Effect of chemical treatment on soluble residual COD in textile wastewaters

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Abstract The effect of chemical treatment on the magnitude of soluble residual COD in the biological treatment effluent is investigated for knit fabric finishing wastewater. Bentonite is selected for its potential to remove soluble COD together with color and particulate components. Chemical treatment using bentonite, when applied prior to biological treatment removes around 40% of the biodegradable as well as soluble inert COD initially present in the wastewater. As a chemical post-treatment, it acts as a polishing step, removing particulate matter and a minor portion of around 20% of the remaining soluble COD. These findings suggest chemical pre-treatment as a better alternative for the optimization of soluble COD removal.
Keywords Biological treatment; COD fractionation; chemical treatment; industrial pollution control; knit fabric finishing wastewater; soluble residual COD; textile industry; wastewater reuse

Introduction

Biological treatment or a sequence of chemical precipitation/biological treatment is generally defined as the appropriate treatment technology for textile mill effluents. The application of chemical treatment prior to biological treatment is commonly used for the minimization of toxic effects of some types of dyes on biological treatability (Pavlostathis and Tincher, 1992; Kuo, 1992) or for the reduction of high inert organic fractions in order to meet the required discharge standards (Jedele, 1982; Abeta *et al*., 1984; Sewekow, 1993).

Soluble residual COD, consisting of initial soluble inert COD of the wastewater and soluble microbial products generated during biological processes, is of primary importance in meeting the discharge standards for biological carbon removal systems. When reuse applications are involved, the level of inert COD concentrations becomes a more important factor with a negative effect in meeting the stringent effluent criteria, as the *remaining* wastewater is expected to have a higher soluble residual COD fraction. Therefore, chemical treatment as a pre-treatment step can be used to lower the soluble inert COD content of the wastewater, which is the main component of soluble residual COD. Chemical treatment after biological treatment (chemical post-treatment) is also a polishing technique used to elevate the water quality to a higher level (Lin and Chen, 1997; Kabdaşlı *et al*., 1992).

Chemical precipitation used to remove COD and color in textile wastewaters is effective on wastewaters originating from insoluble dyeing processes such as disperse dyeing operations (Koprivanac *et al*., 1993; Lin and Liu, 1994; Kabdaşlı *et al*., 2000). On the other hand, chemical treatment with coagulants such as alum, and iron salts is reported to be ineffective in removing COD and color for wastewaters containing soluble reactive dye (Kuo, 1992; Tünay *et al*., 1996).

The objective of the study was to investigate the effect of chemical treatment applying coagulation-flocculation and settling on the magnitude of soluble residual COD in the biological treatment effluent for knit fabric finishing wastewater. Experiments were conducted out on effluent samples of a cotton-synthetic finishing plant as pre- or post-treatment applications of chemical treatment. In this context, chemical treatability studies were carried out on raw wastewater of the mill and *remaining* wastewater after segregation of

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reusable streams, using $FeCl_3$, alum, lime and sodium bentonite as coagulants. The results of chemical treatment applied before and after biological treatment were compared on the basis of soluble residual COD and color removal efficiencies.

Materials and methods

Description of the textile plant

The investigated plant is a typical example for *knit fabric finishing* subcategory, involving batch-wise operations of 20 different processes such as *dyeing* (reactive dye), *bleaching, kiering* etc. applied to cotton, viscose rayon, polyester, polyamide knit fabrics and cotton/polyester, polyester/viscose rayon blend knit fabrics. The average daily production is 10 tons and the water consumption is about 750 m^3d^{-1}, with a wastewater generation rate of 72 $l\,kg^{-1}$ fabric processed.

The textile mill has a treatment plant that includes an equalization basin, a neutralization unit and a conventional activated sludge system operated at a sludge age of 7 days and at a hydraulic detention time of 20 hours. A sludge-thickening unit together with filter press is used for the treatment of produced sludge. The effluent of the treatment plant is discharged to an adjacent receiving water body.

