



Project Summary

Technology Evaluation for Priority Pollutant Removal from Dyestuff Manufacture Wastewaters

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Laboratory-scale studies were conducted to establish the technical feasibility of employing certain processes, including ozonation, GAC adsorption and biophysical (PACT) treatment, for the treatment of dyestuff manufacture wastewaters with special focus on the removal of organic priority pollutants. The GAC adsorption studies showed that GAC provided for excellent removals of both color and priority pollutants but cannot be expected to concomitantly provide for high levels of SOC removal due to comparatively high levels of non-adsorption organics that occasionally are present in dyestuff manufacture wastewaters. Excellent removals of organic priority pollutants were achieved by the PACT process. In addition, SOC and color removals were enhanced by the addition of PAC to an activated sludge system, generally in direct relation to the steady-state concentration of PAC in the reactor. Although ozonation provided for the removal of many organic priority pollutants to levels below detectability, some proved to be comparatively resistant to oxidation by ozone. As for GAC and the PACT process, ozonation provided excellent color removals. Only moderate organic carbon removals were achieved by ozonolysis, however.

A priority pollutants survey showed the presence of a total of 23 organic priority pollutants in the raw wastewaters. With the exception of methylene chloride, removal levels of volatile organic priority pollutants generally exceeded 95 percent.

This Project Summary was developed by EPA's Industrial Environmental Re-

search Laboratory, Cincinnati, OH, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

Many different types of manufacturers of synthetic organic chemicals recently have focused their attention on the treatment and control of toxic chemicals that are contained in their wastewater discharges. One such industry is the dyestuff manufacturing industry. Previous studies conducted on wastewaters obtained from this industry established that ozonation, adsorption on granular activated carbon, and biophysical (powdered activated carbon/biological, PACT) treatment were well suited for removing conventional pollutants from dyestuff manufacture wastewaters and had significant potential for removing priority pollutants from these wastewaters as well. Accordingly, the principal objectives of the present research program were (1) to exhaustively identify and quantify those priority pollutants contained in dyestuff manufacture wastewaters and to establish the performance characteristics of existing BPT (best practical treatment) with respect to the removal of priority pollutants, and (2) to affirmatively establish the effect of the three selected candidate BAT (best available treatment) treatment processes on the removal, conversion, and/or production of priority pollutants.

To ensure that the results of this research program were representative of the entire dyestuff manufacturing industry, studies had to be conducted on a representative number of dyestuff manufacture wastewaters. To select those that were to be included in the

study, the Dyes, Environmental and Toxicology Organization, Inc. was asked to solicit volunteer member companies who would participate. This solicitation resulted in the identification of ten dyestuff manufacturers that indicated a willingness to participate. Because this number was greater than could be accommodated within the budgetary constraints of the cooperative agreement, six dyestuff manufacturers, coded A through F, were selected to participate in the survey. This selection was made on the basis of the following criteria: (1) raw wastewater conventional pollutant characteristics, (2) treated wastewater conventional pollutant characteristics, (3) wastewater treatment plant design characteristics, (4) wastewater treatment plant operational characteristics, (5) class(es) of dyestuff produced, and (6) types of non-dyestuff products manufactured. The six selected were judged to be the most representative of the entire dyestuff manufacturing industry.

Dyestuff Manufacturing Industry Survey

The primary objective of this study was to establish the technical feasibility of employing granular activated carbon adsorption, ozonation, and the PACT process for the removal of priority pollutants from dyestuff manufacture wastewater. Also a study designed to establish the performance characteristics of existing wastewater treatment plants at participating dyestuff manufacturers with respect to the removal, conversion and/or production of priority pollutants was conducted.

Survey Results

To provide the proper perspective for interpretation of these treatability results, it is important to point out that each of the dyestuff manufacturers that were included in the survey had extensive wastewater treatment facilities. Each had provisions for neutralization followed by a conventional activated sludge system that was coupled with an associated sludge handling train. The activated sludge systems were operated at nominal solids residence times (SRTs) that ranged from 7 to 25 days and hydraulic residence times (HRTs) that ranged from 18 to 36 hours. This configuration and associated operational conditions are relatively typical of the dyestuff manufacturing industry.

Several of the manufacturers also had adjunct processes such as granular activated carbon adsorption for the liquid processing train. These adjunct processes, however, are not significant to this analytical survey for

priority pollutants because all samples that herein are reported as effluent samples were collected at the discharge of the solids-liquid separator following the aeration basin and not necessarily at the discharge from the entire wastewater treatment plant. This was done to ensure comparability of the data collected. All influent samples were collected either immediately before or after neutralization, depending on which was most feasible at a particular site.

Organic Priority Pollutants

The results of all analyses conducted for organic priority pollutants are recorded in Table 1. Of the volatile organic priority pollutants found in the four influent wastewater samples, only chlorobenzene and toluene were found in all four samples. Ethylbenzene was noted to be present in three of the four samples. All other volatile organics found were present only as single occurrences. Only toluene and ethylbenzene were detected at concentrations greater than the milligram per liter level.

As expected, removal levels of the volatile organics were very high in the activated sludge systems due to the stripping that occurs as a result of aeration. With the exception of methylene chloride, removal levels generally exceeded 95 percent. Many of the volatile organic materials were removed to levels below detectability.

Of the acid and base/neutral extractable compounds that were found in the influent samples, only phenol, 2,4-Dinitrophenol and Bis (2-chloroethyl) ether were found to be present at concentration levels that exceeded 1 mg/l. Although most acid and base/neutral extractable compounds were removed significantly from the aqueous stream by the activated sludge system, many compounds were found to be present at significant levels even after treatment. This was particularly true in the case of 2,4-Dinitrophenol which was present at a concentration of approximately 4 mg/l after treatment in Wastewater Sample B. Only several compounds were present at less-than-detectable concentration levels after treatment.

