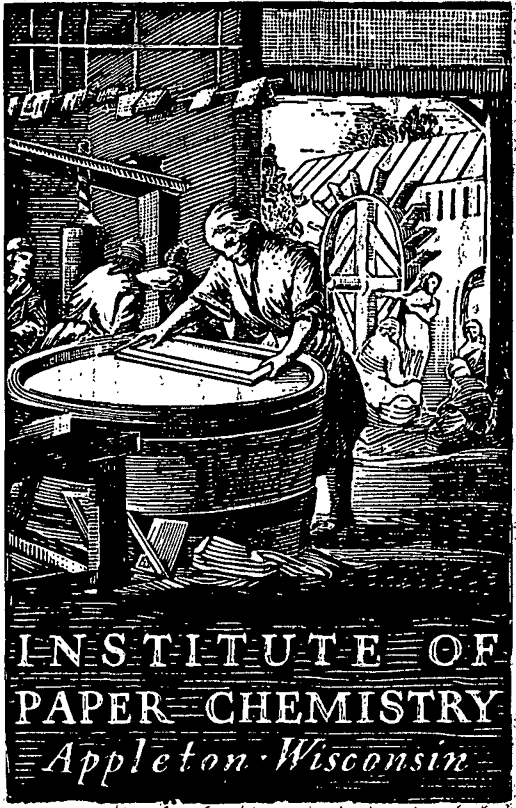


COLOR PROBLEMS DURING THE TREATMENT OF KRAFT EFFLUENTS WITH ACTIVATED CARBON AT ST. REGIS PAPER COMPANY, PENSACOLA

Project 3083

Report One
The Final Report
On Special EPA Grant
to
OFFICE OF RESEARCH AND MONITORING
ENVIRONMENTAL PROTECTION AGENCY

August 25, 1972

THE INSTITUTE OF PAPER CHEMISTRY

Appleton, Wisconsin

COLOR PROBLEMS DURING THE TREATMENT OF KRAFT EFFLUENTS WITH ACTIVATED CARBON AT ST. REGIS PAPER COMPANY, PENSACOLA

Project 3083

Report One

The Final Report

On Special EPA Grant

to

OFFICE OF RESEARCH AND MONITORING
ENVIRONMENTAL PROTECTION AGENCY

August 25, 1972

TABLE OF CONTENTS

THE INSTITUTE OF PAPER CHEMISTRY

Appleton, Wisconsin

COLOR PROBLEMS DURING THE TREATMENT OF KRAFT EFFLUENTS WITH ACTIVATED CARBON AT ST. REGIS PAPER COMPANY, PENSACOLA

SUMMARY

During the treatment of kraft waste water with activated carbon at St. Regis Paper Company, Pensacola, Florida, an overall "true" color reduction was noticed. The filter paper color (FPC) was, however, found to increase manyfold. This increase in FPC was termed as "reversion." True color was defined by St. Regis as the color of mill waste water after it has been filtered through an 0.8 µm. millipore filter. FPC was determined after the mill waste had been filtered through ordinary filter paper.

The study showed that a maximum of 86-87% each of color and T.O.C. are removed during the treatment of kraft waste water by activated carbon. Sand filter also removed some color and T.O.C. Color "reversion" was found to be due to carbon particles in and above the colloidal range. The source of these carbon particles is indicated to be activated carbon.

INTRODUCTION

St. Regis Paper Company has constructed a pilot plant for the treatment of mill wastes by activated carbon under a grant from the Environmental Protection Agency (EPA).

During the course of their pilot-plant studies, St. Regis chose to characterize color after filtration. Filter paper color (FPC) was defined as the color of mill waste water after it has been filtered through an ordinary filter paper. Millipore color (MPC) is the color after the mill waste has been filtered through an 0.8 µm. millipore filter. MPC was also referred to as "true" color. An overall "true" color reduction was noticed during the carbon treatment whereas FPC was found to increase manyfold. Noticeable was the fact, however, that FPC was more black than brown. This increase in color was termed as "reversion" by St. Regis. We will refer to this term from time to time in our report.

We were called in by the EPA to study this problem and what follows is the result of this study.

This report is divided into four main parts:

Background Information

Identification of the "Color Bodies" Responsible for Color Reversion"

Identification of the Source of "Color-Bodies" Responsible for Color "Revision"

Recommendations for the Solution to the "Reversion" Problem

BACKGROUND INFORMATION

St. Regis Paper Company at Pensacola has two pulp mills. Mill No. 1 produces 250-300 tons/day of bleached and unbleached kraft pulp from pinewood. Mill No. 2 produces 630 tons/day of unbleached kraft pulp containing 30% hardwood. Both mills are cross-connected for pulp pumping but washing of the pulp is done at the place of manufacture. At the time samples were taken for this study, the unbleached effluent from Mill No. 2 was being treated in the biooxidation tank followed by a sand filter and the granular carbon columns. The pilot plant also has provisions for treating the effluent with lime and/or pulverized carbon. This treatment may be preceded with or without biooxidation. According to Mr. Winfried Timpe, Project Leader at St. Regis, the raw effluent from No. 2 mill also contains effluent from the bag plant carrying ink discharges, and intermittent washdowns from the lime and caustic area, including some dregs and grits.

The effluent is treated in the pilot plant as follows. Mill effluent containing approximately 1700 units of "true" color (effluent filtered through 0.8 µm. millipore and color measured at 465 nm. by Spectronic 70), B.O.D. 278 p.p.m. and pH 10.5 is treated in an aerated biooxidation tank, capacity 100,000 gallons for five days. After biooxidation the effluent has a pH of 8.5 and shows a color reduction of 35%.

The biotreated effluent is filtered through a sand filter at the rate of 15 g.p.m. According to Mr. Timpe, color reduction of 5% is achieved during this step. Sand filtered effluent containing on an average of 892 color units, T.O.C. 148 p.p.m., B.O.D. 68 p.p.m., and pH 8.5 is passed through four carbon columns in series (3 ft. diam.), each having a carbon bed height of ten feet. I was informed that at times reductions of "true" color of 60-80%, T.O.C. 52-65%, and B.O.D. 75%, have been achieved during carbon treatment. The final pH of carbon-treated effluent is 8.0.

During filtration of effluents through various pore sizes, St. Regis noticed that the MPC values were lower than FPC values. For example, when biotreated effluent was first filtered through an ordinary filter paper and then through 0.8 and 0.45-µm. millipore filters, the following values were obtained (see Table I). All color values were determined at the same pH. The color of the solids on all filters was dark brown or black.

TABLE I

COLOR CHARACTERIZATION AT ST. REGIS PAPER COMPANY

	Color Units	T.O.C.,[a] mg./l.
Biotreated mill effluent, as is	2800	--
Filter paper color (FPC)	1380	150
Millipore color (MPC)		
0.8 µm.	800	150
0.45 µm.	620	150

---

[a] Total organic carbon.

The observation that little or no change in T.O.C. content occurred during filtration is quite surprising (Table I). The independence of T.O.C. and color units may also reflect the possible fact that the mass of colored substances is very small on a relative basis.

Studies at St. Regis have further shown that when a solution containing 0.05% black liquor solids was mixed with 1.0 g./l. of Darco carbon and stored separately under oxygen and nitrogen atmospheres, color was found to increase when no oxygen was present and decrease when oxygen was present in excess (limited oxidation would probably increase color). It was believed that anaerobic conditions might have something to do with the observed color "reversion." It was also established that anaerobic conditions did exist in the carbon columns as no oxygen was found in the samples from carbon columns and H_2S was noticed when columns were back-washed.

Mr. Timpe found that higher color removal by activated carbon occurs at pH 8.5 and below 4.0, whereas lower removal occurs at pH 5.5 and above 9.0. Further, separate studies on kraft effluents at the Institute indicated that absorbance in the visible range, 420 nm. (which is another way of saying "color"), is higher at pH 5.0 and 9.0 and lower at 8.0 and below 4.0. (This behavior can be attributed to the ionization of different chromophores at different pH values.)

The observation that maximum color removal occurs at the pH where lowest color values exist, suggested that color removal by activated carbon is probably a function of particle size.

