EFFECT OF RECENT BLEACHING TECHNOLOGY DEVELOPMENT ON ORGANIC MATTER BALANCE IN EUCALYPT KRAFT PULP BLEACHING EFFLUENTS

Ann H. Mounteer[1*], Renata de Oliveira Pereira[2], Anderson de Assis Morais[2], Daniella Sette Abrantes Silveira[3]

[1]Associate Professor, [2]Master´s Student, Undergraduate Student,
*Civil Engineering Department, Federal University of Viçosa, 36570-000 - Viçosa - MG – Brazil;
Email: ann@ufv.br

ABSTRACT

In the past, a great deal of emphasis was placed on the alkaline bleaching filtrate, since it carried the majority of the organic load in bleaching effluents. However, with modern short ECF bleaching sequences including hot chlorine dioxide treatment as the first bleaching stage a new paradigm has arisen which must be taken into account when planning bleaching filtrate treatability studies and performing organic load balances. We analyzed industrial $D_{HT}EopDP$ acid, alkaline and combined bleaching filtrates and found that over half the organic load (measured as total organic carbon, TOC, and chemical oxygen demand, COD) was found in the acid filtrate, whereas in bleaching filtrates with a conventional Do-stage, the acid filtrates typically account for less than one third of the organic load. In the alkaline filtrate approximately two thirds of the COD and TOC was found in low molecular mass matter (< 500 g mol^{-1}) while in the acid filtrate low molecular mass matter accounted for only one third of the TOC and COD. The high molecular mass matter in the acid filtrate presented a very low biodegradability (BOD/COD = 0.05), a characteristic which has already been shown for DEopDED bleaching filtrates. Bench scale treatability studies of the combined filtrates showed that the proportion of high molecular mass organic matter increased after biological treatment, confirming previous studies. The greater proportion of poorly biodegradable organic matter in bleaching filtrates containing the D_{HT} stage can therefore be expected to lead to greater difficulty in achieving low final effluent COD values, without advanced biological or combined chemical biological treatment.

Keywords: activated sludge, biodegradability, ECF bleaching, high temperature chlorine dioxide, molecular mass

INTRODUCTION

Pulp mill effluent studies generally focus on bleaching effluent treatability, because the bleaching effluents typically account for the major part of the total effluent volume sent to the mill wastewater treatment plant (Springer, 1999). Several comparative effluent treatability studies have been published since the advent of ECF and TCF bleaching technologies (Herstad-Svärd, 1997; Mounteer, 2002; Bjorklund et al., 2003), but few have contemplated the effluents produced in bleaching sequences with a hot chlorine dioxide stage, although this technology has been adopted by several Brazilian mills (Gomes et al., 2007). Initial studies have shown that bleaching filtrates produced using the D_{HT} technology have similar BOD and COD loads, and thus biodegradability, as those produced when using a conventional D_0-stage (Gomes et al., 2007). On the other hand, replacing the D_0-stage with a D_{HT} stage leads to lower effluent AOX and higher effluent color.

Many mills are being faced with increasingly stringent effluent discharge limits, especially with regard to final effluent COD and color loads (Mounteer & Mokfienski, 2005). It is generally accepted that low molecular mass compounds in mill effluents are more harmful to the environment because they can penetrate through membranes of living organisms (Konduru et al., 2001), which also explains why low molecular mass compounds are more readily removed during biological treatment. This results in an increase in the proportion of high molecular mass matter after treatment (Yousefian & Reeve, 2000; Mounteer et al., 2002; Mounteer et al., 2007). There is some indication that high molecular mass compounds may also cause toxic effects in the environment (Kukkola et al., 2006). Although the true environmental significance of release of this recalcitrant COD to the environment is still a matter of debate, it has become the focus of stricter environmental regulations and has motivated research into alternatives for improving its removal during effluent treatment (Archibald et al., 1998; Konduru et al, 2001; Mounteer et al., 2007).

