

## 77 CHARACTERIZATION AND BIOLOGICAL TREATABILITY OF A TEXTILE DYEHOUSE WASTEWATER

Mervyn C. Goronszy,  
Transenviro, Inc.  
Irvine, California 92718

Harry Tomas,  
Olympic Mills  
Guaynabo, Puerto Rico 00651

### INTRODUCTION

Olympic Mills is an integrated textile and apparel manufacturing company which produces T-shirts, men's briefs, panties, etc; production typically operates over three shifts, 5 1/2 days per week. Fabric is knitted from 100% cotton or 50% polyester-cotton yarn, which is bleached and or dyed prior to cutting, sewing and warehousing of the finished articles. Wastewaters are generated from bleaching, dyeing, rinsing, boiler blow-down and water conditioning units. Woven cotton fabrics are bleached (scoured) to generate a brilliant white product prior to direct dyeing procedures. Specific chemical pretreatments are used in dyeing to remove starch based size preparations, to enhance dye absorbency and to counter poor dye penetration due to fiber swelling. Chemicals are also used to increase dye solubility and to improve dye affinity and its fixation. After treatments are used to remove the unfixed dye portions. High concentrations of Glauber's salt or common salt, up to 140 g/L, are used in cotton fabric dye liquors. The yield of color is improved in the case of deep dyeing at the high 140 g/L salt concentration, paler shades are obtained with salt concentrations down to around 6 g/L. Salt additions are based on the mass of cotton fabric, the type of dye and the desired color. When dyeing a polyester/cotton blend with reactive colors it is necessary to dye the polyester fraction first, in a two bath procedure. The dye liquors from the polyester operation are dumped and the appropriate cotton dye recipe followed. It is usual practice to scour the fabric blend. With direct colors, a one bath procedure is used in which the polyester fraction is initially painted with the subsequent additions for the cotton dye recipe without the intermediate rinsing stages that are used in the two bath procedures. While Table I summarizes typical mass usage of major dye chemicals. The concentration of azo dyes in the effluent stream from the dyehouse can be expected to be between 15 and 50 percent of initial calculated values, depending on fiber type. While chloride concentrations in Table I are shown as a mean daily concentration, actual dump load concentrations from a dye machine can be up to the equivalent mass of fiber loaded divided by the volume of dye waters associated with the initial dye operation. In the case of a direct dye for a fiber mass of 1000 lb, the mass of salt can be 1000 lb in a volume of approximately 1000 gal. Significant amounts of paraffin wax are contained in the wastewater generated from the bleaching process.

The dyeing or painting process is conducted using either Beck or jet dyeing machines. The greatest portion of the waste materials is made up of spend dyes and chemical auxiliaries. In addition to dyes, five basic types of chemicals are used, a sequestrant, a surfactant, a leveling agent, a carrier and a pH adjuster. The carrier is typically biphenyl which allows the dyes to penetrate the polyester fibers; an after scour is used to wash out carriers and excess dyes. Waste waters are typically around 180°F. Bleaching is carried out in a J-Box machine. Beck dyeing is a batch process whereby, the fabric is dyed in heated atmospheric dye becks containing dye batch mixtures with constant movement of the cloth through the batch until the desired shade is obtained. The dye batch is then discarded, the fabric is rinsed in the Beck and is then sent to the dryer. Jet dyeing is also a batch process, only the fabric is stationary and the dying process occurs in heated pressurized reactors. Around 15% of the dyes originally introduced into the cotton fiber batches are discharged; around 50% of the dyes introduced into the synthetic fiber batches are discharged. Most of the auxiliary chemicals added to the batches are present in the discharge. These wastewaters contain priority pollutants in the form of aromatics, halogenated hydrocarbons and heavy metals. Dyehouse wastewaters therefore, contain a wide variety of direct colorants, reactive colorants, dispersed colorants, organic solvents, inorganic and organic

Table I. Summary of General Audit Parameters

Date	Total Fabric lb	Total Dye lb	Azo Dye mg/L	Azo Dye %	NaCl lb	NaCl mg/L	Bleach Water gal	Dye Water gal
Jan 15	10104	505	6.5	22.0	4345	2915	48560	130170
Jan 16	11701	348	0.33	0.79	1272	877	46214	178172
Jan 17	16299	408	1.6	5.4	1610	1335	39900	140618
Jan 20	8451	304	26.6	63.3	3435	2692	25540	127703
Jan 21	7213	360	8.9	21.8	2416	1646	31548	144420
Jan 22	10421	437	8.0	23.3	2194	1466	21146	158451
Jan 23	7058	716	8.8	49.2	2695	2112	30862	122789
Jan 24	12392	639	1.7	7.4	5009	3432	24286	150767
Jan 27	7330	340	3.5	2.3	4221	2910	28235	146154
Jan 28	7193	214	2.9	4.5	2095	1535	31175	132457
Jan 29	9779	369	12.8	36.2	4278	3288	29035	127263
Jan 30	8283	588	8.2	35.5	3200	2508	23883	140048
Jan 31	7322	492	7.7	25.4	2589	1734	35400	143673
Feb 1	7514	246	-	-	2473	2879	22759	80693
Feb 3	7308	376	-	-	2687	2120	38248	114280
Feb 4	8489	231	1.6	2.7	4206	3038	35773	130913
Feb 5	8185	214	48.9	74.7	4475	3194	23118	145035
Feb 6	5608	146	5.8	5.7	1906	1291	23355	153846
Feb 7	14162	121	4.9	4.3	1704	1224	21538	145378
Feb 8			-	-			5384	59418
Feb 10	4620	283	13.9	32.5	398	329	24280	120869
Feb 11	10285	649	6.2	2.8	4684	3304	17490	153786
Feb 12	4845	82	8.1	4.7	1597	1126	14214	155786
Feb 13	10592	129	0.48	0.4	2458	1734	20238	149762
Feb 14	7122	373	0.25	0.7	2933	2069	19466	150534
Feb 17	7767	544	55.0	12.8	4537	3200	18283	151717
Feb 18	8288	257	34.7	17.0	4210	2970	18494	151506
Feb 19	6069	505	23.9	5.4	2971	2096	32549	137451
Feb 20	6769	351	44.6	15.9	2706	1910	20475	149525
Feb 21	9072	180	7.1	4.7	2397	1690	26658	143342
Feb 22	4649	89	35.6	20.5	3313	6186	3302	61500
Feb 24	5964	145	9.3	8.0	2507	1768	20660	149340
Feb 25	7199	429	10.6	3.2	3665	2585	14531	155469
Feb 26	8429	114	3.1	3.3	1483	1046	23857	146143
Feb 27	6001	349	4.7	1.7	1913	1350	19550	150450
Feb 28	6863	576	60.8	13.2	2926	2064	19530	150470
Feb 29		256	70.0	16.8	-		5490	73733

salts that are used in the color fixing or painting process. Some of the chemicals used in these operations fall into the hazardous category (Tables II, III). Dyeing requires specific cookbook procedures for chemical additions, fixing temperatures, dyeing times and rinsing relative to textile type and depth of color that is required. Polyester is typically painted at a pH of 5.5 to 6.0 using acetic acid to promote color fixing while cotton is painted at a pH of 11 to 12 with either salt or sodium sulfate, depending on color, for fixing. Figures 1 and 2 show typical time, temperature and addition procedures for the Beck and jet machines when dyeing a polyester-cotton blend.