When used carbon columns were back-washed, highly-colored solutions were obtained. It is believed that, during back-washing, the multilayers of sorbed color bodies are disturbed, released, redispersed, and partially redissolved. Much of this material is suspended, as evidenced by its removal by filtration.

It was further indicated that color bodies appear to contain a disproportionately high amount of metal ions. This applied to the filterable color bodies in the carbon-treated effluent and to the color bodies removed from used carbon by stirring in water or effluent. Pore size of the filter used was not given.

When a slurry tapped from carbon columns was processed through the filtering procedure described earlier, results similar to Table I were obtained. In this case, however, the color was more black than brown.

Upon Dr. Dugal's suggestion that the black color might be due to peptized carbon from the columns, Mr. Timpe pointed out that although the material retained on the filter was black, they had no other evidence that it contained carbon particles. He suggested that it could well be a mixture of metal sulfides, metal-organics and perhaps carbon particles. In their tests for carbon abrasion in a stirred slurry of carbon in distilled water they found no abrasion and no darkening of the water. However, to my knowledge no mill effluents were used in this test.

IDENTIFICATION OF THE "COLOR BODIES" RESPONSIBLE FOR COLOR "REVERSION"

The following seven waste samples were air shipped from Pensacola for study at the Institute.

I. 48-hr. Composite, raw waste
II. After biooxidation
III. After sand filter
IV. After 1st carbon column
V. After 2nd carbon column
VII. After 4th carbon column
VIII. Supernatant from stirred-up carbon taken from 2nd carbon column after 20-min. settling

(Waste No. VI — after 3rd carbon column — was not received.)

CHARACTERIZATIONS OF WASTES BY FILTRATION

Based on St. Regis' work, a qualitative filtration experiment was planned for the initial characterization of these wastes. Filters used in sequence were Whatman No. 1 filter paper and various millipore filters having pore sizes of 1.2, 0.8, 0.45, 0.22, and 0.1 µm.

Visual examination of the filters from the preliminary study showed that negligible amounts of colored material was retained by 1.2, 0.45, and 0.22 µm. millipore filters. Large-scale quantitative filtration experiments were, therefore, carried out using Whatman No. 1 filter paper and 0.8, 0.45, and 0.1 µm. millipore filters in sequence. In spite of the fact that 0.45 µm. millipore filter was not very effective, it was kept in our schedule mainly because St. Regis had used this pore size in their studies.

Aliquots of filtrate after each filtration stage were analyzed for color, total organic carbon (T.O.C.), and absorbance at 280 nm. and 465 nm. Results are given in Table II and are plotted against the filter pore sizes in Fig. 1 to 3. For simplicity, the filter paper pore size has been taken as >3.0 μm. (actual measurements gave an average pore size of this filter paper as 23.0 μm). Pore sizes of the millipore filters were supplied by the manufacturer. It should be noted that in this report color, T.O.C. or any other parameter at a certain pore size have been measured on the filtrate. In other words, 0.45 μm. color means color of mill waste after it has been filtered through 0.45 μm. millipore filter.

Filtration techniques used here are crude for the estimation of particle size and so the values should not be taken as absolute values. These do, however, give a comparative picture.

Figures 1, 2, and 3 show that color, T.O.C., and absorbance at 280 nm. (for 465 nm., see Table II) generally decrease with decreasing pore sizes. The drop in values is maximum from 0.45 μm. to 0.1 μm. Waste VIII is an exception to the above observation. In this case there is a very sharp drop from >3.0 μm. to 0.8 μm. indicating that about 99% of this waste is retained by 0.8 μm. millipore filter. It is well known that colloidal particles fall in the range of 20 to 2000 A. (0.002 to 0.2 μm.). It seems, therefore, that most of the material in the wastes under study is in and above the colloidal range.

"True" color measured by St. Regis was the color of mill waste after it was filtered through 0.8 μm. millipore filter. We have seen above that most of the material in the wastes is larger than 0.1 μm., suggesting that color values obtained by St. Regis were not "true" color values but included an error due to

TABLE II

ANALYTICAL DATA ON VARIOUS WASTES PASSED THROUGH DIFFERENT FILTERS IN SEQUENCE

Through Filter, pore size, µm.	Raw Waste	Waste After Treatment					C-2 Slurry
		Biooxid.	Sand Filt.	C-1	C-2	C-4	
Color Units (Pt-Co)							
>3.0	918	759	651	462	330	244	3630
0.8	1144	651	419	249	248	144	24
0.45	1042	651	419	252	253	134	--
0.1	773	432	224	64	40	25	25
T.O.C., mg./l.							
>3.0	236	178	110	147	66	43	185
0.8	267	168	115	56	77	45	7.5
0.45	248	132	84	61	63	31	--
0.1	241	85	50	21	13	8.8	10.0
Absorbance, cm.$^{-1}$ at 280 nm.							
>3.0	6.0	4.3	3.4	2.6	2.0	1.2	3.4
0.8	6.1	3.7	2.4	1.4	1.4	0.83	0.14
0.45	5.7	3.8	2.3	1.4	1.6	0.75	--
0.1	4.7	2.4	1.4	0.44	0.26	0.11	0.08
at 465 nm.							
>3.0	0.45	0.29	0.23	0.27	0.23	0.14	0.88
0.8	0.55	0.32	0.23	0.22	0.13	0.13	0.03
0.45	0.42	0.23	0.18	0.16	0.11	0.08	--
0.1	0.27	0.16	0.13	0.03	0.03	0.02	0.01
Absorptivity, l./g.cm. at 280 nm.							
>3.0	25.3	24.4	30.5	17.9	29.5	28.6	18.2
0.8	23.0	21.9	21.3	25.3	18.0	18.4	18.7
0.45	23.0	28.7	27.5	23.5	24.7	24.0	--
0.1	19.6	27.7	29.1	21.0	20.2	12.0	11.7
at 465 nm.							
>3.0	1.9	1.6	2.1	1.9	3.5	3.2	4.7
0.8	2.1	1.9	2.0	3.9	1.7	2.8	3.9
0.45	1.7	1.8	2.7	2.7	1.8	2.6	--
0.1	1.1	1.9	2.7	1.4	2.2	1.8	1.5

Biooxid. = after bioxidation; sand filt. = after sand filter; C-1, C-2, C-4 = after 1st, 2nd, and 4th activated carbon columns; C-2 slurry = supernatant from stirred-up carbon taken from 2nd column (settling time 20 min.); T.O.C. = total organic carbon. Absorptivity was calculated by dividing absorbance values by T.O.C. in g./l.

