Combined post-ozonation and biological treatment of recalcitrant wastewater from a resin-producing factory

M.A. Aparicio, M. Eiroa, C. Kennes, M.C. Veiga

Abstract

In this study, effluent from the biological treatment of wastewater from a resin-producing factory containing recalcitrant compounds was ozonated under different conditions. Afterwards, the biodegradability of the ozonated effluent was studied under anoxic conditions. The post-ozonation of the industrial effluent was performed using a wide range of ozone doses, from 1.8 to 29.5 mg L^{-1} min^{-1}. After the biological treatment of the ozonated effluent, organic carbon and nitrogen removals from 27 to 97% and from 27 to 80%, respectively, were achieved. The effect of the contact time was studied at a constant ozone dose of 13.0 ± 1.2 mg L^{-1} min^{-1} and contact times ranging from 30 to 180 min. In this case, organic carbon removals from 55 to 100% and organic nitrogen removals from 41 to 77% were obtained after biological treatment.

Keywords

Post-ozonation; Biodegradability; Recalcitrant wastewater; Resin-producing factory wastewater

1. Introduction

Wastewater from a resin-producing factory contains relatively high concentrations of organic matter (COD 117–6851 mg L^{-1}) and organic nitrogen (TKN 56–1462 mg L^{-1}). The biological treatment of this wastewater requires the accomplishment of a series of objectives: organic matter removal, hydrolysis of the organic nitrogen fraction (urea and polymers) to ammonium, ammonium nitrification to nitrite and/or nitrate and denitrification of both nitrite and nitrate. However, after this biological treatment a significant fraction of residual organic carbon and nitrogen remains present in this type of wastewater [1]. This residual organic carbon and nitrogen is due to waste polymers from the urea–formaldehyde, phenol–formaldehyde and melamine–formaldehyde resins produced in the factory. Therefore, tertiary treatment of these secondary effluents could be required if the concentration of recalcitrant compounds is not in accordance with legal requirements or if the biological treatment is not efficient enough for a possible reutilization of the water. The use of ozone could be useful for this purpose taking into account that post-ozonation can simplify the chemical structure of a bioresistant compound with the concomitant enhancement of its biodegradability [2]. After ozonation, the effluent could be recycled to the biological treatment. The first biological step reduces the concentration of compounds that may compete for the chemical oxidant, thus increasing the overall removal efficiency and lowering treatment costs [3].

Chemical oxidation is a quite widely studied method for the treatment of waters including refractory compounds. Ozone is known to be a powerful oxidant with the highest thermodynamic oxidation potential of the common oxidants. Ozone oxidation has been employed for treating wastewaters from electroplating, textile, pulp and paper, and petroleum industries. In recent years, ozone oxidation has been studied for treating rubber additive wastewaters, landfill leachates and municipal wastewaters [4] and [5].

With post-ozonation, part of the refractory organic matter is usually (but not always) converted into a more biodegradable form. A wastewater constituent highly or completely resistant to conventional biological treatment can be totally mineralised using a combined chemical–biological system [6]. Factors affecting ozonation efficiency are ozone mass transfer, pH, ozone dose and contact time. The ozone mass transfer is influenced by many factors, which can be divided into hydrodynamic and physicochemical effects. Hydrodynamic behaviour is concerned with the movement of the molecules. If intense mixing is applied to a liquid containing gas bubbles, the bubbles are sheared and mixed thoroughly, increasing both the interfacial area and contact time, and reaching therefore higher mass transfer rates. Physicochemical effects include decomposition reactions of ozone, temperature, pressure and chemical composition of the liquid [7]. pH affects the nature of by-products formed and can influence the ozonation efficiency too. In general, the rates of compound elimination and by-product formation increase with pH due to accelerated free radical formation in the presence of hydroxide ions. pH can be controlled either by the use of buffers or by dosing with an acid or alkali.

Another factor affecting the ozonation efficiency is the ozone dose. Molecules which are more sensitive to oxidation react first with small ozone doses, and produce more biodegradable molecules with alcoholic and carboxylic functional groups [8]. At higher ozone doses, biodegradable compounds (both initially present and others formed as a result of ozonation) compete with recalcitrant compounds for the available ozone [9].

