



GAC ADSORPTION OF OZONATED SECONDARY TEXTILE EFFLUENTS FOR INDUSTRIAL WATER REUSE

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ABSTRACT

The paper presents the results obtained at laboratory, pilot and demonstrative scale with granular activated carbon adsorption as a mean to obtain effluent suitable as water supply for textile finishing industries, that require very stringent limits in terms of COD and colour removal. Laboratory scale tests evidenced that the specific carbon adsorption capacity, both for COD and colour, is highest for a sand-filtered + clariflocculated effluent and lowest for the sand-filtered + ozonated secondary effluent. Pilot and demonstrative scale tests were performed on three filters (0.3, 0.3 and 20 m³ of GAC each) fed with the full scale ozonated secondary effluent. © 1999 IAWQ Published by Elsevier Science Ltd. All rights reserved

KEYWORDS

Absorbance; filtration; granular activated carbon; isotherms; ozone; reuse; textile wastewater.

INTRODUCTION

Many textile factories are widespread in the area of Como province and they use large amounts of fresh water, mainly for washing and rinsing operations and discharge appreciable pollution loads. It has been calculated that textile industry uses about 100 m³ of water and emits some 100 kg COD per ton of produced fabric (Jekel, 1997).

Textile industries are supplied by underground water pumped from the water table and, since 1989, by an industrial aqueduct which draws water from the Lake Como and distributes 35,000 m³/d. This industrial water is still rather inexpensive (of the order of 0.25 ECUs for the aqueduct) but its use should be reduced whenever possible because the level of the water table has appreciably decreased during the last decade. Similarly, the lake water, because of its high quality, should be saved or exploited for potable use.

The wastewater from the industrial processes is discharged into the public sewer where it is mixed with domestic sewage (20% as organic load) and treated in centralised plants having a total flow rate of 100,000 m³/d. Half of this capacity is located in the three treatment plants operated by Lariana Depur.

Since 1993 several polishing schemes based on advanced wastewater treatment (AWT) have been tested at pilot scale on the Como area effluents. As described by Bonomo *et al.* (1995) and Rozzi *et al.* (1997), both granular activated (GAC) carbon and nanofiltration, after clariflocculation, make it possible to reach the desired water quality. The addition of ozonation prior to GAC or nanofiltration further reduces colour and surfactants, but with a significant increase in capital and operation costs.

A new research programme was undertaken in 1996 with the objective to develop an integrated process for the provision of recycled water of constant and reliable quality with minimum emission. The research, partly financed by the European Community, involves several European partners and will be concluded at the end of 1998. On the basis of the previous experimental results, scope of the present research is to investigate GAC adsorption at demonstrative scale in biotic/abiotic conditions, to investigate membrane treatments and to verify the suitability of polished effluents as process water in some textile operations.

In the following, the results of the first year laboratory and pilot scale operation related to adsorption on granular activated carbon (GAC) of the effluent of the full-scale treatment plant of Bulgarograsso (25,000 m³/day) are set forth. This plant treats industrial plus domestic wastewater. The percentage of industrial discharges, as hydraulic flow rate, is over 50% during the year but it exceeds 70% of dry weather flow. 92% of incoming industrial wastewater is discharged by textile printing and dyeing factories.

This plant is composed of a conventional secondary treatment, followed by sand filtration and ozonation. The latter treatment was installed in 1993, mainly to reduce effluent colour and surfactants, as required in order to prevent aesthetical impacts on the receiving stream, which has a very low dilution factor.

Table 1. Characteristics of the pilot-scale granular activated carbon columns

Filter	H (m)	D (m)	V of GAC (m ³)	H of GAC (m)	EBRT (min)
S1 (biotic)	5	2.9	20.8	3.15	30 with 40 m ³ /h
S2A (biotic)	1.5	0.586	0.3	1.1	30 with 0.6 m ³ /h
S2B (abiotic)	1.5	0.586	0.3	1.1	30 with 0.6 m ³ /h