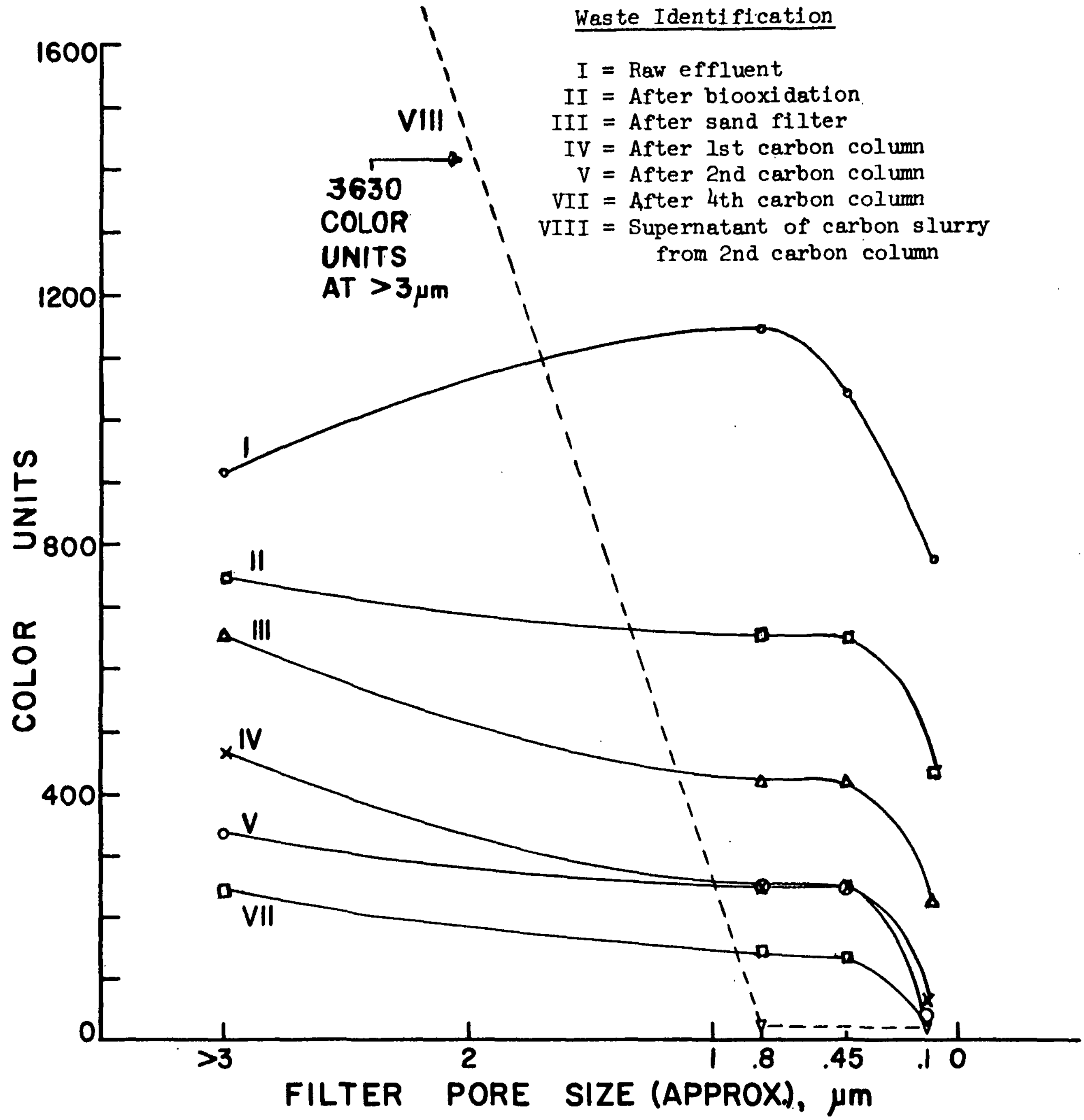


Figure 1. Color of Various Wastes Passed Through Different Filters in Sequence

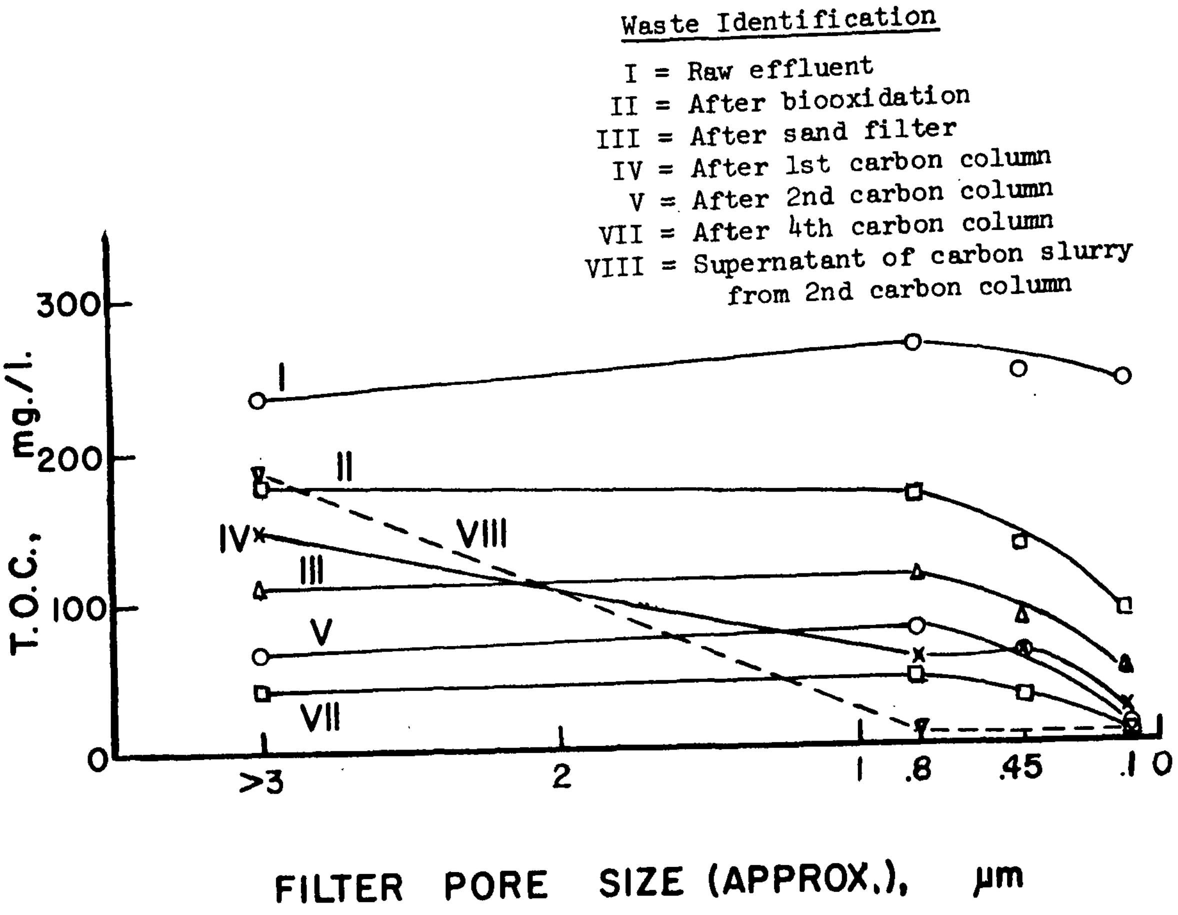


Figure 2. Total Organic Carbon of Various Wastes Passed Through Different Filters in Sequence.