Therefore it is not always worthwhile to increase the ozone dose too high, and it is important to determine the optimum ozone dose so that a higher fraction of dissolved matter can be eliminated by a biological post-treatment. The contact time in the chemical oxidation process is also important in a combined system. Longer oxidation times lead to a higher degree of oxidation and higher removal when chemical oxidation is the sole treatment. However, a higher overall removal does not necessarily occur at long chemical oxidation times in a combined system. When a biological process is receiving the ozonated effluent, excessive chemical oxidation may result in highly oxidized products possessing little metabolic value for the microorganisms. Large ozone doses or contact times could be wasted on easily biodegradable intermediates resulting in decreased system efficiency [3].

The purpose of this work was to evaluate the effect of the ozone dose and the contact time on the biodegradability of recalcitrant industrial wastewater. Effluent from the biological treatment of wastewater from a resin-producing factory was ozonated under different conditions. Afterwards, the biodegradability of the ozonated effluent was studied under anoxic conditions.

2. Materials and methods

2.1. Wastewater composition

The composition of the wastewater from a resin-producing factory and the composition of the effluent after the biological treatment of this wastewater are shown in Table 1. For this study, biologically treated effluent obtained from the industrial wastewater treatment plant was used. The pH was around 8.75 and average values of residual DOC and TKN were 142.4 ± 15.5 mg L^{-1} and 159.5 ± 2.3 mg L^{-1}, respectively.

Table 1.

Composition of the wastewater from a resin-producing factory and of the effluent after the biological treatment of this wastewater (all parameters are in mg L^{-1}, except pH)

Parameter	Industrial wastewater	Biologically treated effluent
DOC	1423.0–99.5	126.9–157.9
TKN	467.8–492.3	157.2–161.8
pH	6.3–7.0	8.6–8.9
CH_2O	2087.0–2200.0	0–10
HCOOH	1384.6–1513.9	0–5
CH_3OH	240.0–264.1	0–5
C_6H_6O	0.9–2.0	–

2.2. Ozonation

The industrial effluent containing a significant fraction of residual organic carbon and nitrogen was submitted to ozonation under different conditions. Several experiments were carried out by modifying the recirculation flow rate, pH, ozone dose and contact

time. The experimental set-up used for the ozonation experiments consisted of a tubular reactor ($h = 63$ cm, i.d. = 6 cm) connected to an ozone generator. All components in the ozone system were made from glass, Teflon®, PVC, stainless steel or polyamide. Ozone gas was produced from oxygen by an Erwin Sander 307.1 laboratory scale generator. The gas pressure in the generator was maintained at 0.5 bar. The gas flow rate to the reactor was maintained at $20 \, L \, h^{-1}$ and controlled using a flow meter. Ozone was continuously bubbled to the reactor through a porous plate (porosity, 10–40 μm hole diameter). Erlenmeyer flasks containing 2% KI solution were connected in series to the reactor in order to determine the input and output concentrations of ozone gas passing through the reactor, and remove the residual ozone in the exit gas. Ozonation was carried out at room temperature (around 20 °C). At the end of the ozonation process, residual ozone was purged out from the liquid phase and reactor headspace by bubbling nitrogen for about 15 min in order to avoid further oxidation. The ozonated effluent was kept refrigerated for at least 24 h in order to make sure that no dissolved ozone was present when biological assays were performed.

2.3. Anoxic batch assays

After ozonation, the biodegradability of the effluent was studied under anoxic conditions. Denitrifying batch assays were undertaken in 300 mL vials filled with 250 mL medium. The initial pH was adjusted to 8.0 ± 0.1. The ozonated effluent was supplemented with 1 mL nutrient solution whose composition was mentioned elsewhere [10], and the suitable quantity of nitrate (as KNO_3) to reach a DOC/N ratio of 1.5. Each flask was inoculated with $2 \, g \, VSS \, L^{-1}$, using sludge obtained from the anoxic chamber of the industrial wastewater treatment plant of a resin-producing factory [11]. Finally, the flasks were sealed and nitrogen gas was passed through the headspace for 10 min in order to remove oxygen. The assays were performed in a thermostatic chamber at 20 °C with a constant shaking at 200 rpm. Experiments were carried out in duplicate. DOC, nitrite and nitrate concentrations were measured at different intervals; the time of the biological assays was around 16 days. TKN, ammonium and pH were determined at the beginning and at the end of the experiments. All samples were filtered over a 0.45 μm membrane prior to analysis.