Heavy Metal Priority Pollutants

All results for heavy metal determinations conducted on Wastewater Samples A, C, and D are given in Table 2; no analyses were conducted on Sample B. Analysis of these data clearly shows that only minor removals of heavy metal priority pollutants were achieved by the respective activated sludge treatment systems. Only in the case of cadmium, copper, antimony and nickel were significant levels of removal achieved, but then only in the case of Wastewater Sam-

ple C. On the basis of these results, one may conclude that the removals achieved were not significant.

GAC Adsorption Treatment Technology

Adsorption Equilibria

Experimental Methodology

Adsorption isotherms were developed using the conventional static bottle technique. This involved placing various selected weights of Calgon Filtrasorb 400 (20 x 30 mesh) into 120 ml French Square bottles and adding 100 ml of the appropriate wastewater. After filling, the isotherm bottles were placed on a gyratory shaker which was operated at 200 cpm. All bottles were removed from the shaker after a ten-day equilibration period since it had been demonstrated that adsorption equilibrium was attained in approximately seven days. The contents of each bottle was then filtered through a 0.45-micrometer millipore filter. Aliquots for soluble organic carbon (SOC) analysis were acidified, using hydrochloric acid, to a pH less than 2 and stored at 4°C in 30 ml screw cap vials until analyzed.

SOC Adsorption Results

Two series of isotherm studies were performed. One was conducted directly on the wastewater itself, and the second was conducted on wastewater samples that had been pretreated by ozonation in an effort to enhance the adsorption characteristics of the organic materials in the wastewater. These latter samples were pretreated at ozone dosage levels that corresponded to those prescribed below for the ozonation studies that were designed for priority pollutant removal.

Analysis of the isotherm data is facilitated by comparison of several adsorption indexes. These include (1) the non-adsorbable fraction, obtained by the intersection of the isotherm trace and the abscissa; (2) the GAC solid-phase concentration or "loading" at the operational-feed concentration; and (3) the associated calculated GAC exhaustion rate. Values for these parameters are summarized in Table 3.

Non-adsorbable organics, usually low molecular weight materials, were present in each of the six raw wastewater samples studied. Significant differences were observed in the level of non-adsorbable organics between the various samples. Samples A through E had non-adsorbable concentrations that ranged from 11 to 75 g SOC/m³, as noted in Table 3. These were in stark contrast to Sample F which had an

Table 1. Organic Priority Pollutant Concentrations Before and After Onsite Activated Sludge Treatment

Sample	Organic Priority Pollutant Observed	Influent ($\mu\text{g/l}$)		Effluent ($\mu\text{g/l}$)	
		Dup #1	Dup #2	Dup #1	Dup #2
A	Acid Extraction				
	2-Nitrophenol	460	[†] -	33	55
	2,4-Dinitrophenol	2700	-	420	440
	Phenol	3200	-	130	190
	Base/Neutral Extraction				
	1,3-Dichlorobenzene	420	-	3.4	3.7
	1,4-Dichlorobenzene	800	-	27	27
	Naphthalene	4.0	-	3.9	4.1
	Acenaphthene	21	-	4.6	4.9
	N-Nitrosodiphenylamine	150	-	4.0	3.6
	Volatiles				
	Toluene	4000	3600	14	11
	Chlorobenzene	180	190	*ND	ND
	Ethylbenzene	270	290	ND	ND
B	Acid Extraction				
	2,4-Dichlorophenol	18	-	*ND	ND
	2,4-Dinitrophenol	5300	-	3900	4700
	Base/Neutral Extraction				
	1,4-Dichlorobenzene	3200	-	11	13
	Nitrobenzene	350	-	91	100
	Di-n-butylphthalate	23	-	ND	ND
	Volatiles				
	Methylene Chloride	5.5	5.5	0.48	0.38
	Chloroform	31	33	ND	ND
	Toluene	800	780	7.2	7.9
	Chlorobenzene	550	550	12	13
C	Acid Extraction				
	2-Nitrophenol	7.7	-	6.6	11.0
	Phenol	4900	-	6.7	6.5
	Base/Neutral Extraction				
	Bis (2-chloroethyl) ether	4700	-	*ND	ND
	N-Nitrosodiphenylamine	310	-	ND	ND
	Volatiles				
	Cis-1,3-Dichloropropene	4.7	5.6	ND	ND
	Toluene	160	160	27	19
	Chlorobenzene	120	100	ND	ND
	Ethylbenzene	4000	4000	ND	ND
D	Acid Extraction				
	2-Nitrophenol	26	-	*ND	ND
	Phenol	150	-	<20	<20
	2,4-Dichlorophenol	^{††} <20	-	<20	<20
	Base/Neutral Extraction				
	1,3-Dichlorobenzene	18	-	1.2	1.2
	1,4-Dichlorobenzene	68	-	4.9	4.9
	Nitrobenzene	660	-	2.6	4.3
	1,2,4-Trichlorobenzene	230	-	36	37
	Naphthalene	120	-	<1.0	<1.0
	Phenanthrene	4.5	-	ND	ND
	Volatiles				
	Carbon Tetrachloride	55	62	ND	ND
	1,1,1-Trichloroethane	220	200	ND	ND
	Trans-1,3-Dichloropropene	130	100	2.9	2.5
	Toluene	7800	7400	300	270
	Chlorobenzene	36	39	ND	ND
	Ethylbenzene	67	55	ND	ND

*ND means not detected (no chromatogram).

