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Impact Of Chemical Oxidation On Biological Treatment Of A Primary Municipal Wastewater.
1. Effects On COD And Biodegradability

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Abstract

Municipal wastewaters taken from a primary sedimentation tank were subjected to different chemical oxidation processes (ozonation or UV radiation alone or combined with hydrogen peroxide) to observe the evolution of COD and BOD/COD ratios. Ozonation of wastewater led to different increases of COD level reduction depending on pH and carbonate-bicarbonate ion concentrations. Direct photolysis or hydrogen peroxide alone were found to be inappropriate technologies. On the other hand, advanced chemical oxidation, that is, oxidation with ozone or UV radiation combined with hydrogen peroxide, increased COD level reduction only when wastewater was previously decarbonated. Thus, elimination of carbonate-bicarbonate ions, increase of pH and addition of hydrogen peroxide (10^{-3} M) yield increases COD level reduction rates. Finally, preozonation also allows improvement of wastewater biodegradability.

Introduction

Due to environmental impacts of wastewaters and possibilities of reutilization, any study aimed at improving the performance of existing technologies in wastewater treatment is highly recommended. As is known, biological oxidation of primary municipal wastewaters is a key process to apply. However, the main parameters to control the degree of pollution, like COD and BOD, could be reduced further if biological oxidation is conveniently combined with other processes like chemical oxidation. In this sense, ozone or hydroxyl radical generating systems (usually called advanced oxidation processes) (Glaze et al., 1987) can play an important role. For example, it is known that ozone is a powerful oxidant and strong disinfectant that reacts both directly with the material (with specific compounds) present in water or indirectly through hydroxyl radicals generated by ozone decomposition (Staehelin and Hoigné, 1985). So far, in Europe ozone has been used mainly in drinking water treatment to improve coagulation or sedimentation, oxidation of pollutants, reduction of THM formation potential or for disinfection (Langlais et al., 1991). However, since ozonation or hydroxyl radical oxidation of organics in water leads to oxygen-containing compounds of lower molecular weight which are more biodegradable (Stephenson et al., 1979, Narkis and Schneider-Rotel, 1980). A process that combines both chemical and biological oxidations could be of interest in the treatment of any kind of wastewaters, as some previous works have pointed out (Stover et al., 1982; Heinzle et al., 1995).

Therefore, the aim of this work was, on one hand, to evaluate the reduction of COD levels of a municipal wastewater, taken from a primary sedimentation unit after being subjected to combinations of ozone, ultraviolet radiation (254 nm) and hydrogen peroxide and, on the other hand, to check the effect of preozonation on the biodegradability of the water. In the following paper (Beltrán et al., 1997) effects of ozonation on the kinetics of a subsequent biological oxidation will be presented.

Experimental

Wastewaters studied in this work were obtained from a municipal wastewater treatment plant in Badajoz (Spain) after being subjected to screening, grit removal and sedimentation. The main characteristics of the effluent at the outlet of the primary sedimentation unit are presented in Table I.

TABLE I. CHARACTERISTICS OF URBAN WASTEWATER USED IN THIS WORK

pH	COD	BOD_5	IC	TC	DO	Alkalinity	$N\text{-}NH_3$	TKN
	$mg{\cdot}L^{-1}$	$mg{\cdot}L^{-1}$	$mg{\cdot}L^{-1}$	$mg{\cdot}L^{-1}$	$mg{\cdot}L^{-1}$	mg $CaCO_3\,L^{-1}$	$mg{\cdot}L^{-1}$	$mg{\cdot}L^{-1}$
7.6 ±0.2	286 ±50	162 ±13	41 ±5	185 ±20	2.0 ±0.4	313 ±21	29 ±2	35 ±3

COD (Chemical Oxygen Demand); BOD (Biochemical Oxygen Demand); IC (Inorganic Carbon); TC (Total Carbon); DO(Dissolved Oxygen); $N\text{-}NH_3$ ($NH_3 + NH_4^+$ measured as nitrogen); TKN (Total Kjeldhal Nitrogen)

Ozone was produced from air in a 500 Fisher ozone generator. Hydrogen peroxide was obtained from Merck. Chemical oxidation was carried out in a bubble column provided at its top with a central inlet to place, if necessary, a quartz tube. In some experiments, inside this tube a 17 cm Hannau low pressure mercury vapor lamp emitting 254 nm UV radiation with a power input of 15 W, according to the manufacturer, was placed. Wastewater was recirculated at the rate of 20 L h^{-1} to ensure good mixing conditions. During ozonation runs, ozone was fed through a diffuser plate situated at the bottom of the reactor. In all cases, pH and temperature were measured in the recirculating line (see Figure 1 for more details about the reactor).

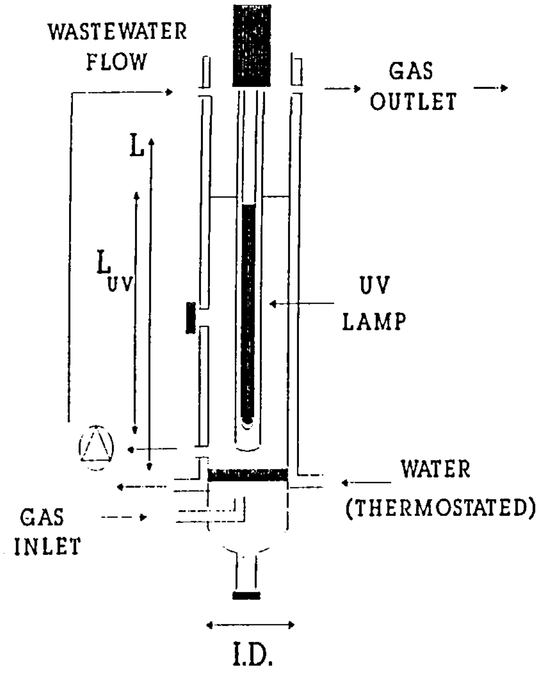

Figure 1. Bubble column: dimensions: L=35 cm; L_{UV}=17 cm; I.D.=9 cm.