LEGEND: H: height; V: volume; D: diameter; EBRT: empty bed retention time

Table 2. GAC general characteristics

Typical analysis*		
Apparent bulk density	g/l	260
Iodine adsorption	mg/g	800
Molasses number		500
Ash content	%	7
Moisture (as packed)	%	2
Particle size		
>3.4 mm	%	1
>2.4 mm	%	25
>1.7 mm	%	55
>1.0 mm	%	92
Density backwashed and drained	g/l	230
D60/D10		1.9
Dechlorinat. halving v.	cm	6
Total pore volume	cm ³ /g	1.2

*Norit data sheet

MATERIALS AND METHODS

Pilot scale plants

Three pilot scale columns have been used: a large column (S1) has been designed to provide treated wastewater for a dyeing and printing factory, the small columns (S2A and S2B) to test adsorption in biological and abiotic conditions. Their geometrical characteristics and operation conditions are indicated in Table 1. The activated carbon (NORIT PK 1-3) has been chosen from among 8 different commercial types tested during previous researches on the secondary effluent of the Bulgarograsso plant. It is a peat based, steam activated granular carbon, having the characteristics reported in Table 2. The columns were equipped with several ports at different height for sampling carbon and oxygen concentration in the column. S1 filter produces 40 m³ per hour with a contact time of 30 minutes and is equipped with 6 water sampling points and 3 carbon sampling points. The frontal piping is equipped with a magnetic flow meter, a delta pressure meter

and a regulation valve. As a result of the oxygen concentration in the feeding water, the filter may be considered as a biological activated GAC filter. Filters S2 are filled with the same carbon and produce 600 litres per hour each. They are equipped with 4 water sampling points. On account of the full oxygen saturation of the feed water, it was necessary to eliminate the biological activity in column S2B via sterilisation by sodium hydroxide (0.1 M solution and 72 hours of contact time) every one or two weeks.

On-line analytical controls are applied to feed water (conductivity, pH, turbidity, colour) and GAC filters effluents (turbidity, colour). The colour analyser measures absorbance in 6 bands chosen between 400 nm and 800 nm. On the influent/effluent of the filters, analyses of COD, TSS, nitrogen compounds, anionic and non ionic surfactants were made according to Standard Methods.

The filters are fed on the ozone treatment effluent of the Bulgarograsso WWTP. The characteristics of the influent differ slightly during the experimental period depending on the ozone dose applied (25 to 35 mgO₃/l). Average values are: COD: 128-135 mg/l; TOC: 16-18 mg/l; TSS: 18 mg/l; ammonia: 1 mgN/l; TKN: 5 mgN/l; nitrate: 9 mgN/l phosphorus: 2 mg/l; anionic surfactants: 0.1 mgMBAS/l; non-ionic surfactants: 0.9 mgBiAS/l; absorbance (0.01 m optical path): 0.054-0.064 (426 nm); 0.023-0.030 (558 nm); 0.01-0.012 (660 nm); ozone: 0.21-0.25 mg/l.

Dissolved oxygen is over the saturation concentration (usually > 20 mg/l) and therefore easily promotes aerobic biological activation of the filters. The BOD concentration is rather low (26-31 mg/l) even if ozonation helps in improving the BOD/COD ratio, that before ozonation is around 0.19 and reaches approximately 0.22 after ozonation (16% increase). Nitrogen and phosphorus concentrations are suitable for the biological degradation of organics (TKN/BOD = 0.16-0.19; P/BOD = 0.06-0.07).

Laboratory scale plant

Laboratory tests have been made on the carbon to determine the adsorption isotherms in terms of COD and absorbance adsorption and the kinetics of adsorption.

To determine the isotherms, different amounts of carbon (100, 200, 400, 800 mg), previously powdered < 63 µm and dried 105°C were placed in stirred 1 l flasks containing the sample streams. After 3 hours contact time, the residual soluble COD (i.e. filtered at 0.45 µm) and 426 nm absorbance were analysed and the amount adsorbed was determined as difference.

To determine the kinetics of adsorption, a fixed amount (200 mg) of carbon was placed in the same apparatus and residual COD and absorbance were analysed after 15, 30, 60, 120 and 180 minutes contact time.