Acid and alkaline bleaching filtrates are generally discharged to separate sewers and mixed before being sent to the mill's wastewater treatment plant. Many treatability studies have been carried out to characterize the filtrates and evaluate the potential for their separate treatment, aimed either at partial filtrate recycle or at pretreatment before conventional biological wastewater treatment plant (Mansilla et al., 1997; Bijan & Mohseni, 2004). Alkaline filtrates from an ECF bleaching sequence such as D_0EoDED have been shown to have higher BOD, COD and color loads than their corresponding acid filtrates (McKague & Carlberg, 1996; Assalin et al., 2004). Use of hydrogen peroxide in the alkaline extraction and/or final bleaching stage (ex. D_0EopDP) can significantly reduce the color of alkaline filtrates to values well below those of acid filtrates (Herstad-Svärd, 1997), although COD values still remain higher for these alkaline filtrates. However, few studies on separate characterization of the acid and alkaline filtrates from

bleaching with the D_{HT}-stage have been published. Furthermore, no information is available on the molecular mass distribution of the organic matter dissolved in these filtrates. The purpose of the present study was therefore to characterize the acid and alkaline filtrates produced in an industrial D_{HT}EopDP bleaching line. In addition, combined effluent biotreatability was evaluated in a bench-scale reactor and removal efficiencies of high and low molecular mass effluent fractions were measured. Filtrate loads and treatment removal efficiencies were compared to those of an industrial D_0EopDP bleaching effluent, without the D_{HT} technology.

EXPERIMENTAL

Effluents

Effluents were collected at a Brazilian pulp mill producing fully bleached eucalypt kraft using the D_{HT}EopDP bleaching sequence. Acid and alkaline filtrates were collected and mixed in equal volumes to produce combined effluent, since approximately equal filtrate volumes are sent to the mill acid and alkaline filtrate sewers. The effluents were pre-filtered (Whatman qualitative filter paper) and stored at 4ºC under a nitrogen atmosphere until used.

Biological treatment

Combined effluent from was treated in bench scale activated sludge systems (600 mL working volume). Before treatment, nitrogen (urea) and phosphorous (phosphoric acid) were added to the effluents at a final BOD:N:P ratio of 100:5:1, and effluent pH was adjusted to 7 ±0.5. Treatment temperature was controlled by placing the reactor in a 35°C water bath and dissolved oxygen was maintained above 2 mg.L^{-1} using porous stone aerators. The reactor was operated at hydraulic retention time of 12 h and a mean cell residence time of 10d, the latter controlled by daily removal of an appropriate amount of biomass directly from the reactor. Effluent feed and sludge recycle were controlled through a peristaltic pump (Gilson Minipuls 4). The reactor was inoculated with biomass from the activated sludge plant at the mill where the effluents were collected. Biomass concentration was estimated by measuring volatile suspended solids (VSS), according to the Standard Method (1998). Treated effluent was collected once each day for six consecutive days after stable operating conditions were achieved (COD variation of less than 10%).

Effluent characterization

Individual filtrates and combined effluents were separated based on molecular mass using an ultrafiltration cell (Amicon 8400, Billerica, MA) equipped with a 500 g.mol^{-1} molecular mass cutoff membrane (Amicon YCO5). Effluents and their high

and low molecular mass fractions were characterized by measuring COD, BOD, TOC and AOX according to the Standard Methods (1998) and color by the Canadian Pulp and Paper Association method (CPPA, 1993). TOC was quantified in a Shimadzu TOC 500 analyzer (Tokyo, Japan) and AOX in a Euroglas 1600 (Delft, Holland) automatic analyzer. All effluent analyses were performed in duplicate on filtered samples and average results are reported.

Average oxidation state (AOS) of effluent dissolved organic matter was calculated using equation 1:

$$AOS = 4.[(TOC - COD)]/TOC \qquad (1)$$

where TOC and COD are reported in mol.L^{-1} of carbon and oxygen, respectively (Stumm & Morgan, 1996).

Degree of chlorination (DCl) of organic matter was calculated using equation 2:

$$DCl = AOX/TOC \qquad (2)$$

where AOX and TOC are reported in mol.L^{-1} of Cl$^-$ and O$_2$, respectively.

RESULTS AND DISCUSSION

Characterization of the untreated acid and alkaline bleaching filtrates and combined D_{HT}EopDP bleaching effluent are presented in Table 1. The acid filtrate organic load to the effluent treatment plant is higher than the alkaline filtrate load, for all parameters quantified. In effluents from eucalypt kraft pulp ECF bleaching with a conventional D_0-stage, the alkaline filtrate accounts for the greatest part of the effluent load (McKague & Carlberg, 1996; Herstad-Svärd et al., 1997). In fact, many studies have focused on forms of treatment of the alkaline filtrate individually, given its relatively larger contribution to effluent pollutant load (Bijan & Mansilla et al, 1997; Herstad-Svärd et al., 1999; Assalin et al., 2004; Bijan & Mohseni, 2004). It is clear from the results in Table 1 that a new paradigm has been established, with acid filtrates contributing even more to the effluent pollutant load than alkaline filtrates, at least for bleaching of eucalypt kraft pulp with a D_{HT}-stage.

