

Ozonation of a landfill leachate: evaluation of toxicity removal and biodegradability improvement

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Abstract

This work shows an evaluation of treatments for the leachate produced at the Gramacho Municipal Landfill in Rio de Janeiro state, Brazil. This leachate has very peculiar characteristics, with a high salinity level and very low biodegradability (BOD₅/COD of 0.05). A sequence of processes was employed in the treatment of this leachate. Initially, a physicochemical treatment was used, while the second stage consisted of application of ozone to improve the biodegradability of the leachate. The final stage comprised a biological treatment. The physical–chemical treatment led to COD and DOC removal levels of 40 and 25%, respectively, with the use of Al₂(SO₄)₃. The sequence of treatments proposed brought good results, with an increase in the BOD₅/COD ratio from 0.05 to 0.3 after ozonation. The toxicity tests performed using *Brachydanio rerio* and *Poecilia vivipara* showed that the toxicity of the leachate had hardly been reduced by ozonation. These results are in agreement with the fact that, despite the higher BOD₅/COD ratio, the biological process did not present a good performance. The total average removal levels of COD and DOC achieved using the combined treatment were 73 and 63%, respectively, for an ozone dose of 3.0 g L⁻¹ by the leachate.

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1. Introduction

Much of society's solid waste is disposed in sanitary landfills, where it undergoes physical, chemical and biological transformations. The solubilization of organic and inorganic components in water produces a leachate, which can be difficult to treat.

The water in a number of regions in Brazil is polluted by leachate, including that of Guanabara Bay in Rio de Janeiro. One of the sources of this contamination is the Gramacho Municipal Landfill, which emits 800 m³ of leachate per day. Located in Duque de Caxias, a city in Rio de Janeiro state, this landfill stands on the edge of Guanabara Bay, and is considered old (more than 10 years old). All kinds of waste

are dumped there, including domestic refuse, rubble from the civil construction industry, hospital and small industry waste. For many years, there was no selective waste collection in Rio de Janeiro, and this practice is still far from being widespread. The result is that the leachate from this landfill has very peculiar characteristics with a low biodegradability, a high concentration of nitrogenated compounds, metals, recalcitrant organic matter and salinity.

Due to the difficulty of treating some effluents, new technologies and new combinations of techniques are being investigated. Ozone is employed in treating drinking water and industrial effluents, as it is a powerful chemical oxidant. Ozonation products are generally less complex, constituted of smaller molecules and are more easily biodegradable than their precursors [1,2].

Leachate often contains a variety of chemical substances that are recalcitrant to conventional biological treatments

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[3]. Ozonation alters the molecular structure of refractory organic compounds present in the leachate, turning them into compounds that are easily assimilated biologically [2]. This is mainly due to the increase in the biodegradability of high molecular weight an organic compound that could not be removed simply through biological treatment. Ozone has been shown to be capable of destroying recalcitrant compounds in effluents and bringing about alterations to biodegradability, as can be seen in a number of studies [2,4–9].

Pre-ozonation can reduce the retention time required for biological treatment, which represents a great improvement in the efficiency of the process. The efficiency of pre-ozonation in bringing about improved biodegradability of leachates for the subsequent biological processes has also been confirmed [2,10]. Ozone has been reported as an alternative agent in leachate treatment from sanitary landfills [2–5,10–12].

In the literature, it is reported that a single, conventional biological treatment is not effective in treating leachates with a high concentration of organic matter resistant to biodegradation [2] and this type of leachate needs to be previously treated in order to become more biodegradable. According to Imai et al. [2], one way of doing this is to employ pre-treatment using physical and oxidative processes.

The aim of this work was to develop a sequence of processes for treating a leachate with very peculiar characteristics, evaluating the following sequence of treatments: coagulation/flocculation, followed by ozonation and biological treatment. Toxicity evaluations were made of ozonated leachate using *Brachydanio rerio* and *Poecilia vivipara*.

2. Materials and methods

2.1. Leachate sampling

The study was done on the leachate from the Gramacho Metropolitan Landfill, Rio de Janeiro, Brazil. The leachate samples were stored at 4 °C and were collected over a period of 11 months.

2.2. Physical–chemical determinations

The characterization of the raw and treated leachate samples was obtained through the determinations of the following parameters: BOD₅, COD, pH, DOC, color, turbidity, heavy metals and chloride. The BOD₅, COD, color, turbidity, chloride and ammonium nitrogen analyses were performed according to the standard methodology [13]. The dissolved organic carbon was determined using the 5000 A Shimadzu TOC analyzer. The heavy metal determination was performed according to the standard methodology using atomic absorption spectrometer Intralab AA1475 [13].