Experimental approach

Experimental investigation covered three different sampling programs. First, a flow-proportional composite sample was prepared to represent 68% (*Composite I*) of the daily total wastewater generation which consists of 7 different processes, namely; cotton knit fabric optical brightening, cotton knit fabric *remazol*® dyeing with kiering, cotton knit fabric *procion*™ dyeing with bleaching, viscose rayon knit fabric *procion*™ dyeing, polyester-viscose knit fabric double bath dyeing, cotton-polyester knit fabric single bath dyeing, cotton-polyester knit fabric double bath dyeing. The second sample, *Composite II*, corresponded approximately to 55% of the total wastewater generation covering the first four processes, mentioned above. This sample program also included the experiments on the remaining wastewater after segregation of reusable streams. In the third sampling program samples were taken from the equalization tank and from the effluent of the activated sludge system to investigate the effect of chemical pre- and post-treatment on soluble inert COD fractions. The effluent sample was taken 20 hours after the sampling time from the equalization tank to be able to represent and maintain approximately the same wastewater quality.

Experimental and analytical methods

All analyses for conventional characterization were performed as defined in *Standard Methods* (1998) except for COD, which was accomplished following the procedure defined by ISO 6060 (ISO, 1986). Filtrates of samples, subjected to vacuum filtration by means of Millipore membrane filters with a pore size of 0.45 μm, were defined as "soluble fractions". The Millipore AP40 glass fiber filters were used for suspended solids (SS) and volatile suspended solids (VSS) measurements. Color measurements were conducted on filtered samples with *Hach DR/2* model spectrophotometer at 455 nm wavelength. The initial soluble inert COD, S_{I1} and the residual soluble microbial product, S_P, components associated with the samples were determined according to a recently proposed experimental procedure by Orhon *et al.*, (1999a). Respirometric procedures were used for the assessment of the readily biodegradable COD, S_{S1} (Ekama *et al.*, 1986). OUR measurements were conducted by a *WTW OXI DIGI 2000* oxygen meter and a *Manotherm RA 1000* respirometer. In the experiments the samples were adjusted to a pH of 7–7.5 by phosphate buffer and the tests were carried out at room temperature.

Chemical precipitation experiments were performed with a lab-scale jar-test apparatus adjusted to provide 5 minutes flash mixing, 30 minutes flocculation and 30 minutes settling. For experiments run with sodium bentonite, on the other hand, three subsequent 3 minutes flash mixing and 3 minutes settling jar-test cycle was adopted. $FeCl_3.H_2O$, alum [$Al_2(SO_4)_3 \cdot 18H_2O$], $Ca(OH)_2$ and sodium bentonite were used as flocculants together with anionic polyelectrolyte, UCE AP273 in different configurations. Optimum pH was adjusted with $Ca(OH)_2$, when necessary.

Evaluation of experimental results

Wastewater characterization

Wastewater characterization studies were mainly conducted on raw and remaining wastewaters after segregation of reusable streams. In textile industry, wastewater recovery and reuse is a commonly used application to decrease the water consumption. The widely used procedure is to segregate the wastewaters originating from the rinsing baths and to reuse them in the appropriate processes after suitable treatment. Reuse application provides savings up to 30–40% of water consumption, but the remained wastewater exhibits a stronger character, which is expected to be more resistant to biological treatment (Orhon *et al.*, 2000a, 2000b, 2001).

Raw wastewater. The first part of wastewater characterization covered their identification in terms of significant conventional parameters in the textile industry. Results, outlined in Table 1, indicate a stronger character, evidenced by high COD and conductivity levels, for composite samples reflecting major processes as compared to the sample from the equalization tank representing the overall effluent quality. This illustrates the typical property of textile effluent quality, which is heavily dependent on the specific processes responsible for their generation. The higher color content in the equalization tank can be explained with the possible discharges of dye baths in the plant at the time of sampling.

Composite II was re-structured by excluding the reusable fraction, which corresponded to a 30% savings in the total water consumption in the plant (Orhon *et al.*, 2001) and subjected to the same evaluation. The *remaining* wastewater reflects, as outlined in Table 1, a stronger character (31% increase of total COD; 38% increase of color) in comparison with the initial raw *Composite II* sample.