Tests of biodegradability were based on the respirometer BOD method (Means and Anderson, 1981). Bottles of 300 mL capacity containing a known amount of wastewater samples and inocula were used. COD was determined according to the dichromate standard method (Moore et al. 1949) with a Dr. Lange photometer. Ozone concentration in the gas stream at the reactor inlet and outlet was monitored with a 919 Anseros Ozomat Analyzer. In the water, ozone concentration also was followed by using the indigo method (Bader and Hoigné, 1981). Variation of UV absorbance at different wavelength was obtained in a 2000 Hitachi spectrophotometer and hydrogen peroxide was analyzed by an iodometric method (AOAC, 1980). TC and IC were measured with a 915B Beckman Carbon Analyzer and DO with a YSI-58 dissolved oxygen transmitter. Finally, nitrogen (total and ammonia) was analyzed by the Kjeldahl method (Standard Methods, 1981).

In some cases wastewaters were decarbonated by separating their carbonate/bicarbonate ions as barium salt precipitate (Burriel et al., 1960). For this, barium chloride and ammonium hydroxide were added. Once the filtrate was separated, the excess ammonia was eliminated by stripping with air.

Results and Discussion

OZONATION

Three variables were investigated: ozone dose rate applied, temperature and pH.

Influence of Ozone Dose Rate Applied

Figure 2 shows the variation of normalized COD with time for experiments carried out at different ozone dose rate (measured as mg of ozone fed per unit time and per unit of wastewater volume). It is seen that at a given time the increase of ozone dose rate, from 94 to 200 mg h^{-1} L^{-1} leads to increases of COD reduction rate. A further increase of ozone dose does not yield any significant effect on the parameter studied. Therefore wastewater ozonation is a process that can be optimized regarding the applied ozone dose rate. Thus, results from Figure 2 indicate that there is an optimum ozone dose rate to remove the maximum amount of COD with lesser ozone consumption.

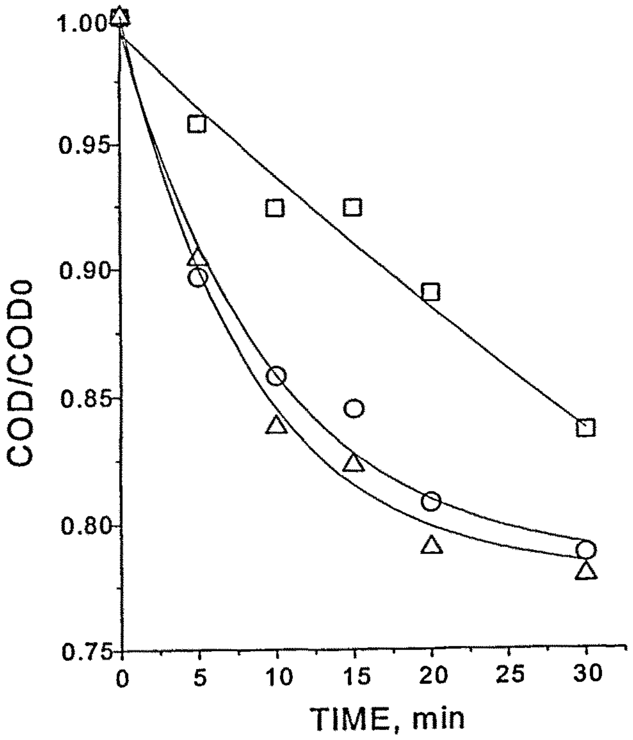

Figure 2. Effect of ozone dose rate on COD/COD_0. Conditions: Temperature: 20°C; pH = 7.7; Reactor volume: 1.5 L; Gas flow rate: 30 L h^{-1}; Recirculation flow: 20 L h^{-1}. Ozone dose rate, mg h^{-1} L^{-1}: □ 94; ○ 200; △ 390.

In Figure 3, both the evolution of COD removed per mg of ozone consumed (CODr), and ozone efficiency (η), measured as percentage of ozone fed that is consumed, needed to reach 5, 10 and 15% COD reduction are plotted versus the ozone dose rate (m_{O3}). It can be observed that approximately 170, 196 and 201 mg L^{-1} h^{-1} ozone dose rates represent the optimum values in each case and that the corresponding ozone efficiency is always higher than 80%. According to these results it also can be deduced that, for the specific system studied herein, ozonation can provide as much as 15% COD reduction, since a further COD reduction will reduce ozone efficiency below 80% and much of ozone would escape from the reactor without being consumed.