Wastewaters from each of nine dye vessels are generated as dump loads typically consisting of a first dump of combined spent dye and fixing chemical solution followed by up to eight drops of lesser concentrations of dye and chemicals through successive rinsing procedures. Mixed yarn is initially painted for polyester adhesion and then painted for cotton adhesion in successive and combined operations. Two dye jets have a 600 gallon (2270 liters) and 630 lb (286 kg), fabric capacity. Five of the six Becks have a 1000 gallon (3780 liters) and 1100 lb (500 kg) fabric capacity; the sixth has a 150 gallon 150 lb (570 liter / 70 kg) (570/70) capacity. The J-Box machine has a similar capacity to the large Becks. The large Becks typically take up to 11 hours for painting comprising four hours for polyester and seven hours for cotton. Liquid dumps can be up to 1000 gallons (3780 liters) at each time. Wastewaters from the facility are directed to a 46,000 gallon, (174,000 liter) collection basin, prior to discharge to the sewer. The bleaching process generates about 40,000 gallons per day,



**Table II. Summary List of Main Chemicals Used in Dyehouse Tradename and Major Constituents**

HOSTATEX LO	Orthochlorotoluene	68%
	Biphenyl	26%
Tanaterge WFF	Isopropyl alcohol	8%
	Ethylhexanol	5%
Tanavol URC	Biphenyl	20%
	Trichlorobenzene	60%
	o-dichlorobenzene	9%
	p-dichlorobenzene	10%
Supersol CSS	Isopropyl alcohol	4%
	2 Butoxy ethanol	10%
	solvent naphtha	12%
	Naphthalene	3%
Tanatex Buffer-IN-A	Phosphoric Acid-75%	< 2%
Sodyefide B Liquid (Sulphide solution)	Sodium Sulphydrate	10-15%
	NaOH	1-3%
Sodyeco Sulfalox 100 Liquid (C10H12O8N2 Na4)	Sodium hydroxide	1-2%
	Trisodium nitrilotriacetate	1-2%
Imacol JN Liquid	Formaldehyde	< 0.2%
	Glycerol Monostearate	14-19%
Tanatex Nostick KOH	KOH	2%
	Isopropyl alcohol	4%
	2 Butoxyethanol	1%
Carolid RNO	Naphthalene	2%
	Solvent naphther	15%
	Biphenyl	27%
	Nonochlorotoluene	55%
Monoethanolamine HO CH <sub>2</sub> CH <sub>2</sub> NH <sub>2</sub>		
NaOH		50%
Acetic Acid	1.051 SG	56%
Remol FRF	KOH	1%
Polyron PB	Organic acid salts	100%
Hostapur DAT	Polyglycol ether (alkyl alcohol polyglycol ether)	39%
Solidum Silicate	Sodium silicate	39%
Sunny SOL	NaO CL	12.5-
	NaOH	15.6%
		0.2-
		2.0%
Soda Ash	Na <sub>2</sub> CO <sub>3</sub>	
Resin 701	Sodium dodecylbenzene sulfonate, Polyvinyl acetate emulsion	< 0.1%
Oxalic Acid		
Nofome J.	Petroleum distillates	2%
Lubit 64	Polyethylene glycol monooleate	2.2%
Alkaflo Liquid Alkali	Sodium hydroxide SG 1.51	3.8%
Resfin 21504	N-Methyl-2 pyrrolidene Triethylamine	6%
		1.2%
Tebolan UF	Urea	73%
	Water	73%
	Ammonia	21%
Fibramoll AFK	Quaternary Amine Salt	

Table II. (Continued)

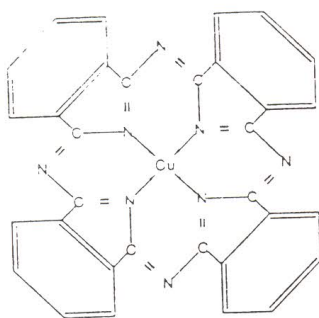
Remol ELA	Surfactant	
Leomin WA	Silicone Emulsion	
Na <sub>2</sub> SO <sub>4</sub>		
Leucophor AC Liquid C42H46N14O16		< 1%
S4-4Na (Monoethanolamine)		
Richsoft 83		
Revatol Sp Powder 060	Substituted benzene derivative	
Dyeset NF	Polyamine Resin	
Plexene D	Chelating Agent	
Hydrogen Peroxide		50%
Chlorothene SM Solvent	1, 1, 1-Trichloroethane	96.5%
	Diethylene Ether	2.5
	1,2 Butylene Oxide	0.47%
	Nitromethane	0.34%
Tanapal M1	2-Butoxyethanol	< 6.0%
	Isopropyl Alcohol	< 7.0%
Tanasoft PNL		

(151,000 liters per day), and the dyeing operations about 160,000 gallons per day, (605,000 liters per day).

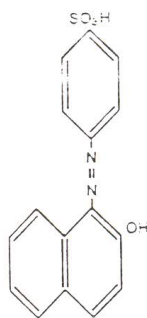
This paper reports on studies that were undertaken to characterize the wastewaters from this dyehouse and to determine a suitable treatment strategy for organics and color removal in order to meet a pre-treatment discharge requirement (Table IV).

### DYE CHEMISTRY

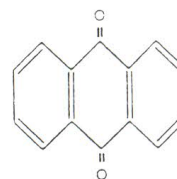
Dyes are produced to yield a color that remains fast for the lifetime of a fabric. Dye stability is necessary so that it will not break down with exposure to sunlight, water, soap or dry cleaning fluids. When a dye is stable under these diverse conditions, it becomes more difficult to treat as a wastewater. The complexity of dye structures is typically demonstrated by the following examples.



Phthalocyanine  
Derivatives



Azo  
Derivatives



Anthraquinone  
Derivatives

The wastewater characteristics in a particular dye house can be highly variable from day to day and hour to hour, depending on the type and color of dye, the type of fabric and the concentration of fixing compounds which are added. Parameters of major interest in the treatment of dye house wastewaters concern degradable organics, re-calcitrant compounds and color. The compound structure of dyes can be very complex and will hence impact on the degree of ready biodegradability. Dye compounds typically exhibit low BOD values and high COD/BOD ratios depending on the structural complexity of those compounds. Data taken from an earlier survey at this mill provided a mean effluent COD/BOD ratio of 3.4 taken from 50 24-hour composite samples spread over a 28-month period. The range varied substantially from 1.1 to 250 indicating the diverse structure apparent and





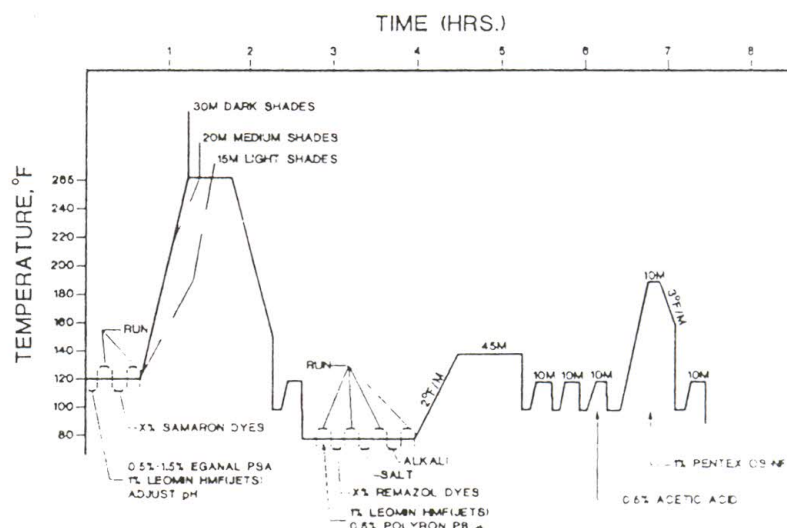


Figure 2. Cotton and polyester dye procedure (Jets).

degradability of the dyes that are used at this facility. Mean and standard deviation values of COD and BOD were  $2910 \pm 8210$  mg/L and  $870 \pm 3220$  mg/L, respectively.

Many of the modern dyes used in the textile garment industry are azo based. A listing of the azo dyes used at this facility is summarized in Table V. Table I shows typical daily variation of the percentage of azo dye to total dye used. These statistics together with total daily water use enable a maximum initial azo dye concentration, based on 24 hour composite sampling, to be derived.

