

Integration of continuous biological and chemical (ozone) treatment of domestic wastewater: 2. Ozonation followed by biological oxidation

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Abstract: A combined chemical–biological treatment, ozonation plus activated sludge, of domestic wastewater was studied and the results were compared with those shown in a previous study where the sequence of oxidation was reversed. Experimental results indicated wastewater preozonation to be an effective pretreatment step for domestic sewage. The goals of ozonation were the improvement in effluent biodegradability and the removal of certain biorefractory organics as aromatic and unsaturated compounds. The percentage of biodegradability was measured by the BOD/COD ratio (eg 0.69 was obtained for an ozonated effluent ($D_{O_3}=40\text{ g m}^{-3}$) while a ratio of 0.57 was measured for raw sewage). Based on continuous experiments of a single activated sludge system (hydraulic retention time=5 h; mixed liquor volatile suspended solids= 1.6 g dm^{-3}) the combined oxidation leads to an improvement of BOD and COD percentage reductions (88% and 66% observed after the combined process for BOD and COD, respectively, compared with 80% and 47% obtained without preozonation). Preozonation also improves the total kjeldahl nitrogen (TKN) removal during subsequent single stage activated sludge treatment. The fraction of autotrophic biomass (f_{nit}) was more important when preozonation took place, so nitrification rates were enhanced in the combined process. The efficiency for the individual and combined process was computed and compared. Among the three processes studied, the sequence of ozonation plus biological oxidation resulted in the highest percentage COD, TKN and UV_{254} reduction.

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Keywords: ozone; activated sludge; domestic sewage; wastewater treatment

NOTATION

AS	Activated sludge
BOD	Biochemical oxygen demand (g m^{-3})
b	Decay rate coefficient of nitrifiers (day^{-1})
C_{O_3g}	Ozone concentration at the reactor inlet (g m^{-3})
COD	Chemical oxygen demand (g m^{-3})
D_{O_3}	Mass of ozone applied per volume unit of wastewater (g m^{-3})
DO	Dissolved oxygen concentration (g m^{-3})
F	Wastewater flow rate ($\text{dm}^3\text{ h}^{-1}$)
F_g	Gas flow rate ($\text{dm}^3\text{ h}^{-1}$)
f_{nit}	Fraction of nitrifiers defined by eqn (2) (dimensionless)
HRT	Hydraulic retention time (h)
MLVSS	Mixed liquor volatile suspended solids (g m^{-3})
N_{nit}	Mass load of nitrified nitrogen defined by eqn (3) (g)

SOUR	Specific oxygen uptake rate [$\text{g O}_2 (\text{g VSS h})^{-1}$]
TKN	Total Kjeldahl nitrogen (g m^{-3})
UV_{254}	Absorbance at 254 nm measured using a 1 cm light path quartz cell
V	Volume of the bioreactor (m^3)
VSS	Volatile suspended solids (g m^{-3})
VSS_{nit}	Nitrifying bacteria expressed as volatile suspended solids (g m^{-3})
Y	Autotrophic yield [$\text{g VSS}_{\text{nit}} (\text{g N})^{-1}$]
α	Biomass activity defined as $\alpha = MLVSS \cdot HRT$ [$\text{g MLVSS dm}^{-3} \text{ h}$]
$\Delta MLVSS$	Heterotrophic biomass growth (g VSS h^{-1})
θ_c	Sludge age defined by eqn (1) (day)

1 INTRODUCTION

In a previous investigation the efficiency of an

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Table 1. Effect of ozone dose on changes in COD, BOD and UV₂₅₄ of the wastewater during ozonation

Run	Ozone dose ($g\ m^{-3}$)		COD _i ($g\ m^{-3}$)	COD _f ($g\ m^{-3}$)	BOD _i ($g\ m^{-3}$)	BOD _f ($g\ m^{-3}$)	UV _{254i}	UV _{254f}
	Applied	Consumed						
1	16.7	13.3	294	279	170	165	1.08	0.92
2	16.7	16.7	291	270	170	162	1.05	0.79
3	41.7	35.8	291	256	165	170	1.11	0.82
4	41.7	39.2	294	260	168	174	0.98	0.65
5	58.3	46.7	296	254	167	175	0.97	0.61
6	58.3	53.3	298	254	170	175	1.09	0.72
7	83.3	64.2	289	238	164	160	1.07	0.71
8	125	99.2	294	235	165	155	1.03	0.64

Conditions: $F_g=30\ dm^3\ h^{-1}$; $T=20^\circ C$; $pH=7.3-7.8$; $F=3.6\ dm^3\ h^{-1}$; $C_{O_3g}=2-15\ g\ m^{-3}$ Subscript notation; i=initial (at the wastewater inlet); f=final (at the wastewater outlet).