2.4. Analytical methods

DOC was determined using a TOC-5050A Shimadzu analyser equipped with an ASI-5000A auto sampler. Nitrite and nitrate were analyzed by capillary electrophoresis using a Hewlett Packard [3D]CE system with a microcapillary tube of fused silica (40 cm × 50 μm i.d.). UV detection was undertaken at a wavelength of 214 nm and 450 nm as reference. VSS, TKN, ammonium and pH were determined according to standard methods [12]. Ozone concentrations in the inlet and the outlet gas streams were measured by iodometric titration [13].

3. Results and discussion

The effluent from the biological treatment reactor from a resin-producing factory containing 142.4 ± 15.5 mg DOC L^{-1} and 159.5 ± 2.3 mg TKN L^{-1} was ozonated under different conditions. The effect of the recirculation flow rate, pH, ozone dose and ozone contact time on the ozonation process were studied. The aim of the ozonation step was to enhance the biodegradability of recalcitrant compounds but minimizing their

mineralization to avoid wasting ozone. Then, anoxic batch assays were undertaken with this ozonated effluent to measure its biodegradability. Biodegradability was evaluated in terms of organic carbon and organic nitrogen removal. Anoxic batch assays were accomplished with the non-ozonated effluent too, in order to evaluate the enhancement of its biodegradability.

3.1. Effect of the recirculation flow rate

In a first step, the effect of the recirculation flow rate on the ozonation efficiency was checked. Ozonation efficiency can be improved by increasing mass transfer through the formation of smaller bubble, by increasing the gas flow rate or by employing a recirculation loop to mix both gas bubbles and the effluent in a circular motion [6] and [14]. In this case, in order to increase the mixing, a peristaltic pump was used to recirculate the liquid in the reactor, using liquid flow rates of 50, 100, and 150 L h^{-1}. An experiment without recirculation was also undertaken. In all cases, the pH, contact time and volume of effluent were set at 8.75, 30 min and 1.6 L, respectively. A fixed ozone dose of 16.8 ± 0.1 mg L^{-1} min^{-1} was selected for all the recirculation rates tested. During the ozonation process under these conditions, no variation on the DOC concentration was observed, and the organic nitrogen removal was below 4%.

In the biological assays performed with the effluent ozonated at increasing recirculation flow rates, DOC removals between 68 and 77% were obtained, whereas the organic nitrogen removal varied between 80 and 88% (Table 2). This indicates that the applied recirculation flow rates during the ozonation process did not affect the biodegradability of the wastewater. For this reason, no recirculation was applied in subsequent ozonation experiments.

Table 2.

DOC and organic nitrogen removals in the biological assays performed with the effluent ozonated at different recirculation flow rates

Ozonation conditions			Anoxic assays	
Ozone dose (mg L^{-1} min^{-1})	pH	Recirculation flow rate (L h^{-1})	DOC removal (%)	Organic N removal (%)
16.8 ± 0.1	8.75	0	69	83
		50	77	81
		100	68	88
		150	75	80

3.2. Effect of the pH

The influence of the pH was checked in a second step to verify how its increase could affect the efficiency of ozonation process and the subsequent biological treatment. In general, at pH 8 or above, the formation of highly reactive products, such as hydroxyl radical, are expected to oxidize more persistent products. However, optimal ozonation efficiency and biodegradability improvement have been found by many workers to

occur at pH 7, where free radical generation balanced the self-decomposition rate [15] and [16]. Ozonation experiments were performed at three different pH values of 7.4, 8.75 and 11.0. An ozone dose of 13.5 ± 1.6 mg L^{-1} min^{-1} was applied for 30 min to 1 L of effluent. During ozonation, the percentage of DOC removal was lower than 0.5% in the assays at pH 7.4 and 8.75, but it increased to 12% at pH 11.0. The organic nitrogen removals at pH 7.4, 8.75 and 11.0 were 3, 5 and 9%, respectively.

Carbon and nitrogen removals obtained in the biological assays performed with the effluent ozonated at different pH are presented in Table 3. DOC removals between 51 and 55% and organic nitrogen removals between 40 and 49% were achieved. The pH normally decreases during ozonation, but in our case the alkalinity content of the effluent (around 750 mg $CaCO_3$ L^{-1}) conferred it a buffer behaviour. Differences between the assays performed at different values of pH are insignificant probably due to the content of radical scavengers in the effluent, and the similar biodegradability of the products obtained with the ozonation. Therefore, in the next ozonation experiments, it was chosen the pH value of 8.75, which corresponds to the original pH of the effluent.