[†]- means not measured.

^{††}< means a chromatogram was observed, but response was insufficient to quantify.

extremely high non-adsorbable concentration of 590 g SOC/m³. Pretreatment of these wastewater samples served to alter the non-adsorbable fraction of organic materials only slightly. Generally, ozonation led to an increase in the non-adsorbable fraction in all samples with the exception of Sample E.

Calculated GAC exhaustion rates must be indexed to the operational aqueous-phase feed concentration of organics that one would expect to be present in the feed stream to the adsorber. For the present studies, the feed stream concentrations were assumed to be equal to the concentration of organics that existed in the samples either before or after ozonation. These are tabulated in the third column of Table 3, while the associated calculated GAC exhaustion rates are tabulated in the last column. Generally, it is apparent that the GAC exhaustion rates vary rather dramatically from one dyestuff manufacturing wastewater sample to another. In all but two cases, ozonation pretreatment led to an increased GAC exhaustion rate. In the case of Sample B, the slightly lower GAC exhaustion rate was due to the greater non-adsorbable fraction that was present after ozonation. Conversely, the lower GAC exhaustion rate for Sample E was due primarily to the fact that ozonation served to significantly increase the adsorption capacity. This was the only sample for which this observation was made. For all other samples the adsorption capacity either decreased or did not change appreciably.

Continuous-Flow Adsorption Studies

Experimental Methodology

Since this phase of the research focused on the ability of GAC to remove priority pollutants from dyestuff manufacture wastewaters, a continuous-upflow GAC adsorption system was constructed using five columns-in-series. The columns and their connecting lines were constructed of glass to minimize the adsorption of organics onto column surfaces. Each column was 1.2 m in length and 2.54 cm in internal diameter. The inlet section of each column was filled with 3 mm glass beads to a depth of 20 cm to provide for even distribution of flow across the surface of the GAC bed. Each column was charged with 203 gm of the 20 x 30 mesh Calgon Filtrasorb 400 GAC. Prior to each run, the GAC was immersed in distilled water for 24 hours to ensure complete wetting of the GAC prior to operation.

These experiments were conducted by passing each of the dyestuff manufacture wastewaters through the columnar GAC adsorbers that were charged with virgin GAC.

Table 2. Heavy Metal Priority Pollutant Concentrations Before and After Onsite Activated Sludge Treatment

Sample	Heavy Metal Priority Pollutant Observed	Influent ($\mu\text{g/l}$)	Effluent ($\mu\text{g/l}$)
A	Cadmium	22	17
	Chromium	142	134
	Copper	23	24
	Antimony	33	33
	Lead	111	66
	Nickel	140	102
	Zinc	56	56
	Thallium	45	¹ <5
	Silver	30	15
	Arsenic	114	83
C	Cadmium	124	28
	Chromium	12	12
	Copper	3250	82
	Antimony	176	59
	Lead	*ND	ND
	Nickel	160	80
	Zinc	14	288
	Thallium	ND	ND
	Silver	ND	ND
	Mercury	3	4
	Arsenic	ND	ND
	Selenium	20	12
D	Cadmium	8.7	12.5
	Chromium	180	<500
	Copper	5650	4750
	Antimony	200	200
	Lead	130	130
	Nickel	130	130
	Zinc	70	70
	Thallium	*ND	125
	Silver	ND	ND

*ND means Not Detected.

¹< means response was observed, but was insufficient to quantify.

Table 3. GAC Adsorber Design Factors for SOC Removal

Wastewater Sample	Non-Ads. Fraction (g SOC/m ³)	Oper. Feed Conc. (g SOC/m ³)	Ads. Cap. at Feed Conc. (g SOC/kg GAC)	GAC Rate of Exhaustion (kg GAC/1000 m ³)
No Pretreatment				
A	11	160	165	903
B	40	181	165	850
C	75	320	105	2330
D	70	290	175	1260
E	45	445	128	3120
F	590	960	140	2640
Ozone Pretreatment				
A	14	148	100	1340
B	50	189	165	840
C	75	300	87	2590
D	91	300	160	1310
E	22	390	190	1940
F	600	995	135	2930

The wastewater was placed in a 50-liter carboy that was mixed with air to maintain homogeneity, was allowed to equilibrate at room temperature, was sampled for priority pollutant analysis, and was passed through

the GAC columns using a peristaltic pump. The flow rate through the columns was set at 0.082 m/min (2 gpm/sq ft) which provided an empty bed residence time of 45 minutes for all five columns. The wastewater was

pumped through the system to waste for a period of four hydraulic retention times to ensure displacement of the distilled water. Thereafter, the system effluent was collected in a thirteen-liter glass carboy for a period of four hours. At the end of each run conducted on a dyestuff manufacture wastewater, the total effluent was mixed and sampled for subsequent priority pollutant analysis.

Priority Pollutant Adsorption Results

The results of these GAC adsorption studies are given in Table 4. No analyses for volatile organic priority pollutants were conducted in this study. The analytical program was limited to the acid and base/neutral extractable priority pollutant fractions.

Results for all samples showed that in all cases GAC adsorption effectively removed all of the priority pollutants initially present in the wastewater to below detectable levels. Since these results were achieved for five dyestuff manufacture wastewaters that have widely divergent compositions and matrixes and had widely varying concentrations of priority pollutants, it appears safe to conclude that GAC adsorption appears to be a reasonably universal treatment technology for the removal of organic priority pollutants, neglecting economic considerations. It is important to note, however, that adsorber design criteria were not elaborated by these studies. Such criteria can only be developed by conducting extensive pilot-scale studies.