ozonation step after biological oxidation of domestic sewage with respect to any variation of COD, BOD and UV₂₅₄ was studied.¹ Other literature reports describe works aimed at increasing the biodegradability of wastewaters that contain specific biorefractory compounds by means of previous chemical oxidation. The results obtained after chemical oxidation, however, are highly dependent on the nature of the wastewater.² In these works a significant increase of the biodegradable fraction is observed when ozone is used. This is probably due to the formation of low molecular weight substances that are more easy to biodegrade.³⁻⁵ An extensive review of the literature of studies about the combination of chemical and biological degradation (usually oxidative) of organic contaminants in water has been presented by Scott and Ollis.⁶

In this work, domestic wastewaters have been treated in a continuous semi-pilot scale process with both chemical and aerobic biological oxidation. The main aims of this work were to evaluate the beneficial effects of the integrated chemical (ozone) plus biological oxidation (activated sludge) to improve the water biodegradability and to reduce the organic compound levels. For this purpose, ozone alone is used as a chemical oxidant since the combination of other agents like hydrogen peroxide or UV radiation do not improve the COD and BOD elimination in the domestic wastewaters studied, as was shown in a previous work.⁷

2 EXPERIMENTAL

The characteristics of domestic wastewater and the activated sludge used were described in the first paper in this series.¹ Activated sludge units were acclimatized to ozonated wastewaters for periods of approximately 4 weeks. Acclimatization was necessary to adapt the microorganism to different ambient and physical conditions (pH, temperature, sludge age, etc) and because after ozonation the molecular structure of the feed changes. After this acclimatization time the sludge settling characteristics and oxygen uptake rate were both improved.

The experimental set-up was described in detail in the first part of this work although the sequence of steps was changed. In this case, the ozonation reactor and an additional tank to strip the residual ozone by bubbling air through the liquid were placed before the biological aeration basin. The operational procedures and analytical methods were given in the previous paper.¹

3 RESULTS

3.1 Changes induced by ozonation

The effects of a single step ozonation on parameters like COD, BOD, TKN and aromatic and/or unsaturated substances measured by UV₂₅₄ were first considered. For that purpose, continuous ozonation experiments were conducted to treat the wastewater at ozone doses between 15 and 125 g of ozone per m³ of wastewater. The results are shown in Table 1.

As can be observed from Table 1, the increase of ozone dose leads to an increase of both COD and, especially, UV₂₅₄ reductions. Figure 1 shows the remaining normalized COD and UV₂₅₄ and the dissolved ozone concentration as a function of the ozone consumed. Notice that in all figures presented herein, the variation of parameters is plotted versus the ozone consumed instead of the ozone dose applied, which is more usual in other works. The objective is to avoid the effect of particular hydrodynamics and mass transfer conditions in the discussion of results. As can be deduced from Fig 1, reductions of COD and UV₂₅₄ mainly occurred in a first period and only small additional removals were achieved at higher ozone consumptions.

Regarding the elimination of total Kjeldahl nitrogen, the reductions observed were always less than 15%, which is in accordance with the low reaction rate of ozone with ammonia at pH values lower than 8.⁸ The variation of BOD with ozonation, observed in Table 1, implies an improvement of biodegradability measured as the ratio BOD/COD.⁹ As can be observed from Fig 2, the highest value of this ratio corresponds to an optimum ozone consumed dose of approximately 40 g m⁻³.

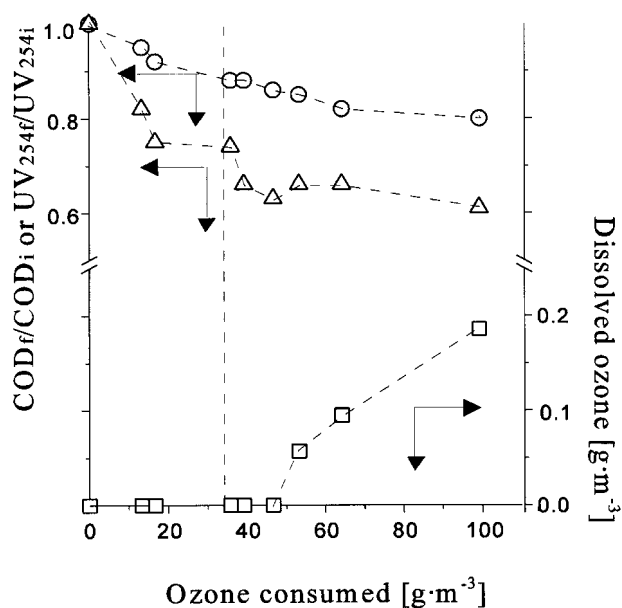


Figure 1. Effect of ozone consumed on (□) the dissolved ozone and remaining normalized (○) COD and (△) UV₂₅₄ during continuous ozonation of the wastewater. Conditions: $F_g=30\text{ dm}^3\text{ h}^{-1}$; $T=20^\circ\text{C}$; $\text{pH}=7.3\text{--}7.8$; $F=3.6\text{ dm}^3\text{ h}^{-1}$; $C_{O_3g}=2\text{--}15\text{ g m}^{-3}$; $\text{COD}_i=286\pm 50\text{ g m}^{-3}$; $\text{UV}_{254i}=1.0\pm 0.2$.

