Color Removal
From Textile Plant Effluents

By 0. Marmagne, C. Coste,
Degremont S.A.,
Cedex, France

Note-(Author's title is Research Engineer with the Industrial Technical Department, Degremont S.A., Co-author's Manager, Industrial Technical Department, Degremont S.A.)

Abstract

Textile plants, particularly those involved in finishing processes, are major water consumers and the source of considerable pollution. The American and European directives on effluent quality to be issued in coming years will be increasingly restrictive; conventional treatment lines and discharge into municipal systems will no longer be tolerated by water authorities at the various levels. Therefore, it is of paramount importance to minimize pollution and to know its exact nature, in order to implement an appropriate treatment process.

Pollution measurement

BOD_5(biochemical oxygen demand) is usually measured after five days. This so-called BODs corresponds to the phases of assimilation and synthesis by microorganisms. It is sometimes useful to know the ultimate BOD, measured after 21 days, which includes the phase of auto-oxidation of bacteria. In France, BOD is measured in accordance with the standard NF.T90. 103 .

COD (chemical oxygen demand) represents all oxidable matter, particuarly certain oxidable minerals (e.g., sulides, sulfites) as well as the majority of organic compounds. Only certain nitrogenous and hydrocarbon compounds are unaffected by this potent oxidation. The standardized method of analysis of COD in wastewater NF.T90.101) uses potassium dichromate in a heated sulfuric medium.

Table I: Selected textile dyes.

Acid dyes		Cationic dyes	
AcidBlue 142	Triphenylmethane	BasicBlue 41.1	Azoic
Acid Blue 113	Azoic	Basic Yellow 13	Methine
Acid Blue 260	Anthraquinone	Basic Blue 3	Oxazine
Mordant dyes		Vat dyes	
Acid Brown 298	Azoic 1/2	Vat Blue 4	Anthraquinone
Acid Black 142	Azoic 1/1	Vat Green 1	Anthraquinone
Disperse dyes		Reactive dyes	
Disperse Blue 56	Anthraquinone	Reactive Blue 204	Oxazine (MFT)
Disperse Yellow 235	Anthraquinone	Reactive Blue 209	Formazan FCP
Direct dyes		Reactive Red 184	Azoic (MFT)
Direct Blue 199	Phtalocyanine	Reactive Blue 41	Phtalocyanine (MCT)
Direct-Red 89	Azoic	Reactive Blue 49	Anthraquinone (MCT)
Sulfur dyes			
I specimen of Black dye			

Color is measured using the standardized method of comparison with a color scale, the Hazen scale (NF.-T90.034). The latter is determined using various dilutions of a potassium chloroplatinate solution. Although this method is not satisfactory for the measurement of color in industrial wastewater, it is used for lack of a standardized alternative. In the following study, a more reliable method, called the "area method" has been used. For all solutions, the visible spectrum is scanned in order to obtain a curve of Optical Density = f(λ). The area beneath the resulting peak is then considered representative of the color intensity of the sample.. Color removal achieved by various treatment processes can then be determined by simple comparison with the scale. To date, this relatively precise analytical method has not become standardized.

Naturally, a considerable battery of other methods (suspended solids, heavy metals, nitrogen, phosphorus) is also available, but will not be discussed in this article.

Nowadays, many of the world's textile manufacturers are equipped with their own wastewater treatment plant which usually combines an aerobic biological process and a physical-chemical process. In some cases, only one of these steps is needed to obtain satisfactory treatment efficiency.

In general, the COD/BOD_5 ratio of a textile industry effluent ranges from 3 to 4, meaning that the effluent is moderately biodegradable. A 40 to 50% color removal can be anticipated due to biodegradation and to the adsorption of the dyes on flocculated sludge. COD removal can be expected to reach 70%. Physical-chemical processes alone cannot provide satisfactory results, even with the addition of specific coagulants that can enhance color removal considerably (such as Kemazur 45-39, manufactured by ERPAC). Color removal of insoluble dyes is insufficient, and COD removal is only moderately efficient (about 50%). Furthermore, this alternative entails high reagent consumption and substantial sludge production.

Fact is, a combination of biological and physical-chemical processes will remove more than 85% of the COD. This results in an effluent containing a COD refractory to these conventional processes (between 150 and 300 mg/L), low BOD_5 and usually high color. Ideally, a complementary treatment process is needed to remove the color and, if possible, the residual COD (Figure 1).