Biophysical (PACT) Treatment Technology

A typical flowsheet of the biophysical or PACT treatment system involves the addition of powdered activated carbon (PAC) to the aeration basin of a conventional activated sludge treatment process. The addition of PAC to the aeration basin provides for increased removals of BOD, COD, TOC, color, and toxic compounds; provides for added stability of the biological process; and improves the settling characteristics of the sludge. PAC addition also allows for adsorption of organic compounds, provides surfaces for biological attachment, and creates the possibility for the elaboration of beneficial biomass-PAC interactions.

Experimental Methodology

The experimental program was limited to evaluating this process on three dyestuff manufacture wastewaters, Samples A, B, and F. These were carefully selected to ensure that the wastewaters generated from the production of three distinctly different product line mixes were evaluated to obtain the broadest-based technology evaluation information possible.

Table 4. Organic Priority Pollutant Concentrations Before and After GAC Treatment

Sample	Organic Priority Pollutant Observed	Influent ($\mu\text{g/l}$)		Effluent ($\mu\text{g/l}$)	
		Dup #1	Dup #2	Dup #1	Dup #2
A	Acid Extraction				
	Phenol	110	120	*ND	ND
	2,4-Dinitrophenol	350	340	ND	ND
	Base/Neutral Extraction				
	2-Nitrophenol	40	35	ND	ND
	1,4-Dichlorobenzene	3.4	3.1	ND	ND
B	Naphthalene	1.6	1.4	ND	ND
	Acid Extraction				
	2,4-Dichlorophenol	1.3	1.3	ND	ND
	2,4-Dinitrophenol	3200	3300	ND	ND
	Base/Neutral Extraction				
	1,4-Dichlorobenzene	5.0	6.2	ND	ND
C	Nitrobenzene	51	47	ND	ND
	Di-n-butylphthalate	22	24	ND	ND
	Acid Extraction				
	Phenol	1900	-	ND	ND
	Base/Neutral Extraction				
	Bis (2-chloroethyl) ether	2300	-	ND	ND
D	N-Nitrocodiphenylamine	29	-	ND	ND
	Acid Extraction				
	Phenol	240	-	ND	ND
	Base/Neutral Extraction				
	1,3-Dichlorobenzene	1.4	-	ND	ND
	1,4-Dichlorobenzene	9.4	-	ND	ND
F	Nitrobenzene	830	-	ND	ND
	1,2,3-Trichlorobenzene	8.5	-	ND	ND
	Naphthalene	26	-	ND	ND
	Acid Extraction				
	Phenol	57	59	ND	ND
	Base/Neutral Extraction				
	Di-n-octylphthalate	1800	1800	ND	ND

*ND means Not Detected.

Approximately 1.51 m³ of raw wastewater was collected from the equalization basin of each of the three wastewater treatment systems sampled. The waste was stored at 4°C to minimize degradation and was neutralized to pH 7.0. The requisite nutrients, essential for biological growth, were added prior to use as reactor feed.

Nuchar S-A 15,* manufactured by Westvaco Corporation, was the powdered activated carbon (PAC) used in this study. Due to the fact that biological plate counts showed the presence of significant concentrations of microorganisms in the virgin PAC, the PAC was sterilized in an autoclave prior to use and then stored at 103°C. Daily PAC make-up requirements were supplied to the PACT reactors using an aliquot of a 10 kg/m³ aqueous PAC slurry. Changes in reactor PAC concentration, however, were made by adding a specific weight of dry PAC.

The laboratory-scale, continuous-flow reactor system consisted of a glass percolator which was fitted with a diffuser through which compressed air, which has been filtered and humidified, entered the bottom of the reactor vessel. This provided for completely mixed aerobic conditions in the reactor. Exhaust gases were drawn off through a vacuum connection. Feed solution was supplied to the reactors by a peristaltic pump. The wastewater passed from a completely-mixed, 20-l plastic feed tank to the reactor vessel through tygon tubing. Cam cycle timers were used to aid in control of the flowrate such that low flow rates (2.08 ml/min) could be achieved.

Treated wastewater was removed directly from the reactor by a vacuum line connected to a cylindrical vyon cup. The vyon cups allowed the soluble portion of the treated wastewater to pass into the effluent collection bottles while eliminating most biological solids. This provided for positive control of the biological and PAC solids contained within the reactor.

To determine the effectiveness of the PACT process for treating the dyestuff manufacture wastewaters, two reactors were run in parallel for each of the three wastewaters studied. One system was operated as a conventional activated sludge process and the other, containing PAC, was operated as a PACT system. Both systems were operated at a nominal solids residence time of 20 days and a nominal hydraulic residence time of 24 hours.

Reactor start-up consisted of charging both the biological and biophysical reactors with 3 liters of mixed liquor obtained from the aeration basin of one of the dyestuff manufacturer's activated sludge wastewater treatment facilities. An initial aliquot of nutrients was also added to both of the reactors to promote biological growth and to shorten the acclimation period, while an appropriate amount of prewashed, dry, sterilized PAC was added to the biophysical reactor. An initial acclimation period of 40 days was necessary to develop an adequate population of acclimated microorganisms. During this period, the flow rate to the reactors was set to maintain a one-day hydraulic residence time (HRT). Biological and biophysical solids were wasted daily by removing 150 ml of the mixed liquor from each reactor to maintain a solids residence time (SRT) of 20 days. To account for the loss of PAC from the biophysical system due to wasting, an appropriate quantity of virgin PAC was subsequently added to maintain a steady-state PAC concentration in the reactor.