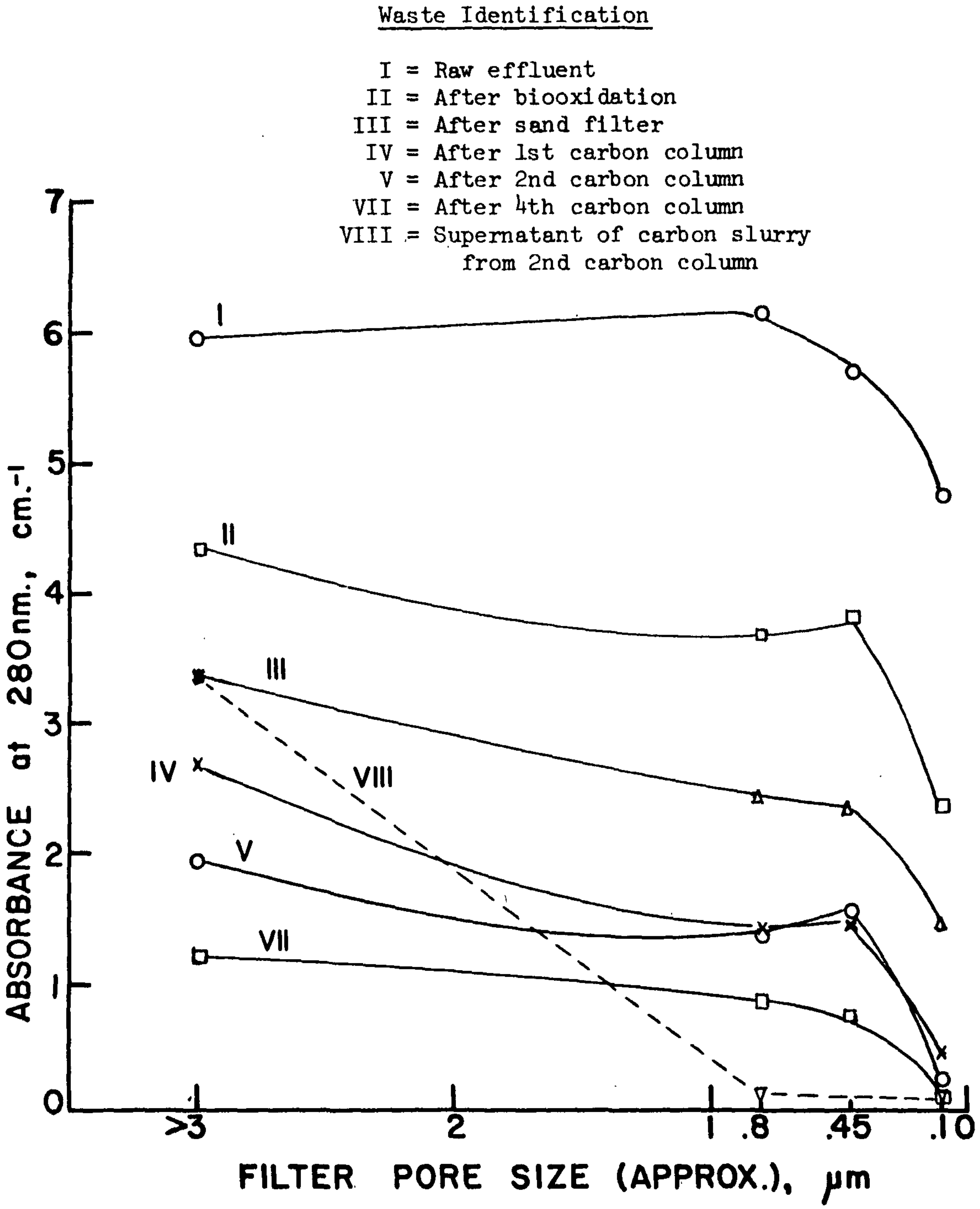


Figure 3. Absorbance of Various Wastes Passed Through Different Filters in Sequence

scattering, especially in the activated carbon-treated wastes. It seems logical to say that filtering through 0.8 µm. millipore filter is not enough and that this pore size is, therefore, not suitable for clearing a colloidal system that is present in these wastes.

With the thought that 0.1 µm. values should be more comparable, the color, T.O.C., absorbance, and absorptivity (absorbance/T.O.C. in g./l.) values of various wastes filtered through 0.1 µm. millipore filter are plotted against the treatment stages in Fig. 4. The waste treatments are in the same order as located in the mills treatment program.

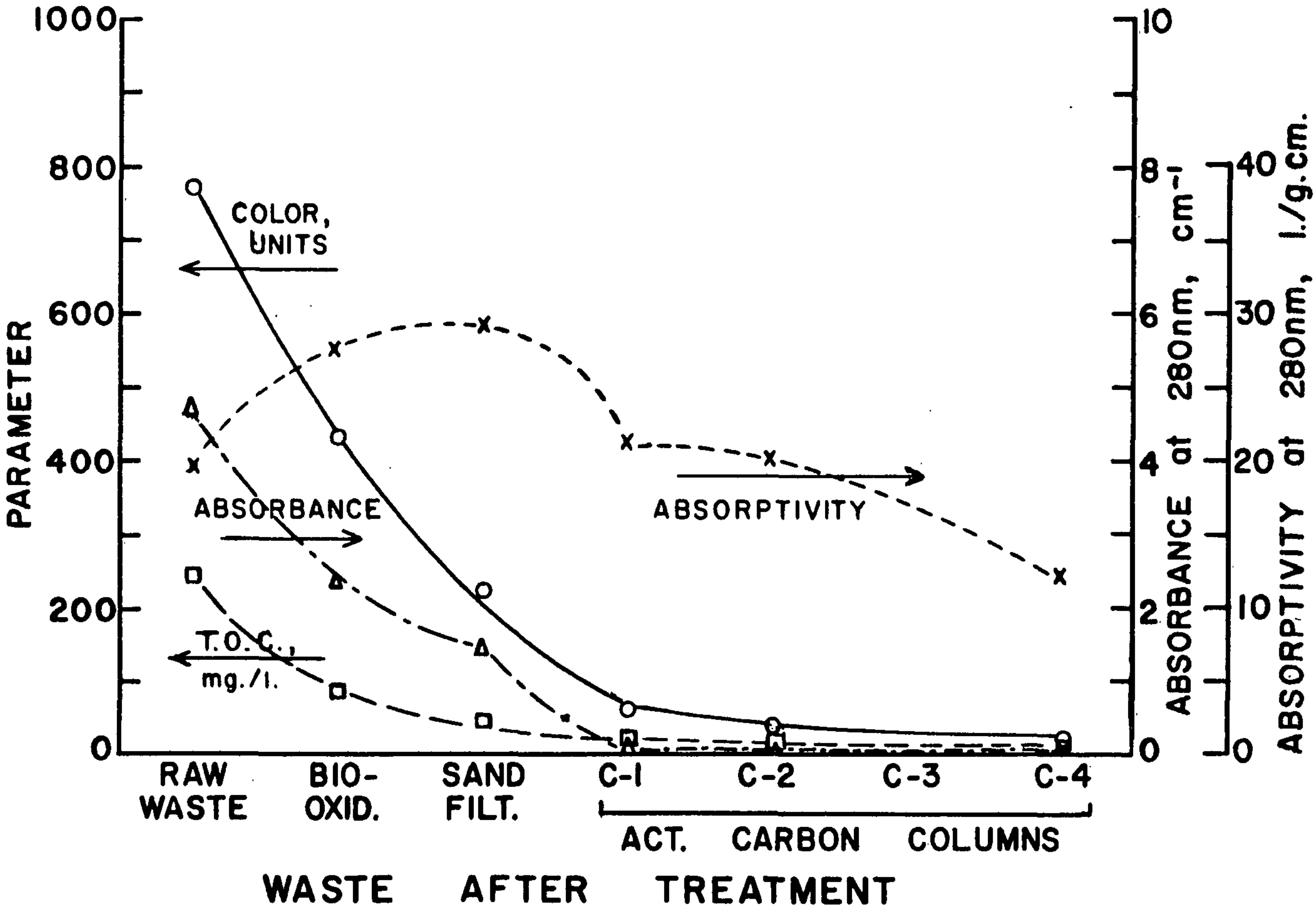


Figure 4. Color, Total Organic Carbon, Absorbance and Absorptivity of Various Wastes Filtered Through 0.1 µm. Millipore Filter

Figure 4 shows that color, absorbance, and T.O.C. values decrease sharply until after the wastes have come in contact with the 1st carbon column, and then the decrease is very slow. Absorptivity values, on the other hand, show an interesting fact. Absorptivity increases until after the waste has been passed through the sand filter, indicating that more of nonabsorbing carbon (kraft lignin absorbs more at 280 nm.) is being removed during biooxidation and sand-filteration steps. As soon as the waste comes in contact with the carbon column the absorptivity drops.

The efficiency of the treatment system at different stages was calculated from the data available. Cumulative percentages of removal of color and T.O.C., at different stages of treatment of wastes passed through various filters in sequence, were calculated taking raw waste as 100. Average percentage of removal was then determined from these values. Results are given in Table III and are plotted in Fig. 5 and 6. These figures show that maximum average removal of color and T.O.C. after carbon treatment is 86-87%. It is surprising to note that color and T.O.C. removal (about 20% each) occurs as the waste passes through the sand filter which probably acts as an ordinary filter as well as a trickling filter. No data in support of this mechanism are available at this time.