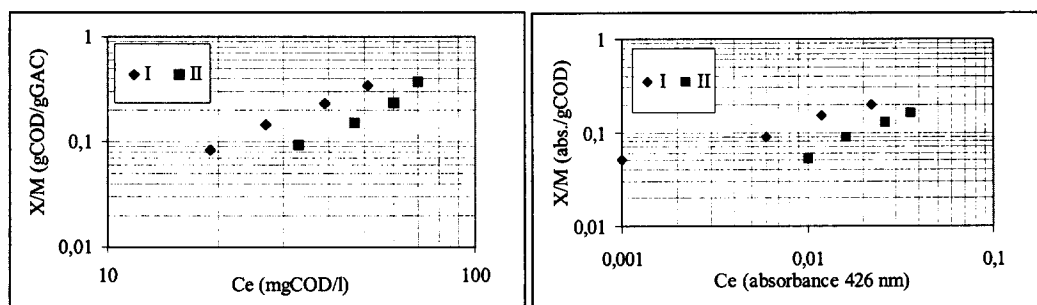


Figure 1. (a) COD experimental isotherm (Freundlich expression); (b) Absorbance 426 nm experimental isotherm (Freundlich expression).

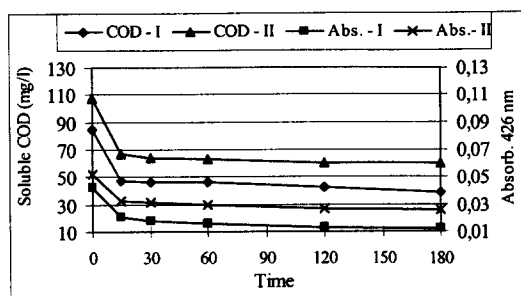


Figure 2. Residual COD and absorbance vs time.

Table 3. Freundlich adsorption isotherm experimentally determined ($X/M = \text{gCOD/gGAC}$ or absorbance/gGAC; $C = \text{mgCOD/l}$; $A = \text{absorbance 426 nm (optical path} = 0.01 \text{ m)}$)

	Equation	R ²
<i>COD isotherms</i>		
I	$X/M = 0.00134 \cdot C^{1.4089}$	0.998
II	$X/M = 0.000171 \cdot C^{1.7836}$	0.973
<i>Absorbance 426 nm isotherms</i>		
I	$X/M = 1.1016 \cdot A^{0.4418}$	0.967
II	$X/M = 2.893 \cdot A^{0.857}$	0.984

LABORATORY SCALE TEST RESULTS

The diagrams in Figure 1a and 1b show the isotherms experimentally determined for COD and absorbance on two samples of the effluent of the Bulgarograsso plant, i.e. the sand-filtered and ozonated effluent and in Table 3 the equations of the isotherms are reported. As may be seen, there is a noticeable difference in adsorption capacity with respect to the two samples, both in terms of COD and colour. Sample I is characterised by lower COD and absorbance with respect to sample II (85 mg_{soluble} COD/l and 0.042 absorbance against 107 mg_{soluble} COD/l and 0.052 absorbance) and is the one with which the highest specific adsorption capacity is achieved. In textile wastewater a considerable number of variable organic substances (dyes, surfactants, thickeners, etc.) may be present depending on the specific manufacture and differences in the composition and characteristics of the COD residual may be expected.

The diagrams in Figure 2 plot the residual COD and absorbance for the two samples as a function of contact time. COD is very rapidly adsorbed and equilibrium concentration is obtained in roughly 15 minutes. Absorbance is adsorbed more slowly but with a higher efficiency than COD.

The great variability of specific adsorption capacity is further evidenced by the isotherms that were determined on the following streams, in order to compare the adsorption capacity on different streams (Fig.3a and 3b):

- A. effluent of biological treatment + sand filtration;
- B. effluent of biological treatment + sand filtration + flocculation at laboratory scale (by 10 mg/l of alum);
- C. effluent of biological treatment + sand filtration + ozone treatment.