The second part of the characterization study basically involved COD fractionation. Despite the differences depicted for the values of conventional parameters, the results for COD fractions, as shown in Table 2, were quite consistent with the typical pattern

Table 1 Conventional characterization of cotton-synthetic wastewaters

Parameters	Unit	Composite I	Composite II		Equalization Tank
			Overall	Remaining	
Total COD	mgl^{-1}	1,980	1,125	1,475	925
Soluble COD	mgl^{-1}	1,210	870	1,215	530
TSS	mgl^{-1}	170	100	115	175
VSS	mgl^{-1}	130	90	95	155
TKN	mgl^{-1}	25	14	15	40
NH_3-N	mgl^{-1}	21	12	–	35
TP	mgl^{-1}	27	13	18	–
PO_4-P	mgl^{-1}	12	–	–	2
Alkalinity	mg $CaCO_3$ l^{-1}	2,150	1,675	2,380	610
Conductivity	μMhos cm^{-1}	21,800	14,500	19,800	9700
Color	Pt-Co unit	810	720	990	1840
pH	–	10.2	10.3	10.6	9.17

Table 2 COD Fractionation of Cotton-Synthetic Wastewaters

Parameters	Unit	Composite I	Composite II		Equalization Tank
			Overall	Remaining	
Total COD, C_T	mgl^{-1}	1,980	1,125	1,475	925
Particulate COD, X_T	mgl^{-1}	770	255	260	395
Soluble COD, S_T	mgl^{-1}	1,210	870	1,215	530
Readily Biodegradable COD, S_S	mgl^{-1}	190	120	135	175
Soluble Hydrolysable COD, S_H	mgl^{-1}	740	500	770	235
Slowly Hydrolysable COD, X_S	mgl^{-1}	705	200	260	355
Soluble Inert COD, S_I	mgl^{-1}	280	250	310	120
Particulate Inert COD, X_I	mgl^{-1}	65	55	≈0	40
S_S/C_T	%	10	11	9	19
S_H/C_T	%	37	44	52	26
X_S/C_T	%	35	18	18	38
S_I/C_T	%	14	22	21	13
X_I/C_T	%	3	5	≈0	4

associated with textile wastewater (Germirli Babuna, *et al.*, 1998; Orhon *et al.*, 2001). They underline the importance of the initial soluble inert fraction, S_{I1}, which may reach levels as high as 250–280 mgl^{-1} when a given set of processes become the major source for wastewater generation, as in *Composites I and II*. The result for the equalization sample shows the mixing and dilution effect of wastewater streams more compatible with biological treatment for lowering S_{I1} to120 mgl^{-1}. The relative changes in the S_S and S_H content of the equalization tank with respect to other samples, may be attributed to partial hydrolysis taking place during equalization. The similar COD fractionation study was also performed on remaining wastewater sample and the important feature of the COD fractionation summarized in Table 2 is the 20% increase in the inert COD content after recovery of the reusable fraction.

Effect of chemical treatment prior to activated sludge treatment

Chemical treatment of raw wastewater. Chemical treatment before activated sludge treatment was first conducted on raw wastewater samples using different coagulants. The optimum coagulant type and dosage were assessed on Composite I with the evaluation of the COD and color removal efficiencies. Figures 1a and 1b illustrate the results of the chemical treatment studies.

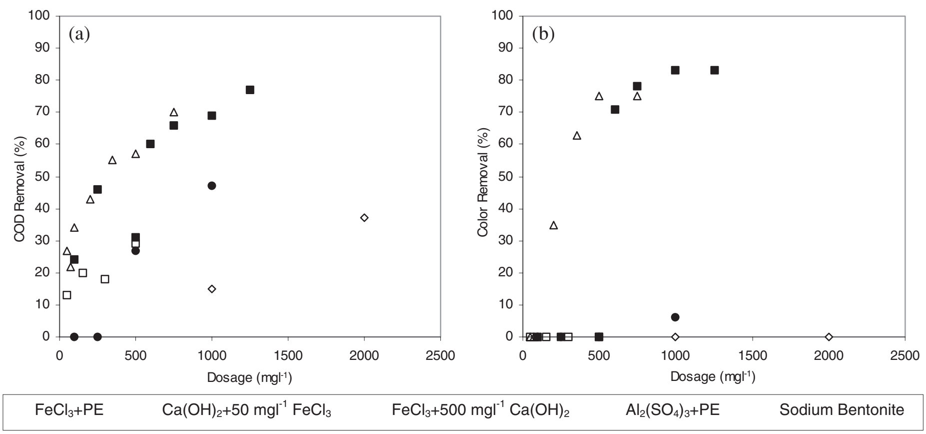

Figure 1 (a) COD and (b) color removal efficiencies of chemical treatability studies conducted on Composite I