During the acclimation period daily measurements of pH, suspended solids, and soluble organic carbon (SOC) were made to follow the operating conditions of the system. Adjustments in pH were made to maintain the pH of the system in the range of 6.5 to 7.5. The SOC levels in the influent to and the effluent from each reactor were monitored daily to establish the onset of steady-state conditions. Once steady state had been achieved (determined on the basis of SOC analyses), effluent samples were collected from each reactor and analyzed for color, organic priority pollutants, and heavy metals.

SOC Removal Results

Based on PAC isotherm studies, four PAC reactor concentration levels, 1, 3, 5, and 7 kg/m³, were selected for experimental evaluation. A parallel or "control" biological reactor that received no PAC feed was operated under identical conditions throughout the duration of the study.

Summarized data for these studies are shown in Table 5. Qualitative analysis of the data shows that PAC addition to an activated

*Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

Table 5. SOC Removals Obtained in Parallel PACT and Biological Reactor Systems

Steady-State PAC Conc. (g/m ³)	Influent SOC Conc. (g/m ³)	Biol. Eff. SOC Conc. (g/m ³)	PACT Eff. SOC Conc. (g/m ³)	Biol. Rem. Efficiency (%)	PACT Rem. Efficiency (%)	Sig. Dif. Between Systems @ 95% Conf. Level
Wastewater Sample A						
1000	250	103	102	58.8	59.2	no
3000	217	99	65	54.5	70.0	yes
5000	236	96	51	59.3	78.4	yes
7000	240	101	49	57.9	79.6	yes
Wastewater Sample B						
1000	164	106	97	35.4	41.0	yes
3000	142	107	68	24.6	52.0	yes
5000	171	105	58	38.6	66.0	yes
7000	157	105	52	33.1	66.7	yes
Wastewater Sample F						
1000	664	380	357	42.8	46.2	no
3000	814	489	433	39.9	46.7	yes
5000	817	352	373	56.9	54.3	no
7000	857	481	389	43.9	54.6	yes

sludge system appears to enhance system performance and that system performance improved with increasing steady-state concentrations of PAC in the reactor up to 5 kg/m³. Performance did not increase substantially for PAC concentrations greater than 5 kg/m³.

To provide a more rigorous interpretation of the data, the significance of the differences between the observed removal efficiencies for the PACT and activated sludge systems was determined using the "t" statistical test. Reference to the last column of Table 5 shows that, at steady state, the PACT system was statistically more efficient in removing SOC in nine of the 12 experiments conducted. Exceptions were noted for wastewater sample A (PAC level of 1 kg/m³) and wastewater sample F (PAC levels of 1 and 5 kg/m³). In the case of sample F, this occurrence is likely due to the fact that a significant quantity of the soluble organic carbon present in the wastewater (ca. 40 percent) is non-adsorbable. Since one of the predominant functional mechanisms of the presence of PAC in a PACT system is simple adsorption, it is obvious that addition of PAC to an activated sludge system would have lesser beneficial effects for wastewaters having greater proportions of non-adsorbable materials.

A statistical analysis was also conducted to establish whether or not significant differences existed in system performance between the various steady-state PAC concentration levels. This analysis shows that statistically significant differences were observed between PAC concentrations of 1/3 and 3/5 but not for 5/7 kg/m³ for samples A and B. Because sample F had a comparatively high level of non-adsorbable organics, a significant difference was observed only for the 3/5 kg/m³ PAC concen-

tration pair. On the basis of these results, one may conclude that system performance was not enhanced for PAC concentration levels greater than 5 kg/m³ for the wastewater samples studied.

Color Removal Results

Color analyses were performed on effluent samples from both the PACT and biological systems as well as the raw feed at each steady-state PAC concentration level. The results of these analyses are given in Table 6. Statistically significant biological removal of color was achieved only for sample A. The removal levels achieved for samples B and F were not found to be statistically different than zero. Addition of PAC to the biological reactors proved to significantly enhance color removal levels only for sample A. Only minor increases in color removal were observed for samples B and F as a result of PAC addition.

It is interesting to note, furthermore, that color removal levels generally decreased with increasing steady-state PAC concentration levels for samples A and F. Since physical adsorption appears to be the principal mechanism of color removal, this result cannot be rationally explained. The relative removals achieved in the case of sample B are consistent with the anticipated performance.

Metallic Priority Pollutants Removal Results

Because one major focus of this investigation was removal of priority pollutants and because the PACT process has been reported to remove heavy metals, heavy metal analyses were performed on filtered raw feed and effluent samples obtained from the PACT system that was operated with a

Table 6. Color Removals Obtained in Parallel PACT and Biological Reactor Systems

Steady-State PAC Conc. (g/m ³)	Influent Color Conc. (ADMIU)	Biol. Eff. Color Conc. (ADMIU)	PACT Eff. Color Conc. (ADMIU)	Biol. Rem. Efficiency (%)	PACT Rem. Efficiency (%)
Wastewater Sample A					
1000	3800	3830	690	0.0	81.8
3000	4350	3810	2530	12.5	41.8
5000	4120	3790	1880	7.9	54.2
7000	4040	3680	1780	9.0	56.3
Wastewater Sample B					
1000	16700	16700	16400	0.1	2.1
3000	17000	16630	15600	2.4	6.2
5000	16900	16900	15200	0.0	10.2
7000	16600	16500	14100	0.8	14.3
Wastewater Sample F					
1000	22200	21800	18900	2.0	15.2
3000	22500	22600	20100	0.0	10.4
5000	22300	20300	20300	8.8	9.1
7000	21700	22100	20200	0.0	6.8

steady-state PAC concentration of 5 kg/m³ and its corresponding parallel biological system. The data from these analyses are shown in Table 7.