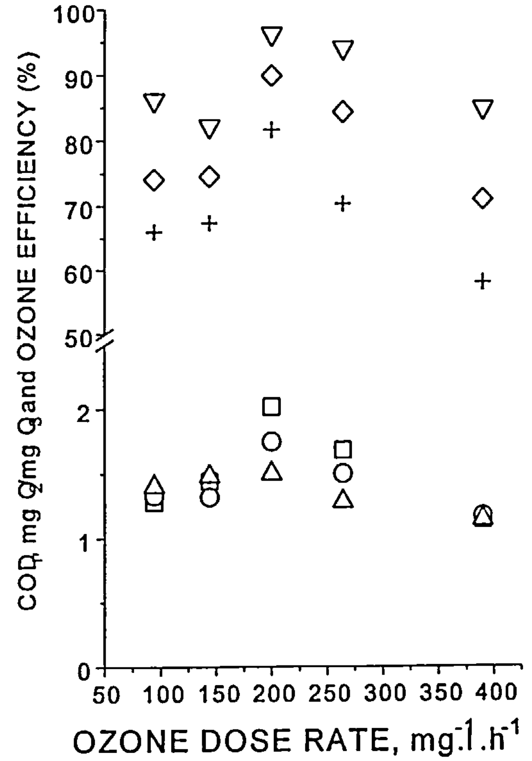

Figure 3. Ozone efficiency (η) and COD eliminated per mg ozone consumed (COD_r) versus ozone dose for different COD percentage reductions. Conditions: Temperature: 20° C, pH = 7.7; Reactor volume: 1.5 L; Gas flow rate: 30 L h^{-1}; Recirculation flow: 20 L h^{-1}. % COD reduction: (for η): □ 5%; ○ 10%; Δ 15%. (For COD_r): ▽ 5%; ◇ 10%; + 15%.

Influence of Temperature

Figure 4 shows the effect of temperature on COD reduction. As observed in Figures 2 and 4, temperature and ozone dose rate applied present similar effects on COD reduction.

Thus, for temperatures between 15 and 20°C there is a positive effect, while no significant difference in COD reduction is observed between 20 and 30°C. It seems that both ozone solubility and reaction rate constant are responsible for what is observed, since temperature has opposite effects on both parameters. Thus, the increase of temperature yields a decrease of ozone solubility and an increase of the reaction rate constants, hence, higher chemical reaction rates. Accordingly, it is not convenient to reach temperatures of ozonation above ambient conditions.

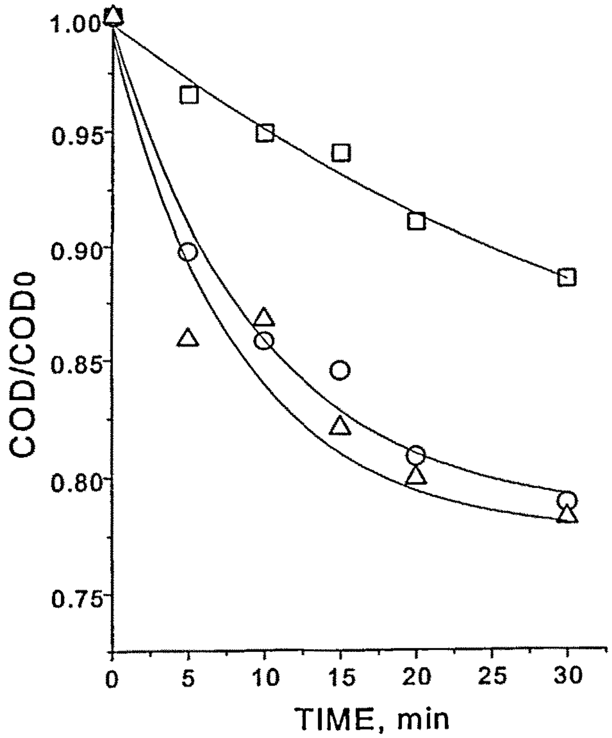

Figure 4. Effect of temperature on COD/COD$_0$ during ozonation of wastewater. Conditions: Ozone concentration in the gas inlet: 10 mg L^{-1}; pH = 7.7; Reactor volume: 1.5 L; Gas flow rate: 30 L h^{-1}; Recirculation flow: 20 L h^{-1}. T, °C: □ 15; ○ 20; Δ 30.

Influence of pH

A priori, pH can be the most important parameter of an ozonation process. This is due to the strong effect of hydroxide ions on ozone decomposition, especially when pH is raised above 8 (Staehelin and Hoigné, 1982). However, as shown in Figure 5, there is no pH effect on COD reduction at short ozonation times (less than about 10 minutes), while for higher times a slight increase of COD reduction is observed with the increasing pH. Different COD reduction rates at different pH could be explained if it is considered, on one hand, that reacting organic compounds can have different reactivities at different pH values due to their dissociation and electron activities and, on the other hand, that ozone at high pH may decompose into free radicals (like the hydroxyl free radical) that could increase the oxidation rate of the compounds present. During the first reaction minutes, since pH has no influence on the oxidation rate (similar COD reductions) it is evident that direct ozone reactions are important. In fact, during this initial period there is no accumulation of dissolved ozone in water regardless of pH, which supports that fast direct ozone reactions develop (Beltrán, 1995).