TABLE III

CUMULATIVE PERCENTAGE OF REMOVAL AT DIFFERENT STAGES OF TREATMENT

Treatment Stage	Removal, % Color	Removal, % T.O.C.
Biooxidation	35.5	43.3
Sand filter	56.0	63.8
Act. carbon columns		
C-1 (First)	73.6	71.3
C-2 (Second)	78.2	78.1
C-4 (Fourth)	86.2	87.2

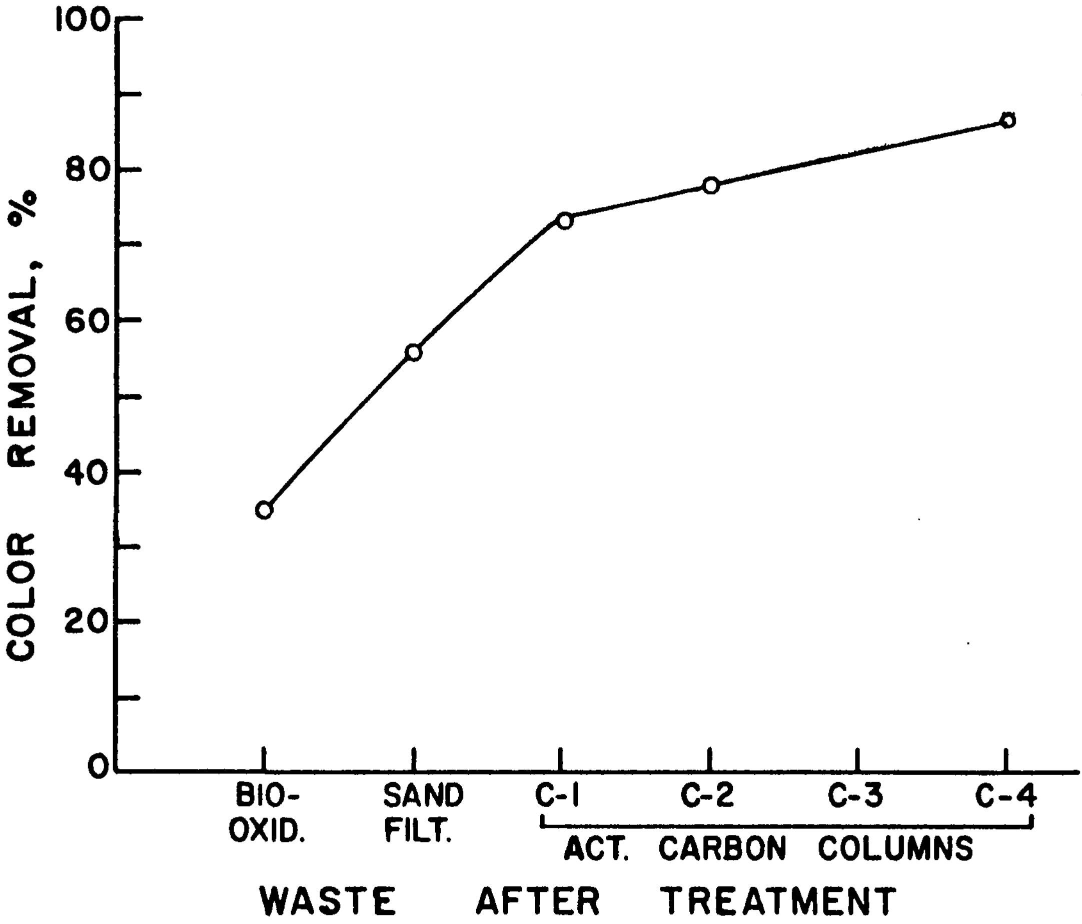


Figure 5. Cumulative Percentage of Color Removal at Different Stages of Treatment

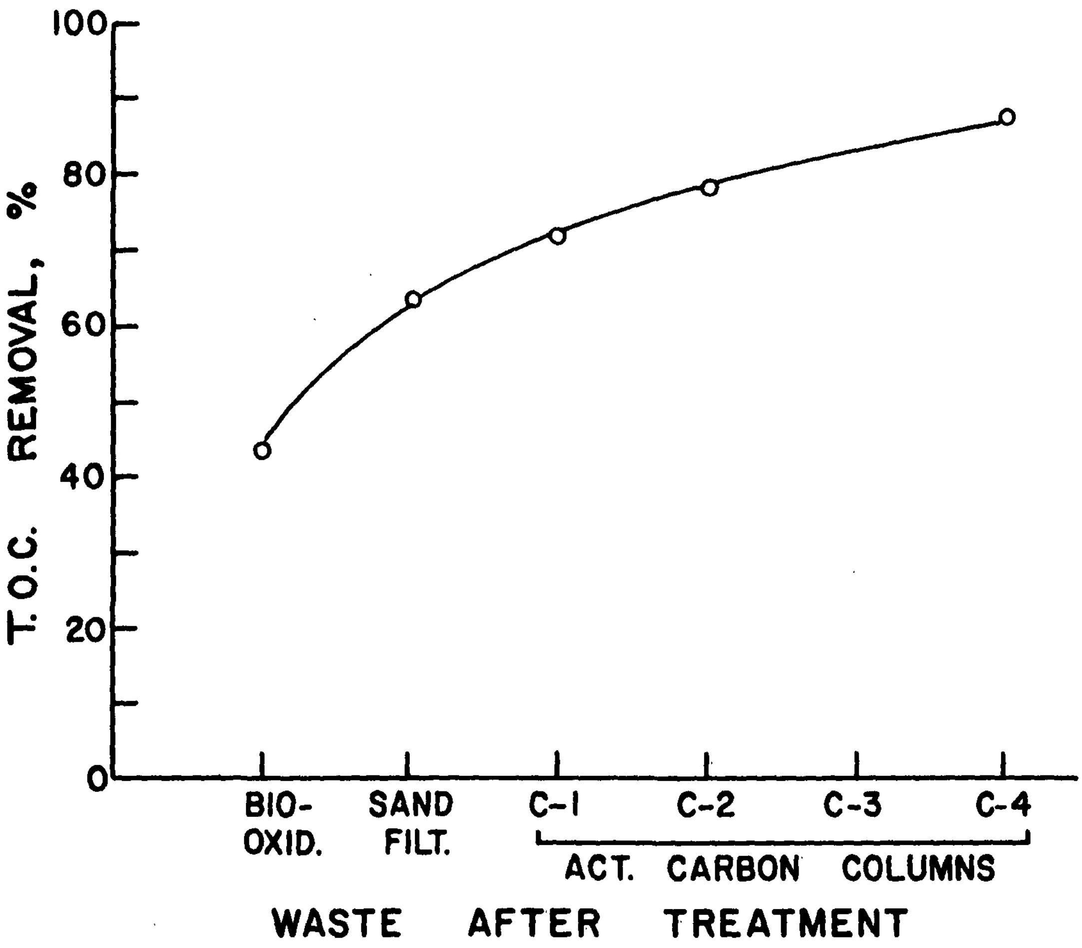


Figure 6. Cumulative Percentage of T.O.C. Removal at Different Stages of Treatment

EMISSION SPECTROGRAPHIC ANALYSIS

Mill wastes I through VIII were centrifuged at 3000 r.p.m. until clear. The solid material was washed once with water and centrifuged again on a bench top centrifuge. The water was decanted and the solids were dried in vacuum over P_2O_5. Emission spectrographic analysis was performed on the moisture-free solids. Activated carbon (unused Darco) was also analyzed.

Although the amounts fluctuated, the following metals were found in all samples without exception: Al, B, Ba, Ca, Cr, Cu, Fe, Mg, Mn, Na, Ni, Pb, Si, Ti, and Zn. The metals present in amounts above the measurable limits were totalled. The percentages of calcium and sodium were also not included in the totals. Further, the metals which give gray or black colored sulfides were totalled separately for each waste. The results are given in Table IV. Total percentage of metals which form black sulfides ranged from 0.75 to 3.04% of which 78.5-98% was iron. Even if these metals were present as sulfides in the wastes, their amounts (0.75 to 3.04%) were not enough to account for the quantity of material involved in the "reversion" of color, suggesting the presence of something other than metal sulfides which is responsible for the major portion of the black color.

INFRARED SPECTROSCOPIC ANALYSIS

Keeping in mind the observations at St. Regis Paper Company that an overall "true" color reduction was noticed during the carbon treatment, whereas the FPC (filter paper color) was found to increase manyfold and that this color was more black than brown, the following four samples were chosen for the infrared spectroscopic study.

Waste after biooxidation (Sample II)
C-2 slurry (Sample VIII)
C-2 slurry-EtOH (Sample VIII, ethanol washed)
Activated carbon (unused)

The activated carbon spectrum was used for comparison. Samples VIII, water-washed and ethanol-washed, were chosen because they had the highest FPC values and were black in color. Ethanol washing was carried out to desorb any organic impurities that might be present in this system, mainly because Sample

VIII was the supernatant from stirred-up carbon taken from the 2nd carbon adsorption column. Sample II (after biooxidation) was used as a control.