Table 3.

DOC and organic nitrogen removals in the biological assays performed with the effluent ozonated at different values of pH

Ozonation conditions			Anoxic assays	
Ozone dose (mg L^{-1} min^{-1})	pH	Recirculation flow rate (L h^{-1})	DOC removal (%)	Organic N removal (%)
13.5 ± 1.6	7.40	0	52	49
	8.75		55	41
	11.00		51	40

3.3. Effect of the ozone dose

A third series of experiments were carried out for a wide range of ozone doses, between 1.8 and 29.5 mg L^{-1} min^{-1}. The gas flow rate and volume of effluent were fixed at 20 L h^{-1} and 1 L, so the increase in ozone dose was due to the rise of the ozone concentration in the input gas. In all cases, pH and contact time were set at 8.75 and 30 min. During the ozonation experiments, DOC removal was negligible for the lower doses, while values between 10 and 13% were observed for the experiments with applied doses higher than 12.6 mg L^{-1} min^{-1}. The nitrogen removal percentages were slightly lower, being negligible till reaching an applied ozone dose of 18.3 mg L^{-1} min^{-1}, in which 6% of organic nitrogen was eliminated. Organic nitrogen removals around 10% were obtained for doses of 24.8 and 29.5 mg L^{-1} min^{-1}.

Biological experiments using non-ozonated effluent and the effluent treated at different ozone doses were undertaken. DOC evolution in these anoxic assays is shown in Fig. 1. The DOC concentration decreases in a greater extent during the first day of assay in all experiments, being this reduction larger for the assays performed with the effluent ozonated at doses higher than 12.6 mg L^{-1} min^{-1}. From there on, a slower degradation was observed. The initial and final DOC concentrations for the experiment performed

with the effluent submitted to an ozone dose of 12.6 mg L^{-1} min^{-1} were 134.4 mg DOC L^{-1} and 60.5 mg DOC L^{-1}, respectively. The reduction during the first day to 103.4 mg DOC L^{-1} implies approximately a removal of 23%. For the experiments performed with the effluent treated with applied ozone doses higher than 12.6 mg L^{-1} min^{-1}, more than 50% of the DOC content was removed in the first day of the biological assay. When the applied ozone dose was 18.3 mg L^{-1} min^{-1}, the initial and final DOC concentrations were 116.7 and 18.7 mg DOC L^{-1}, respectively, and the concentration corresponding to the first day of the assay was 52.9 mg DOC L^{-1}. The high removals obtained in the first day of the assays are important since in continuous biological reactors hydraulic retention times of few days are generally used.
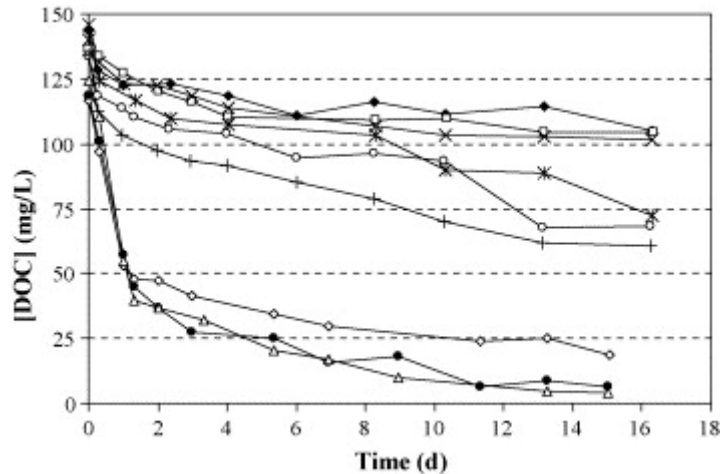

Fig. 1.

DOC evolution in the biological assays performed with the effluent ozonated at different ozone doses: without ozonation (♦), 1.8 mg L^{-1} min^{-1} (□), 4.3 mg L^{-1} min^{-1} (×), 6.0 mg L^{-1} min^{-1} (✳), 8.4 mg L^{-1} min^{-1} (○), 12.6 mg L^{-1} min^{-1} (+), 18.3 mg L^{-1} min^{-1} (◇), 24.8 mg L^{-1} min^{-1} (●) and 29.5 mg L^{-1} min^{-1} (△).