The largest differences between acid and alkaline filtrates are their color and AOX loads. The acid filtrate has double the color and AOX of the alkaline filtrate. Color is lower in the alkaline filtrate because the alkaline bleaching stages use hydrogen peroxide which is known to produce low effluent color (Mounteer et al., 2002). The higher AOX in the acid filtrate reflects the ability of the high temperature chlorine dioxide stage to dissolve partially degraded chlorinated compounds.

Acid and alkaline filtrate, as well as combined effluent, show similar, relatively low biodegradability (BOD/COD values, Table 1). Effluents that present biodegradability of less than 0.3 are considered more difficult to treat with biological processes, and may indicate the presence of toxic substances (Metcalf & Eddy, 2003). COD removal efficiency in biological treatment of eucalypt bleached kraft pulp mill effluent typically ranges from only 40 to 70% (Pokrel & Viraraghavan, 2004) because of the presence of non-biodegradable (recalcitrant) organic matter. The low biodegradability of the effluents evaluated in this study does not appear to be caused by organochlorine compounds, as has been previously reported (Jokela et al., 1993) since the degree of chlorination of the acid filtrate is almost twice that of the alkaline filtrate, yet both have similar BOD/COD values (Table 1).

Table 1. Characteristics of untreated $D_{HT}EopDP$ bleaching effluents (averages and standard deviations)

Parameter		Effluent		
		Acid	Alkaline	Combined
COD	mg O_2 L^{-1}	1274 (18)	1146 (21)	1133 (4)
	kg O_2 ton^{-1}	15.3	13.8	13.6
BOD	mg O_2 L^{-1}	362 (4)	307 (5)	315 (13)
	kg O_2 ton^{-1}	4.3	3.7	3.8
Color	mg Pt L^{-1}	940 (16)	487 (13)	658 (17)
	kg Pt ton^{-1}	11.3	5.8	7.9
TOC	mg C L^{-1}	522 (4)	453 (5)	530 (2)
	kg C ton^{-1}	6.3	5.4	6.4
AOX	mg Cl$^-$ L^{-1}	16	8.3	13.9
	kg Cl$^-$ ton^{-1}	0.19	0.10	0.17
$\frac{BOD}{COD}$	-	0.28	0.27	0.28
DCl*	-	0.011	0.006	0.011
AOS**	-	0.34	0.20	0.79

* DCl = degree of chlorination
**AOS = average oxidation state

The average oxidation state of the dissolved organic matter is slightly positive in all cases. AOS values can vary from -4 to +4, and values between 0 and +1 indicate the presence of partially oxidized compounds, such as carbohydrates (Stumm & Morgan, 1996). The slightly higher AOS of the combined effluent as compared to the acid and alkaline filtrates suggests partial oxidation, possibly caused by alkaline hydrolysis of organochlorine compounds upon mixing of the filtrates (McKague & Carlberg, 1996).

The molecular mass distribution of the dissolved organic matter in the acid and alkaline filtrates and the combined $D_{HT}EopDP$ effluent is presented in Figure 1 while the biodegradability and average oxidation state of the effluent fractions are presented in Table 2. The high molecular mass fraction accounts for the majority of all parameters measured except BOD. The higher BOD in the low molecular mass fraction reflects the fact that low molecular mass compounds are more

