bath. Ref. Intracolor Ex 6.2.1 (3/3/69). Dye bath. Cloth ratio 40/1.

DISPERSE BLUE 3

Preparation:

1. Add Carolid to warm water bath and adjust pH to 6.5 with monosodium phosphate; then add Intravon G.
2. Disperse dyestuff in one liter of water at 110-120°F. In making the one-gallon formulation, be sure to use one liter of the amount of warm water specified because of the effect of reduced volume on the colorization.
3. Add dispersed dye solution to bath.

	For 1 Gallon
Warm tap water, gal	1 3.79 liters
Carolid (ortho phenylphenol; Tanatex Co.), g	1.51
Monosodium phosphate	To adjust bath to pH of 6.5
Dyestuff, g	1.51
Intravon G (wetting agent), g	0.084

NOTE 1:

Based upon a 2000$^+$ pound solution (approximately 267 gallons)
Theoretical dye application for 100 pounds cloth
Ref: Intracolor Ex-2.11.1 (1/1/68) Cloth ratio 40/1.

REACTIVE RED 3

Prepare a concentrate of this dye as follows:

Lantex	10 parts by wt.
Dyestuff	10 parts by wt.
Sodium bicarbonate	5 parts by wt.
Urea	18 parts by wt.
Ludigol	2 parts by wt.
Tap water	155 parts by wt.

Dilute this dye concentrate as follows:

	For 1 Gallon
Concentrate, ml	4.7
Warm tap water, gal	1 3.79 liters

NOTE 1:

Formulation by William Turner of Cranston Print Works.

APPENDIX C

Calculation of Radiation Cost

Gamma radiation is a major cost element for this process. Since pilot plant design was not a part of this study, a determination of radiation cost only was made. Other costs such as pretreatment for solids removal, storage of effluents, and plant capital equipment costs were not made but are expected to be approximately the same as for conventional processes. Cobalt-60 costs to yield the required gamma radiation were estimated.

The tank volume provides 10 min of solution/charcoal contact time at a flow rate of 5×10^5 gal/day. The diameter was selected for maximum utilization efficiency of ^{60}Co gamma.

Assumptions		
	Charcoal adsorption tank size	5 ft diam
		23.6 ft high
	Tank volume, ml	1.315×10^7
	Weight of charcoal in tank	6.58×10^6 g

Percent by weight of organic adsorbed on charcoal at equilibrium (equilibrium is defined as the rate of organic adsorption onto charcoal being equal to the rate of removal by oxidation and requiring a 10^6 R gamma radiation dose to the adsorbed organic) is 2.88%. The time chosen for this equilibrium to occur is 24 hr.

Organic content of feed effluent	100 ppm
Effluent flow rate	5×10^5 gal/day

Cobalt-60 required

To deliver 10^6 R dose to organic in 24 hr, the dose rate to the organic will be $\frac{10^6 \text{ R}}{24} = 4.17 \times 10^4$ R/hr.

The energy of the ^{60}Co gamma is 1.17 and 1.33 MeV or 2.50 MeV per disintegration.

The yield per curie of ^{60}Co in ergs/hr is:

$$\frac{3.7 \times 10^{10} \text{ dis/sec} \times 2.5 \text{ Mev/dis} \times 3600 \text{ sec/hr}}{6.24 \times 10^5 \text{ Mev/erg}} = 5.33 \times 10^8 \text{ erg/hr/Ci}$$

The density of the media in which the organic is irradiated (charcoal plus water) is approximately 1 g/ml (determined experimentally); therefore,

$$\underset{\text{(total grams in tank to be irradiated)}}{1.315 \times 10^{7}\ \text{g}} \times \underset{\text{(dose rate)}}{4.17 \times 10^{4}\ \text{R/hr}} \times 100\ \text{erg/g/R} = \underset{\text{(required total dose)}}{5.48 \times 10^{13}\ \text{erg/hr}}$$

$$\text{Curie cobalt-60} = \frac{5.48 \times 10^{13}\ \text{erg/hr}}{5.33 \times 108 \times 0.8} = \text{1.283} \times 10^{5}\ \text{Ci of }^{60}\text{Co required for delivery of a } 10^{6}\ \text{R dose in 24 hr to load in irradiator}$$

$$\left[\frac{\text{Required total dose}}{\text{Dose/Ci} \times \text{efficiency of energy utilization}}\right]$$