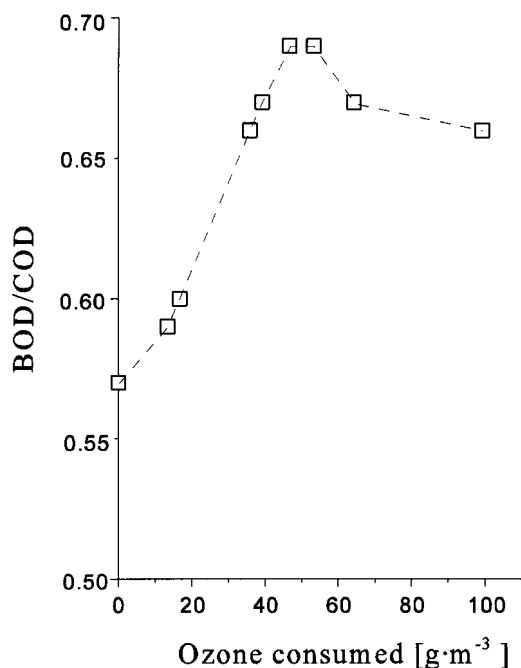


Figure 2. BOD/COD ratio as a function of ozone consumed during continuous ozonation of the wastewater. Conditions: $F_g=30\text{ dm}^3\text{ h}^{-1}$; $T=20^\circ\text{C}$; $\text{pH}=7.3\text{--}7.8$; $F=3.6\text{ dm}^3\text{ h}^{-1}$; $C_{O_3g}=2\text{--}15\text{ g m}^{-3}$; $\text{COD}_i=286\pm 50\text{ g m}^{-3}$; $\text{BOD}_i=162\pm 13\text{ g m}^{-3}$.

3.2 Effect of the combined process: ozonation and biological oxidation

3.2.1 BOD and COD removal

The influence of ozonation on a subsequent biological oxidation step was subsequently determined by carrying out a series of combined experiments (ozonation followed by activated sludge). In all cases, the same

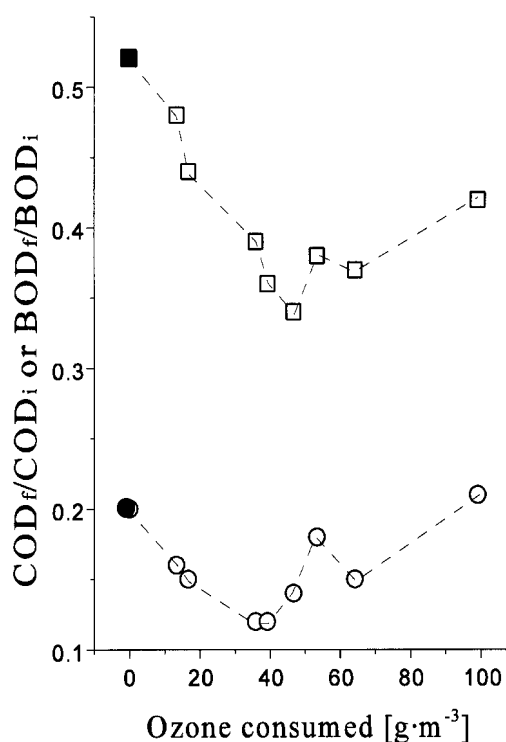


Figure 3. Effect of ozone consumed on remaining normalized (□) COD and (○) BOD during continuous combined (ozone plus activated sludge) treatment of the wastewater. Ozonation conditions: $F_g=30\text{ dm}^3\text{ h}^{-1}$; $T=20^\circ\text{C}$; $\text{pH}=7.3\text{--}7.8$; $F=3.6\text{ dm}^3\text{ h}^{-1}$; $C_{O_3g}=2\text{--}15\text{ g m}^{-3}$; $\text{COD}_i=286\pm 50\text{ g m}^{-3}$; $\text{BOD}_i=162\pm 13\text{ g m}^{-3}$. Biological oxidation conditions: $T=20^\circ\text{C}$; $\text{pH}=7.2\text{--}7.6$; $\text{DO}=2.5\text{--}3.5\text{ g m}^{-3}$; $\text{HRT}=5\text{ h}$; $\text{MLVSS}=1.6\text{ g dm}^{-3}$; $F=3.6\text{ dm}^3\text{ h}^{-1}$. Black symbols correspond to single biological oxidation.

conditions for the biological oxidation step were employed ($\text{MLVSS}=1.6\text{ g dm}^{-3}$; $\text{HRT}=5\text{ h}$). Firstly the ozone dose was varied in order to find out optimum operating conditions.