In fact, isotherm referred to stream C in Figure 3a shows a lower specific adsorption capacity than the isotherms reported in Figure 1a. Figure 3a and 3b show that, at the same equilibrium concentration, carbon has the lowest specific adsorption capacity in treating the ozonation effluent, and the highest in treating the filtered and flocculated effluent. This confirms that carbon adsorption is less effective after the ozonation, probably due to the lower dimension of the molecules, as frequently reported in the literature (inter alia Kuribayashi, 1992, De Laat *et al.*, 1991). The significant increase in specific adsorption capacity after flocculation may be explained with the removal of colloidal organics that evidently compete with the adsorption of dissolved organics. The main differences between stream A and C, however, are in terms of absorbance adsorption. This must be considered when evaluating the opportunity to use the GAC in the full scale scheme after ozonation or after sand filtration alone. In fact, taking into account that the suitable 426 nm absorbance for textile reuse is considered to be 0.01, it may be seen in Figure 3b that at this equilibrium concentration the adsorption capacity for unit weight of carbon is 0.1 for stream A and 0.033 absorbance/gGAC for stream C, that is the specific adsorption capacity is one third for stream C with respect to stream A. However, the absorbance in stream A is of the order of 0.105, four to five times the absorbance of stream C. Therefore, as regards ozonated effluent, a unit weight of carbon may treat higher volumes of water than in the case of sand filtered water effluent.

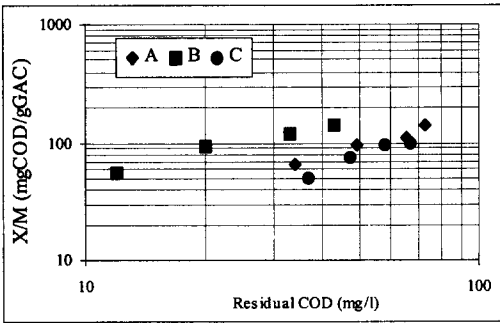


Figure 3a. COD isotherms determined on streams A, B, and C.

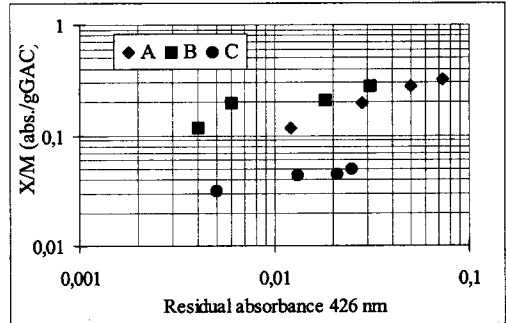


Figure 3b. Absorbance isotherms determined on streams A, B, and C.