Dyes

Residual color is usually due to insoluble dyes which have low biodegradability. The following COD/BOD_5 ratios are given as examples:

Direct Blue 80	COD/BOD_5 = 17.7
Disperse Red 68	COD/BOD_5 = 7.0
Reactive Blue 21	COD/BOD_5 = 59.0
Vat violet 21	COD/BOD_5 = 10.8

Discharge standards will undoubtedly restrict color to a maximum value of 100 mg Pt.Co/L. The results of the conventional treatments mentioned above are far from being in compliance with this level. It is therefore indispensable to become more familiar with the behavior of organic dyes in order to determine the color removal technology that best meets the needs of each user company.

Processes studied and results

The aim of this study is to learn how various dyes react to water treatment techniques that can have a color-removing effect.

- The COD of the dyes studied is

Table II: COD resulting from the select dye.

Dye	Structure	COD (g O_2/g of dye)
Acid Blue 142	Triphenylmethane	1900
Acid Blue 113	Azoic	1500
Acid Blue 260	Anthraquinone	1551
Basic Blue 41.1	Azoic	1100
Basic Yellow 13	Methine	1400
Basic Blue 3	Oxazine	1000
Vat Blue 4	Anthraquinone	1600
Vat Green 1	Anthraquinone	1800
Direct Blue 199	Phtalocyanine	700
Direct Red 89	Azoic	500
Disperse Blue 56	Anthraquinone	1500
Disperse Yellow 235	Azoic	1500
Acid Brown 298	Azoic 1/2	700
Acid Black 142	Azoic 1/1	1000
Reactive Blue 204	Oxazine (MFT)	650
Reactive Blue 209	Formazan (FCP)	800
Reactive Red 184	Azoic (MFT)	850
Reactive Blue 41	Phtalocyanine (MCT)	1150
Reactive Blue 49	Anthraquinone (MCT)	1250
Sulfur	–	650

Table III: Efficiency of treatment by coagulation-flocculation.

Dye	Structure	COD removal (%)	Color removal (%)	Floc notation
Acid Blue 142	Triphenylmethane	95.4	98.6	6
Acid Blue 113	Azoic	90.2	97.2	6
Acid Blue 260	Anthraquinone	33.3	93.2	6
Basic Blue 41.1	Azoic	0.0	0.0	0
Basic Yellow 13	Methine	0.0	0.0	0
Basic Blue 3	Oxazine	0.0	0.0	0
Vat Blue 4	Anthraquinone	35.5	49.1	4
Vat Green 1	Anthraquinone	52.6	52.1	4
Direct Blue 199	Phtalocyanique	90.6	97.0	6
Direct Red 89	Azoic	89.9	90.3	6
Disperse Blue 56	Anthraquinone	89.7	95.1	8
Disperse Yellow 235	Azoic	62.7	93.5	8
Acid Brown 298	Azoic 1/2	53.4	48.8	4
Acid Black 142	Azoic /1	88.9	68.0	4
Reactive Blue 204	Oxazine (MFT)	28.2	53.0	4
Reactive Blue 209	Formazan (FCP)	31.0	88.8	6
Reactive Red 184	Azoic (MFT)	23.4	22.6	2
Reactive Blue 41	Phtalocyanine (MCT)	60.0	38.3	2
Reactive Blue 49	Anthraquinone (MCT)	19.0	35.4	4
Sulfur	–	83.9	96.1	8

reported as grams of O_2 per gram of dye. Note that the COD corresponds to a commercial dyestuff and includes any and all additives contained in the formula. The results are shown in Table II.

The following rule of thumb may be derived:

Direct = Sulfur < Mordant = Reactive < Cationic < Dispersed < Acid < Vat

- Biological processes were not implemented due to the long period needed for biological organisms to become acclimated and to the low biodegradability of dyes.
- Coagulation-flocculation: the aim is to know whether dyes can be easily coagulated and flocculated. No effort is made to optimize coagulant dosages. The coagulation is carried out in bench flocculators (six l-liter units).

Following a mixing time of 10 minutes, the floc is allowed to settle for 15 minutes. The accepted system of floc notation is as follows:

0: no floc
2: slightly visible floc, opalescent water
4: small floc
6: medium-sized floc with clear interstitial water
8: well-formed floc with clear, shining interstitial water
10: very well-formed floc with clear, shining interstitial water

The results obtained are compiled in Table III.

Cationic dyes do not coagulate at all; making their removal by physical-chemical (coagulation-flocculation) process impossible.