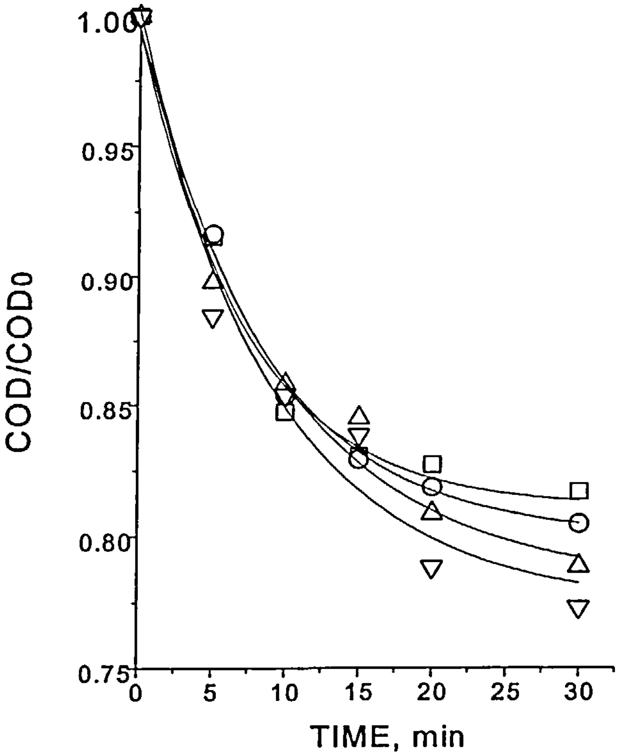

Figure 5. Effect of pH on COD/COD$_0$ during ozonation of wastewater. Conditions: Ozone concentration in the gas inlet: 10 mg L^{-1}; Temperature: 20°C; Reactor volume: 1.5 L;Gas flow rate: 30 L h^{-1}; Recirculation flow: 20 L h^{-1}. pH: □ 2; ○ 4; Δ 7; ∇ 9.

After this initial period, dissolved ozone concentration was found to increase with time. It is possible then, that at high pH ozone decomposes into free radicals that promote the increase of the oxidation rate observed. One way to ascertain if hydroxyl radical reactions are taking place is based on the elimination of carbonates present in wastewaters, since these species are strong inhibitors of reactions between the hydroxyl free radical and the organic matter (Buxton et. al., 1988). It is also possible that the municipal wastewaters studied in this work contain significant amounts of carbonates (Weeks and Rabani, 1966) since alkalinity and inorganic carbon were high (about 313 mg CaCO$_3$ L^{-1} and 41 mg C L^{-1}, respectively, according to Table I). Thus, a series of experiments was carried out on wastewaters whose bicarbonate-carbonate ions were previously removed. Figure 6 shows the results obtained. It can be seen that for the first initial period (about 10 minutes) results are similar to those shown in Figure 5, that is, there is no pH influence on COD removal rate, a logical consequence of the pH independent ozone direct reactions that presumably develop at the start of ozonation. At higher reaction times, on the other hand, the increase of pH is now more clear, yielding significant increases of COD removal rates, especially at pH 9 (i.e., at 30 minutes of ozonation, percentage removal of COD varies from 20% to about 37% for pH 4 and 9, respectively, carbonates being previously removed from wastewater). It has to be noticed that removal of carbonates from wastewaters is not a recommended procedure for a practical case, but at the laboratory level and from a scientific point of view, it permits the establishment of some characteristics of the ozonation mechanism. Also, notice that other free radicals like organic peroxy radicals and inhibiting species likely are present in the complex matrix of wastewaters.

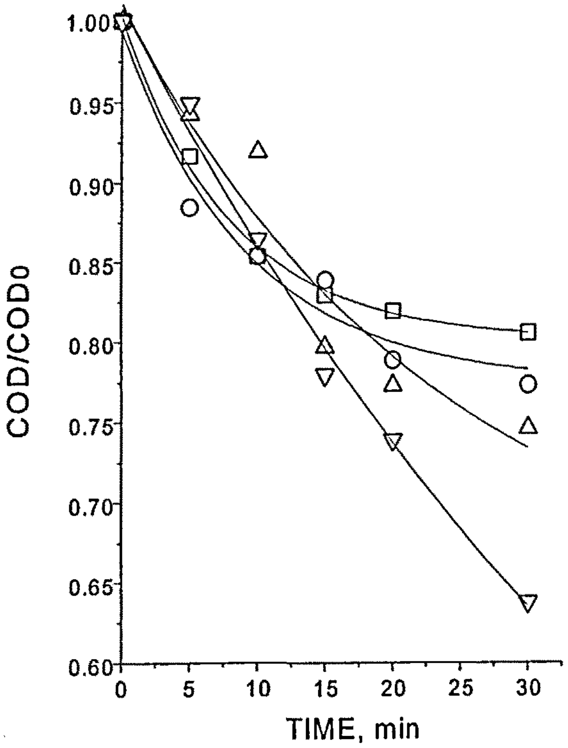

Figure 6. Effect of the presence of carbonate/bicarbonate ions on COD/CODo during ozonation of wastewater at different pH values. Conditions: Ozone concentration in the gas inlet: 10 mg L^{-1}; Temperature: 20°C; Reactor volume: 1.5 L; Recirculation flow: 20 L h^{-1}. pH (with carbonate/bicarbonate present): □ 4; ○ 9; (without carbonate/-bicarbonate): Δ 4; ∇ 9.

WASTEWATER OXIDATION WITH UV RADIATION ALONE AND COMBINED WITH HYDROGEN PEROXIDE

The COD analytical method then was tested in wastewater samples of different carbon content at varying hydrogen peroxide concentrations. It was observed that hydrogen peroxide at concentration below 10^{-2} M does not interfere in COD determination. As a consequence, in this work hydrogen peroxide concentrations $\leq 10^{-3}$ M were used during hydrogen peroxide-involved advanced oxidations (UV/H_2O_2 and O_3/H_2O_2). Also, it was observed that hydrogen peroxide alone did not exert any effect on COD of wastewaters treated.

In a second stage, single UV photolysis of wastewaters was studied. This process did not result either in significant COD removal rates (only about 7% COD reduction was observed during 30 minutes of UV radiation, see Figure 7) although this could be attributed primarily to the low actual power output of the lamp used (1.11 watts), since the quantum yield of wastewater (see below) was not negligible.