Summary

Flow:	5×10^{5} gal/day or 7470 gal/min
Quantity of Charcoal:	463 ft^{3}, $\frac{6.58 \times 10^{6}\ \text{g}}{453.6\ \text{g/lb}} = 14{,}500$ lb
Organic loading on charcoal	2.88%
Curies of ^{60}Co	128,300
Cost of ^{60}Co (\$0.40/Ci)	\$51,320
Cost of ^{60}Co/yr ($T_{1/2}$ = 5 yr)	\$6,620
Cost of ^{60}Co/day	\$18.18
Cost of ^{60}Co/1000 gal of throughput	3.6¢

Table 1. Variation in Irradiation Cost as a Function of Organic Loading on Charcoal and Dose Rate to a Total Dose of 10^6 R

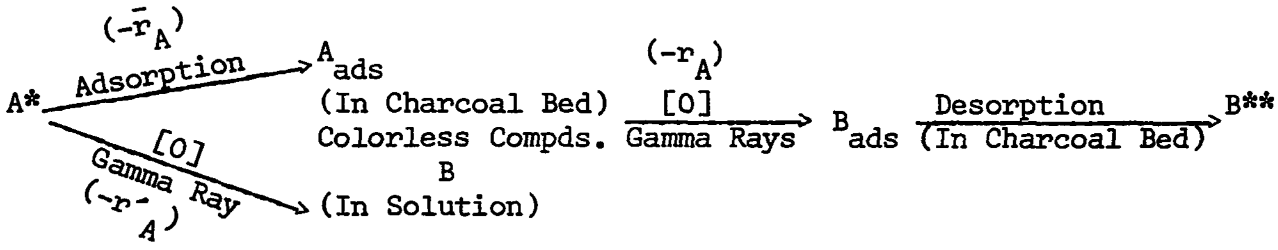
Organic loading, (%)	2.88	5.76	8	10	20
Exposure time available for organic oxidation, (hr)	24	48	66.7	83.3	166.5
Required dose rate (erg/hr)	5.48×10^{13}	2.74×10^{13}	1.97×10^{13}	1.58×10^{13}	0.79×10^{13}
Curies of ^{60}Co	12.83×10^{4}	6.415×10^{4}	4.62×10^{4}	3.70×10^{4}	1.85×10^{4}
Cost of ^{60}Co ($0.40/Ci)	$51,320	$25,660	$18,480	$14,800	$7,400
Cost of ^{60}Co/yr ($T_{1/2}$ - 5 yr)	$6,620	$3,310	$2,380	$1,909	$955
Cost of ^{60}Co/ 1000 gal	3.6¢	1.8¢	1.3¢	1.0¢	0.5¢

APPENDIX D

Mathematical Model to Describe Effluent Treatment by Irradiation of Dye Effluent on a Fixed Charcoal Bed

A packed charcoal bed (Fig. 1) is initially saturated with radiation-sensitive colored organic contaminants "A" from untreated plant effluents. The contaminants "A" under gamma irradiation in the presence of oxygen are either degraded or converted to colorless compounds "B". Under steady-state operation, the untreated plant effluents containing C_{Ai} (mole/volume) of "A" are fed through the bed continuously at a rate of ν (volume/time). In the charcoal bed, the colorless compounds "B" are preferentially eluted by the solution while the contaminants "A" are adsorbed onto the bed. The treated solution being discharged at ν from the system contains C_{Af} (mole/volume) of "A".

The process scheme in the packed bed system is:



*Colored Contaminants (In Solution)
**Colorless Compounds (In Solution)