Acid, direct, vat, mordant and reactive dyes usually coagulate, but the resulting floc is of poor quality and does not settle well even after introduction of a flocculant. Thus, a coagulation-flocculation treatment will yield mediocre results. It is not inconceivable that this property could be an advantage in membrane processes.

Sulfur and dispersed dyes coagulate well and settle easily, thanks to the fornation of good-quality floc. Accordingly, color removal is practically complete. Thus, the efficiency of the coagulation-flocculation process is excellent for this type of dye.

From the standpoint of water recycling, membrane techniques hold great promise. The various dyes are studied to see if removal is possible by microfiltraion, ultrafiltration or nanofiltration mod-

Table IV: Efficiency of membrane treatment.

Dye	Structure	Microfiltration COD rem (%)	Microfiltration Color rem (%)	Ultrafiltration COD rem (%)	Ultrafiltration Color rem (%)	Nanofiltration COD rem (%)	Nanofiltration Color rem (%)\
Acid Blue 142	Triphenylmethane	20. 1	14.5	91.7	96.8	95.8	98.6
Acid Blue 113	Azoic	1.6	5.0	86.7	98.0	95.6	99.1
Acid Blue 260	Anthraquinone	1.6	13.3	88.6	95.0	96.2	98.2
Basic Blue 41.1	Azoic	2.9	11.0	88.0	98.9	96.0	99.5
Basic Yellow 13	Methine	0.4	7.0	80.4	96.8	88.0	98.2
Basic Blue 3	Oxazine	4.4	6.0	88.0	96.2	92.0	98.1
Vat Blue 4	Anthraquinone	29.1	80.5	92.7	95.6	97.6	98.2
Vat Green 1	Anthraquinone	31.2	89.3	91.3	97.2	95.9	98.4
DirectBlue 199	Phtalocyanine	1.4	3.0	81.5	96.2	92.3	98.0
Direct Red 89	Azoic	1.6	1.7	84.0	96.0	92.0	97.7
Disperse Blue 56	Anthraquinone	33.3	69.6	91.4	95.4	96.4	98.5
Disperse Yellow	Azoic	35.7	99.1	89.1	99.2	96.4	99.6
Acid Brown 298	Azoic 1/2	2.0	6.7	86.7	97.1	92.0	98.1
Acid Black 142	Azoic 1/1	3.7	0.5	81.3	96.2	90.0	97.4
Reactive Blue 204	Oxazine (MFT)	2.3	5.2	80.0	95.5	89.6	97.9
Reactive Blue 209	Formazan (FCP)	0.9	4.2	76.5	94.0	94.2	97.0
Reactive Red 184	Azoic (MFT)	0.6	6.7	80.9	96.2	89.1	98.3
Reactive Blue 41	Phtalocyanine (MCT)	0.4	7.4	76.1	94.0	93.3	97.2
Reactive Blue 49	Anthraquinone (MCT)	0.5	5.0	81.3	92.3	93.8	96.9
Sulfur	–	1.1	1.7	80.0	93.4	92.0	99.3

Table V: Efficiency of activated carbon treatment.

Dye	Structure	COD removal (%)	Color removal (%)
AcidBlue 142	Triphenylmethane	71.4	93.7
Acid Blue 113	Azoic	70.9	95.6
Acid Blue 260	Anthraquinone	58.8	86.8
Basic Blue 41.1	Azoic	84.7	100.0
BasicYellow 13	Methine	81.5	99.7
Basic Blue 3	Oxazine	67.8	98.5
Vat Blue 4	Anthraquinone	0.0	10.1
Vat Green 1	Anthraquinone	0.0	12.9
Direct Blue 199	Phtalocyanique	25.6	71.7
Direct Red 89	Azoic	45.5	59.0
Disperse Blue 56	Anthraquinone	0.0	30.2
Disperse Yellow 235	Azoic	59.3	83.4
Acid Brown 298	Azoic 1/2	91.5	97.1
Acid Black 142	Azoic 1/1	82.1	98.1
Reactive Blue 204	Oxazine (MFT)	70.6	69.0
Reactive Blue 209	Formazan (FCP)	89.8	78.5
Reactive Red 184	Azoic (MFT)	69.4	77.6
Reactive Blue 41	Phtalocyanine (MCT)	74.6	57.4
Reactive Blue 49	Anthraquinone (MCT)	19.2	94.6
Sulfur		45.5	40.9

ules. Permeate quality is analyzed. Tests involving microfiltration are conducted on filters of 0.45 μ/m pore size. The ultrafiltration and nanofiltration processes are implemented on a laboratory-scale pilot as illustrated in Figure 2.