If COD is representative of the concentration of oxidizable matter present in water, the rate of COD removal due to photolysis can be expressed as follows (Beltrán et al., 1992; 1993):

$$-\frac{dCOD}{dt} = I_o\phi[1-\exp(-2.303\,L\epsilon COD)] \qquad [1]$$

where L, I_0, ϵ and ϕ represent the effective path of radiation through the photoreactor, intensity of incident radiation, extinction coefficient and quantum yield of wastewater, respectively. For our case, the exponential term becomes unity ($2.303L\epsilon COD > 2$, $L = 4{,}5$ cm; $\epsilon = 0.004$ L mg^{-1} cm^{-1}) and equation [1] can be simplified to yield:

$$-\frac{dCOD}{dt} = I_o\phi \qquad [2]$$

According to equation [2], the removal rate of COD is independent of COD, which confirms the results of single UV photolysis presented in Figure 7. In this figure it is seen that COD varies linearly with time. The slope of this line, according to equation [2] is $-I_0\phi$. Since I_0 is known (1.6×10^{-6} Einstein L^{-1} s^{-1}) (Beltrán et al., 1993), ϕ was found to be 5417 ± 924 mg O_2 $photon^{-1}$.

The combined effect between UV radiation and hydrogen peroxide at a concentration lower than 10^{-2} M only results in a slight increase (with respect to UV photolysis alone) in COD removal rate. At first sight, this suggests that all incident radiation could be absorbed by the wastewater and hence hydrogen peroxide photolysis does not develop to generate hydroxyl radicals (Christensen et al, 1982). However, another possible explanation can be due to the presence of carbonate/bicarbonate ions that would inhibit the oxidizing action of some free radicals like hydroxyl radicals. In fact, when these ions were removed, COD reduction rates increased (data not shown). According to this, in the absence of carbonate/bicarbonate ions, hydrogen peroxide photolyzes to yield hydroxyl radicals which in turn increase the rate of COD level reduction. As also shown in Figure

7, direct radiation of wastewaters in the presence and absence of carbonates leads to similar COD level reductions.

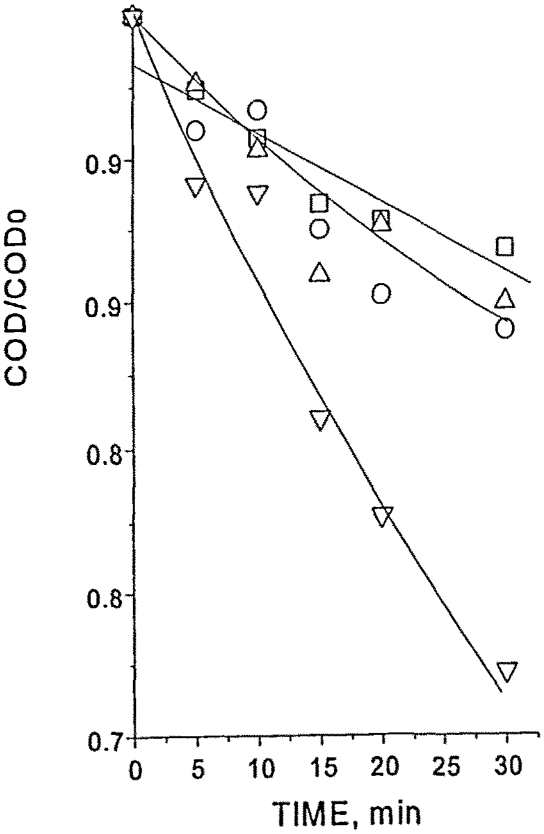

Figure 7. Effect of single UV radiation and UV/H_2O_2 oxidation on COD/COD_0 in the presence and absence of carbonate/bicarbonate ions: Conditions: Temperature: 20°C; pH = 7.7; Reactor volume: 1.5 L; Recirculation flow: 20 L h^{-1}. Radiation intensity: 1.6×10^{-6} Einstein L^{-1} s^{-1}. Type of treatment: (with carbonate/bicarbonate present) □ UV; Δ UV/H_2O_2 (10^{-3} M); (with carbonate/bicarbonate removed) ○ UV; ∇ UV/H_2O_2 (10^{-3} M).

WASTEWATER OXIDATION WITH OZONE COMBINED WITH HYDROGEN PEROXIDE OR UV RADIATION

As shown in Figure 8, addition of hydrogen peroxide to wastewater ozonation does not result either in any improvement of COD removal rate compared to single ozonation. In fact, during the first 10 minutes of reaction, no increase of ozonation rate was expected if it is admitted that only ozone direct reactions develop. For longer oxidation times, an increase of COD removal rate with increasing hydrogen peroxide concentration also was expected because, under these conditions, it is likely that the concentration of hydroxyl radicals formed from the direct ozone-hydrogen peroxide reaction increases (Staehelin and Hoigné, 1982). However, the COD removal rate was kept practically independent of hydrogen peroxide concentration as shown in Figure 8. As it happens with single ozonation, it is reasonable to admit that at the conditions investigated (that is, with a concentration of hydrogen peroxide lower than 10^{-2} M), hydroxyl radical concentration is not high enough to overcome the inhibiting action of carbonate or like substances. Thus, another series of experiments with ozone-hydrogen peroxide oxidation was carried out after removing carbonates from wastewater. Figure 8 also presents some of the results of this series. It can be observed that after the first period of reaction (about 10 minutes), the process becomes hydrogen peroxide-dependent (after 30 minutes, COD level reduction is 33% for single ozonation and 40% when ozone is combined with hydrogen peroxide at a concentration of 10^{-3} M).