ORNL-DWG 72-2141

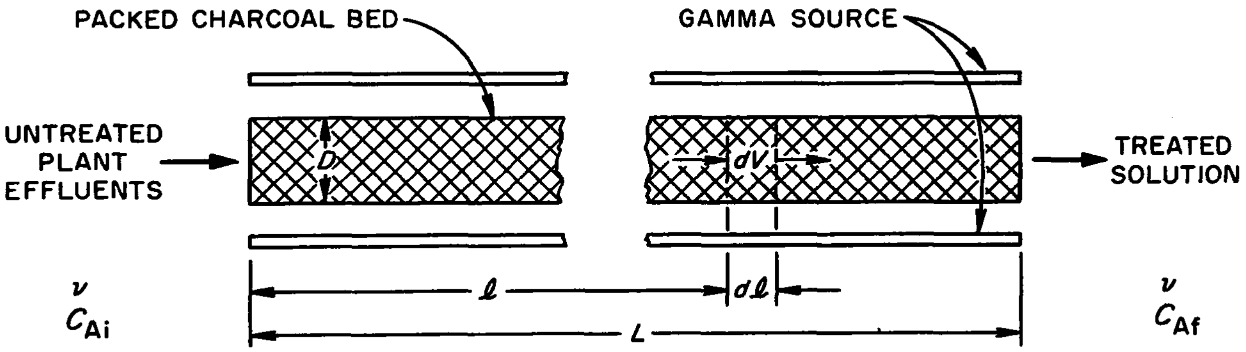


Fig. 1. Packed Charcoal Bed

Development of Mathematical Model

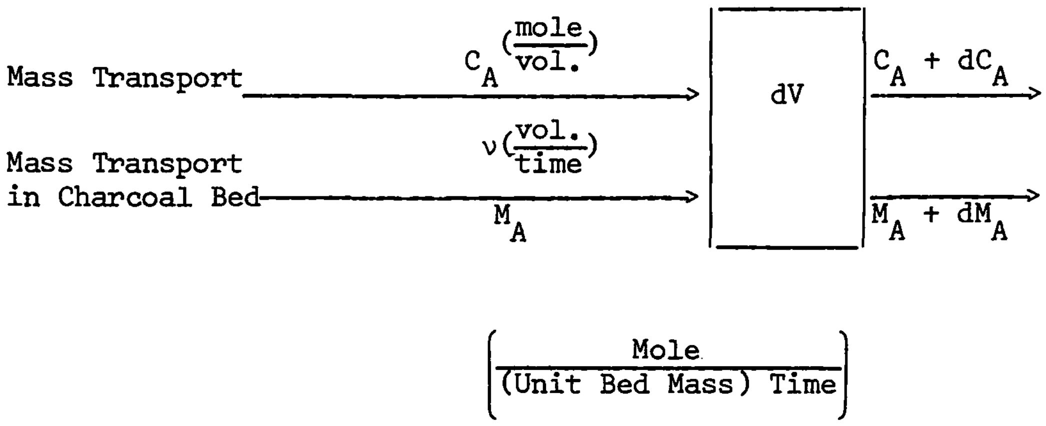


Figure 2. Differential Volume Element in Charcoal Bed

Assumptions:

1. Plug flow condition prevails in the packed charcoal bed system, i.e., there is no composition gradient in the radial direction, and the composition varies only in the longitudinal direction.
2. The gamma radiation sources are arranged in such a way that the dose rate is constant and uniform throughout the charcoal bed.
3. A steady-state isothermal operation is in progress.
4. Physical properties (solution density, bulk density of charcoal bed, viscosity, etc.) of the system remain constant.

Consider a differential volume element dV in the bed. Transport of organic contaminants "A" takes place in two separate streams, one in solution occupying the void volume and the other in the charcoal bed.

Material balance on "A" in the solution stream is:

$$[\nu C_A + (-\underline{r}_A)\rho_b dV] - [(-r'_A)\varepsilon dV + (-\bar{r}_A)\rho_b dV] - \nu(C_A + dC_A) = 0 \qquad (1)$$

Material balance on "A" in the charcoal bed is:

$$[M_A\rho_b dV + (-\bar{r}_A)\rho_b dV] - [(-r_A)\rho_b dV + (-r_{\underline{A}})\rho_b dV] - (M_A + dM_A)\rho_b dV = 0 \qquad (2)$$

where,

$(-r'_A)$ = rate of disappearance of "A" by radiolysis in solutions, moles/(volume)(time)

$(-\bar{r}_A)$ = rate of disappearance of "A" from solution by adsorption onto charcoal bed, moles/(wt. of bed)(time)

$(-r_A)$ = rate of disappearance of "A" by radiolysis in charcoal bed, moles/(wt. of bed)(time)

$(-r_{\underline{A}})$ = rate of disappearance of "A" from charcoal bed due to desorption from charcoal bed by solution, moles/(wt. of bed)(time)

ε = porosity of charcoal bed

ρ_b = bulk density of charcoal bed.