Experimental results are compiled in Table IV.

A large proportion of dispersed and vat dyes are removed by a 0.45 μ/m pore microfiltration membrane. Thus, a good degree of color removal may be achieved using this type of membrane. The proportion of other classes of dye removed on these membranes is small or nil.

Ultrafiltration achieves complete color removal for all classes of dye, but care is needed to avoid membrane clogging, which appears to occur rapidly. Naturally, nanofiltration also allows complete removal of color, but with less membrane fouling.

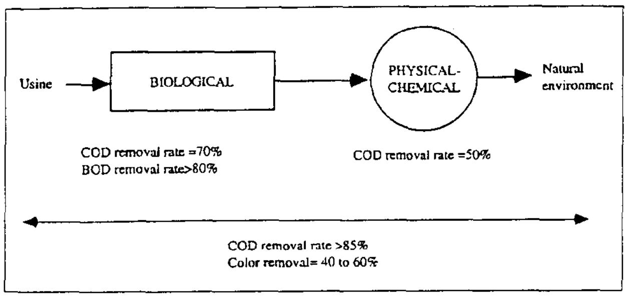
It is important to note that membrane techniques achieve a sharp reduction in COD, since the dyes are removed from the permeate. However, this is offset by the formation of a heavily-loaded concentrate which will ultimately require disposal.

Powdered Activated Carbon (PAC) will be studied at a single concentration for the sole purpose of determining whether it has any color-removing action. These tests are performed in laboratory flocculators. The carbon is left to act for a few minutes in an agitated reactor, and the supernatant is analyzed following settling and filtration. Notably, powdered activated carbon can be introduced "as is" into a physical-chemical or biological process. Results are compiled in Table V. The decisive parameter seems to be the class of dye rather than its chemical structure.

High removal rates (over 90%) are achieved using activated carbon for cationic, mordant, and acid dyes . For direct, sulfur, dispersed, and reactive dyes, efficiency is moderate (over 40%), or can be improved using massive dosages of activated carbon. For vat dyes, color removal is very low (under 20%). These rates may, therefore, be viable for companies working with animal or acrylic fibers. For other fibers, efficiency is either unpredictable or dependent on massive carbon dosages.

An effort is made to determine the efficiency of ozone as a function of the chemical structure of the dyes. Indeed, ozone can be hoped to have an oxidiz-

Figure 1: Conventional treatment line.



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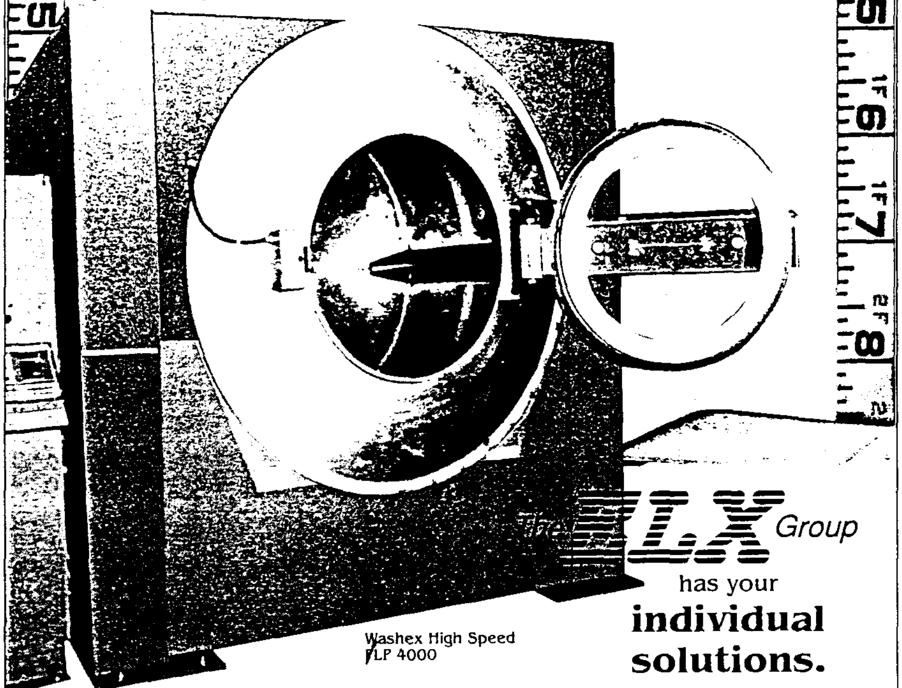

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Table VI: Efficiency of ozonation.