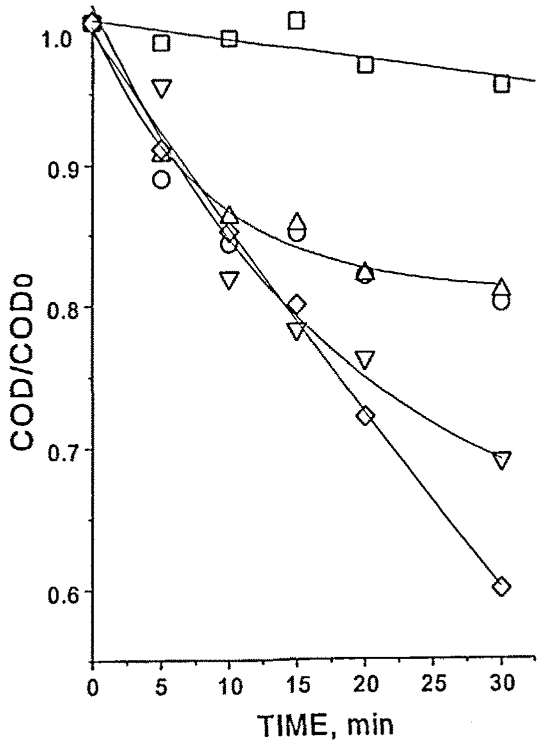

Figure 8. Effect of hydrogen peroxide concentration on COD/COD_0 during O_3/H_2O_2 oxidation of wastewater with and without carbonate/bicarbonate removed. Conditions: Temperature: 20°C; pH = 7.7; Reactor volume: 1.5 L; Gas flow rate: 30 L h^{-1}; Recirculation flow: 20 L h^{-1}; C_{H2O2}, M and C_{O3g} mg L^{-1} (without carbonate/bicarbonate removed): □ 10^{-3} and 0; ○ 0 and 10; Δ 10^{-3} and 10; (with carbonate/bicarbonate removed): ∇ 0 and 10; ◇ 10^{-3} and 10.

Finally, experiments of ozone combined with UV radiation showed similar results to those obtained with the combination ozone-hydrogen peroxide, that is, there were no significant differences between this advanced oxidation and single ozonation when carbonates were present in the wastewater (see Figure 9).

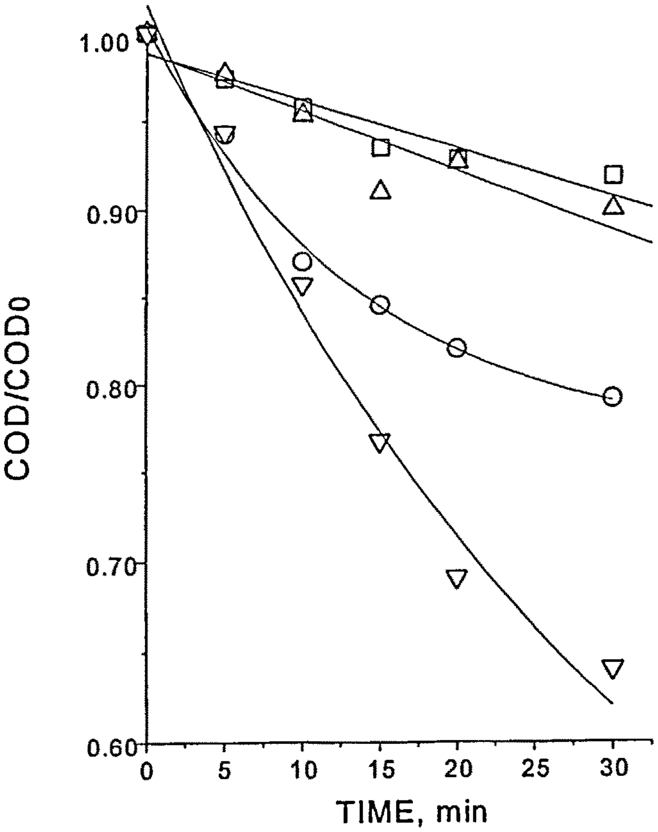

Figure 9. Effect of single UV radiation and O_3/UV oxidation on COD/COD_0 in the presence and absence of carbonate/bicarbonate ions. Conditions: Temperature: 20°C; pH = 7.7; Reactor volume: 1.5 L; Gas flow rate: 30 L h^{-1}; Recirculation flow: 20 L h^{-1}; Ozone concentration in the gas inlet: 10 mg L^{-1}; Radiation intensity: 1.6 x 10^{-6} Einstein L^{-1} s^{-1}. Type of treatment: (with carbonate/bicarbonate present): □ UV; ○ O_3/UV; (with carbonate/bicarbonate ions removed): Δ UV; ∇ O_3/UV.

BIODEGRADABILITY TEST

From the above comments it can be concluded that single ozonation is the most appropriate technology among those studied in this work to increase COD level reduction of wastewaters. Combined advanced oxidations do not seem to significantly improve COD level reduction unless elimination of carbonates is made. Thus, tests of biodegradability of wastewaters were only applied to wastewater samples subjected to single ozonation. Figure 10 shows the evolution of BOD/COD ratio with time corresponding to unozonated and ozonated wastewaters at different ozone doses. It can be seen that for unozonated wastewater, the evolution of BOD/COD presents the typical curve found for this analysis with BOD/COD ratio stabilized approximately after 4 to 5 days from the beginning of tests. For the case of ozonated wastewater, a lag period is observed at the start of tests where BOD/COD ratio increases with time very slowly as a result of the acclimatization of the inocula fed to the sample (notice that since ozonated wastewater is disinfected, activated sludge has to be added to the sample for the BOD test). In these cases, however, BOD/COD ratio always stabilizes after 6 to 8 days of biodegradation. It is also seen that the bio-test of an ozonated wastewater for 10 days leads to a BOD/COD ratio equal to or even higher than that found for the unozonated wastewater.