From Eqs. (1) and (2), neglecting the second-order differential:

$$-\nu dC_A = [(-r'_A)\varepsilon dV + (-r_A)\rho_b dV] \tag{3}$$

Integrating between the inlet and discharge ends of the charcoal bed:

$$\frac{V}{\nu} \int_{C_{Af}}^{C_{Ai}} \frac{dC_A}{\varepsilon(-r'_A) + \rho_b\,(-r_A)} \tag{4}$$

or

$$\bar{t} = \frac{\varepsilon V}{\nu} = \varepsilon \int^{C_{Ai}} \frac{dC_A}{\varepsilon(r'_A) + \rho_b\,(-r_A)} \tag{5}$$

where $\bar{t}$ is the residence time of the untreated plant effluent solutions in the charcoal bed. Integration of the right-hand side of Eq. (5) can be completed only after the functional forms of $(-r'_A)$ and $(-r_A)$ have been established.

For the proposed process to be economically attractive, the rate of radiolysis in the charcoal bed $(-r_A)$ must be considerably greater than that in the solution $(-r'_A)$. That is, $(-r_A) \gg (-r'_A)$. This probably would be the case since the concentration of "A" in the charcoal bed would be much higher than that in the solution, provided that a sufficient amount of oxygen is available for the radiolysis reaction to proceed. If $(-r'_A)$ is small enough to be neglected, Eq. (5) becomes:

$$\bar{t} = \frac{\varepsilon}{\rho_b} \int_{C_{Af}}^{C_{Ai}} \frac{dC_A}{(-r_A)} \qquad (6)$$

Thus, Eq. (5) or (6) with a given value of C_{Ai} and known functional forms of $(-r_A')$ and $(-r_A)$ would describe how the contaminant concentration of the solution discharged from the charcoal bed, C_{Af}, varies with the residence time $\bar{t}$.

Experimental Data to be Acquired

To confirm the mathematical model developed above, the experimental data listed below are required.

1. Bulk Density (ρ_b) and Porosity (ε) of charcoal bed:

   These two properties are related to the true density of charcoal being used (ρ) by $\rho_b = (1 - \varepsilon)\rho$.

2. Radiolysis Rate Expressions $(-r_A')$ and $(-r_A)$:
   The bulk density and the porosity of charcoal bed are known.

   The radiolysis rates are presumably functions of several parameters as in:

$$(-r_A') = -\frac{dC_A}{dt} = f_1(1, C_A, C_o) \qquad (7)$$

$$\text{and } (-r_A) = -\frac{dM_A}{dt} = f_2(1, M_A, M_o) \qquad (8)$$

where t is time, 1 represents the gamma radiation dose rate, and C_o and M_o are the oxygen concentrations in the solution and in the charcoal bed, respectively. Both equilibrium values of C_o and M_o are related to the partial pressure of oxygen in the fixed charcoal bed system.

One of the possible functional forms for Eqs. (7) and (8) may be a power function of the type:

$$(-r'_A) = k' l^s C_A^n C_0^m \quad (9)$$

$$\text{and } (-r_A) = k l^b M_A^a M_o^c \quad (10)$$

where the rate constants k' and k, and exponential constants s, n, m, b, a, c can be determined by the batch type of experiments. Frequently, it may be more convenient to use the partial pressure of oxygen (P_o) instead of concentrations, and Eq. (9) and (10) are rewritten as:

$$(-r'_A) = k'_p l^s C_A^n P_0^{\bar{m}} \quad (11)$$

$$(-r_A) = k_p l^b M_A^a P_o^{\bar{c}} \quad (12)$$

If the gamma irradiation source can be designed such that l is kept constant and uniform throughout, two dependent variables (concentration of "A" and P_o) would be left in each of the above two equations. Furthermore, if P_o could be fixed at a value that is technically and economically most desirable, only one variable (concentration of "A", C_A, or M_A) remains. Thus, Eqs. (11) and (12) can be simplified to give Eqs. (13) and (14) to yield functional forms for $(-r'_A)$ and $(-r_A)$.