TABLE IV

EMISSION SPECTROGRAPHIC ANALYSIS OF UNTREATED AND CARBON TREATED MILL WASTES

Wastes	Total Metals, %	Total-S[a], %
Raw waste	2.6	1.13 (79.5% iron)
After biooxidation	6.9	0.79 (78.5)
After sand filter	2.8	0.75 (81.5)
After 1st carbon column (C-1)	7.3	2.83 (85.0)
After 2nd carbon column (C-2)	7.5	1.37 (80.5)
After 4th carbon column (C-4)	8.5	3.04 (89.0)
C-2 slurry[b]	11.4	1.53 (85.0)
C-2 slurry-EtOH[c]	11.5	1.53 (85.0)
Activated carbon	15.3	0.94 (98.0)

All values, except in parentheses, are calculated on moisture free centrifuged solids. The percent of Ca and Na have been excluded from the total.

[a] Total of metals which form gray or black sulfides. Values in parentheses are percent iron in individual total-S amounts.

[b] Supernatant from stirred-up carbon taken from 2nd carbon column. Supernatant was centrifuged to get solids and washed with water for this analysis.

[c] Same as "b" but washed with ethanol.

The samples were centrifuged until clear, and the centrifuged solids were mixed with potassium bromide, formed into pellets and used for IR-spectroscopic study. Infrared spectra obtained for the above four samples are given in Fig. 7.

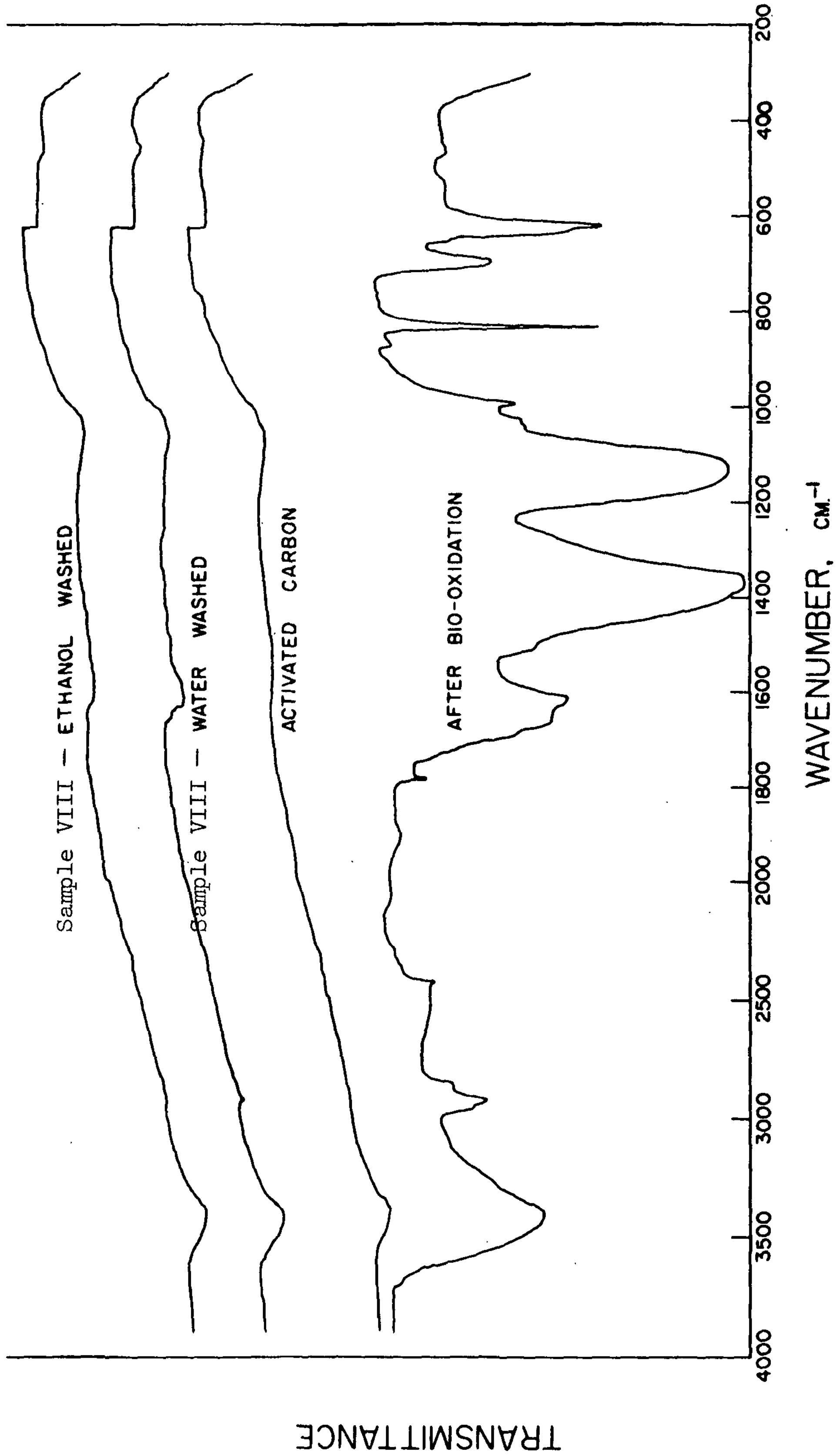


Figure 7. Infrared Spectra of Activated Carbon and Solids from Kraft Mill Waste Water After Biooxidation and Sample VIII (Supernatant from Stirred-up Carbon Taken from 2nd Carbon Column)

The control sample (i.e., waste after biooxidation) gave a number of absorption bands indicating the presence of hydroxyl groups (at 3400 cm.$^{-1}$), organic material giving C-H stretching vibrations of aliphatic CH_3- and CH_2-groups (2920 cm.$^{-1}$), color giving unsaturated conjugated groups containing carbonyl groups (1600-1700 cm.$^{-1}$), and possibly inorganic salts like sodium sulfate (1130 and 620 cm.$^{-1}$), and sodium nitrate (1785, 1370, and 833 cm.$^{-1}$). Aromatic structures probably contribute to the weak shoulder at 1505 cm.$^{-1}$. This is the only indication of the presence of lignin or lignin related materials. Other lignin bands may well be obscured by the intense bands of the inorganic components (the medium bands at 992 and 695 cm.$^{-1}$ are not good group frequencies and, therefore, no assignment can be made with any confidence).

The spectra of Samples VIII, water-washed and ethanol-washed, are similar to that of unused activated carbon in that very limited signs of functional groups are apparent. Weak -OH absorption is seen near 3400 cm.$^{-1}$ in all cases, which is almost certainly due to water absorbed on the potassium bromide during the preparation of the pellet. Water-washed Sample VIII showed some weak absorption at 1600 and 2910 cm.$^{-1}$ which became even weaker after ethanol washing indicating the removal of adsorbed organics by ethanol.

In summary, the material responsible for color "reversion" (Sample VIII) is similar to activated carbon.

X-RAY DIFFRACTION ANALYSIS

The samples (Sample VIII and activated carbon) were separately ground in an agate mortar and pestle and packed in a glass-bottomed aluminum sample holder. X-ray powder diagrams were prepared for these samples using a Norelco x-ray diffractometer and a Cu-tube with Ni-filter for CuKα radiation at 35 Kv. and 20 ma. The scanning rate was 0.5° 2θ per minute.