Analysis of BOD tests confirms the ozone capacity to transform the matter present in water into compounds more amenable for microorganisms as biokinetic data confirm. Thus, BOD can be expressed as a function of time as follows (Ramalho, 1991):

$$BOD = L_0(1 - e^{-kt}) \quad [3]$$

where L_0 represents the total amount of biodegradable matter and k is the biodegradation rate constant. After applying equation [3] to the experimental results, L_0 and k were obtained by least squares analysis of experimental data under different conditions as presented in Tables II and III. As seen in these tables, values of k corresponding to non-ozonated wastewaters with different COD are approximately constant (0.70 ± 0.06 day^{-1}) while those of ozonated wastewaters increase with increasing ozone dose and temperature.

On the other hand, Tables II and III also present the percentage of wastewater biodegradability of wastewaters calculated as $(L_0/COD) \times 100$. Thus, it is observed that biodegradability of wastewater increases when ozone is used (i.e., for an ozone dose of 100 mg L^{-1} at 20°C [run 2] biodegradability increases from 54%, for non-ozonated wastewater, to 71%, for ozonated wastewater). On average, ozonation of wastewater increases wastewater biodegradability about 25%.

TABLE II. NON-OZONATED WASTEWATER BIOKINETIC DATA

Run	COD_0	k	L_0	% biodegradability
	mg $O_2 \cdot L^{-1}$	day^{-1}	mg $O_2 \cdot L^{-1}$	$(L_0/COD_0) \times 100$
1	263	0.81	165	63
2	303	0.75	164	54
3	272	0.78	161	59
4	234	0.66	168	72
5	234	0.81	165	70

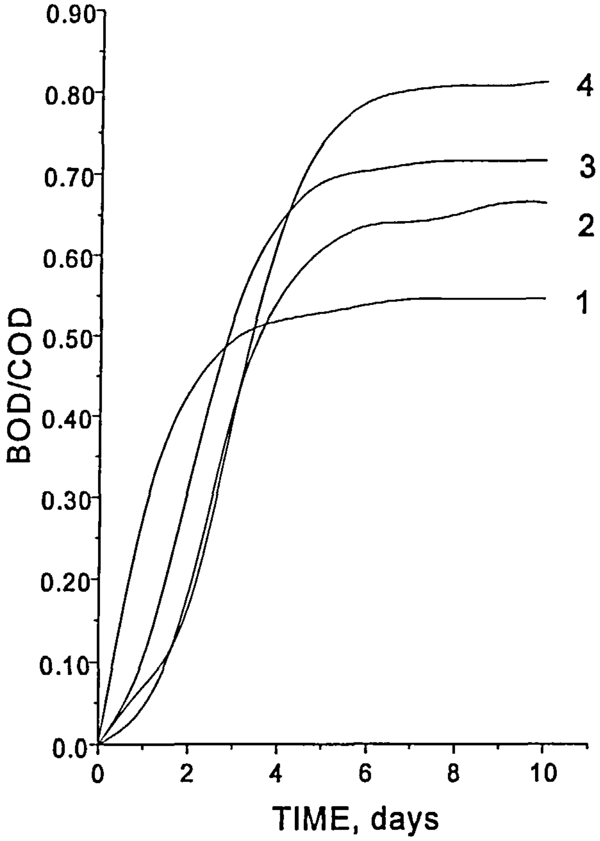

Figure 10. Biodegradability test: Variation of BOD/COD of non-ozonated and ozonated wastewater with time. Conditions: During ozonation: Temperature: 20°C; pH = 7.7; Reactor volume: 1.5 L; Gas flow rate: 30 L h^{-1}; Recirculation flow: 20 L h^{-1}; Reaction time: 30 min. Run number and ozone dose, mg L^{-1} : 1, 0; 2, 47; 3, 100; 4, 195.

In Figure 11 variation of total, biodegradable and non-biodegradable fractions of non-ozonated and ozonated wastewater at different conditions is shown. It can be seen that for the lowest ozone dose applied (47 mg L^{-1}) both biodegradable and non-biodegradable fractions are reduced about 7 and 10%, respectively, but higher ozone doses applied lead to increases of the non-biodegradable fraction reduction. From these results it seems that there exists a critical ozone dose (100 mg L^{-1} approximately) above which ozone mainly attacks the non-biodegradable fraction resulting in a net increase of biodegradability (see Figure 11).