In Fig 3, the remaining values of normalized COD and BOD corresponding to the combined process are plotted versus the consumed ozone dose in the chemical step. Both parameters decrease with an increase in the ozone dose to reach minimum values after an ozone consumption of approximately 40 g m^{-3} . At higher ozone doses the remaining COD and BOD increase. In the case of BOD, the final value obtained at the most stringent ozonation conditions used in this work is slightly higher than that from the non-preozonated biological oxidation.

3.2.2 Specific oxygen uptake rate

Since the wastewater BOD/COD ratio increases with ozonation, an improvement in effluent biodegradability induced by ozonation is also assumed. It is therefore of interest to investigate what effect pre-ozonation could have on the oxygen uptake rate during subsequent biodegradation. Preozonated wastewater has SOUR values quite similar to the non-preozonated one. For instance SOUR values were 11.7 and $12.7\text{ mg O}_2\text{ (g MLVSS h)}^{-1}$ for non-ozonated and preozonated ($D_{O_3}=40\text{ g m}^{-3}$) wastewaters. However, since ozona-

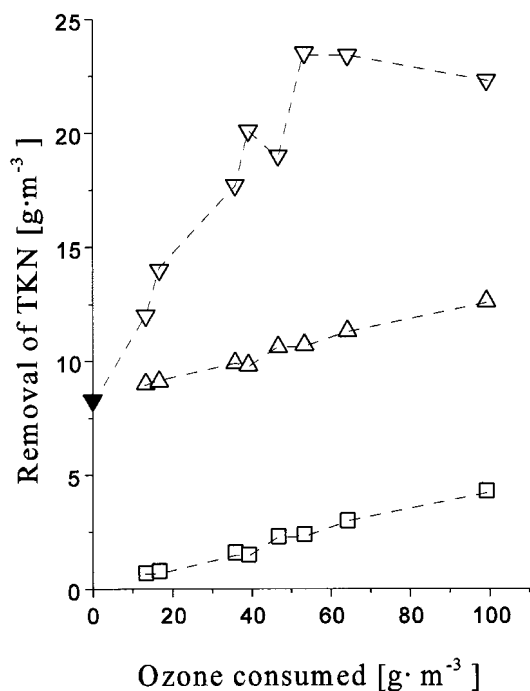


Figure 4. Removal of total Kjeldahl nitrogen during ozonation and the combined ozone plus activated sludge treatment of the wastewater. Ozonation conditions: $F_g=30\text{ dm}^3\text{ h}^{-1}$; $T=20^\circ\text{C}$; $\text{pH}=7.3\text{--}7.8$; $F=3.6\text{ dm}^3\text{ h}^{-1}$; $C_{O_3g}=2\text{--}15\text{ g m}^{-3}$; $\text{TKN}_i=35\pm 2\text{ g m}^{-3}$. Biological oxidation conditions: $T=20^\circ\text{C}$; $\text{pH}=7.2\text{--}7.6$; $\text{DO}_i=2.5\text{--}3.5\text{ g m}^{-3}$; $\text{HRT}=5\text{ h}$; $\text{MLVSS}=1.6\text{ g dm}^{-3}$; $F=3.6\text{ dm}^3\text{ h}^{-1}$. Symbols: \square ozonation; \triangle , sums of contributions of ozonation and biological oxidation individually considered; ∇ , integrated ozone–biological oxidation. Black symbol corresponds to single biological oxidation.

tion applied at optimum conditions allows much better water biodegradability higher differences of SOUR should be expected when comparing results from ozonated and non-ozonated wastewaters.

3.2.3 Evolution of nitrogen compounds

Figure 4 presents values for total Kjeldahl nitrogen removal from single and combined oxidations as a function of the ozone consumption. From this figure it is observed that for low ozone consumed doses ($<40\text{ g m}^{-3}$) there is little TKN elimination during ozonation but it is increased at higher ozone doses. On the other hand, nitrification during biological oxidation was higher than that obtained during single ozonation under the conditions investigated here. However, when ozonation was applied prior to biological oxidation, nitrification was strongly improved, as is also shown in Fig 4. Thus, for an MLVSS of 1.6 g dm^{-3} and HRT of 5 h in the aerobic digester, the use of ozone at the optimum conditions (D_{O_3} between 40 and 60 g m^{-3}) allows an increase in the reduction of total Kjeldahl nitrogen from 24% to 51%. It should be noted that TKN eliminated during the combined oxidation is also much higher than the sum of nitrogen removals from the ozonation and biological oxidation considered individually.