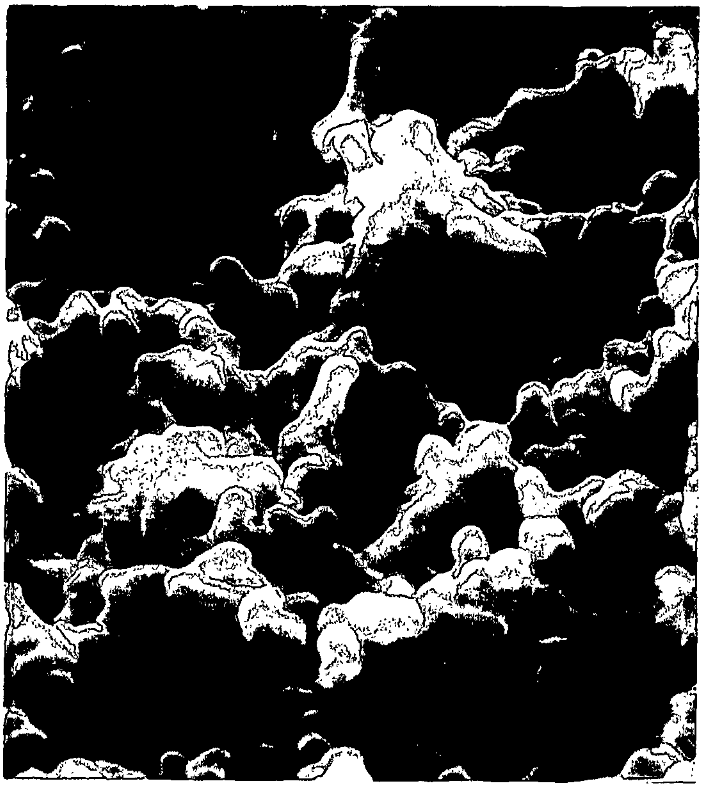
The diffractograms (not included in report) showed that both samples contained silica. Activated carbon contained slightly more than Sample VIII. It also had considerably larger amorphous background, a halo, but the general shape of the amorphous halo of the two samples was similar. The difference in intensity was due to the larger quantity of activated carbon sample used in the analysis. Since the two amorphous backgrounds are somewhat similar, it appears that the two samples are similar in composition.

SCANNING ELECTRON MICROSCOPIC (SEM) STUDY

Scanning electron microscopic study was conducted in order to be able to actually see the similarity between Sample VIII and the unused activated carbon. It was thought that such a study supported by IR and x-ray studies would pinpoint whether or not the material responsible for color "reversion" is actually carbon.

All samples were air dried on 0.8 μm. millipore filter, or clean metal stub. These were then coated with 200 A. of gold-palladium (60:40 mixture) before examining under the microscope. For such a study, millipore filters are not a requirement but as we already had used these in our filtration experiments, material retained on 0.8 μm. filters was examined under the scanning electron microscope (SEM).

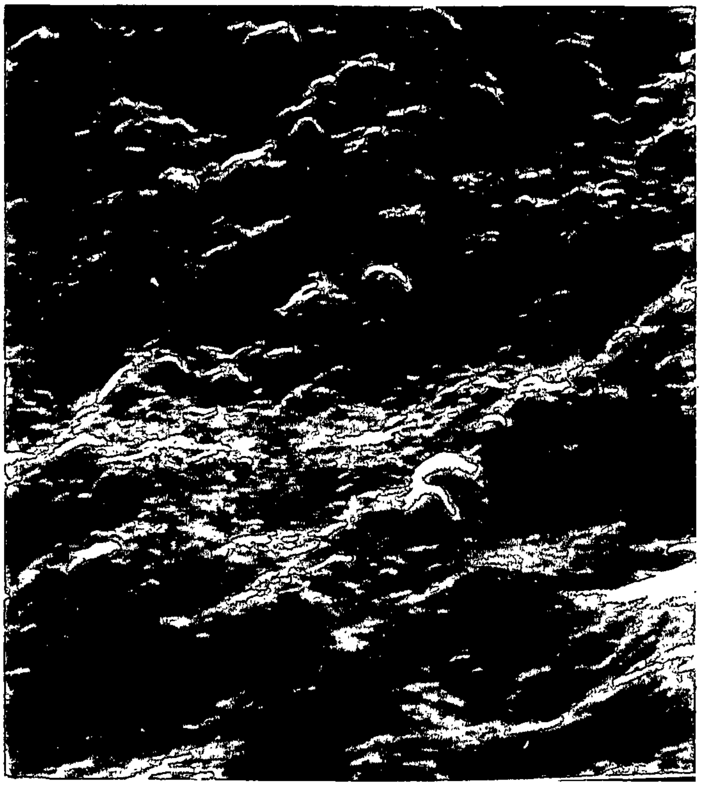
SEM micrographs at 10,000X magnification of 0.8 μm. millipore filter surface, Sample I (raw waste), Sample II (after biooxidation), Sample VII (after 4th column), Sample VIII (supernatant from stirred-up slurry from 2nd carbon column), and unused activated carbon surface are given in Fig. 8a-g.



a. 0.8 µm. Millipore Filter Surface
10,000X

Figure 8. Scanning Electron Micrograph

b. Sample I — Raw Waste
10,000X



c. Sample II — After
Biooxidation
10,000X

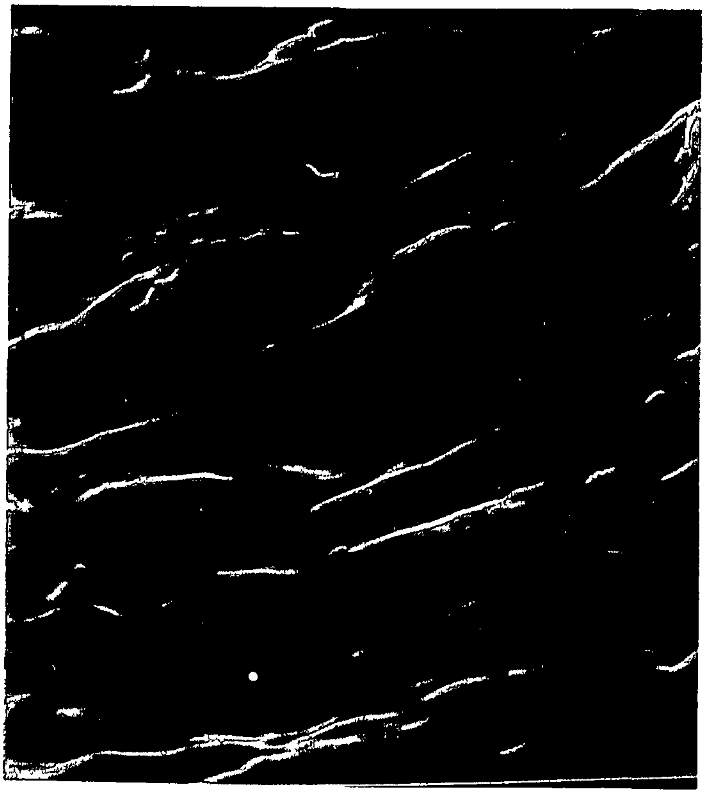
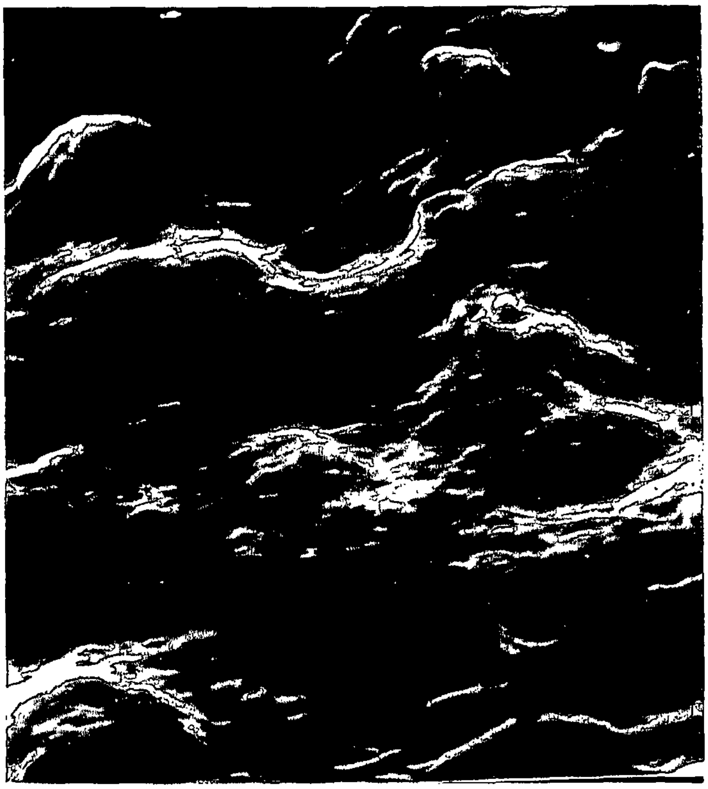