Analysis of the data shows that it is not particularly conducive to reaching significant conclusions. This is likely due to the fact that the three wastewater matrixes were dramatically different both in the solution- and particulate-phase fractions. Nonetheless, several general observations are appropriate. In the case of sample A, two heavy metals, nickel and antimony, were removed by the PACT at levels that were statistically significantly greater than the removals achieved in the corresponding biological control reactor. For sample B, the PACT system performed better for chromium, copper, nickel, antimony and zinc, while the PACT system performed better only in the case of chromium for sample F. The situation for sample F is somewhat confused by the fact that the biological control reactor provided better removals of antimony and zinc than did the parallel PACT reactor. On the basis of these results one may conclude that PAC addition to a biological reactor may result in enhanced removals for certain heavy metals, but that the situation is very specific and related to the composition of the aqueous matrix.

Organic Priority Pollutants Removal Results

To establish the technical feasibility of using PACT systems for providing for the removal of organic priority pollutants from dyestuff manufacture wastewaters, analyses for organic priority pollutants were performed on composite samples obtained from the feed and the effluent of the PACT system that was operated with a steady-state concentration of PAC of 5 kg/m³. The data from these analyses are shown in Table 8.

The results for all samples showed that the PACT system effectively removed all of the organic priority pollutants initially present in the wastewaters to below detectable levels, with a single exception. This was in the case of phenol that was present in sample B at a level of 5300 µg/l. An average residual level of 8.1 µg/l was observed to be present after PACT treatment. This represents a treatment efficiency in excess of 99.8 percent. Had a similar analyses been performed on a composite sample obtained from the PACT reactor that was operated with a steady-state PAC concentration of 7 kg/m³ is it probable that the phenol in this sample would also have been decreased to a concentration level that was less than detectable.

Since these results were obtained for three dyestuff manufacturing wastewaters that

Table 7. *Metallic Priority Pollutant Removals Obtained in Parallel PACT and Biological Reactor Systems*

<i>Metal</i>	<i>Influent Conc. (g/m³)</i>	<i>Biol. Eff. Conc. (g/m³)</i>	<i>PACT Eff. Conc. (g/m³)</i>	<i>Biol. Rem. Efficiency (%)</i>	<i>PACT Rem. Efficiency (%)</i>
<i>Wastewater Sample A</i>					
<i>Ag</i>	0.08	0.06	0.06	25.0	25.0
<i>Cd</i>	0.005	0.005	0.005	0.0	0.0
<i>Cr</i>	0.05	0.05	0.05	0.0	0.0
<i>Cu</i>	0.10	0.48	0.35	*	*
<i>Ni</i>	0.97	0.66	0.59	32.0	39.2
<i>Pb</i>	0.58	0.15	0.15	74.1	74.1
<i>Sb</i>	2.65	2.04	1.21	23.0	54.3
<i>Tl</i>	0.36	0.36	0.47	0.0	*
<i>Zn</i>	0.38	0.66	0.59	*	*
<i>Wastewater Sample B</i>					
<i>Ag</i>	0.04	0.04	0.04	0.0	0.0
<i>Cd</i>	0.005	0.005	0.005	0.0	0.0
<i>Cr</i>	1.50	0.74	0.05	50.7	96.7
<i>Cu</i>	5.71	4.38	1.02	23.3	82.1
<i>Ni</i>	1.09	0.72	0.22	33.9	79.8
<i>Pb</i>	0.15	0.15	0.15	0.0	0.0
<i>Sb</i>	1.21	1.21	1.01	0.0	16.5
<i>Tl</i>	0.12	0.12	0.12	0.0	0.0
<i>Zn</i>	2.60	1.71	0.92	34.2	64.6
<i>Wastewater Sample F</i>					
<i>Ag</i>	0.12	0.12	0.12	0.0	0.0
<i>Cd</i>	0.45	0.21	0.21	53.3	53.3
<i>Cr</i>	3.18	2.84	2.68	10.7	15.7
<i>Cu</i>	55.2	55.4	53.7	*	2.7
<i>Ni</i>	1.65	1.78	2.03	*	*
<i>Pb</i>	0.37	0.30	0.30	18.9	18.9
<i>Sb</i>	2.04	1.94	2.04	4.9	0.0
<i>Tl</i>	0.24	0.24	0.24	0.0	0.0
<i>Zn</i>	0.80	0.54	0.79	32.5	1.2

*Negative removal.

Table 8. *Organic Priority Pollutant Concentrations Before and After PACT Treatment*

Organic Priority Pollutant Observed	Influent (µg/l)	Effluent (µg/l)	
		Dup #1	Dup #2
Wastewater Sample A			
2-Nitrophenol	570	*ND	ND
Phenol	4400	ND	ND
2,4-Dichlorophenol	2500	ND	ND
1,4-Dichlorophenol	65	ND	ND
1,3-Dichlorobenzene	12	ND	ND
Acenaphthene	40	ND	ND
N-Nitrosodiphenylamine	32	ND	ND
Wastewater Sample B			
2,4-Dinitrophenol	2500	ND	ND
Phenol	5300	8.5	7.7
1,4-Dichlorobenzene	77	ND	ND
Nitrobenzene	120	ND	ND
Fluoranthene	13	ND	ND
Wastewater Sample F			
Bis (2-ethylhexyl) phthalate	560	ND	ND
Di-n-octylphthalate	1200	ND	ND

*ND means Not Detected.

have widely divergent compositions and matrixes and widely varying concentrations of priority pollutants, it is reasonable to conclude that the PACT process is effective for the removal of organic priority pollutants.