Dye	Structure	Ozone (mg/l)	COD reml (%)	Color rem (%)
Acid Blue 142	Triphenylmethane	49.5 112.1	30.7 44.3	11.6 91.5
Acid Blue 113	Azoic	54.8 117.5	5.2 54.6	87.8 98.7
Acid Blue 260	Anthraquinone	31.7 99.3	8.5 47.9	82.3 99.3
Basic Blue 41.1	Azoic	44.5 72.0	14.4 35.6	97.6 100.0
Basic Yellow 13	Methine	48.1 81.6	39.6 50.0	95.2 100.0
Basic Blue 3	Oxazine	44.2 **83.9**	9.4 **39.6**	83. 100.0
Vat Blue 4	Anthraquinone	40.2 84.6	2.9 36.7	0.0 19.8
Vat Green I	Anthraquinone	43.5 103.5	13.2 35.5	11.1 53.1
Direct Blue 199	Phtalocyanique	44.2 73.4	46.9 84.4	62.8 98.8
Direct Red 89	Azoic	44.9 79.9	40.0 100.0	94.4 100.0
Disperse Blue 56	Anthraquinone	27.2 88.3	4.0 34.1	1.4 99.6
Disperse Yellow 235	Azoic	36.8 60.8	18.5 36.1	3.2 11.5
Acid Brown 298	Azoic 1/2	57.2 110.8	58.6 72.9	86.1 98.7
Acid Black 142	Azoic 1/1	31.4 103.3	21.8 72.4	66.7 99.3
Reactive Blue 204	Oxazine (MFT)	49.2 83.1	13.3 67.3	83.2 99.7
Reactive Blue 209	Formazan (FCP)	43.1 80.3	19.4 45.8	90.1 99.0
Reactive Red 184	Azoic (MFT)	40.7 82.2	24.3 85.2	83.2 99.7
Reactive Blue 41	Phtalocyanine (MCT)	43.3 88.7	25.8 44.8	69.0 99.5
Reactive Blue 49	Anthraquinone (MCT)	48.0 81.4	50.6 85.9	95.9 99.4
Sulfur		50.9 92.7	46.8 83.0	62.0 95.5

ing effect and show preference for the double bonds of the dye molecules. Oxidation of indigo by ozone is one example (Figure 3).

Flow data

Ozonized oxygen is injected into a PVC column through a porous diffuser. The column has a capacity of 8 liters of colored effluent. The typical flow diagram for the ozonation pilot unit is shown in Figure 4. Experimental results are compiled in Table VI.

Color removal

Color removal is generally effective and fairly rapid using ozone. Again, it is the class of dye that is most significant in determining the behavior of the dyes. To a lesser extent, the chemical structure, if highly compact (phtalocyanine, triphenylmethane, etc.) can have a negative impact on the rate of reaction.

Reasonable ozone dosages (50 mg/L) usually allow very efficient color removal for acid, mordant, cationic, direct, reactive, and sulfur dyes. Removal of a significant portion of the COD can also be anticipated, even if it is sometimes necessary to push the ozone dosage somewhat higher.

Dispersed and vat dyes are generally difficult to remove, even at high ozone dosages. Ozone is not an efficient treatment solution for these dyes.

Future prospects

As stated, biological and coagulation-flocculation treatments have proven insufficient to remove color from a textile plant effluent. They produce an effluent characterized by relatively few COD, low biodegradabiiity and high color.

The use of coagulants specific to color removal applications may be considered. But although the removal efficiencies will improve slightly, the result will often remain insufficient. The same observation can be made regarding powdered activated carbon, which can be used as a complement to a biological or physical-chemical treatment. This will lead to somewhat enhanced performance. This option is viable only for solutions with low residual color. The use of granular activated carbon (GAC) would be prohibitively costly.

Alternative answers

The only alternatives remaining are ozone and membrane processes. With membranes, the significant danger of clogging would undoubtedly call for filtering a coagulated effluent (with ferric chloride as the coagulant, for example), unless care is taken to select the type of membrane best suited to the effluent. This would yield a non-colored permeate that could either be returned to the process or discharged to the sewer. However, the resulting concentrate would need to be treated and placed in landfill.

Ozone emerges as the most universal solution offering satisfactory efficiency. It produces an effluent with no color, low COD, and suitable for discharge into the environment or return to the process.