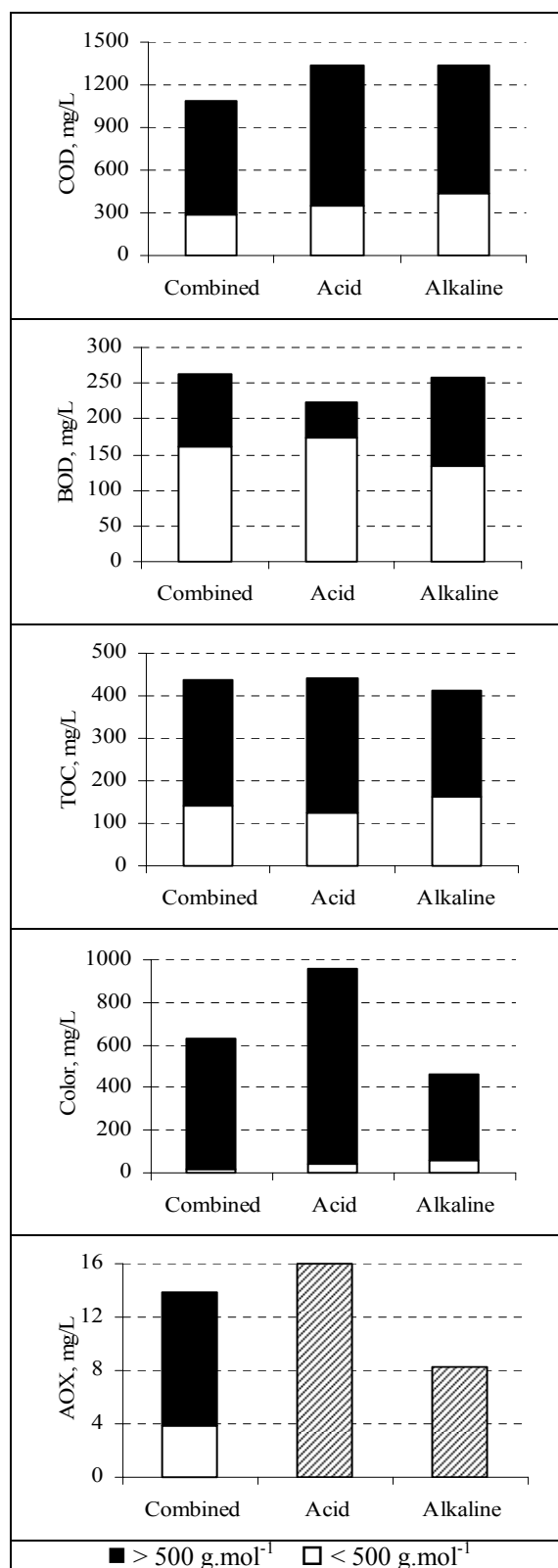readily assimilated by microorganisms than high molecular mass compounds (Bitton, 1994).

Figure 1. Organic matter in high (> 500 g.mol^{-1}) and low (< 500 g.mol^{-1}) molecular mass fractions of untreated acid and alkaline filtrates and combined $D_{HT}EopDP$ bleaching effluent. (For AOX, only total acid and alkaline filtrate values are reported).

Similar percentages of COD (73%), TOC (72%) and AOX (68%) are found in the high molecular mass fraction, while almost all color (98%) is found in this fraction. It is thus obvious that efficient biological treatment depends on the capacity of reactor biomass to attack and degrade the high molecular mass matter.

Unfortunately, the high molecular mass effluent fractions present low biodegradability, in particular that of the acid filtrate that has a BOD/COD value of only 0.05 (Table 2). Low biodegradability of the high molecular mass fraction of the acid filtrate from an industrial D(Eop)DP bleaching effluent has been reported previously (Mounteer et al., 2007). On the other hand, the low molecular mass effluent fraction of the acid filtrate has a higher biodegradability than the low molecular mass fraction of the alkaline filtrate, as a result of both higher BOD and lower COD in the acid filtrate fraction.

AOS values of both high and low acid and alkaline filtrate fractions are similar and close to 0, while the low molecular mass fraction of the combined effluent has a slightly higher AOS, illustrating that the partial oxidation that occurs upon mixing of filtrates as previously mentioned occurs almost entirely in low molecular mass compounds.

Table 2. Biodegradability (BOD/COD) and average oxidation state (AOS) of high (> 500 g.mol^{-1}) and low (< 500 g.mol^{-1}) molecular mass effluent fractions

Effluent	Fraction	BOD/COD	AOS
Combined	Low	0.55	0.87
	High	0.13	-0.02
Acid	Low	0.51	-0.0005
	High	0.05	-0.005
Alkaline	Low	0.31	-0.0002
	High	0.14	-0.009

Effluent quality after biological treatment as well as removal efficiencies for the different parameters evaluated are reported in Table 3. Removal efficiencies for the whole effluent are typical of values reported in the literature (Pokrel & Viraraghavan, 2004). COD, BOD and TOC removal efficiencies are higher for the low molecular mass fraction than for the high molecular mass fraction of the effluent. This is the same trend already reported for other eucalypt ECF bleaching effluents (Herstad-Svärd et al., 1997; Mounteer et al., 2002). Low molecular mass compounds are more readily assimilated by microorganisms present in the biological reactor, whereas removal of high molecular mass compounds may require efficient biomass adaptation to ensure their removal (Mounteer et al., 2007).