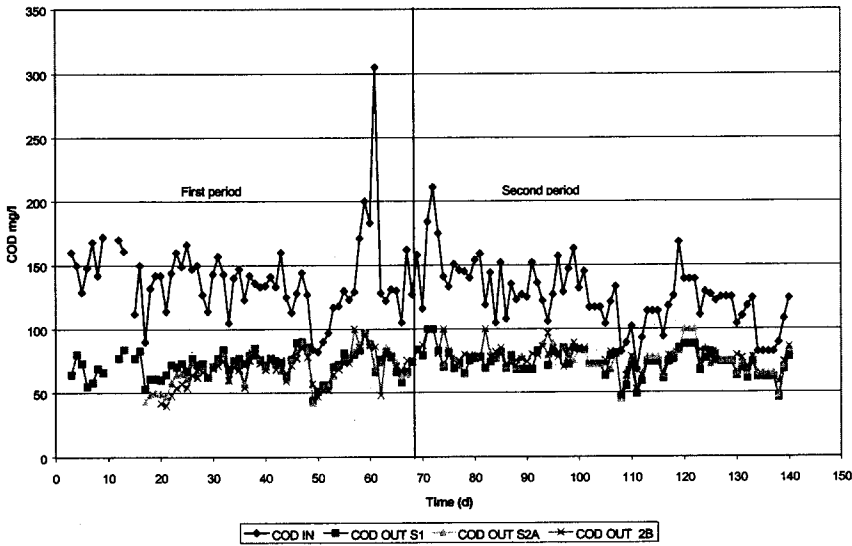


Figure 4. Influent and effluent COD in the three GAC columns vs. time

PILOT SCALE RESULTS

In a first operation period S1 was fed at different flow rate (20-30-40 m³/h) to verify the performances at different EBCT (60, 45 and 30 minutes). COD removal did not change at different flow rate, probably because the adsorption of COD reaches its maximum after few minutes. On the contrary colour removal, referring to absorbance at 426 nm, was lower at the higher flow (around 35% abatement of 426 nm absorbance at 40 m³/h and around 50 % abatement at 20 m³/h). In the second period the flow rate was maintained at 30 m³/h to provide an adequate colour removal of the effluent supplied to the factory.

The influent and the effluent COD concentrations for the second period related to the three GAC columns are plotted vs. time in Figure 4. It may be observed that the COD concentration in the three effluents follows the same trend and that their value is fairly constant with respect to time and to variations in the influent concentrations. A similar behaviour was found with respect to colour absorbance, although the deviations are slightly higher. COD removal is of the same order of magnitude for the three filters (around 40-45%, including the contribution due to TSS removal). In terms of soluble COD, assuming a COD/TSS ratio of 1.2,

the removal is slightly lower and of the order of 40%, a value comparable with the one obtained at laboratory scale (see Figure 2).

Colour abatement is higher in filters S2B then in filter S2A, which is the biological activated one because the sterilization with NaOH caused a partial desorption of colour and COD, as explained in the following.

Table 4 reports the average results of the whole experimental period for filters S2 and of the second experimental period for filter S1.

The amounts of filtered water and total COD removed at the termination of the experimental period, when the COD breakthrough was approaching, are reported in Table 5.

The amount of COD removed per mass unit of GAC is of the order of 0.9–1 kg_{soluble}COD/kgGAC for all the three filters and no significant differences between S2A (biological activated) and S2B (abiotic) are observed, taking into account the fact that the soluble COD adsorbed has been estimated on the basis of the average TSS removal.

Table 4. Average operation results in the experimental period

	pH	Total COD (mg/l)	TSS mg/l	Soluble COD mg/l(1)	NTU	Absorbance 426 nm	Absorbance 558 nm	Absorbance 660 nm	Aldehydes (mg/l)
Filter S1 -Flow rate 30 m ³ /h EBCT 45 min (73 days of operation)									
In	7.4	126	15	108	15.5	0.057	0.025	0.010	0.40
Out	7.4	73	6	66	7.6	0.043	0.018	0.007	0.22
Removal %		42	60	39	51	24	28	30	45
Filter S2A Flow rate 600 litres/h EBCT 30 min (114 days of operation)									
In	7.7	132	18	110	16.7	0.058	0.026	0.011	0.42
Out	7.6	72	6	65		0.040	0.017	0.007	0.21
Removal %		45	67	41		31	34	36	50
Filter 2B Flow rate 600 litres/h EBCT 30 min (103 days of operation)									
In	7.7	132	18	110	16.7	0.058	0.026	0.011	0.42
Out	7.7	74	6	67		0.035	0.014	0.006	0.21
Removal %		43	67	39		39	46	45	50

(1) Estimated on the basis of the TSS content and a ratio COD/TSS = 1.2

Table 5. Filters production

	Water filtered (m ³)	Water/GAC (m ³ /m ³ GAC)	Water/GAC (m ³ /kgGAC)	COD Removed (kg)	Soluble COD removed (1) (kg)	X/M (kgCOD/kg GAC)	X/M (kg _{soluble} COD/kg GAC)
S1	100,999	4,856	21.112	5,703	4,249	1.192	0.888
S2A	1,642	5,473	23.797	94	70	1.362	1.014
S2B	1,469	4,896	21.289	86	65	1.246	0.942

(1) Estimated on the basis of a 12 gTSS/m³ removal and a ratio COD/TSS = 1.2

BIOLOGICAL ACTIVITY IN THE GAC FILTERS

Respirometric tests have been carried out by using GAC plus the effluent of ozone treatment. The carbon samples, collected at various depths, were washed in order to remove organic suspended solids.