The ability to remove azo dyes by activated sludge primarily depends on the molecular structure and on the type, number and position of the substitution radicals in the ring structures. Degradability is increased by the presence of hydroxy groups, nitro groups and azo groups in the molecule. Sulfo groups reduce the ability to remove by activated sludge. Adsorptive removal of dyes on activated

Table IV. Final Discharge Limitations and Final Monitoring Requirements

Parameter	Discharge Limits	Outfall 002 Monitoring Requirements	
		Sample Type	Frequency
1. Temperature (c)*	40	Grab	Continuous
2. pH (s.u.)*	6.5-9.0	Grab	Continuous
3. Copper	1.0	Composite	Continuous
4. Mercury (mg/L)	0.05	Composite	Continuous
5. Nickel (mg/L)	0.5	Composite	Continuous
6. Chromium (mg/L)	1.0	Composite	Continuous
7. Silver (mg/L)	0.05	Composite	Continuous
8. Cadmium (mg/L)	0.10	Composite	Continuous
9. Zinc (mg/L)	0.50	Composite	Continuous
10. Lead (mg/L)	0.20	Composite	Continuous
11. Aluminum (mg/L)	1.0	Composite	Continuous
12. Selenium (mg/L)	0.20	Composite	Continuous
13. Iron (mg/L)	2.0	Composite	Continuous
14. Manganese (mg/L)	2.0	Composite	Continuous
15. Tin (mg/L)	5.0	Composite	Continuous
16. Cyanide (mg/L)	0.10	Composite	Continuous
17. Phenols (mg/L)	0.50	Composite	Continuous
18. Oil and Grease (mg/L)	50.0	Grab	Continuous
19. BOD <sub>5</sub> (mg/L)	250.0	Composite	Continuous
20. Settleable Solids (ml/L)	125.0	Grab	Continuous
21. Flow, GPD	250,000.0	Continuous	Continuous
22. COD (mg/L)	300.0	Composite	1/Year
23. Sulfides (mg/L)	-	Grab	1/Year
24. Color	75 Pt-Co	Grab	1/Year

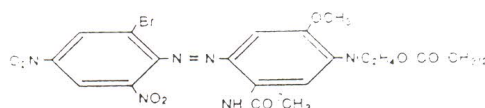
\* Temperature and pH shall be monitored continuously 180 days after EDP.



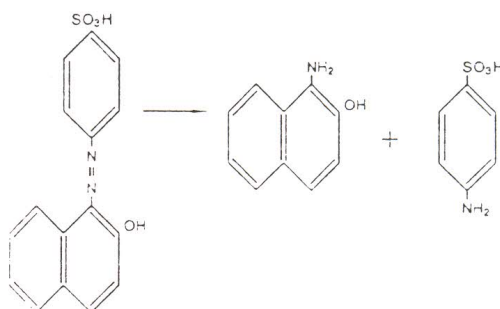
sludge varies between 0.01% to 4% by weight. The primary reductive degradation of the azo group -N=N- in a number of dyes can proceed in an aerobic environment.

Degradation may be enhanced through the anaerobic sequencing which occurs in variable volume activated sludge systems. Reduction of the azo group is inhibited by the presence of nitrites and nitrates in the mixed liquor. Azo compounds are therefore not decolorized during biological treatment until all nitrites and nitrates in the medium have been denitrified. Chlorine and nitro groups in the aromatic ring can enhance the rate of reduction. In considering degradation of dye compounds, the rate of biological degradation depends upon the ease with which the molecule can penetrate the cell wall and reach the appropriate enzyme site, the extent to which steric effects interfere with enzyme bonding and the extent to which electronic effects either interfere with enzyme bonding or alter the energy required to break the critical bonds in the molecule. For example, there is evidence to show that the main factor determining the reduction rate of sulfonated azo dyes is the electron density in the region of the azo group.

C.I. Disperse Blue 79, a large production volume dye, in the blue jean industry, is a water insoluble bromodinitroaniline derived compound which exhibits limited aerobic degradability has the formula.



Substrates consisting of complex dye sources alone (with nutrients) are unlikely to be significantly degraded.<sup>1</sup> The degradation of azo dyes, for example, consists of an initial cleavage of the azo bond followed by degradation of the aryl intermediates, many of which are aromatic amines. For example Acid Orange 7 breaks down to 1-amino-2-naphthol and sulfanilic acid as follows.



Fortunately Olympic dyehouse wastewaters also contain a source of degradable organics (other than dye compounds) for use as a supplemental carbon source with which a net biological growth can be established. Once cleavage of the nitrogen bond is established, various rules for the degradation of substituted aromatics can be applied. For example, substituents which generally facilitate biodegradation include OH, COOH, CHO, CH<sub>3</sub> while substituents which associate with decreasing degradability include NH<sub>2</sub>, NO<sub>2</sub>, SO<sub>3</sub>H and halogens. Theoretically, the first group can increase electron density on the aromatic ring while the second group can decrease the electron density on the aromatic ring. The rate of biodegradation usually decreases with increasing number of substituents on the aromatic ring. The order of degradability can also be influenced by the position of substituents on the aromatic ring. For example aromatic trisubstituted derivatives with positions 1, 2, 3 or 1, 2, 4 occupied are usually degraded more readily than derivatives in which, positions 1, 2, 5; 1, 2, 6 and 1, 3, 5 are occupied and OH, NH<sub>2</sub>, CH<sub>3</sub> or COOH groups are in position 1. A high COD/BOD ratio is indicative of difficult degradability. The BOD/TOD (Theoretical Oxygen Demand) ratio can also be used to indicate degradability. A value of between 0.4 and 0.7 indicates a ready and rapid degradability or that the culture used for the degradation was not sufficiently acclimated. For example, biphenyl with a TOD value of 3.01 g/g and a BOD<sub>5</sub> of 0.85 g/g exhibits a ratio of 0.28; indicative of a slow degradability. 1, 3 dichlorobenzene exhibits a ratio of 0.08; 1, 4 dichlorobenzene has a zero value.<sup>8</sup> Various dye types are used to formulate a specific fabric color. These include mixtures of direct, reactive and disperse colorants. For example the blue jean dye Navy 106, although not used at this dye house, consists of three reactive azo dyes, Remazol red, Remazol black and Remazol yellow. Operation of a full scale municipal cyclical activated sludge process has shown the feasibility of 100 percent removal of

Table V. List of Azo Dyes

Altafix B. Blue RW	Drimarene B, Red A-4G
Atlantic D. Yellow 4 GLN	Drimarene B, Red X-2BN
Atlantic F. Blue 7GUL	Drimarene B, Yellow X-4GL
Polycron B. Orange 2RL	Drimarene Blue XBL (PAT)
Polycron Black ET 200%	Drimarene Disch. Orange X-3LG
Polycron Blue G-B8	Drimarene Navy X-RBL
Polycron Yellow 3G	Drimarene Rubine X-3LR
Intracron B. Orange VS-3RA	Drimarene Scarlet A-2G
Intracon G. Orange VS-3G	Drimarene Violet X-2 RL
Intralite Orange 3-GL	Foron B. Orange B-RL
Remazol B, Blue BB (new)	Foron B. Violet S-3RL
Remazol Black B	Foron B. Yellow SE GGFL
Remazol G, Yellow RNL	Foron Rubine RD-GFL (Granules)
Remazol Navy Blue R-GB	Pyrazol F. Blue 2 GLN
Samaron Blue RL% 200%	Pyrazol F. Red 7 BSW (Powder)
Samaron D, Blue BB-A 150	Pyrazol F. Rubine BLN
Samaron Red HGF	Pyrazol F. Violet B.
Carta Violet 2-BP	Drimarene B. Red RX-4BL
Cartasol Red 2GF	

apparent color derived from indigo blue dye removal in a prewash denim wastewater with flow ratios up to 25%.<sup>2</sup>

### WASTEWATER CHARACTERIZATION

A combined characterization and treatability study was conducted over an approximate 12 week period from November 12, 1991 to the end of February, 1992. Table I summarizes water, total dye, azo dye and salt use for the weights of fabric shown some 90 different dyes are used in the various formulations Table II lists the main chemicals used at the facility. Table III identifies the hazardous associated materials as per the Superfund Amendments and Re-authorization Act (1986). Table V summarizes the azo dyes that are used. Tables VI, VII, and VIII summarize typical daily chemical use for the bleaching (J-Box), jet and Beck operations. The mass of salts used per day varies depending upon fiber type and product color. GC/MS analyses were conducted on representative samples of dyehouse wastewater. Typical color measurements of this wastewater are shown in Table IX; the ADMI tristimulus method was used.