Effluent color increased after biological treatment, especially in the low molecular mass fraction. Color formation through biological treatment systems has been well documented, and may be caused by creation of novel chromophores in the partially degraded organic substances (Yousefian & Reeve, 2001; Mounteer et al., 2002; Milestone et al., 2004). Additionally, the biologically treated effluent has a lower AOS (-1.22) than the untreated effluent (0.79) which is consistent with the removal of partially oxidized substances during treatment.

Table 3. Characteristics of biologically treated whole D$_{HT}$EopDP bleaching effluent and its high and low molecular mass fractions

Parameter		Whole Effluent	Fraction High	Fraction Low
COD	mg.L^{-1}	466	405	49
	Removal, %	63.4	49.4	83.2
BOD	mg.L^{-1}	11	9	< 2
	Removal, %	96.9	91.2	> 98
TOC	mg.L^{-1}	134	110	16.8
	Removal, %	74.3	63.1	88
Color	mg.L^{-1}	677	634	55
	Removal, %	-3.0	-2.6	-323
AOX	mg.L^{-1}	4	2.1	1.5
	Removal, %	71.2	79	61.5
AOS*	-	-1.22	-1.52	-0.38

*AOS = average oxidation state

The percentage of the organic matter in the high and low molecular mass fractions of the untreated and biologically treated D$_{HT}$EopDP bleaching effluent is presented in shown in Figure 2.
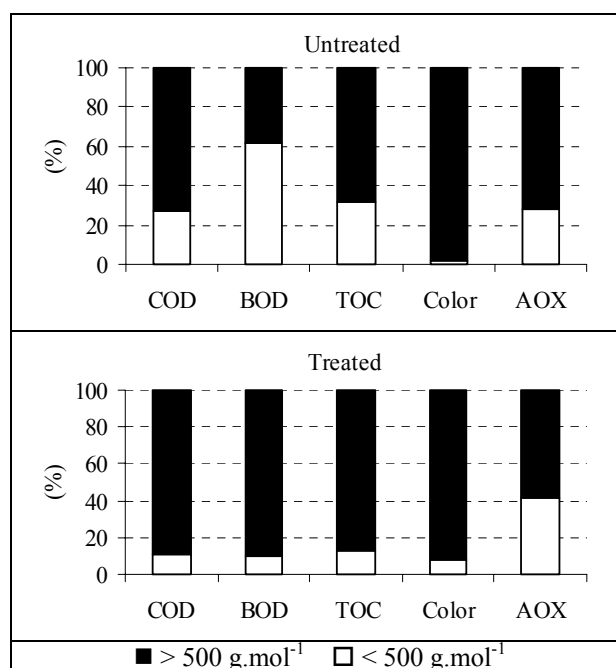

Figure 2. Percent distribution of organic matter in high (> 500 g.mol^{-1}) and low (< 500 g.mol^{-1}) molecular mass fractions of D$_{HT}$EopDP bleaching effluent, before and after biological treatment.

It is readily observed from Figure 2 that biological treatment is more efficient in removing low molecular mass compounds. The result is that over 85% of the treated effluent COD, BOD, TOC and color is found in the high molecular mass fraction. It has been shown that adaptation of biomass to high molecular mass organic matter can improve efficiency of removal this material in ECF bleaching effluents in the laboratory (Mounteer et al., 2007), and this strategy should be tested on an industrial scale, given the increasing concern about the release of this material to the environment (Kukkola et al., 2006).

Comparisons of the dissolved organic matter in industrial oxygen-delignified eucalypt kraft pulp $D_{HT}EopDP$ and D_0EopDP bleaching effluents are presented in Figure 3 (untreated effluents) and Figure 4 (biologically treated effluents).