$$(-r'_A) = K'_{P,l} C_A^n \quad (13)$$

$$(-r_A) = K_{P,l} M_A^a \quad (14)$$

Although this model was proposed for a dye mixture, it could be most easily checked for a single dye solution. A sample of the dye solution could be irradiated in equilibrium with charcoal under the selected pressure and selected radiation dose. These irradiations could be made over a suitable range of dye concentrations to get the necessary data to determine the constants in Eqs. (13) and (14). The solution with the charcoal could be agitated during the period of time of irradiation with a mechanical shaker. The C_{Ai} and C_{Af} could be read directly on the spectrophotometer as absorbance and the constants of Eq. (13) could be determined. The determination of M_{Af} is more difficult. Since the ratio of C_{Af}/M_{Af} should be constant for each value of C_{Af} when agitated in the same manner and for the same period of time, it should be possible to calculate the M_{Af} from the C_{Af}. The C_{Af}/M_{Af} could be determined for the range of C_{Af} as needed in an experiment without radiation and without oxygen agitating the mixture for the same length of time. Hence, it should be possible to find the amount of A on the charcoal (M_{Af}). The constants of Eq. (14) can be determined.

3. Equilibrium Relationship:

The functional forms of $(-r_A')$ and $(-r_A)$ determined in the preceding step are to be substituted into Eq. (5) to obtain an explicit relation between C_{Af} and $\bar{t}$. However, before Eq. (5) can be integrated, a relation between C_A and M_A must be known. Their relation can assume the form:

$$M_A = KC_A^{\alpha} \tag{15}$$

The constants K and α in such a relation can also be determined by the batch experiments. Since in an actual operation a true equilibrium condition is not obtainable within a convenient time, it will be necessary to investigate how fast the system approaches the equilibrium.

The absorption of A on charcoal can be investigated for this same dye by using an equivalent shaking (by mechanical shaker). A plot of absorption of A on charcoal (M_A) is made as a function of time until there is no further increase of M_A. The K and α can be determined for Eq. (15).

Treatment of Experimental Data

Rate expressions $(-r_A')$ and $(-r_A)$ together with the relation of Eq. (15) can now be employed in Eq. (5) to perform an integration. Equation (6) can be used if the experimental data confirm that $(-r_A')$ is negligibly small compared with $(-r_A)$. The integration can be carried out analytically if rate expressions are relatively simple. When complex expressions are obtained, Eq. (5) or (6) is integrated more conveniently by the graphic method or solved by the method of numerical integration. It is to be noted that the relation between $\bar{t}$ and C_A in Eq. (5) is also valid for the constant volume batch system since physical properties of the system are assumed to be constant in the present case.

The mathematical model developed in this section is confirmed when the values of C_{Af} at various residence times $\bar{t}$ predicted from Eq. (5) or (6) agree with the experimental values within a desired accuracy. Otherwise need for modification of the model is indicated.

1 *Accession Number* **W**	2 *Subject Field & Group*	**SELECTED WATER RESOURCES ABSTRACTS** **INPUT TRANSACTION FORM**

5 *Organization* Oak Ridge National Laboratory, Oak Ridge, Tennessee
Isotopes Development Center
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6 *Title* Study of Gamma Induced Low Temperature Oxidation of Textile Effluents

10 *Author(s)* Case, Forrest N. Ketchen, Eugene E.	16 *Project Designation* Project Contract #12090 FWD 21 *Note*

22 *Citation*

Environmental Protection Agency report number EPA-R2-73-260, May 1973.

23 *Descriptors (Starred First)*

*Color Removal, *COD Removal, Reactivation of Charcoal

25 *Identifiers (Starred First)*

*Color Removal, Textile Effluents

27 *Abstract*

Gamma irradiation of textile mill effluents under oxygen pressures up to 1500 psi, with and without activated charcoal present, was studied as a method for removing color and removal of substances contributing to the chemical oxygen demand (COD). Both color and COD reduction are directly related to the radiation dose and pressure of the oxygen over the dye solution samples during irradiation. Color removal was achieved in solutions of dye prepared in the laboratory for process evaluation and for authentic textile mill waste effluents; however, the variation in the radiation dose required for various dye compounds was large. The study revealed a new method for in-situ reactivation of charcoal by gamma-radiation-induced oxidation of organic compounds adsorbed on charcoal. This discovery permits a large reduction in the gamma source size required for processing textile mill effluents because the water fraction of the effluent does not need to be irradiated to the same degree as the organic material contained in the effluent. A methematical model for the process, developed late in this study, has not yet been experimentally verified.

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