Olympic Mills is required by the regulatory authority to meet a *Pt-Co* color standard. This conventional test for color measurement is not applicable to textile wastewaters. While it was recognized that the ADMI (American Dye Manufacturers Institute) method, is more applicable, and since the discharge permit was given as *Pt-Co* units, the *Pt-Co* method was used. The ADMI method, which gives results that are independent of hue, i.e., water containing blue, red, yellow and of equal visual appearance regarding depth and intensity will have the same ADMI color value. For highly colored textile wastewaters, it is more important for the color measurement to be related to the "visual perception" and not the concentration of the color bodies since the identity of the colored bodies in this type of wastewater is usually unknown and difficult to determine.

The ADMI Tristimulus Filter (Tentative) Method, is described by Section 204D of *Standard Methods* or the alternate method (Section 204D4) utilizing a spectrophotometer. A Bausch and Lomb Spectronic 20 spectrophotometer, with a 1 cm path length is suitable. Suitable wavelengths for measuring textile colors are, 590 nanometers for T1, 540 nanometers for T2 and 438 nanometers for T3. Distilled water blanks are used for 100% transmittance. Sample measurements are conducted at a pH of 7.6.

The wastewaters were also characterized by total and soluble COD, suspended solids, oil and grease, chloride, pH and BOD.

### TREATABILITY STUDIES

The treatability studies that were conducted were based on the premise that, the basic unit operations in the proposed treatment system would include the following:



**Table VI. Dyebecks Typical Daily Chemical Consumption**

Chemical	Purpose	Consumption (lb/d)
Plexene D	sequestering agent	24
Tanatex Nonstick	cleaner for rolls	1
Tanaterge WWF	surfactant	77
Polyron PB	stabilizer sequesterns peroxide	73
Caustic Soda	adjust pH	304
Hydrogen Peroxide	bleach	198
Acetic Acid	adjust pH	71
Sodium Thiosulfite	neutralize peroxide in fabric	29
Hostatex Lo	carrier poly	151
Sodium Sulfate	cotton color fix	540
Revatol SP	color oxidant cotton	50
Sodium Chloride	fix color	5000
Nofone J	anti-foam	2
Lubit 64	lubricant cotton	25
Tanapal Me	color leveling poly	39
Buffer-In-A	pH stabilizer poly	33.3
Dyeset NF	fixer cotton	50
Sodium Hydrosulfite	strip cotton	60
Fibranol AFK	softener	450
Remol ELA	detergent	150
Jer State Resin 701	adds body cotton	10
Super Sol CSS	emulsifier stain remover	100
Soda Ash	adjust pH	249
Leonin WA	lubricant cotton	90
Silsoft 2069 B	softener	125

- lint screens
- balance tank
- pH correction
- energy recovery and wastewater cooling
- nutrient addition

- cyclic activated sludge system
- sludge digestion (aerobic)
- sludge dewatering
- color removal using chlorine
- (Possible dechlorination with sulphur dioxide)

A schematic layout of the full-scale treatment facility is shown in Figure 3. This biological treatability study was based on the premise of initially maximizing biological degradation of organics and at

**Table VII. Dyejets Typical Daily Chemical Consumption**

Chemical	Purpose	Consumption (lb/d)
Defoamer DSV	anti-foam	15
Penetrant EH-MOD	penetrating agent	23
Reducer RDT	sulfur based dyes (black)	175
Lyogen DFT	Polyester carrier	10

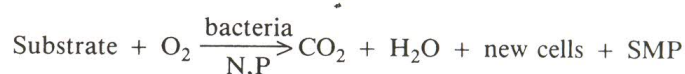
**Table VIII. J-Box (Bleaching) Typical Daily Chemical Consumption**

Chemical	Purpose	Consumption (lb/d)
Sodium Silicate	stabilizer peroxide	528
Caustic Soda	adjust pH	360
Plexene D	sequestering agent	108
Polyron PB	sequestering peroxide	120
Leucophor AC	optical bleach	84
Hydrogen Peroxide	bleach	714
Tebolan 02	cotton lubricant	120
Tanaterge WFF	surfactant	108

established when the rate of substrate addition results in a net growth of biomass. Proper acclimation of a mixed substrate, containing various components exhibiting different degradability and toxicity levels, consists of a gradual increase in loading up to a target organic loading consistent with overall removal performance and process stability. The target loading depends on many factors including toxicity limits which, determine feed protocol; slow or fast. Where significant toxicity exists, reaction rate and threshold toxicity concentrations determine fill-rate and fill-volume in variable volume activated sludge systems.

Acclimation period cannot be predetermined; it may last 15 days, or 150 days, depending on the chemical structure of the substrate components and the specific growth rates of the responsible microorganisms. Elements of co-metabolism may be required to sustain an initial growth response. Once acclimation and equilibrium reaction conditions are established, kinetic studies can then be conducted. Complex wastewaters typically require a long sludge age to accommodate their low rates of degradation.

The basic equation for aerobic bio-oxidation is useful for describing the principles of the procedures relative to the parameters that were monitored during the treatability study.



The generation of soluble microbial products (SMP) is not easily quantifiable. These compounds will manifest as effluent COD and may contribute to the BOD. Their contribution is determined by initial loading conditions ( $S_0/X_0$ ). Bio-degradability is quantifiable through substrate removal, its rate of removal and oxygen utilization rate (both expressed in terms of units of reactive biomass) or formation parameters such as  $\text{CO}_2$  or new biomass. In this case, multiple substrates are involved. As biological discharge parameters are principally concerned with BOD, COD and TSS reduction, then these parameters were used to quantify biological degradation of substrate and the efficacy of solids-liquid separation that is associated with the method of activated sludge treatment. Degradability was principally measured by substrate decrease in terms of COD. Some BOD analyses were also conducted to check that COD removal performance was sufficient to meet BOD discharge parameters. Yield factors for COD removal and new cell growth as volatile suspended solids were included. Typically, measurements that are made to assess biodegradability in terms of biomass increase are not practical. No attempt was made to determine fractions of effluent COD, which could be considered to be biologically resistant or to have been generated as biological byproducts (soluble microbial products).

Degradation rate was determined through separate batch studies using mg COD removed/g VSS/hr as a measure of the substrate removal velocity. Rate was also inferred through biomass respiration rate. The potential of the biomass to enter into degradation was assessed using acetic acid spikes as a readily degradable soluble substrate and one that was known to be contained in the mixed waste stream in comparative biomass respiration analyses. Oxygen utilization rate was determined during fill-react and react sequences in the main aeration zone and in the captive selector zone of the demonstration unit. Most of the organic compounds listed in Table II exhibit a sufficient level of degradability even though the presence of the three chloro groups in the structure of the benzene ring in trichlorobenzene has a negative influence on degradability rate. Naphthalene, 1-2 dichlorobenzene and 1-4 dichlorobenzene can be removed with an acclimated biomass.

Biodegradability of these determined wastewaters was in a demonstration Cyclic Activated Sludge System (CASS<sup>TM</sup>).