TABLE III. OZONATED WASTEWATER BIOKINETIC DATA[a]

Run	T[a]	Ozone dose	COD[b]	k	L_0	% biodegradability
	°C	mg L^{-1}	mg $O_2 \cdot L^{-1}$	day^{-1}	mg $O_2 \cdot L^{-1}$	$(L_0/COD_0) \times 100$
1	20	47	220	54	146	66
2	20	100	239	60	171	71
3	20	195	212	85	178	84
4	15	100	210	58	170	81
5	30	100	183	84	159	87

[a]Ozonation time: 30 min. Initial COD values as in Table 1. [b]COD values after ozonation

Conclusions

Two main conclusions can be drawn from this work: preozonation of a primary municipal wastewater (1) reduces levels of COD and (2) improves biodegradability. More specifically, the results obtained allow the conclusion that, apart from economic reasons, ozone is an appropriate technology to be combined with biological oxidation if proper experimental conditions are applied. Thus, there exists an optimum ozone dose for which both ozone efficiency and COD level reduction per ozone consumed are maximum. In this work and for the specific system studied, the optimum ozone dose is 100 mg L^{-1}. The temperature of the wastewater should be around 20°C. Regarding the pH effect, decarbonation of the wastewater prior to ozonation allows ascertaining to what extent contribution of hydroxyl radical reactions develop. In this way, once ozone fast-reacting compounds are eliminated from direct ozonation during the first minutes, radical oxidation takes place to further increase COD level reduction. This indirect method of oxidation is favored with increase of pH, presence of hydrogen peroxide and/or UV radiation in the absence of carbonate-bicarbonate ions. Direct photolysis of wastewaters is not appropriate. In this work it was observed that ozonation yields about 25% increase of biodegradability compared to non-ozonated wastewaters.

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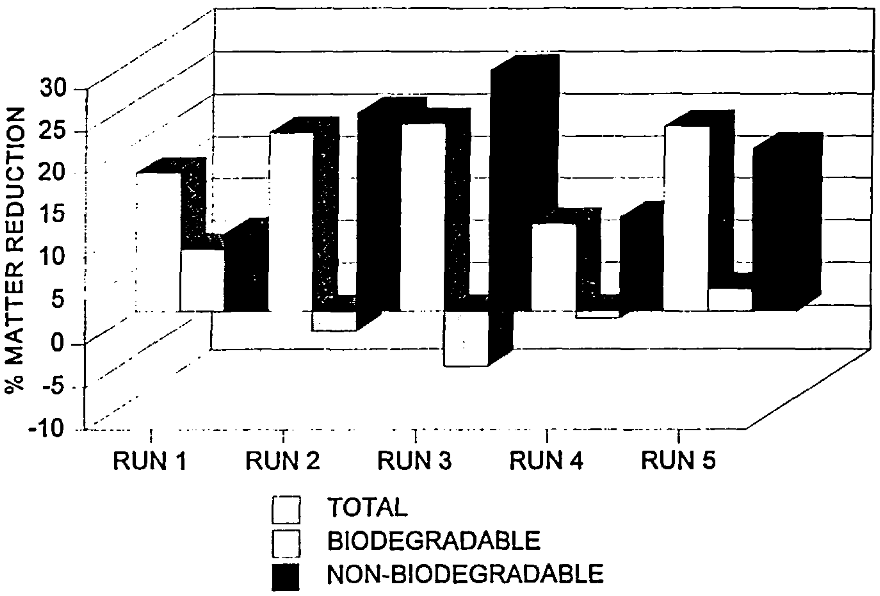

Figure 11. Reduction of total, biodegradable and non-biodegradable fractions of wastewater during ozonation. Conditions of ozonation: Temperature: 20°C; pH = 7.7; Reactor volume: 1.5 L; Recirculation flow: 20 L h^{-1}; Reaction time: 30 min; Run number, ozonation temperature (°C), and inlet ozone dose (mg L^{-1}): 1, 20, 45; 2, 20, 100; 3, 20, 195; 4, 15, 100; 5, 30, 100.

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Key Words

Ozone; Primary Municipal Wastewater; Chemical Oxidation; Biologtical Treatment; COD; Biodegradability;

Résumé

Les eaux résiduaire urbains prélevées après décantation primaires ont été soumises à différents procédés d'oxydation chimique (ozonation ou radiations UV, seules ou combinés avec le peroxyde d'hydrogène) pour évaluer l'évolution de la DOC et du rapport DBO/DCO. L'ozonation de l'eau résiduaire a conduit à accroître la réduction de la DCO, dépendant du pH et de la concentration en ions carbonate et bicarbonate. Le traitement par radiations UV or par peroxyde d'hydrogène utilisés seuls n'ont pas été trouvés des procédés appropriés. Par ailleurs, le procédé d'oxydation avancée (par combinaison de l'ozone avec UV or peroxyde d'hydrogène) a permis d'accroître la réduction de la DCO sous réserve que l'eau soit au préalable décarbonatée. L'élimination des ions carbonate et bicarbonate, l'augmentation du pH, at l'addition de peroxyde d'hydrogène (10^{-3} M) augmentent le pourcentage d'élimination de la DCO. Enfin, la préozonation permet également d'améliorer la biodégradabilité de l'eau résiduaire.

Zusammenfassung

Mit kommunalem Abwasser aus dem ersten Absetzbecken wurden verschiedene Oxidationsversuche durchgeführt (Ozon und UV sowohl allein als auch kombiniert mit H_2O_2), um die Entwicklung des COD und des BOD/COD-Verhältnisses zu untersuchen. Die Ozonung führte zu unterschiedlichen COD-Erniedrigungen in Abhängigkeit von pH-Wert und Carbonat/Bicarbonatkonzentration. Direkte Photolyse oder H_2O_2 allein waren ungeeignet. Die Oxidation mit Ozon oder UV zusammen mit H_2O_2 erniedrigte den COD nur, wenn vorher Carbonat aus dem Abwasser entfernt wurde. Die Entfernung der Carbonat/Bicarbonationen, eine pH-Erhöhung und der Zusatz von H_2O_2 (10^{-3} M) erhöhte die COD-Entfernung. Die Vorozonung erhöhte die biologische Abbaubarkeit des Abwassers.