Test results are reported in Table 6. Data in column A and B refer to the test performed at the half of the first period and at the termination of the second respectively. The Oxygen Uptake Rate decreases along the bed showing a different biomass colonisation. The high value at the first sampling point of S1 for B column is mainly on account of an incomplete TSS removal from the sample. The OUR of the sample collected on the top of the S2B is not very different to the one of S2A sample, partly because tests are carried out at the end of the interval between one sterilization and another.

Table 6. GAC oxygen consumption

	GAC bed Depth (m)	Test A	Test B
		MgO ₂ /h/g GAC * 20°C	mgO ₂ /h/g GAC * 20°C
S1	0.57	0.68	5.93
	1.57	0.55	1.06
	2.57	Not available data	0.88
S2A	Top	0.74	0.81
S2B	Top	0.55	0.54
Unused GAC		0.12 **	
		mg O ₂ /l	mg O ₂ /l
Water without GAC		0	0

* GAC dried (105°C and burned 850°C)

** GAC conditioned in distilled water at oxygen saturation for 6 hours

The oxygen concentration detected inside the filters is reported in Figure 5, for the S1, S2A and S2B at different influent temperature. The oxygen consumption as determined from the gradients along the filters axis in the first layers of the filters is very similar to the one detected in the laboratory (Table 6). Significant differences are found at different bed depths. Probably this is due to the organic suspended solids retention on the upper layer of the filter and to the low DO concentration for the deeper layers. Obviously the total oxygen consumption decreases with the influent temperature because the biomass activity is slower and because the oxygen solubility is higher.

The oxygen consumption in filters S2A (biotic) and 2B (sterilised) is approximately the same at the upper layers, but not in the inner depth. Three days following the sterilisation procedure, the oxygen consumption at 0.36 m depth was 0.490, 0.105 and 0.000 mgO₂/h/gGAC for S1, S2A and S2B respectively.

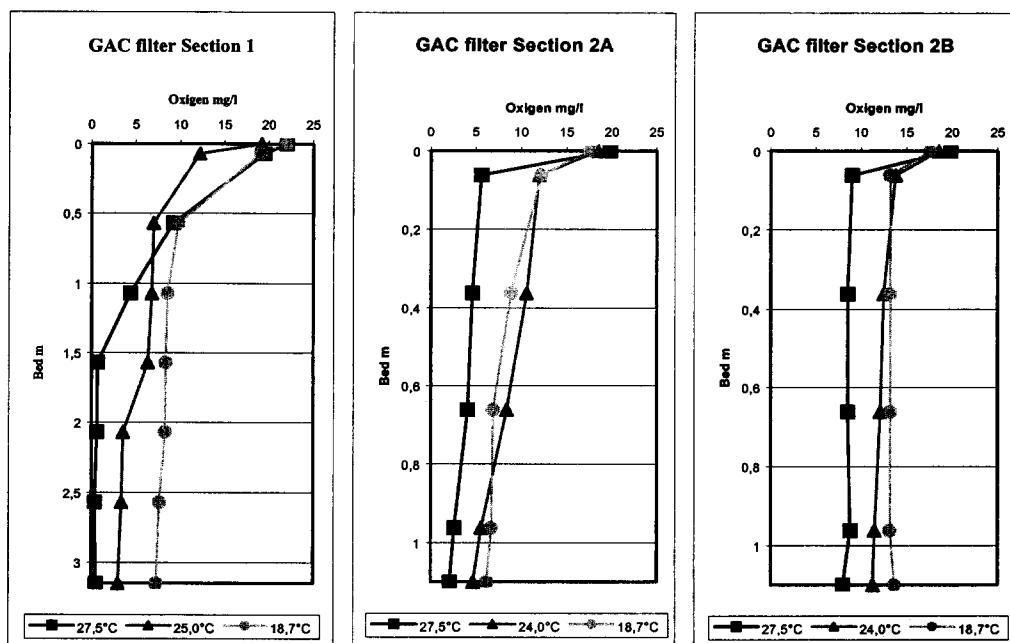


Figure 5. Oxygen profiles into GAC filters at different temperatures.