### CYCLIC ACTIVATED SLUDGE SYSTEM (CASS<sup>TM</sup>)

Details of the use of CASS<sup>TM</sup> fed-batch reactor technology for both municipal and industrial wastewater treatment have been reported previously.<sup>4-7</sup> CASS<sup>TM</sup> is a simple periodic process, operated under time (or volume) based cycles. CASS<sup>TM</sup> technology incorporates variable volume activated sludge processing in a single basin. Operation is based on sequences that are set for filling the reactor, aerobic biological degradation of the wastewaters, separation of the activated sludge solids from the treated liquid phase and removal of a volume of the liquid phase as treated effluent. This technology uses the same basin for biological degradation mechanisms and solids-liquid separation. No clarifiers are required for this technology, which typically represents a cost savings, to the order of thirty percent of the total cost of the plant. CASS<sup>TM</sup> facilities are configured to allow simultaneous filling and reaction to take place, without generating biological growth conditions, which may encourage the proliferation of filamentous microorganisms. Sludge bulking caused by the overgrowth of filamentous microorganisms can deleteriously impact on effluent quality. CASS<sup>TM</sup> is configured with an inlet



captive selector, which is responsible for containing the growth of a large number of filamentous species. This is a notable feature of the CASS<sup>TM</sup> technology which permits simple and reliable operation of the activated sludge process in a variable volume reactor, without filamentous sludge bulking concerns. The CASS<sup>TM</sup> batch reactor basin is configured with an inlet captive selector to insure the biomass undergoes sequenced initial aerobic and anaerobic feed-starve loading conditions. This has proven to be a most reliable and flexible methodology for minimizing filamentous sludge bulking and for obtaining high levels of biological nutrient removal.<sup>6,7</sup> Waste is typically introduced via the captive selector during REACT, SETTLE and an optional IDLE non-aeration sequence when it is necessary to effect an additional initial anaerobic reaction component in the cyclic operation. The break down of complex organic compounds can be assisted through this mechanism. This type of operation is independent of reaction filling protocols as has to be practiced by other variable volume (fed-batch) systems which do not have the captive selector feature. Proper initial bio-loading conditions ( $S_0/X_0$ ) are always established for maximum conversion to cellular storage products of available soluble substrate. Solids-liquid separation occurs during SETTLE and the effluent is withdrawn during a SURFACE SKIM sequence after which the reactor is ready to receive wastewater again. A CASS<sup>TM</sup> unit having dimensions of 5.5 m long  $\times$  2.1 m wide  $\times$  2.4 m high, with operation at a liquid depth of 2.3 m, was used to demonstrate the biological treatability of this wastewater and the efficacy of using the system. The unit is fitted with a plexiglass side panel in order to observe and to properly quantify in-basin sludge settling properties. Feed and operational sequences were automatically controlled through a programable logic controller (PLC).

### MATERIALS AND METHODS

Wastewater flows at the facility are manually corrected for pH. Temperature of the wastewaters discharged from the premises were monitored. Approximately, 3000 gallons (11,300 liters) of activated sludge from the Humacao Wastewater Treatment Facility was used to seed the demonstration facility which has an approximate volumetric capacity of 10,000 gallons (37,800 liters). The working volume can be changed through adjustment of the designated bottom water level, (lower operating volume). The unit can be operated manually or, automatically through a programmable logic controller. Acclimation procedures were initiated with process wastewaters taken from the central collection/equalization basin, using an air actuated double acting diaphragm pump. A semi-continuous cultivation technique was used based on a once a day feeding protocol, effectively simulating a single 24 hour CASS<sup>TM</sup> cycle of operation.<sup>8</sup> Acclimation was accomplished using co-metabolic techniques, (added degradable substrate), until it was determined that the biomass was self-sustaining using the wastewater only as feed. Volumetric additions were gradually increased from the initial 200 gallon (750 liters) per day, until the designated bottom water level position was reached. A slow-fill protocol was adopted, to minimize impact of potential toxicity effects. Without the captive selector this feed protocol can select for filamentous sludge bulking. An initial screening test was conducted, with an un-acclimated biomass. Later tests used an acclimated biomass. Combinations of wastewater and activated sludge were mixed and aerated prior to measuring the resulting oxygen utilization rate response. Immediate toxicity effects were not observed. Ammonium hydroxide was added to the basin in order to maintain balanced growth conditions, relative to nitrogen. Sufficient phosphorus was found to be contained in the wastewater. The rule of thumb BOD:N:P ratios in excess of 100:5:1, were complied with. Initial degradation was monitored on the basis of soluble COD concentrations, which were measured during and at the end of 24 hours aeration, in samples taken from the reactor. Influent samples were monitored for COD total, COD, soluble, Color, Oil and Grease, TSS and available nutrients (during the initial phase only). Filtered reactor samples were also analyzed for color and soluble COD. Some analyses of biomass concentrations measured as mixed liquor suspended solids and mixed liquor volatile suspended solids, were also conducted.

Following acclimation, the facility was then operated with variation to aeration cycle time and reactant fill-volume to assess the performance of this treatment method. On-site respirometric analyses were conducted on biomass samples taken at various times during react-aeration sequences, both in the captive selector zone and in the main aeration zone. Nutrient addition was practiced to maintain an effluent ammonia nitrogen of around 2 mg/L. The operating bottom water level of the reactor was set at a number of different positions in order to adjust for the various fill-volumes. Reaction conditions were maintained such that the settled biomass never exceeded 50% of the top water volume. During most of the study, the settled solids fraction after one hour rarely exceeded 400 mm in a depth of 2200 mm. Effluent was removed from the unit at a rate of 32 L/sec/m of weir length. Aeration was provided via 8 stainless steel coarse bubble diffusers at gas rates up to 3.7 m<sup>3</sup>/min. Loading conditions were such that the dissolved oxygen concentration was in excess of 4 mg/L during the latter phase of the aeration sequence. Samples of biomass were periodically taken for microscopic analyses. Cycles of various duration were used during the study, particularly during the onsite kinetic



Table X. In-Basin Parameters During Acclimation

Date	Settled Volume %	MLSS mg/L	MLVSS mg/L	COD <sub>s</sub> mg/L	Color Pt-Co	N mg/L	P mg/L	Cl mg/L
11/19		8838	6162	420	35	0.8 < 2	129	
11/21		2900	2147	368	70	0.5	94	
11/22				230	50	2.46	55	
12/05		3750	2625	255	250		62	
12/06	17.5	3680	2600	280	100		62	
12/09	17.0				305		7.5	
12/10	15.0	3300	2350	280	400	6.0	67	
12/11	15.0	2425	1750	215	350	6.6	60	
12/12	14.5	850	650	327	350	6.9	7.8	
12/13	13.0	2790	1990	254	350	8.4	8.4	
12/16		3000	2100	332	250	7.4	53	
12/17*		432	321	192	250	12.4	56	
12/18		3040	2060	255	190		50	
12/19		2210	1500	215	230		44	
12/20		2530	1690	205	200		50	
12/23*		880	620	225	300		40	
12/26*		143	96	190	250	1.9	36	
12/24*		8.0	2.0	230	300	1.6	40	
12/27*		194	128	200	350	1.2	44	
01/08*		13	10	250	250	4.8	33	3241
01/09*		15	5	160	250	0.26	22	2590
01/13*		43	37	275	200	0.16	18	3220
01/14*		77	57	200	200	.23	23	3334

\* Supernatant.

studies. All cycles operated with no inflow during effluent removal. Fill sequences were extended to 3.5 hours in some cycles depending on the loading condition that was being studied. This fill-rate was maintained for all cycles, to minimize risk of toxicity to the system through fast-fill operation. Fill-ratio was always less than 20%. Aeration sequences were varied to assess limits on biodegradability; times of 2 to 14 hours were used. Settle sequences were always of a one hour duration. Following acclimation and a steady state period of operation, analyses were conducted to achieve a treated effluent having less than 300 mg/L of total COD. Checks were made on the apparent viability of the biomass during particular runs oxygen uptake rates were conducted with the addition of, a single readily degradable substrate, (acetic acid). These tests were conducted with a volume addition to yield a concentration of 25 mg/L of acetic acid. Other tests were done with different combinations of substrate, (raw wastewater) and biomass ratios. Checks were made on the apparent viability of the biomass. During the course of a number of stimulus response in track runs where organic loading and hydraulic retention time varied. Biomass oxygen utilization rates were routinely monitored during the course of a track run. These were conducted using a magnetically stirred aerated sample, contained in a BOD bottle. Dissolved oxygen depletion and time were recorded to derive the oxygen utilization rate. Concentration of MLVSS was used to derive a specific oxygen utilization rate. Batch kinetics were conducted in a separate 200 liter reactor using acclimated biomass, a dump-fill and a continuous aeration protocol. Samples of mixed liquor were taken and filtered to establish a soluble COD removal velocity, this reactor was operated at 36° to 38°C. Some difficulty was encountered with excessive foaming, due to the intensity of aeration and mixing and from the amount of detergents that were contained in the wastewater. Color removal from the biologically treated wastewater using a five percent chlorine solution was assessed.