Figure 5 shows changes of nitrate and nitrite concentration, measured as nitrogen, plotted versus

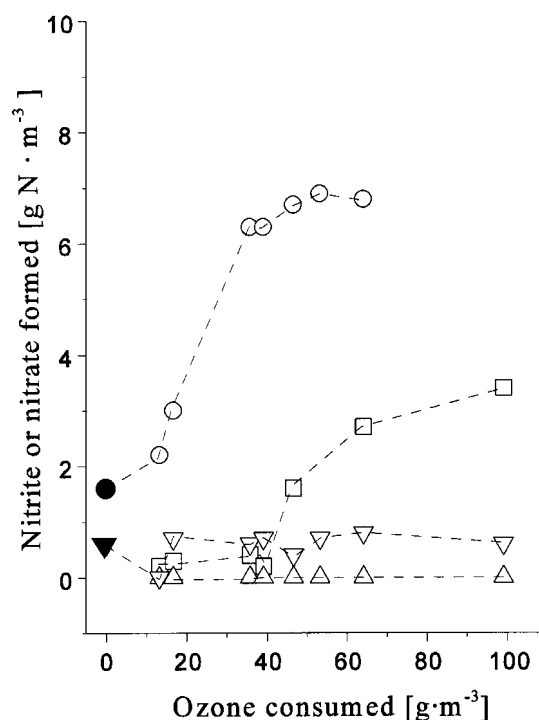


Figure 5. Formation of nitrite and nitrate during ozonation and the combined ozone plus activated sludge treatment of the wastewater. Ozonation conditions: $F_g=30\text{ dm}^3\text{ h}^{-1}$; $T=20^\circ\text{C}$; $\text{pH}=7.3\text{--}7.8$; $F=3.6\text{ dm}^3\text{ h}^{-1}$; $C_{O_3g}=2\text{--}15\text{ g m}^{-3}$; $\text{TKN}=35\pm 2\text{ g m}^{-3}$. Biological oxidation conditions: $T=20^\circ\text{C}$; $\text{pH}=7.2\text{--}7.6$; $\text{DO}_i=2.5\text{--}3.5\text{ g m}^{-3}$; $\text{HRT}=5\text{ h}$; $\text{MLVSS}=1.6\text{ g dm}^{-3}$; $F=3.6\text{ dm}^3\text{ h}^{-1}$. Symbols: \triangle , nitrite formed during ozonation; ∇ , nitrite formed during combined treatment; \square nitrate formed during ozonation; \circ nitrate formed during combined treatment. Black symbol correspond to single biological oxidation.

the ozone consumed corresponding to different oxidation processes. As seen in this figure, after the combined oxidations, accumulation of nitrate follows a similar trend to that observed in Fig 4 for the removal of total Kjeldahl nitrogen, that is, the increase of ozone consumption leads to an increase of the accumulation of nitrate. On the other hand, the concentration of nitrite is always lower than 1 g dm^{-3} , as would be expected, due to the two classical steps of nitrification: slow nitrite (reaction for formation of nitrite from ammonia) and fast nitrate (formation of nitrate from nitrite).

Some integrated ozone–activated sludge experiments, at an applied ozone dose of 58 g m^{-3} (the best one for carbonaceous matter removal according to Fig 1 and 2) and different MLVSS in the bioreactor, were also carried out. Table 2 summarizes the TKN results obtained from the influent and effluent wastewater of the aerobic digester. The heterotrophic biomass growth (ΔMLVSS) and sludge age (θ_c) are also presented, the latter calculated as follows:

$$\theta_c = \frac{\text{MLVSS} \cdot V}{\Delta\text{MLVSS}} \quad (1)$$

Analysis of the experimental data shown in Table 2 indicates a high effective TKN removal in the

Table 2. Changes in TKN and nitrate levels during activated sludge treatment with and without preozonation

Run	MLVSS ($g\ m^{-3}$)	Δ MLVSS ($g\ h^{-1}$)	θ_c (days)	TKN _i ($g\ m^{-3}$)	TKN _f ($g\ m^{-3}$)	NO ₃ ⁻ -N formed ($g\ m^{-3}$)
9 ^a	485	0.167	2.2	38.1	31.5	0.4
10 ^a	1620	0.174	7.0	34.6	26.3	1.6
11 ^a	2028	0.181	8.4	35.7	23.5	5.6
12	650	0.251	1.9	33.6	21.5	1.3
13	1150	0.270	3.2	32.1	17.7	4.3
14	1650	0.258	4.2	33.6	16.3	6.1
15	2540	0.241	7.9	32.4	5.6	12.2