Inspection of the data in Figure 1 qualifies sodium bentonite as the most efficient coagulant for both COD and color removal. In this context, following experiments on *Composite II* and equalization tank samples were conducted with sodium bentonite. As seen in Figure 2a, COD removal efficiencies for *Composite II* remained in the narrow range of 45–52%, with no appreciable improvement with increased bentonite doses between 1,000–4,000 mgl^{-1}. A slightly higher and increasing removal trend was observed for color in the range of 70–80%. A bentonite dose of 2,000 mgl^{-1}, corresponding to around 45% COD and 70% color removal was interpreted as the optimum level, as further increase was not economically justifiable with no indicative increase in color removal. Slightly higher but similar results were also obtained for the equalization tank sample, as shown in Figure 2b.

The chemical sludge resulting from the precipitation experiment on the equalization tank sample appears to have, as expected, good settling characteristics under laboratory conditions with a sludge volume of 80 mll^{-1}, a SVI of 43 mlg^{-1} and a dry solids content of 2.4%.

Chemical treatment of remaining wastewater. In the chemical treatment of the remaining wastewater sample, the optimum sodium bentonite dosage was estimated as 3,000 mgl^{-1} as shown in Figure 3, higher than the value obtained for the raw wastewater, in parallel to the stronger characteristics of the sample. At this dose, the COD removal achieved was calculated as 53%, and color removal, as 69%.

Effect of chemical pre-treatment on COD fractionation

COD fractions of the raw wastewater after chemical treatment. COD composition of the two samples characterizing the textile wastewater in the study were experimentally

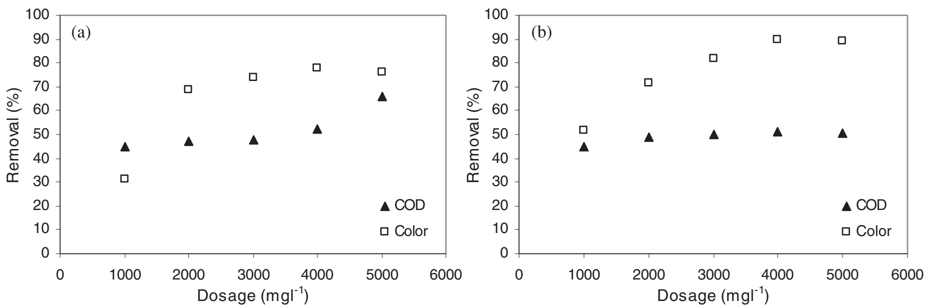

Figure 2 Color and COD removal efficiencies of chemical precipitation with sodium bentonite on (a) Composite II and (b) Equalization tank

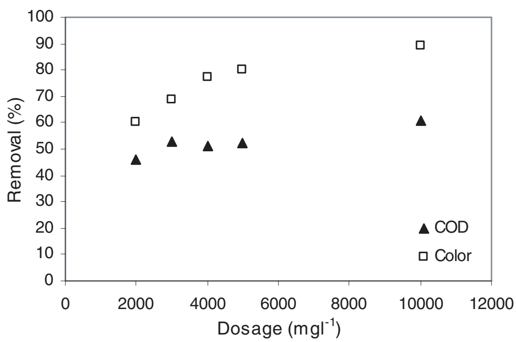

Figure 3 COD and color removal efficiencies of chemical precipitation on remaining wastewater

Table 3 COD fractionation after chemical treatment

Parameter	Composite II		Equalization	
	Concentration, (mgl^{-1})	Removal, (%)	Concentration, (mgl^{-1})	Removal, (%)
C_T	620	45	355	62
X_T	85	67	60	85
S_T	535	39	295	44
S_S	70	42	90	49
S_H	325	35	125	47
X_S	85	58	60	83
S_I	140	44	80	33
X_I	≈0	100	≈0	100

assessed after chemical treatment with 2,000 $mgl^{-1}$of sodium bentonite, previously selected as the optimum coagulant dose for the experiments. The results obtained are listed in Table 3.