In general, organic matter is distributed more equally between the high and low molecular mass fractions in the untreated effluent including the D_0-stage than in the untreated effluent containing the D_{HT}-stage. The use of the D_{HT} technology results in an increase in biodegradability and decrease in degree of chlorination of the low molecular mass fraction compared to the D_0 technology. On the other hand, effluent generated with the hot chlorine dioxide stage has a high molecular mass fraction with lower biodegradability than that generated with the D_0-stage, probably due to the very low biodegradability of the high molecular mass material contained in the D_{HT} acid filtrate (Table 2). The greater color in effluent incorporating the D_{HT} stage is contained in high molecular mass matter. On the other hand, the greater AOX in effluent incorporating the D0-stage is contained in low molecular mass compounds.

After biological treatment, the D_{HT}-stage derived effluent has a lower BOD and AOX levels and higher color than the D_0-stage derived effluent. Both effluents present similar COD and TOC levels but the D_{HT}-stage derived effluent contains a greater proportion of high molecular mass recalcitrant organic matter (COD, TOC and color) than the D_0-stage derived effluent. It can be seen by comparing the untreated and treated effluents that there is a greater percent removal of low molecular mass material in the D_{HT}-stage derived effluent. For the D_0-stage derived effluent, the relative proportions of high and low molecular mass fractions remain fairly constant before and after biological treatment. The greater recalcitrance of dissolved organic matter in D_{HT}-stage effluents represents a new challenge for mill wastewater treatment plant managers and operators, who are being faced with increasingly stringent effluent discharge limits. Research should be focused on increasing removal efficiency of this high molecular mass material in order to improve final effluent quality and minimize potential environmental impacts of its release to the environment.
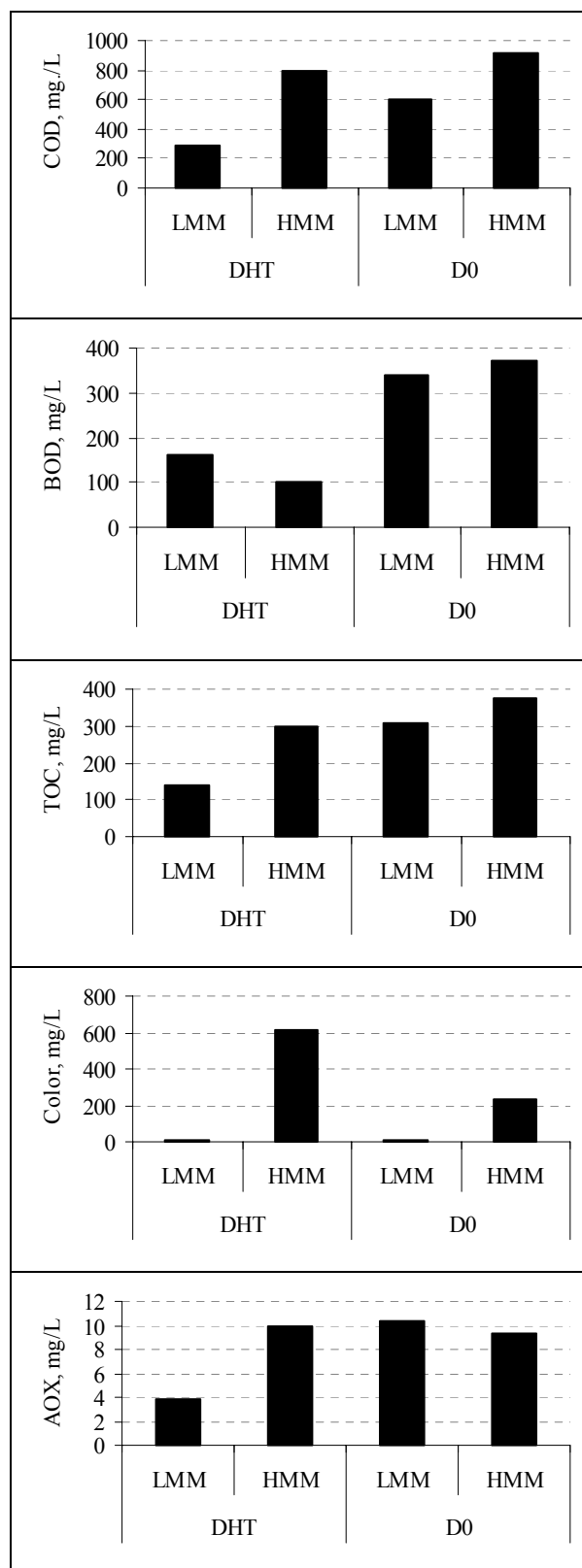