The sterilisation by sodium hydroxide of the filter Section 2B is not long-term effective. Probably bacteria grow within a few days after sterilisation according to the oxygen concentration detected in the filter during the first operation period when the filter was sterilised every two weeks. A more frequent sterilisation (every week) has been used in the second operation period. In virtue of such management the filter has been subject

to an enhanced biological deactivation, but verification indicated that the contribution of sodium hydroxide to chemical regeneration of carbon was significant. In fact about the 17% of COD adsorbed during a week of operation is desorbed by sterilisation, as evidenced from the COD analyses of the sterilisation solution. Both phenomena (not efficient sterilisation and chemical regeneration by sodium hydroxide) could invalidate the comparison between the biological filter and the abiotic one.

CONCLUSIONS

According to the laboratory isotherms, the specific adsorption capacity of the carbon in terms of COD is not very different for the secondary + sand filtration and the secondary + sand filtration + ozonation effluent. Roughly, double adsorption capacity could be achieved with a flocculation-clarification stage that removes the colloidal fractions. In terms of absorbency, no significant differences in the adsorption capacity are observable between the sand filtered and the sand filtered + flocculated effluent, but a reduction to one third is evidenced in case of the ozonated effluent. However, in terms of global balance and considering the composition of the water treated at the Bulgarograsso plant, a unit weight of carbon can treat higher volumes of ozonated effluent than of sand-filtered effluent.

Significant variations in the COD specific adsorption, however, were evidenced for different samples of the same effluent, probably as a consequence of the variability of organic substances (dyes, surfactants, thickeners, etc.) that may be present, depending on the specific manufacture.

At pilot scale, the initial COD breakthrough was evidenced after the treatment of 20-23 m³ of effluent for kg GAC, corresponding to 1.2-1.36 kg COD or 0.9-1 kg_{soluble} COD adsorbed for kg GAC.

However, due to the not efficient sterilisation of filter S2B and to the contribution of TSS, the role played by the biological activity in the results obtained at pilot scale cannot be clearly explained. A different sterilisation procedure is currently being studied and the periodic dosage of mercury, which is very efficiently adsorbed and highly toxic for biomass seems a promising solution.

Actually the water produced by GAC filtration is not suitable for all the textile processes. The organic pollutants have still high concentrations (COD > 70 mg/l) and the residual colour is over the optical detection. Performances at different contact time are about the same and therefore it is necessary to reduce COD and colour in the GAC influent by flocculation in order to achieve better GAC effluent quality. As it is not possible to carry out flocculation at demonstrative scale at Bulgarograsso plant, filter S1 will be moved to another plant managed by Lariana and fed on textile + domestic wastewater, where flocculation + ozonation treatments of the secondary biological effluent will start up soon.

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REFERENCES

- Bonomo, L., Malpei, F., Mezzanotte, V., Rozzi, A. and Bianchi, R. (1995). Possibilities of treatment and reuse of wastewater in textile industrial settlements of Northern Italy. *Proc. WEFTEC '95 68th Annual Conference and Exposition of the Water Environment Federation*, 539-548.
- De Laat, J., Dore, M. and Mallevalle, J. (1991). Influence d'une preozonation sur l'adsorbabilité et la biodégradabilité des substances humiques d'origine aquatique et sur les performances des filtres de charbon actif en grains. *Water Research*, **25**(2), 151-164.
- Kuribayashi, S. (1992). Experimental studies on advanced treatment of wastewater for amenity use. *Wat. Sci. Tech.*, **26**(9-11), 2401-2404.
- Jekel, M. (1997). Wastewater treatment in the textile industry. *Proc. of "Treatment of Wastewaters from Textile Processing" TU Berlin, Schriftenreihe Biologische Abwasserreinigung des Sfb 193*, Berlin.
- Rozzi, A., Bianchi, R., Liessens, J., Lopez, A. and Verstraete, W. (1997). Ozone, granular activated carbon and membrane treatment of secondary textile effluents for direct reuse. *Proc. of "Treatment of Wastewaters from Textile Processing" TU Berlin, Schriftenreihe Biologische Abwasserreinigung des Sfb 193*, Berlin., 25-47.