Organic carbon and nitrogen removals obtained in these biological assays are shown in Fig. 2. The DOC removal percentages increased from 27 to 97% in assays with effluent ozonated at increasing ozone doses. No improvement was observed with doses lower than 6.0 mg L^{-1} min^{-1} since the same DOC removals were obtained in these assays and in the assays with non-ozonated effluent, around 27%. For ozone doses between 6.0 and 12.6 mg L^{-1} min^{-1}, an increase in DOC removal was reached, rising up to 55%. At ozone doses higher than 12.6 mg L^{-1} min^{-1}, DOC removals raised more than 55% with regard to assays with non-ozonated effluent, reaching 96%. With regard to organic nitrogen removal, the percentages increased gradually from 27 to 80% in assays with effluent ozonated at increasing ozone doses. In the assays with non-ozonated effluent a removal of only 16% was obtained. With ozone doses lower than 8.4 mg L^{-1} min^{-1} similar nitrogen removals were observed, around 27%. A greater rising was achieved with doses higher than 12.6 mg L^{-1} min^{-1}. Thus, a maximum organic nitrogen removal of 80% was obtained with an ozone dose of 24.8 mg L^{-1} min^{-1}.
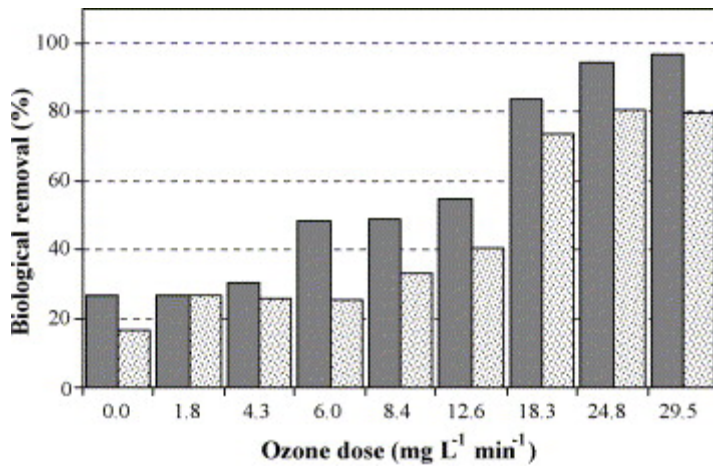
Fig. 2.

Removal percentages of DOC (grey bars) and organic nitrogen (dotted bars) in the biological assays performed with the effluent ozonated at different ozone doses.

The purpose of this study was to combine chemical with biological oxidation, enhancing the biodegradability of recalcitrant compounds but minimizing their mineralization in the ozonation step to avoid wasting ozone. Therefore, for the next experiments (effect of the contact time) an applied ozone dose around 12.6 mg L^{-1} min^{-1} was selected ($2.6\,\mathrm{g\,ozone\,g\,DOC_0^{-1}}$ 2.6 g ozone g DOC0−1). This is in good agreement with the optimum ozone dose range found in literature, for maximum biodegradable improvement, between 1.2 to $3.5\,\mathrm{g\,ozone\,g\,DOC_0^{-1}}$ 3.5 g ozone g DOC0−1[6] and [17].

3.4. Effect of the contact time

In a final step, ozonation experiments were performed at different contact times, between 30 and 180 min. An ozone dose of 13.0 ± 1.2 mg L^{-1} min^{-1} was applied to 1 L of effluent and the pH was set at 8.75 in all cases. During the ozonation, DOC removal was lower than 3% in the assays with less than 60 min of contact time. For longer times, increasing removal percentages were achieved. Thus, 16% of organic matter was removed with 90 min of ozonation, 21% with 120 min, and 40% for the highest contact time that was applied. In the case of organic nitrogen removal, lower percentages were obtained, being the removal negligible when ozone was applied for 30 min, but increasing its value whenever the contact time was increased. The largest value of 13% was obtained with 180 min of ozonation.