Ozonation Treatment Technology

Experimental Methodology

The ozone used was generated by a Grace Model LG-2-L2 corona ozone generator using bottled dry oxygen as the gas source. Oxygen was first dried and filtered through a TekLab FD-0235 transparent filter/drier then directed to the ozone generator via 0.95 cm polyethylene tubing. The ozonator was operated at a pressure of 86.2 kPa, an oxygen flowrate of 10 scfh, and a variable power setting of 0 to 300 watts.

Ozone was directed to the reactor through polyethylene tubing, where it entered the bottom of the column. A porous stone diffuser was used for initial ozone dispersion. To aid in gas transfer, 6.3 mm ceramic Raschig rings were placed in the column to a depth of 1.52 m. The reactor consisted of two 1.52-m sections of 5.08 cm diameter pyrex glass tubing with an expansion globe located at the top which served as an aid in breaking foam generated during the experiments.

The test wastewater samples were removed from the bottom of the column through a glass recirculation line and returned to a spray nozzle located in the expansion globe. Glass tubing was used wherever possible to minimize the potential for desorption of phthalates during the ozonation studies. Tygon tubing was used only for making connections between the various sections of glass tubing. The wastewater was recirculated at a rate of four liters per minute by a peristaltic pump.

The off-gas from the reactor was directed via 0.95 cm Eastman polyethylene tubing to two 500-ml gas washing bottles arranged in series for ozone analysis. Three sets of gas washing bottles were arranged in parallel. Two sets contained a solution of buffered potassium iodide while the third contained distilled water to detect gas flow. Any unreacted ozone that passed through the gas washing bottles was vented to a 20-l tank containing a saturated solution of sodium thiosulfate. The exhaust from the 20-l tank was discharged to the atmosphere.

Preliminary Studies

Preliminary ozonation characterization studies were directed toward evaluating the degradation of color, organics, pH changes and ozone consumption levels to define the

experimental conditions required for the conduct of the subsequent priority pollutant oxidation study. Experimental samples were collected from the influent to the wastewater treatment facilities of the six participating dyestuff manufacturers and were ozonated batchwise to an ozone application level of three grams ozone per gram of COD initially present. All preliminary studies were conducted at a temperature of 20°C and all wastewaters were neutralized to a pH of 7.0 prior to ozonation with the exception of wastewater sample A which had been collected after neutralization. The pH of this neutralized wastewater was 7.7.

For the present studies the maximum absorbance occurred near the low end of the visible span for all but the B and F samples. Upon ozonation, all spectra shifted into the ultraviolet region. Complete elimination of the visible spectra was not achieved, even with an ozone application level of three grams per gram of COD initially present. Degradation of the color value for each of the samples was rapid as a result of ozonation. Essentially complete color removal was observed for the B and F samples for ozone application levels of 1.76 and 2.25 g O₃/g initial COD. The remaining dyestuff manufacture wastewater samples (A, C, D, & E) proved somewhat more resistant to complete color value removal. Nonetheless, color value removals ranged from 88 to in excess of 95 percent for these samples at an ozone application level of 3 g O₃/g initial COD. A baseline color value of 0 to 300 ADMI units was attained in all cases.

During these preliminary studies TOC removals ranged from 15 to 42 percent at an ozone application level of 3 O₃/g COD initially present at which point each experiment was terminated. The associated initial ozone consumption rate expressed as percentage of the ozone application rate ranged between 90 and 100 percent for all samples. At the termination of each study, consumption rates were approximately 2 to 10 percent of the ozone application rates with the exception of sample F for which the final ozone consumption rate was equal to approximately 40 percent of the application rate.

The ratio of ozone utilized per unit of TOC removed did not change appreciably throughout these preliminary experiments although a slight increase in the ratio was observed for several of the studies as they progressed. The highest O₃/TOC ratios, 20 to 30 g O₃/g TOC, were observed for the A, C, and D samples which proved to be most refractory in character. The B and F samples were observed to have comparatively low ozone utilization ratios, in the range of 7 to 10 g O₃/g TOC oxidized, while the E sample

was observed to have an intermediate ozone utilization ratio.

Organic Priority Pollutant Removal Studies

To establish the technical feasibility of using ozonation for removing organic priority pollutants from dyestuff manufacture wastewaters, a treatability study was conducted on each of the six wastewaters. These were conducted batchwise at ozone application levels determined on the basis of the preliminary studies.

Initially, three criteria were defined for determining the appropriate ozone application levels. These were: (1) mass of ozone utilized per unit mass of total organic carbon oxidized, (2) TOC degradation, and (3) color value degradation. Because the time dependent traces of TOC degradation and the ratio of O₃ utilized/TOC oxidized showed no significant discontinuities that could serve as the basis for establishing ozone application levels, the time trace of color value degradation was selected for establishing ozone application levels for all organic priority pollutant ozonation studies.

Degradation of the color value could be described by a first-order kinetic relationship. For this reaction order, the associated time constant of the system is equal to the time required to attain 63 percent color value removal in a batch system. To attain removals of approximately 95 percent in a continuous-flow, plug-flow reactor operating at steady state, the design hydraulic residence time for the system would have to equal a minimum of three time constants. Accordingly, these ozonation studies were conducted batchwise on 4 liter samples for a period of time that equalled three characteristic time constants for the system at ozone application rates that were identical to those used in the preliminary studies.