In any case, pilot studies will be necessary prior to any decision, in order to determine the appropriate chemical dosages and technologies. Figure 5 provides some possible flow diagrams. Textile plant effluents are highly variable in nature. So then, are the treatment solutions to be proposed. □ □ □

Figure 2: Membrane pilot.

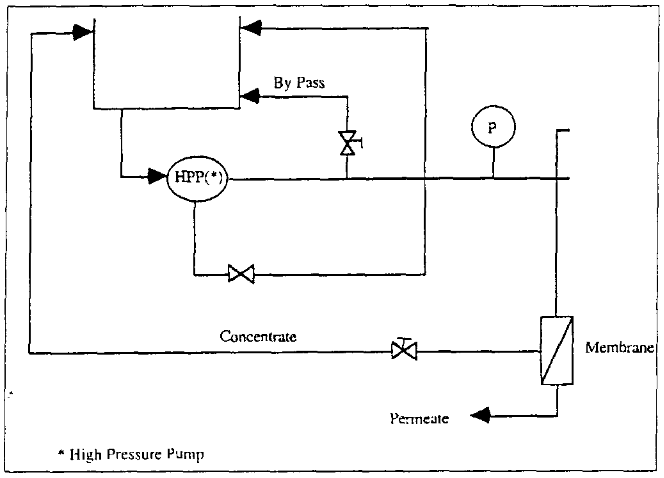


Figure 3: Reaction of ozone with indigo.

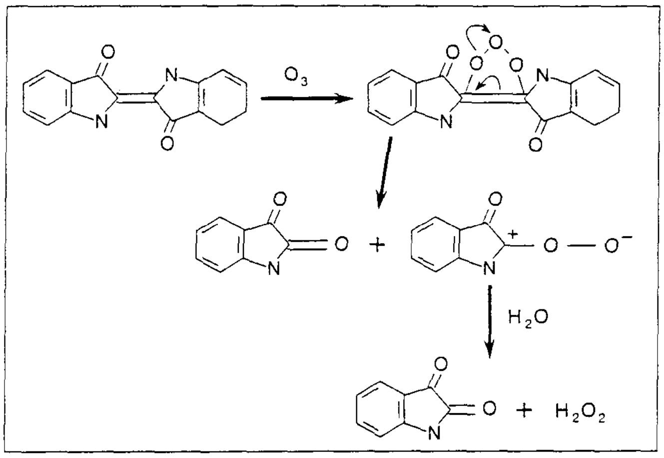


Figure 4: Ozone pilot flow diagram.

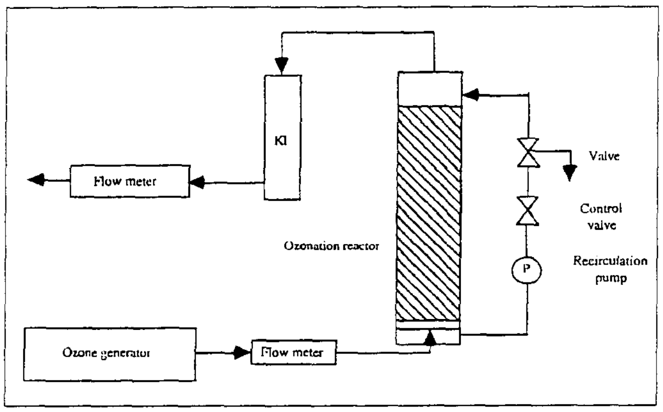
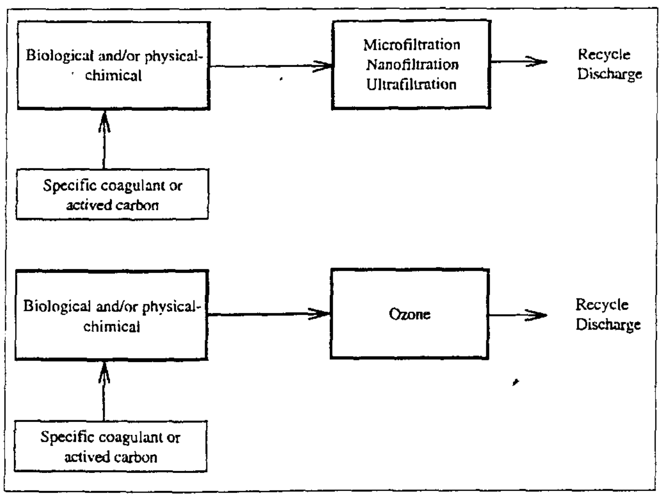


Figure 5: Proposed treatment lines.



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