Wastewater testing procedures were conducted in accordance with procedures outlined in *Standard Methods*.<sup>3</sup> Parameters analyzed included, oil and grease, total and soluble COD, total and soluble BOD (infrequent) TSS, nutrients and color using both *Pt-Co* and *ADMI* techniques. The biological treatability study included the same parameters plus in-basin information on pH, MLSS, MLVSS, dissolved oxygen, oxygen uptake rate, temperature and flow (mass load).

An acclimation operational protocol was followed from 11/19/91 to 01/14/92. Table X summarizes the in-basin operating parameters during this period. Table XI summarizes the major influent parameters during the demonstration period. Table XII summarizes effluent and in-basin parameters while operating on four six hour cycles per day. The data shown is representative of two of the four



Table XI. Major Influent Parameters

Date	COD <sub>T</sub> mg/L	COD <sub>S</sub> mg/L	Cl mg/L	TSS mg/L	O&G mg/L	Color	BOD mg/L
11/19	420	266			30		
11/21	812	468			38	50	
11/22	1150	775			38		
12/11	825	725			31		
12/10	750	430			24		
12/09	525	353			6.3		
12/06	1048	725			3.5		
12/05	660	379			16		
12/12	667	254			0.22		
12/13	776	406			39		
12/16	500	400			16		
12/17	857	579			0.22		
12/18	720	505			9.1		
12/19	890	545			31		
12/20	595	400			-	200	
12/23	620	400			36	200	
12/24	595	422			14		
12/26	570	350			20	80	
12/27	410	325				60	
01/08	250	74	3356		5.2		
01/09	1560	850			108		
01/13	500	400	1272		17		
01/14	1110	765	3422		24		
01/19	765	610			48	200	163
	610	590			47	200	
01/20	1380	610		54	43	200	
01/21	1050	910			28	500	
	980				42	250	
01/22	700	525		36	23	750	
	1049	980		33	30	750	
	850	800		100	36	750	
01/23	1000	900		90	10	750	
	910	850		110	9.9	750	
	945			100	3.3	750	
01/24	790	400		200	10	500	
	465				.5	1000	
01/27	750	550					
01/28	490	400					
	675	510					
01/29	650	610					
	475	475					
01/30	425	340					
	840	675					
01/31	800	550					
	1090	680					
02/03	275	125		72	13	150	
	650	375		68	15	1500	
02/04	1310	840		208	25	1500	
02/05	850	550		143		1750	
	1150	780		143		1250	
02/06	1200	580		173		500	
	1050	860		63		1000	
02/07	1190	800		87		750	
02/11	970	650		300		1750	
02/12	1200	750		109		1750	
02/13	1390	600		333		1000	
	1070	960					
02/14	1020	800		107		1500	
	1025	780		103		1000	

Table XI. (Continued)

Date	COD <sub>T</sub> mg/L	COD <sub>S</sub> mg/L	Cl mg/L	TSS mg/L	O&G mg/L	Color	BOD mg/L
02/17	400	340		78		500	
	660	570		90		2000	
02/18	540	540		140		1500	
	520	600		70		1250	
02/19	1300	1220		100		1250	
02/20	980	475		190		750	
	630	420					
02/21	1040	900		230		500	
	750	700					
02/24	480	290					
02/25	1200	1050					
	1200	1025					
02/26	1150	1040		157		1500	
	1200	1025		64		300	
02/27	1025	820					
	1375	1100					
02/28	1400	1050					

cycles per day. Table XIII summarizes the main influent and effluent biological treatability performance. Table XIV summarizes data on the chlorine decoloring experiments. Figure 4 summarizes fractional removal of COD versus organic loading (COD based). Figure 5 summarizes effluent COD versus COD based organic loading.

### WASTEWATER FINGERPRINTING

Two production wastewater samples were taken from the influent line to the demonstration unit and "fingerprinted" using gas chromatography and mass spectrometry techniques. In both cases individual samples were collected during specific track runs for the preparation of a representative composite influent sample. Biologically treated effluent samples were also taken for comparative analyses. USEPA methods 8270 and 8240 for semi-volatile and volatile organics were observed.<sup>9</sup> Method 8270 is used to quantify most neutral, acidic, and basic organic compounds that are soluble in methylene chloride and capable of being eluted without derivatization as sharp peaks from a gas chromatographic fused silica capillary column coated with a slightly polar silicone. Such compounds include polynuclear aromatic hydrocarbons, chlorinated hydrocarbons, pesticides, phthalate esters, organophosphate esters, nitrosamine, haloethers, aldehydes, ethers, ketone, anilines, pyridenes, quinolines, aromatic nitro compounds, and phenols including nitro phenols. Method 8240 is similar to method 8270, but uses a megabore capillary column in place of a narrow bore capillary column. Standardization procedures require the addition of compounds in the EPA target compound list (TCL), plus a five point matrix standard together with surrogate standards, as described for the methodology, to properly enable qualitative and quantitative identification. Both samples were analyzed for the presence of TCL compounds in addition to compounds obtained from comparative searches of the EPA/NIH Mass Spectral Library. Compounds identified from the library are collectively categorized as Tentatively Identified Compounds (TIC). A number of strict guidelines are followed in assigning a tentative identification. Sample dilutions, when necessary, were made after the introduction of the surrogate compounds. Typical gas chromatograms for influent and biologically treated samples were made at dilutions of 1:10 and 1:1, respectively. Tables XV to XXI summarize concentrations of target list compounds and the tentatively identified compounds that were matched with the mass spectra library for the two sampling events.

For fingerprinting purposes, the relative retention time peaks relative to sample dilution together with the quantitation of compounds based on the integrated abundance from the Extracted Ion Current Profile (EICP) of the primary characteristic ion are of use. The equipment required to carry out these analyses included a Hewlett-Packard GC/MS system consisting of a HP5890 GC coupled to an HP 5970 Mass Selective Detector which allows the continuous acquisition and storage on machine readable media of all mass spectra obtained throughout the duration of the chromatographic program. The computer has software that can search any GC/MS data file for ions of a specific mass and that can plot such ion abundances versus time or scan number. It is a relatively simple matter to compare both qualitative and quantitative parameters of the two samples. While it is expected that



Table XII. Summary of CASS<sup>TM</sup> Performance

Date	TSS mg/L	COD <sub>T</sub> mg/L	COD <sub>S</sub> mg/L	Color Pt-Co	O & G mg/L	BWL gal	COD <sub>S</sub> mg/L	MLSS mg/L	MLVSS mg/L	Vol. gal
01/27	-		190			6210				797
		175	175							
01/28		190	190			6170				478
		140	140			6210				797
01/29		230	230			6130				638
		150	140			6170				638
01/30		180	180			5090				638
		220	200			6050				718
01/31		240	200			5971				558
		310	300			6250				478
02/03	120	205	120	500	0.12	6025	270	1240	880	1190
	136	225	180	150	2.6	5985	575	2620	2020	1390
02/04	43	230	180							
02/05	277	210	140			6025	160	4760	3500	991
	90	240	225			6184	130			1030
02/06	77	250	225	1000		6100	400	3380	2640	793
	90	270	210	1000		5985	220	3240	2480	951
02/07	73	280	160	750				3020	2280	
02/11	98	230	220	1000		6025	170	3380	2600	912
02/12	60	240	205	750		5946	-			1070
02/13	33	225	175	1000		6104	170	3260	2520	1270
	52	260	220	625		6104	200	4060	3080	1270
02/14	73	225	170	500		6262	170	3220	2360	753
	30	270	200	500		6184	350	5020	3800	753
02/17	43	220	300			6540	220	5520	4440	1150
	26	175	500			6382	125	-	-	1230
02/18	93	225	190	300		6540	220	5520	4440	1150
	25	210	125	500		6382	125	-	-	1230
02/19	53	260	260	1000		6302	280	4640	3640	1070
02/20	93	280	275	1000		6184	210	3160	2566	1150
	30	210	180	500		6263	-			1189
02/21	73	250	250	500		6290	125			1036
	60	240	180	500		6130	220			1156
02/24	135	225	220	350		6342	70	5300	4360	714
02/25	67	110	100	300		6342	60	5520	4580	714
		90	50			6342	50			714
02/26	42	140	125	400		6130	220			997
	64	120	75	250						
02/27		135	70			6170	80			1036
		125	75			6090	90			1156
02/28		180	130			6090	210			1196

subsequent production run samples might show some differences in constituents and relative differences in concentration of constituents, the analytical technique provides a powerful tool for characterizing the major organic constituents in this wastewater. Similarly, the same technique provides a means of identifying removal and or degradation resulting from aeration and activated sludge treatment.