The results of these ozonation studies are given in Table 9 for the dyestuff manufacture wastewater samples coded A through D and F, respectively. Results for the A and B samples showed that all of the priority pollutants initially present in these wastewater samples were removed to levels below detectability. It is important to note, furthermore, that no organic priority pollutants were produced as a result of ozonation. For sample C, both bis (2-chloroethyl)ether and N-Nitrosodiphenylamine were removed to non-detectable levels. Nonetheless, phenol which was initially present at a concentration level of 1900 µg/l was reduced to an average concentration of 12 µg/l representing a removal level in excess of 99 percent.

The situation for samples D and F was somewhat different, however. In the case of

Table 9. Acid and Base/Neutral Fraction of Priority Pollutants Prior to and After Ozonation

Sample	Compound	Concentration ($\mu\text{g/l}$)			
		Initial		Final	
		Dup #1	Dup #2	Dup #1	Dup #2
A	2-Nitrophenol	40	35	*ND	ND
	Phenol	110	120	ND	ND
	2,4-Dinitrophenol	350	340	ND	ND
	1,4-Dichlorobenzene	3.4	3.1	ND	ND
	Naphthalene	1.6	1.4	ND	ND
B	2,4-Dichlorophenol	1.3	1.3	ND	ND
	2,4-Dinitrophenol	3200	3300	ND	ND
	1,4-Dichlorobenzene	50	6.2	ND	ND
	Nitrobenzene	51	47	ND	ND
	Di-n-butylphthalate	22	24	ND	ND
C	Phenol	1900	#-	13	11
	Bis (2-Chloroethyl) ether	2300	-	ND	ND
	N-Nitrosodiphenylamine	29	-	ND	ND
D	1,3-Dichlorobenzene	1.0	-	ND	ND
	Phenol	240	-	15	16
	1,4-Dichlorobenzene	9.4	-	ND	ND
	Naphthalene	16	-	ND	ND
	1,2,3-Trichlorobenzene	8.5	-	ND	ND
F	Nitrobenzene	830	-	360	400
	Phenol	59	57	26	32
	Di-n-octylphthalate	1800	1800	360	350

*ND means not detected.

#- Duplicate samples were not run.

sample D, four of the organic priority pollutants initially present were removed to less-than-detectable levels. Phenol was present in the ozonated sample at an average concentration of 15.5 $\mu\text{g/l}$ representing a removal efficiency of approximately 93 percent. In contrast, the concentration of nitrobenzene which was initially 830 $\mu\text{g/l}$ was decreased to only 380 $\mu\text{g/l}$ (54 percent removal). The two organic priority pollutants present in sample F proved to be even more resistant to degradation by ozonation. For this sample, residual levels of phenol of 29 $\mu\text{g/l}$ and of Di-n-octylphthalate of 355 $\mu\text{g/l}$ were observed after ozonation. This represents treatment levels of 50 and 80 percent, respectively.

The lower treatment level observed for the F sample is likely attributable to the fact that the concentration of organic materials expressed as TOC was approximately three times the magnitude of the TOC in the other four samples. The comparatively higher concentrations of competing compounds would tend to inhibit the rate of degradation of specific organic compounds by ozone, thereby resulting in lower removal efficiencies at specific ozone application levels.

Conclusions

Results of an analytical survey conducted on the wastewaters of four dyestuff manu-

facturers showed the presence of a total of 23 organic priority pollutants in the raw wastewaters. Of these, six were present at concentration levels greater than 1 mg/l. Removal levels of these organic priority pollutants by the activated sludge systems that existed at the sites sampled generally exceeded 95 percent in the case of the volatile organics with the exception of methylene chloride. Although most acid and base/neutral extractable compounds were removed significantly from the aqueous stream by the activated sludge system, many compounds were found to be present even after treatment. Only several of these compounds were present at less-than-detectable concentration levels after treatment.

Analyses for heavy metal pollutants conducted during this survey showed that only minor removals were achieved by the respective activated sludge treatment systems. With the exception of copper, most heavy metals were found to be present in the raw wastewater in the 20 to 200 $\mu\text{g/l}$ concentration range. In two of the three wastewaters sampled, copper was found to be present in the 3 to 6 mg/l concentration range.

Granular activated carbon (GAC) adsorption studies conducted on six dyestuff manufacture wastewaters showed that while excellent removals of both organic priority pollutants and color can be obtained, ad-

sorption of soluble organic carbon (SOC) is not particularly efficient due to the fact that comparatively high concentrations of non-adsorbable organics occasionally are present in these wastewaters. Moreover, it was shown that ozonation pretreatment of these wastewaters generally served to degrade adsorption characteristics.

Parallel PACT (biophysical) and biological (activated sludge) studies conducted on three dyestuff manufacture wastewaters showed that powdered activated carbon (PAC) addition provided for enhanced SOC and color removals, generally in direct relation to the steady-state concentration of PAC in the reactor. Excellent removals of organic priority pollutants were achieved by the PACT system. Heavy metal removal levels were small.

Ozonation studies conducted on six dyestuff manufacture wastewaters showed that ozone provides for excellent color removals but only moderate organic carbon removals as indexed by total organic carbon (TOC). Although many organic priority pollutants were removed to levels below detectability some proved to be comparatively resistant to oxidation by ozone. It was demonstrated, furthermore, that no priority pollutants were produced as a result of ozonation.

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The complete report, entitled "Technology Evaluation for Priority Pollutant Removal from Dye stuff Manufacture Wastewaters," (Order No. PB 84-157 064;

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