Ozonation conditions: $F_g = 30\ dm^3\ h^{-1}$; $T = 20^\circ C$; $pH = 7.3-7.8$; $F = 3.6\ dm^3\ h^{-1}$; $C_{O_3g} = 5\ g\ m^{-3}$ Biological oxidation: $T = 20^\circ C$; $pH = 7.2-7.6$; $DO = 2.5-3.5\ g\ m^{-3}$; $F = 3.6\ dm^3\ h^{-1}$; HRT = 5h Subscript notation: i = initial (at the wastewater inlet); f = final (at the wastewater outlet)

^a Biological oxidation without preozonation.

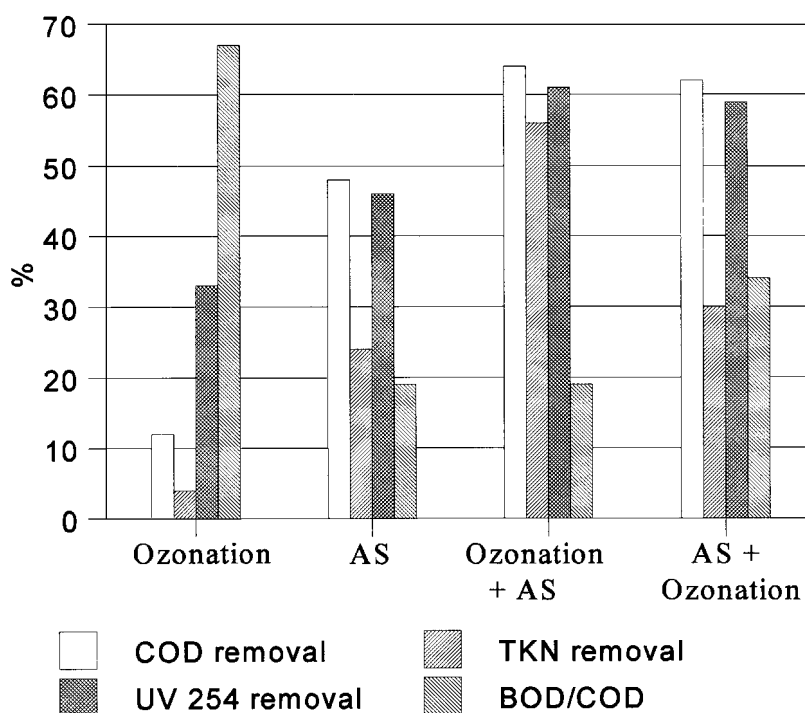


Figure 6. Comparison of processes studied regarding percentage elimination of COD, TKN and UV₂₅₄ and changes in biodegradability measured as BOD/COD. AS is activated sludge. Ozonation conditions: $F_g = 30\ dm^3\ h^{-1}$; $T = 20^\circ C$; $pH = 7.3-7.8$; $F = 3.6\ dm^3\ h^{-1}$; $C_{O_3g} = 5\ g\ m^{-3}$. Biological oxidation conditions: $T = 20^\circ C$; $pH = 7.2-7.6$; $DO = 2.5-3.5\ g\ m^{-3}$; HRT = 5h; MLVSS = $1.6\ g\ dm^{-3}$; $F = 3.6\ dm^3\ h^{-1}$.

experiments corresponding to preozonated wastewater compared with those without preozonation.

3.2.4 Comparison of processes

Figure 6 presents a summary of the results obtained with the different processes studied regarding the percentage elimination of COD, TKN, UV₂₅₄ and BOD. The results shown correspond to experiments carried out at fixed experimental conditions for both chemical and biological oxidations, but with a different sequence of treatments. Biodegradability of treated wastewater is expressed as BOD/COD ratio. The results indicate that the combined processes allow improvements of parameters studied compared with the individual chemical or biological oxidation. The best integrated process is the sequence ozonation plus biological oxidation which leads to the highest COD, UV₂₅₄ and especially TKN reductions. Ozonation alone, on the other hand, leads to the higher biodegradability in the final effluent. It is also likely that the sequence biological oxidation plus ozonation

presents an appropriate disinfection performance as far as water reuse is concerned.