In the biological experiments using the previous effluent treated at different contact times, the trend was clear both for organic carbon and nitrogen removal. An experiment with non-ozonated effluent was also undertaken. DOC evolution in these anoxic assays is shown in Fig. 3. Organic matter concentration decreased with time for all experiments. A pronounced decrease is observed in the first day for contact times of ozone greater than 30 min, in which DOC removals were around 40%, except for the biological experiment with effluent ozonated during 180 min. In this experiment, a removal greater than 50% was obtained during the first day (the DOC concentration decreased from 86.9 to 41.0 mg DOC L^{-1}) and the total DOC removal was achieved in approximately 10 days.
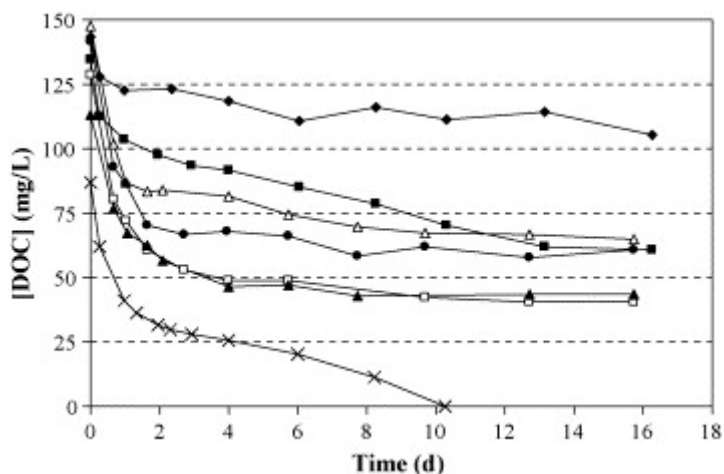
Fig. 3.

DOC evolution in the biological assays performed with the effluent ozonated at different ozone contact times: without ozonation (♦), 30 min (■), 45 min (△), 60 min (●), 90 min (□), 120 min (▲) and 180 min (×).

The organic carbon and nitrogen removals obtained at the end of these biological assays are shown in Fig. 4. DOC percentages from 55 to 100% were achieved for the assays performed with effluent treated at increasing ozone contact times. The same trend was observed for organic nitrogen removal, from 41 to 77% were achieved in the biological oxidation of the nitrogen matter previously treated with ozone. DOC and organic nitrogen removal obtained with the non-ozonated effluent were around 27 and 16%, respectively. Therefore, the application of an ozone dose of 13.0 ± 1.2 mg L^{-1} min^{-1} between 30 and 180 min clearly enhanced the effluent biodegradability. As the aim of the ozonation step was to enhance the biodegradability of recalcitrant compounds but minimizing their mineralization to avoid wasting ozone, at an ozone dose of 13 mg L^{-1} min^{-1} contact time larger than 60 min would not be recommended. As well an ozone dose higher than 13 mg L^{-1} min^{-1} and lower contact time could be used.
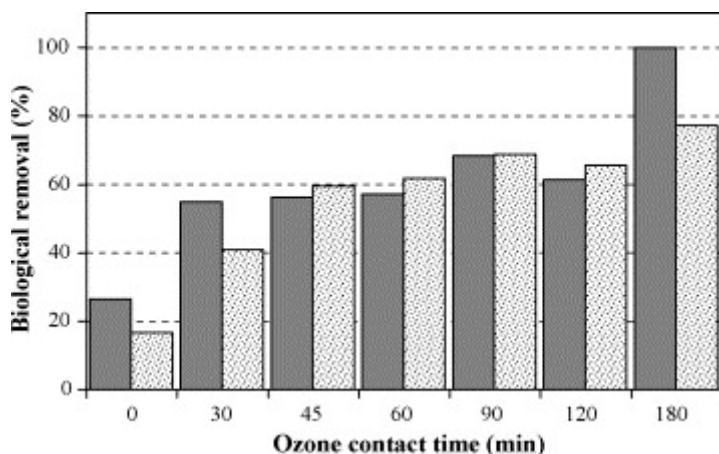

Fig. 4.

Removal percentages of DOC (grey bars) and organic nitrogen (dotted bars) in the biological assays performed with the effluent ozonated at different ozone contact times.

4. Conclusions

In this study, effluent from the biological treatment of wastewater from a resin-producing factory containing recalcitrant compounds was ozonated under different conditions. Afterwards, the biodegradability of the ozonated effluent was studied under anoxic conditions.

Enhancement in organic carbon and nitrogen removal was observed in the biological assays after the post-ozonation. Organic carbon removals from 27 to 97% and organic nitrogen removals from 27 to 80% were obtained when the applied ozone dose was increased from 1.8 to 29.5 mg L^{-1} min^{-1}.