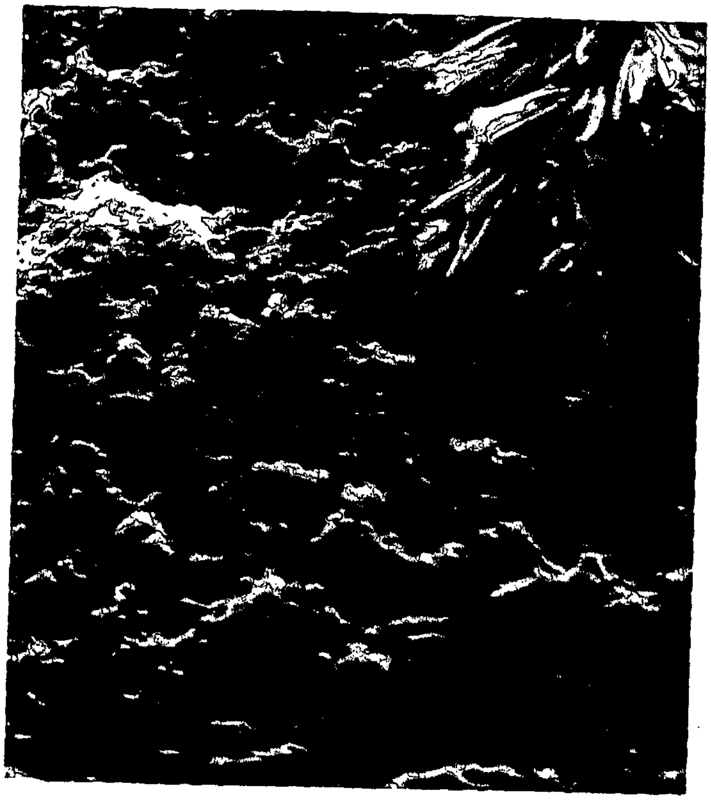
Figure 8 (Continued). Scanning Electron Micrographs

d. Sample VII — After 4th
Carbon Column
10,000X



e. Sample VIII — Supernatant
from Stirred-up Slurry
from 2nd Carbon Column
10,000X

Figure 8 (Continued). Scanning Electron Micrographs



f. Sample VIII — Diluted
10,000X

g. Unused Activated Carbon
10,000X

Figure 8 (Continued). Scanning Electron Micrographs

Samples I and II (Fig. 8b and 8c) contain a nongranular material which fills up the pores and evens out the filter surface (8a). A small amount of granular material is noticeable in Sample VII (upper half of Fig. 8d). Sample VIII (Fig. 8e), on the other hand, seems to be full of structured material which upon filtration deposits in multilayers. Sample VIII was, therefore, diluted twenty times its original concentration and dried on a metal stub. A sample of unused activated carbon was also prepared in this manner. Both samples (Fig. 8f and 8g) show similarity, suggesting the possibility that the material responsible for color "reversion" is carbon.

IDENTIFICATION OF THE SOURCE OF "COLOR BODIES" RESPONSIBLE FOR COLOR "REVERSION"

From the results obtained so far, it is clear that "carbon" is responsible for the major part of color "reversion." Data also suggest that the particle size of this "carbon" is in and above the colloidal range. (Metal sulfides may also partly contribute to color reversion.)

There could be two possible sources of 'carbon' in the system under study, namely, activated carbon used in adsorption columns and organic material present in mill effluents.

"Carbon" from activated carbon could go into a nonsettleable colloidal form by peptization. According to Mr. Edgar Dickey of the Institute, lignosulfonates are known to peptize carbon. Work done by him on kraft wastes and activated carbon also showed peptization of carbon.

Anaerobic digestion of organic material is known to give black smelly suspensions which probably contain "carbon" particles. We are also aware of the fact that anaerobic conditions exist in carbon columns. It is, therefore, safe to assume that "carbon" could have been produced by anaerobic digestion of organics in carbon columns. The most difficult job is to differentiate between "carbons" from these two different sources. To our knowledge, no analytical procedure for achieving this aim is available at this time.

We, therefore, tried to create anaerobic column conditions in the laboratory in order to pinpoint the source of colloidal carbon.

SIMULATION STUDIES OF ADSORPTION BY ACTIVATED CARBON

Sample II (after biooxidation) was filtered through Whatman No. 1 filter before use. Eighty ml. of this sample were mixed separately with unwashed- and ethanol-washed activated carbon (2 g. each). The mixtures were treated with N_2 or H_2S gas for 30 min. and were kept for 60 hours at room temperature. After this time the mixtures were filtered on tared filter papers, washed 8 times with ethanol and dried at 105°C. for 3 hours. Loss or gain in the weight of activated carbon was then determined on an o.d. basis. Results are given in Table V.

TABLE V

SIMULATION STUDIES OF ADSORPTION COLUMNS

Expt. No.	Treatment	Supernatant Color	Loss or Gain, %
1	Waste + C-EtOH	Amber, clear	-0.22
2	Waste + C-EtOH + N_2	Amber, clear	-0.36
3	Waste + C-EtOH + H_2S	Murky amber	+1.36
4	Waste + H_2S	Murky yellow	None
5	Waste + C (unwashed) + H_2S	Murky gray	-8.7

Note: Waste = 80 ml. of Sample II (after biooxidation).
C-EtOH = Activated carbon washed with ethanol.
N_2 and H_2S gases were bubbled through the solutions for 30 min.

Maximum loss (8.7%) occured when unwashed carbon was used. No black or gray precipitates were obtained when Sample II was treated with H_2S (Experiment 4) ruling out the formation of metal sulfides, which are gray or black in color. Even if such sulfides are formed their overall effect on "reversion" seems negligible. The gain in weight in Experiment No. 3 is probably due to the sorption of metal sulfides on carbon. From Table V it is clear that losses, although small, do occur during such treatments, indicating the possibility of peptization of activated carbon. One must keep in mind that, in a very complex system such as adsorption columns, peptization may be one of the solutions to the problem.

SEM STUDIES

Scanning electron micrographs of the supernatant from the following mixtures were prepared (Fig. 9a-c) and compared with the ones in Fig. 8a-g.

Sample II + carbon (Fig. 9a)
Sample II + H_2S (Fig. 9b)
Sample II + carbon + H_2S (Fig. 9c)

Study shows that Fig. 9a is similar to 8e and 9c to 8d, indicating the presence of "carbon." This, however, is no proof. No "carbonlike" character was noticeable in the sample containing waste and H_2S only.

a. Sample II + Carbon
10,000X

b. Sample II + H_2S
10,000X

Figure 9. Scanning Electron Micrographs

c. Sample II + Carbon + H_2S
10,000X

Figure 9 (Continued). Scanning Electron Micrographs

RECOMMENDATIONS FOR THE SOLUTION OF THE "REVERSION" PROBLEM

1. Carbon should be thoroughly washed before use, preferably before packing in columns.

2. A filtering device after the 4th carbon column should be used. Sand filter may be tried.

3. Minimum quantities of polyelectrolytes may be used to flocculate colloidal carbon before the sand filter located after the 4th carbon column.

4. Simulation studies of adsorption columns on a large scale should be performed in the laboratory to check losses due to peptization of carbon and/or carbon production during anaerobic digestion of kraft mill wastes.

CONCLUSIONS

The following conclusions are drawn from a study on the causes for increase (termed as "reversion") in the filter paper color (FPC) during the treatment of kraft wastes with activated carbon. FPC was defined as the color of mill waste water after it has been filtered through an ordinary filter paper.

1. "Color bodies" responsible for color "reversion" are predominantly carbon particles in the colloidal or larger particle size range.
2. Metal sulfides play little part in color "reversion."
3. Activated carbon used for adsorption seems to be the source of colloidal carbon responsible for color "reversion."
4. Studies indicate that products from the anaerobic digestion of organics in carbon columns contribute very little, if at all, to color "reversion."

ACKNOWLEDGMENTS

The authors wish to thank Mr. Norman L. Colson and Drs. R. A. Parham, D. C. Johnson, and Robert M. Leekley for their help in areas of their specialty.

The support of this work by the Office of Research & Monitoring, Environmental Protection Agency and the help provided by Mr. George R. Webster is acknowledged with sincere thanks.

THE INSTITUTE OF PAPER CHEMISTRY

Dugal

Hardev S. Dugal
Research Associate

John W. Swanson

John W. Swanson, Director
Division of Natural
Materials & Systems