4 DISCUSSION

Results obtained from the ozonation of domestic wastewaters can be explained by considering the two mechanisms of ozone attack on the organic matter in water.¹⁰ For low ozone consumption (up to approx $40\ g\ m^{-3}$) there is no dissolved ozone remaining in solution and the highest reduction rates of COD and UV₂₅₄ were achieved, which probably suggests that ozone is consumed through fast reactions with compounds in water.¹¹ On the other hand, for ozone consumptions higher than $40\ g\ m^{-3}$, dissolved ozone starts to accumulate in the wastewater and reduction rates of COD and UV₂₅₄ diminish, which suggests indirect ozone oxidation develops (ie through the action of hydroxyl radicals). The small COD and UV₂₅₄ reductions observed in this second stage are likely due to the presence of substances, like carbo-

nates, that scavenge the hydroxyl free radicals.¹⁰ From these results it can be concluded that large quantities of ozone would be required to destroy significant amounts of the organic matter by direct ozonation. Even then, a sizeable ozone refractory organic fraction would remain in solution.

Taking into account the moderate reduction of COD observed (no complete destruction of the organic matter to CO₂ occurred), the improvement of biodegradability caused by ozonation can be explained because ozone removes recalcitrant substances or inhibitory effects by changes in the molecular structure of chemicals, leading to the formation of oxygenated byproducts more amenable to biotreatment.¹² It seems that at more drastic ozonation conditions (ozone doses above the optimum), ozone was able to also react with biodegradable compounds (both originally in the wastewater and/or formed during the first oxidation stage, corresponding to low ozone dose) resulting in a decrease of final BOD.

Since BOD after ozonation at mild conditions (ozone consumption $\leq 40 \text{ g m}^{-3}$) slightly increases, while COD diminishes (see Table 1), ozone would be used to increase the biodegradability of refractory organic matter, which would require less ozone. The results shown in Fig 2 confirm the beneficial effects of a preozonation step to biodegrade the organic matter through a subsequent activated sludge treatment. Thus, at optimum conditions for ozonation, COD and BOD percentage reductions observed after a subsequent biological oxidation are 66% and 88%, respectively, compared with 47% and 80% obtained without preozonation. However, when ozone is fed in excess ($D_{O_3} > 41.7 \text{ g m}^{-3}$), chemical oxidation results in highly oxidized products with little metabolic value for the microorganisms, so that large amounts of ozone are wasted on easily biodegradable reaction intermediates and hence the system efficiency is decreased.

The increase of effluent biodegradability induced by ozonation is not reflected by a much higher SOUR during the subsequent biotreatment, when comparing preozonated and non-preozonated wastewater. These results can be explained if it is considered that after ozonation the oxygen requirements for substrate biological oxidation (g of oxygen consumed per g of BOD reduced) are lower than that required without preozonation (0.72 against 0.57 for non-ozonated and ozonated wastewaters, respectively) which is likely due to the more oxygenated byproducts formed during ozonation.

On the other hand, ozonation is not an appropriate method to remove nitrogenous compounds from wastewater. As observed from Fig 4 it is deduced that for low ozone doses there is no nitrification (see also Fig 5 in which no formation of nitrate and nitrite is observed) since at these conditions ozone reacts directly with organics. At higher ozone doses there is enough ozone available (dissolved ozone starts to increase as was shown in Fig 1) to react with organics and to decompose into radicals that can slightly

oxidize the ammonia present in wastewater. Notice that, as has been discussed previously, at the pH of the wastewater (pH=7.3–7.9), ozone does not react directly with ammonia and total nitrogen is practically in the form of ammonia. As deduced from Fig 5 ozonation of ammonia present in wastewater gives approximately stoichiometric amounts of nitrate which means that intermediate nitrites do not accumulate in water. This is a logical consequence of the high reactivity of ozone and hydroxyl radical with nitrite.^{13,14} However, ozonation increases the efficiency of a subsequent biological treatment to remove nitrogenous compounds. There are several possible explanations for this behavior. With regard to the net heterotrophic biomass growth ($\Delta MLVSS$), one explanation can be the higher amount of nitrogen metabolized when preozonation occurred because of the more elevated biomass growth (see Table 1). On the other hand, it is evident that a more intensive nitrification process develops after biological oxidation in the preozonated runs due to the higher observed formation of nitrates. In order to establish an explanation of this behavior, the fraction of nitrifiers in the mixed liquor (f_{nit}) was calculated according to the following equation:¹⁵

$$f_{nit} = Y \frac{\theta_c}{1 + b \cdot \theta_c} \frac{N_{nit}}{V \cdot MLVSS} \quad (2)$$

where Y is a yield coefficient expressed as mass of autotrophic biomass (VSS_{nit}) formed per mass of nitrogen metabolized, b is the decay rate of nitrifiers and N_{nit} the mass load of nitrified nitrogen.