The biodegradability of the effluent also increased with the contact time. For an applied ozone dose of 13.0 ± 1.2 mg L^{-1} min^{-1}, the organic carbon removal increased from 55 to 100% when the contact time was increased from 30 to 180 min. Under this conditions, organic nitrogen removals from 41 to 77% were obtained.

On the basis of these results, a combined post-ozonation and biological treatment can be applied to recalcitrant wastewater from a resin-producing factory. The aim of the ozonation step is to enhance the biodegradability of recalcitrant compounds but minimizing their mineralization to avoid wasting ozone. Therefore, an ozone dose around 13 mg L^{-1} min^{-1} and contact times between 45 and 60 min or an ozone dose higher than 13 mg L^{-1} min^{-1} and lower contact times could be used.

References

M. Eiroa, A. Vilar, C. Kennes, M.C. Veiga
Biological treatment of industrial wastewater containing formaldehyde and formic acid
Water SA, 32 (2006), pp. 115–118

C. Di Iaconi, A. López, R. Ramadori, R. Passino
Tannery wastewater treatment by sequencing batch biofilm reactor
Environ. Sci. Technol., 37 (2003), pp. 3199–3205

J.P. Scott, D.F. Ollis
Integration of chemical and biological oxidation processes for water treatment: review and recommendations
Environ. Prog., 14 (1995), pp. 88–103

R.G. Rice
Application of ozone for industrial wastewater treatment: a review
Ozone Sci. Eng., 18 (1997), pp. 477–515

F.J. Beltrán
Kinetics of the ozonation of wastewaters
Ozone Reaction Kinetics for Water and Wastewater SystemsLewis Publishers, Boca Ratón, Florida (2004) pp. 113–150

A.B.C. Alvares, C. Diaper, S.A. Parsons
Partial oxidation by ozone to remove recalcitrance from wastewaters—a review
Environ. Technol., 22 (2001), pp. 409–427

C.H. Kuo, F.H. Yocum
Mass transfer of ozone into aqueous systems
R.G. Rice, A. Netzer (Eds.), Handbook of Ozone Technology and Applications, 1Ann Arbor Science, Michigan, USA (1982), pp. 105–141

A. López, G. Ricco, G. Mascolo, G. Tiravanti, A.C. Di Pinto, R. Passino
Biodegradability enhancement of refractory pollutants by ozonation: a laboratory investigation on an azo-dyes intermediate
Water Sci. Technol., 38 (4/5) (1998), pp. 239–245

P. Haapea, S. Korhonen, T. Tuhkanen
Treatment of industrial landfill leachates by chemical and biological methods: ozonation, ozonation + hydrogen peroxide, hydrogen peroxide and biological post-treatment for ozonated water
Ozone Sci. Eng., 24 (2002), pp. 369–378

M. Eiroa, C. Kennes, M.C. Veiga
Formaldehyde and urea removal in a denitrifying granular sludge blanket reactor
Water Res., 38 (2004), pp. 3495–3502

M. Cantó, J. Gómez, C. Kennes, M.C. Veiga
Integrated anoxic–aerobic treatment of wastewaters from a synthetic resin-producing factory
European Conference on New Advances in Biological Nitrogen and Phosphorus Removal for Municipal or Industrial Wastewaters, Narbonne, France (1998), pp. 289–292

APHA
Standard Methods for the Examination of Water and Wastewater
(20th ed.)APHA, Washington DC, USA (1998)

K. Rakness, G. Gordon, B. Langlais, W. Masschelein, N. Matsumoto, Y. Richard, C.M. Robson, I. Somiya
Guideline for measurement of ozone concentration in the process gas from an ozone generator
Ozone Sci. Eng., 18 (1996), pp. 209–229

F.J. Beltrán, J.F. García-Araya, P.M. Álvarez
pH sequential ozonation of domestic and wine-distillery wastewaters
Water Res., 35 (4) (2001), pp. 929–936

C.D. Adams, R.A. Cozzens, B.J. Kim
Effects of ozonation on the biodegradability of substituted phenols
Water Res., 31 (1997), pp. 2655–2663

N.J. Karrer, G. Ryhiner, E. Heinzle
Applicability test for combined biological–chemical treatment of wastewaters containing biorefractory compounds
Water Res., 31 (1997), pp. 1013–1020

J.C. Jochimsen, H. Schenk, M.R. Jekel, W. Hegemann
Combined oxidative and biological treatment for separated streams of tannery wastewater
Water Sci. Technol., 36 (2/3) (1997), pp. 209–216