Figure 3. Dissolved organic matter in low (LMM) and high (HMM) molecular mass fractions of untreated $D_{HT}EopDP$ (DHT) and D_0EopDP (D0) bleaching effluents.
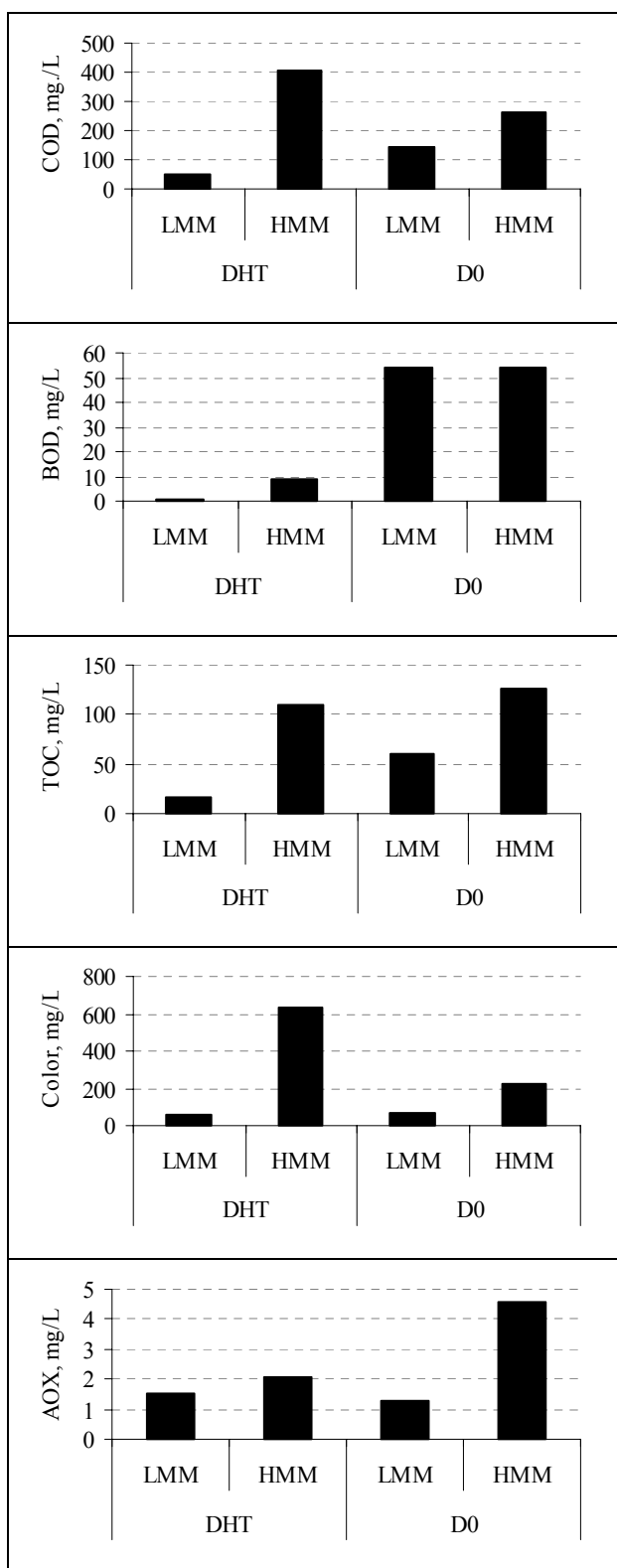
Figure 4. Dissolved organic matter in low (LMM) and high (HMM) molecular mass fractions of biologically treated $D_{HT}EopDP$ (DHT) and D_0EopDP (D0) bleaching effluents.

CONCLUSIONS

Bleaching filtrate organic mass balance is significantly altered by substituting the conventional D_0-stage with a D_{HT}-stage. In particular, acid filtrates contain greater color and AOX loads and equal or greater COD, TOC and BOD loads than alkaline filtrates. Moreover, more than 60% of the COD, BOD, TOC and over 90% of the color in acid and alkaline filtrates, as well as combined effluent is caused by substances with molecular mass >500 g.mol^{-1}. This high molecular mass material is more recalcitrant to biological treatment than high molecular mass matter dissolved in effluent produced with the D_0-stage. Over 85% of the COD, BOD, TOC and color in biologically treated $D_{HT}EopDP$ effluent is found in high molecular mass substances, highlighting the need for continued research into ways to transform this recalcitrant matter into biodegradable substances.

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