The amount of nitrified nitrogen (N_{nit}) can be calculated from a mass balance as follows:

$$N_{nit} = F(TKN_i - TKN_f) - 0.12 \Delta MLVSS \quad (3)$$

where F is the wastewater flow rate, TKN_i and TKN_f the total Kjeldahl nitrogen at the inlet and outlet of the bioreactor, respectively, and $\Delta MLVSS$ the total biomass generated during 1 h of biological oxidation. The last term of the right side of eqn (3) is due to metabolic nitrogen fixation and represents the accumulation of nitrogen in the biomass. A factor of 0.12 has been assumed, considering an average biomass formula of $C_5H_7NO_2$.¹⁶ The yield coefficient ($Y = 0.16 \text{ g } VSS_{nit} (\text{g N})^{-1}$) and the decay coefficient ($b = 0.12 \text{ day}^{-1}$) have been obtained from literature.¹⁷

The estimated fraction of nitrifiers has been plotted in Fig 7 versus the total biomass activity, measured as the product $\alpha = MLVSS \cdot HRT$ for the experiments of Table 2. As can be seen, on one hand, the percentage of nitrifiers in the MLVSS increases with the increasing biomass activity for both ozonated and non-ozonated effluents and, on the other, the nitrifiers percentage for a given value of α is higher when the wastewater had been ozonated. This latter observation suggests that preozonation favors the growth of *Nitrosomas* species. A possible explanation of the results of Fig 7 is the feasible presence of nitrification

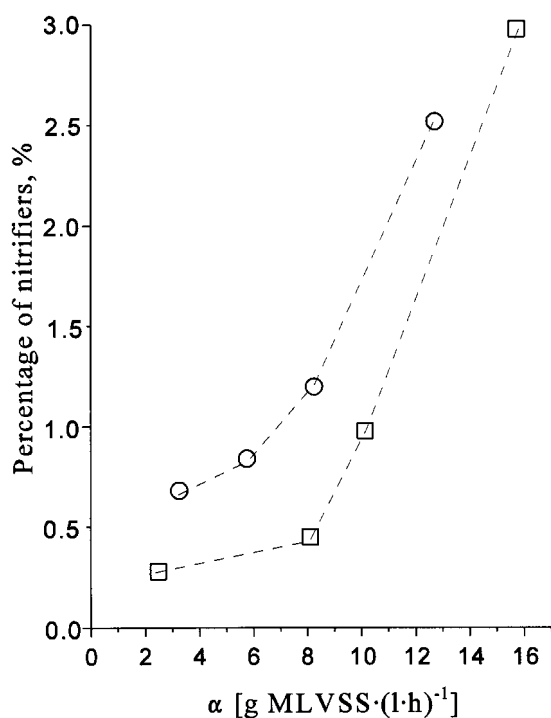


Figure 7. Variation of nitrifiers percentage as a function of biomass activity ($\alpha = \text{MLVSS} \cdot \text{HRT}$) during biological oxidation (○) with and (□) without preozonation. Ozonation conditions: $F_g = 30 \text{ dm}^3 \text{ h}^{-1}$; $T = 20^\circ \text{C}$; $\text{pH} = 7.3\text{--}7.8$; $F = 3.6 \text{ dm}^3 \text{ h}^{-1}$; $C_{\text{O}_3\text{g}} = 5 \text{ g m}^{-3}$. Biological oxidation conditions: $T = 20^\circ \text{C}$; $\text{pH} = 7.2\text{--}7.6$; $\text{DO} = 2.5\text{--}3.5 \text{ g m}^{-3}$; $\text{HRT} = 5 \text{ h}$; $\text{MLVSS} = 0.5\text{--}3.1 \text{ g dm}^{-3}$; $F = 3.6 \text{ dm}^3 \text{ h}^{-1}$.

inhibitory compounds in wastewaters, which could be partially removed by ozonation. The presence of these inhibitory substances would exert a negative influence on the growth of the autotrophic microorganism, thereby affecting the nitrification rate. This hypothesis is supported by the fact that the nitrifiers fraction estimated for non-preozonated wastewaters was much lower than others obtained from literature.¹⁸

5 CONCLUSIONS

From the results of this investigation it can be concluded that:

- (1) Ozonation removes organic material from the wastewater, especially compounds which absorb light at 254 nm.
- (2) Ozonation improves water biodegradability.
- (3) The extent of organic matter removal and improvement of water biodegradability highly depends on the ozone dose transferred from the gas to the water.
- (4) Ozonation enhances the nitrification in a subsequent aerobic biological stage.

Among all processes treated, the combined chemical-biological oxidation system was observed to be the most appropriate as far as the ozone efficiency is concerned. Preozonation strongly improves the effec-

tiveness of the biological process and hence the global efficiency.

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