### BIOMASS ANALYSES

A sample of biomass was taken from the demonstration CASS<sup>TM</sup> unit during the quantitation track runs. This sample was analyzed for metal content and for content of hazardous organics in accordance with EPA method. The principal results of this analysis are summarized in Table XXII. These data reflect a propensity for the activated sludge to adsorb dye compounds, as evidenced by the copper and other metal concentrations contained within the biomass. Activity measurements of the biomass during the quantitative track runs using acetate spike substrate addition techniques indicated a ready propensity for the biomass to utilize readily degradable simple organics such as acetate. While biomass oxygen utilization rate during react fill sequences, exhibited low values, the spike addition

Table XIII. Summary of Influent Data

	COD <sub>T</sub> mg/L	COD <sub>S</sub> mg/L	TSS mg/L	O & G mg/L	Color Pt-Co
Mean	853	621	125	24	797
Minimum	250	74	33	0.2	38
Maximum	1560	1220	333	108	2000
Standard Deviation	303	248	71	20	561
Mean + Std. Dev.	1156	869	196	44	1358

Summary of Effluent Data

	COD <sub>T</sub> mg/L	COD <sub>S</sub> mg/L	TSS mg/L	O & G mg/L	Color Pt-Co	BOD mg/L
Mean	214	203	83	2.7	556	6
Minimum	70	50	15	0.1	150	2
Maximum	310	500	277	10.0	1000	10
Standard Deviation	54	79	63	3.0	252	2
Mean + Std. Dev.	268	281	146	5.7	809	8

Table XIV. Treated Effluent Color Removal

Sample Number	Before Chlorine Pt-Co	After Chlorine Pt-Co	Chlorine Dose mL
2		50	
2		70	
4	400	10	3.0
5	300	15	1.0
6	150	15	0.3
7	200	35	0.5
8	250	50	0.3
9	500	300	0.3
9	500	30	1.0
10	750	70	0.8
11	500	70	0.6
12	500	40	
13	500	50	1.0
14	500	60	1.0
15	500	60	1.0
16	500	70	1.0
17	500	60	1.0

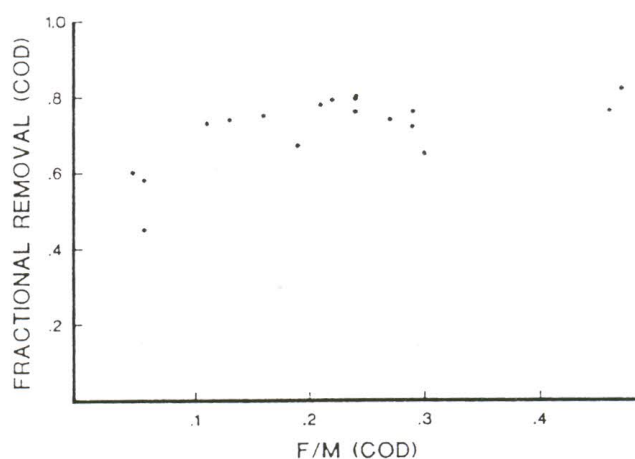


Figure 4. Fractional COD removal.



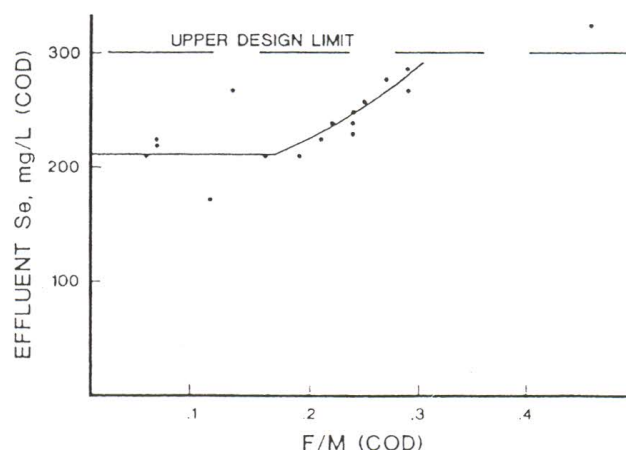


Figure 5. Effluent concentration versus organic loading.

Table XV. Tentatively Identified Compounds-Influent (Sample 1, Dilution Factor 10)

CAS Number	Compound Name	RT, min	Concentration $\mu\text{g/L}$
111762	2 Butoxy Ethanol	6.36	820
108703	1, 3, 5 - Trichlorobenzene	16.21	210
92524	1, 1 - Biphenyl	20.09	730
4860031	1 - Chlorohexadecane	20.81	130
143077	Dodecanoic acid	23.44	160
	Unknown Alkane	25.43	160
	Unknown Alkane	28.87	100
	Unknown Alkane	29.20	280
112801	9 - Octadecenoic Acid	31.22	110
57114	Octadecenoic Acid	31.50	120
	Unknown Alkane	32.52	200
7225641	9 Octal-Heptadecane	33.01	110
646311	Tetracosane	34.09	80
629992	Pentacosane	35.12	110
	Unknown Alkane	35.73	90
5533998	7 Hexyl Eicosane	36.13	140
593497	Heptacosane	37.24	170
630024	Octacosane	38.54	300
	Unknown Alkane	39.04	140
630079	Pentatriacontane	41.20	170
7098228	Tetratetracontane	42.21	160
	Unknown Alkane	42.28	240

Table XVI. Tentatively Identified Compounds-Effluent (Sample 1, Dilution Factor 1)

CAS Number	Compound Name	RT, min	Concentration $\mu\text{g/L}$
108703	1, 3, 5 Trichlorobenzene	16.43	4.0
	Unknown Alkane	21.03	7.0
	Unknown Alkane	25.71	5.0
930029	1 - (ethenyloxy) - Octadecane	27.54	39.0
	Unknown Alkane	27.94	45.0
	Unknown Alkane	28.09	18.0
	Unknown Alkane	28.29	34.0
	Unknown Alkane	28.48	12.0
	Unknown Alkane	28.58	15.0
	Unknown Alkane	28.94	6.0
	Unknown Alkane	30.37	5.0
	Unknown Alkane	30.94	13.0
	Unknown Alkane	31.44	6.0

**Table XVII. Tentatively Identified Compounds – Effluent (Sample 1, Dilution Factor 2)**

CAS Number	Compound Name	RT, min	Concentration $\mu\text{g/L}$
95498	1, Chloro - 2 - Methyl Benzene	25.10	130
1758889	2 - Ethyl - 1, 4 - dimethyl Benzene	27.38	26
535773	1 - Methyl - 3 - (1 - Methyl Ethyl) Benzene	28.01	58
25155151	Methyl (1 - Methyl Ethyl) Benzene	28.17	74
488233	1, 2, 3, 4 - Tetra Methyl Benzene	28.83	110
527537	1, 2, 3, 5 - Tetra Methyl benzene	28.47	150
	Alkyl Benzene	29.16	60
	Halogenated Alkyl Benzene	29.32	38
	Alkyl Benzene	29.52	28
	Halogenated Alkyl Benzene	29.63	76
	Alkyl Benzene	29.75	70
	Alkyl Benzene	29.91	66

test was used to indicate the reactivity and viability of the biomass. Of important note was the two three times specific oxygen utilization rate of the biomass in the captive selector zone.