The total COD reduction at the selected coagulant dose for *Composite II* was determined as 45%, lowering C_T from 1,125 mgl^{-1} to 620 mgl^{-1}. At this stage the particulate inert COD, X_I was not specifically determined and assumed to be totally removed, since its fraction in the raw wastewater before chemical treatment was negligible. The important point is that chemical precipitation with sodium bentonite, aside providing around 70% removal of particulate COD, was also effective on soluble components. A removal efficiency varying from 35–44% was observed for soluble COD fractions. In this context, two observations merit further emphasis: (i) Total biodegradable COD was reduced by 42%; (ii) the soluble inert COD concentration, S_I, was lowered to 140 mgl^{-1}, corresponding to a 44% removal, quite significant in terms of meeting the effluent discharge standards.

Results obtained for the equalization tank sample indicate a similar trend with a slightly higher removal of total COD and soluble COD components: C_T was reduced by 62% and S_S by 49%. The soluble inert COD, S_I was found as 80 mgl^{-1}, 33% lower than the level in the untreated sample before chemical treatment with bentonite.

The effect of bentonite on soluble COD components is also illustrated by the oxygen utilization rate, (OUR), measurements using the filtered equalization tank sample, before and after chemical treatment. Comparison of the OUR profiles plotted in Figure 4, gives a clear indication of biodegradable COD reduction achieved by bentonite treatment. The total area under the OUR curve commonly serves as a convenient tool for the calculation of C_S (Orhon and Artan, 1994) and the first part of the curve yields the value of S_S using the procedure proposed by Ekama *et al*. (1986).

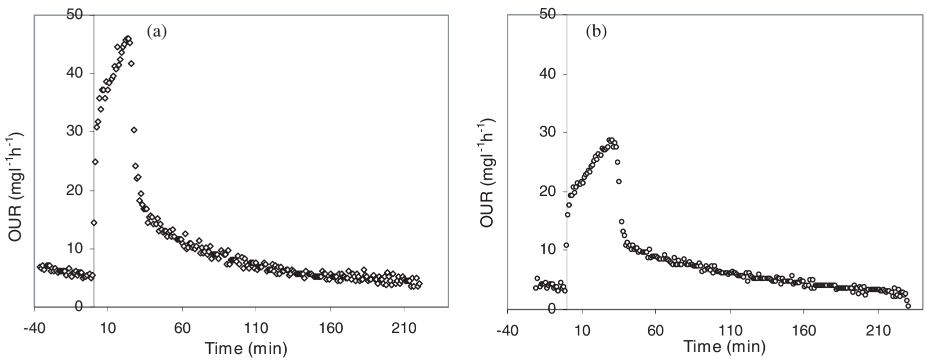

Figure 4 OUR profiles of equalization tank (a) raw sample and (b) after chemical precipitation

Table 4 Characterization of biologically treated cotton-synthetic wastewaters

Parameters	Unit	Effluent of biological treatment
Total COD	mgl^{-1}	195
Soluble COD	mgl^{-1}	160
TSS	mgl^{-1}	15
VSS	mgl^{-1}	15
TKN	mgl^{-1}	–
NH_3-N	mgl^{-1}	<1
TP	mgl^{-1}	–
PO_4-P	mgl^{-1}	5
Alkalinity	mg $CaCO_3$ l^{-1}	800
Conductivity	µMhos cm^{-1}	1,380
Color	Pt-Co unit	1,250
pH	–	8.5

Remaining Wastewater. As previously mentioned, chemical treatment application to the *remaining* wastewater after segregation of the recoverable portions from *Composite II*, was observed to reduce the total COD level to 700 mgl^{-1}, with a removal efficiency of 53%. On this sample, the soluble inert COD was the only fraction that was experimentally investigated and it was calculated as 170 mgl^{-1}, indicating a reduction level of 45%, similar to those obtained with the chemical treatment of the other samples.