After an extensive acclimation period it was shown that cycle times of 4 to 12 hours, using the same fill volume generated a statistically similar COD concentration in the biologically treated effluent. of around 200 mg/L concentration. Associated BOD values were generally less than 10 mg/L. Using the primary data base initial theoretical azo dye concentration based on daily water usage, averages 47 mg/L. Depending on the type of fabric being painted this equates to a mean range of between 7 mg/L (total cotton fiber) to 23.3 mg/L (polyester fiber). The data base covers a range of azo dye concentration in the wastewaters of 0.4 to 63.3 mg/L. For cotton fiber this equates to a range of 0.06 to 9.5 mg/L and for polyester fiber, the range is 0.2 to 31.7 mg/L of residual azo dye, respectively, in the raw wastewater.

## RESULTS AND DISCUSSION

Standard wet chemistry and specialized gas chromatography – mass spectrometry techniques were used to characterize the wastewaters from the Olympic Mills dyehouse facility. All chemical sources were audited in conjunction with daily use and daily water use. These data provided information for the calculation of the approximate concentrations of these chemicals in the wastewater.

GC/MS profiling enabled the concentration of all organics in the wastestream and in the biologically treated wastewater to be identified and quantified.

Effective aerobic pre-treatment of these wastewaters using the cyclic activated sludge system was demonstrated. The treatability data suggest there is an approximate 200 mg/L of soluble COD that is non-degradable in terms of the reaction time and sludge age criteria on which the facility was

**Table XVIII. Environmental Protection Agency Target Compound List (Sample 1)**

Compound Name	Influent $\mu\text{g/L}$	Effluent $\mu\text{g/L}$
Acetone	180	–
Chloroform	6.4	–
Benzene	11	–
Tetrachlorethane	21	–
Toluene	27	–
Xylene	17	–
1, 2-Dichlorobenzene	99	–
Fluorene	15	–
Naphthalene	39	1
1, 2, 4-Trichlorobenzene	940	18
2, Methyl naphthalene	2	–
4, Nitroaniline	13	10
2, 4-Dichlorophenol	6	–
2, 4, 6-Trichlorophenol	11	18
4, Methylphenol	33	–



**Table XIX. Tentatively Identified Compounds-Influent (Sample 2, Dilution Factor 10)**

CAS Number	Compound Name	RT, min	Effluent $\mu\text{g/L}$
111762	2 - Butoxy Ethanol	6.41	78
87616	1,2,3 Trichlorobenzene	16.24	36
92524	1, 1 - Biphenyl	20.13	87
643583	2 - Methyl - 1, 1 - Biphenyl	22.06	9
143077	2, 4 Dodecanoic Acid	23.42	8
1632708	5 - Methyl Undecane	25.45	12
	Unknown Alkane	29.23	19
	Unknown Alkane	32.25	5
	Unknown Alkane	32.34	4
	Unknown Alkane	32.54	19
646311	Tetracosane	34.12	8
	Unknown Alkane	35.23	7
	Unknown Alkane	35.49	19
	Unknown Alkane	35.76	9
	Unknown Alkane	35.97	6
55333998	7 Hexyl Eicosane	36.16	18
630024	Octacosane	37.25	18
629970	Docosane	38.59	28
630079	Pentatricontane	41.23	14
7098228	Tetratetracontane	42.24	11
	Unknown Alkane	43.36	7
	Unknown Halogenated Hydrocarbon	7.25	5
	Unknown	21.93	6

operated. The biological unit was operated under near nitrogen limited conditions at times, even though nitrogen in the form of ammonium hydroxide was added daily. Microbiological examination of the biomass showed occurrence of filamentous species, namely type 021N, 0675, 1851 and *Nostocoida limicola*. Sludge settling problems may occur in the full-scale system if proper attention is not placed on nutrient balance maintenance. Effective biological treatment was obtained even with the relatively high concentrations of dissolved solids in the raw wastes.

Residual color in the biologically treated wastewaters was easily removed with chlorine at contact times of 5-20 minutes using concentrations of around 25 to 100 mg/L.

While sludge settling tests were not conducted on a routine basis, it was found that sludge settling velocity was quite rapid and easily settled to a fractional volume of 30% of the reactor in the set, 60 minutes allocated for this sequence. There was a tendency for layering of straggler floc in the upper

**Table XX. Tentatively Identified Compounds - Effluent (Sample 2, Dilution Factor 1)**

CAS Number	Compound Name	RT, min	Concentration $\mu\text{g/L}$
74381401	1 - (1, 1 - Dimethyl)		
	2-2 Methyl Propanoic Acid	23.94	6.0
87616	1,2,3 Trichlorobenzene	16.05	7
	Unknown*	20.72	11
	Unknown	24.60	5
	Unknown	27.01	7
	Unknown	27.21	33
	Unknown	27.59	22
	Unknown	27.74	25
	Unknown	27.92	27
	Unknown	18.14	13
	Unknown	28.73	23
	Unknown	28.63	28
	Unknown	30.61	30

\* Compounds closely resemble one another.

**Table XXI. Environmental Protection Agency Target Compound List (Sample 2)**

	Influent $\mu\text{g/L}$	Effluent $\mu\text{g/L}$
Acetone	1300	8.8
1, 2 Dichlorobenzene	240	-
Fluorene	16	-
Naphthalene	23	-
1, 2, 4 Trichlorobenzene	1700	18
2, 4 Dichlorophenol	6.6	-
2, 4, 6 Trichlorophenol	16	-
4 Methylphenol	5.8	-

**Table XXII. Biomass Analyses**

Parameter	Concentration $\mu\text{g/L}$
Phenolics	16
Cyanide	40
Antimony	6.4
Arsenic	< 1.0
Beryllium	< 5
Cadmium	4
Chromium	120
Copper	840
Lead	42
Mercury	6.7
Nickel	60
Selenium	< 1.0
Silver	3
Thallium	< 1
Zinc	3187
MLSS	3740 mg/L
MLVSS	2740 mg/L

EPA TCL for semi-volatiles and volatiles all below detectable limits.

volume of the reactor at low solids flux. With increase in mixed liquor suspended solids concentration, this phenomenon markedly reduced.

Design data for the full-scale system was based on 85 percentile values.

## REFERENCES

1. Horner, C., P. Bishop, H. Yongjie, E. Holder, and P.U. Scarpino. "Biofilm Processes for Removal of Azo Dye from Municipal Wastewaters." *Proceedings, 46th Purdue Industrial Waste Conference, Purdue University, (1991)*.
2. Young, K. "Techniques for Treating Pre-washed Denim Laundry Wastes." *Proceedings 44th Purdue Industrial Waste Conference, Purdue University, (1988)*.
3. *Standard Methods for the Examination of Water and Wastewater*. 17th Edition, American Public Health Association, Washington (1989).
4. U.S. Patent Nos. 4663044, 4693821, 4891128, 5013441.
5. Goronszy, M.C. "Design Considerations for Cyclically Operated Activated Sludge Systems Treating Domestic Wastewater," *Proc., 41st Annual Industrial Waste Conference, Purdue University, (1986)*.
6. Goronszy, M.C., and Rigel, D. "Biological Phosphorus Removal in a Fed-Batch Reactor without Anoxic Mixing Sequences." *Research J. Water Pollut. Control Fed.*, 63(3): 248-258 (1991).
7. Goronszy M.C., and Costello, J. "Treatment of Fragrance Manufacturing Wastewaters, A Case History," *Proceedings, 46th Purdue Industrial Waste Conference, Purdue University, 1992*.



8. Chudoba, J., J. Albokova, and J. Cezh. "Determination of Kinetic Constants of Activated Sludge Microorganisms Responsible for Degradation of Xenobiotics," *Wat. Res.* 23(11): 1431-1438 (1989).
9. "Methods for the Determination of Organic Compounds in Finished Drinking Water and Raw Sewage Water," *Method 524.2; US EPA. Office of Research Development* Cincinnati, OH, 1986.