Effect of chemical treatment after activated sludge treatment

In this part of the study, chemical treatment was applied to a composite sample collected to represent the effluent of the full-scale activated sludge plant in operation for the investigated textile mill. The quality of the effluent in terms of conventional parameters was measured as indicated in Table 4. The activated sludge plant was operated effectively, an effluent TSS concentration of only 15 mgl^{-1}, and a soluble COD concentration of 160 mgl^{-1}. An OUR test was also run for the effluent. As shown in Figure 5, no appreciable biodegradable substrate, could be detected in the resulting OUR profile, indicating that all biodegradable COD was removed in the activated sludge systems and the effluent COD consisted only of residual fractions. It should be noted that the influent stream from the equalization tank contained only an S_I of 120 mgl^{-1}, and the 40 mgl^{-1} increment in the effluent was due to residual metabolic product generation in the course of biological treatment (Orhon *et al*., 1999b).

Results of chemical treatment applied to the biological treatment effluent are shown in Figure 6. Chemical treatment provided, as expected, high color removal efficiencies in the range of 80–90%, but the COD removals achieved remained limited to 20–30%. As far as COD was concerned, it generated basically a polishing effect by removing the particulate

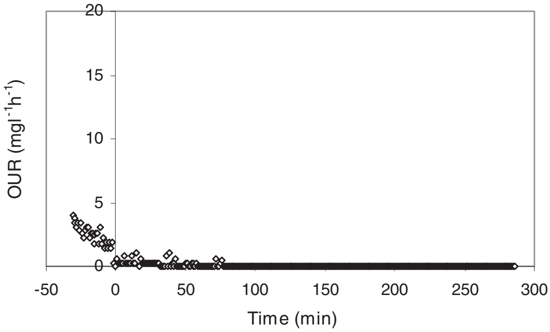

Figure 5 OUR profile of biological treatment effluent

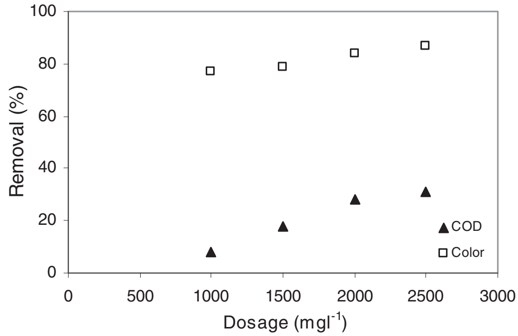

Figure 6 COD and color removal efficiencies of chemical precipitation after biological treatment

matter and a small portion of the residual COD as no biodegradable COD was available at this stage. Chemical treatability with 2,000 mgl^{-1} sodium bentonite, for the purpose of comparative evaluation with the results derived for the equalization tank sample, reduced soluble COD to 140 mgl^{-1} with complete removal of particulate COD; indicating only a 20 mgl^{-1} reduction in the effluent soluble inert COD level. Color removal, on the other hand, was achieved as 76%.

Conclusions

The following may be expressed as the concluding remarks of the study.

The selected knit fabric processing wastewater has a high soluble residual COD content, a typical characteristic for the textile industry. Chemical treatment is tested in the study, as a complementary step to biological treatment, for the achievement of an optimum soluble residual COD removal.

The experiments single out bentonite as the most suitable coagulant for the selected wastewater, mainly based on its potential to remove soluble COD components along with particulate COD. Chemical treatment with bentonite, when applied prior to biological treatment removes around 40% of the biodegradable as well as soluble inert COD initially present in the wastewater. This observation is quite important in view of the fact that residual COD in the activated sludge effluent includes significant portion of non-biodegradable metabolic products generated in proportion to the amount of substrate (biodegradable COD) utilized. In this context, the role of chemical pre-treatment should be evaluated in terms of its potential to (i) remove 40% of the initially present soluble inert COD, (ii) reduce the organic load by 40%, and this way, (iii) to reduce the potential of additional residual COD generation by the same rate.

A well designed activated sludge system is capable of removing all biodegradable organic matter so that the effluent contains, as also observed in this study, only residual COD, both initially present and generated during the course of treatment. Chemical post-treatment acts as a polishing step, removing particulate matter and a minor portion (around 20% in this study) of the remaining soluble COD.

In this framework, chemical treatment with bentonite as pre-treatment has distinct advantages over the post-treatment alternative if the objective is the optimization of soluble COD removal.

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