2.3. Acute toxicity determination

Tests with the fish species *B. rerio* basically followed the methodology proposed by the Standard Methods (8910) [13]. The protocol used was based on the methodology developed by the local environmental agency [14]. The percentage of mortality was observed in the incubation period (48 and 96 h). To determine the acute toxicity parameters EC50 or LC50, the experimental results were submitted to statistical tests, using the Spearman–Karber method [15], which supplies the parameter values and 95% confidence intervals. All the toxicity tests were performed on non-filtered samples.

For the fish species *P. vivipara*, two acute toxicity tests were performed on each sample to test the sensitivity of the newly hatched *P. vivipara*. In each test, five effluent concentrations were used (1, 5, 10, 15 and 20%), with at least two replicas for each concentration and for the control. The tests were static, lasted 96 h and were performed in 1000 mL beakers containing 900 mL solution. Three of the 7–15-day-old fish, obtained from a laboratory culture, were positioned randomly in each beaker. The beakers were kept in an aerated incubator at 25 ± 1 °C with alternating 12 h periods of light and dark. Everyday, the dead organisms were counted and removed. At the beginning and end of each toxicity test, the pH, dissolved oxygen and water salinity were measured.

At the end of the tests, the LC50-96h was calculated (lethal concentration to 50% of the organisms after 96 h exposure) using the trimmed Spearman–Karber method [15].

At the same time as these tests on *P. vivipara*, other acute toxicity tests were performed with copper to see whether the test organisms responded within the sensitivity range predicted for the species.

Survival levels were 100% for all control tests. Dissolved oxygen concentrations varied between 5.9 and 8.1 mg O₂ L⁻¹. These values were always greater than 4 mg O₂ L⁻¹, which is the value recommended for toxicity tests [16]. pH values varied little, staying around 8.0 (7.9–8.8). Water salinity in the tests with *P. vivipara* stayed around 30 g L⁻¹.

2.4. Coagulation/flocculation tests

The experiments were held simultaneously on six samples in 2000 mL Jar Test beakers. Thousand milliliters leachate samples were coagulated, achieving final coagulant concentrations of 400, 450, 500, 550, 600, 650, 700, 750, 800, 850, 900, 950 mg L⁻¹. The pH of the initial samples was varied between 4.0 and 10.0 for each product utilized. The samples were stirred vigorously (150 rpm, 5 min) while the coagulant was added, and then more slowly (15 rpm, 15 min), while a 0.2% (v/v) polyelectrolyte solution was added, so that the final concentrations were 3.0, 6.0, 9.0, 12, 15, 20 mg L⁻¹. After this time, the stirring was stopped and the sample was left to settle for 30 min. The experiments were made using four coagulants – aluminum sulfate, ferric chloride, cationic tannin and aluminum polychloride – and four polyelectrolytes.

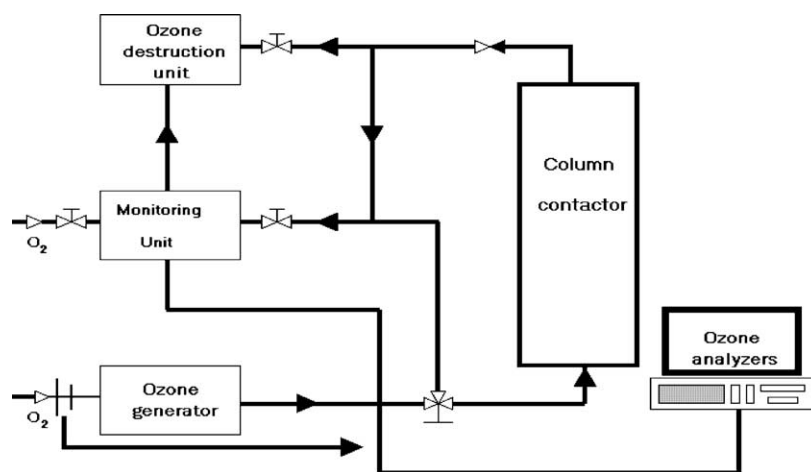


Fig. 1. Experimental set-up used for wastewater ozonation.

2.5. Ozonation tests

The ozonation of the leachate were held in an ozone pilot plant, the scheme of the pilot plant used is shown in Fig. 1. A PCI ozone generator was used, in which up to 40 g h^{-1} ozone can be generated, using commercial oxygen as the feed gas. An acrylic contact column measuring 1.0 m high and 0.1 m diameter was used. The ozone concentration at the inlet and outlet of the contact column was monitored. The diffuser at the bottom of the column was a 316 L stainless steel porous disk with a pore diameter of $10 \mu\text{m}$, which generated oxygen bubbles with a diameter of approximately 3 mm. Both the gases that emerged from the contact column and the gases from the ozone analyzers passed through the catalytic ozone destruction unit, which contained manganese dioxide, copper dioxide and aluminum dioxide.

The quantity of ozone consumed by the sample was determined by comparing the mass between the inflow and outflow of gases through the contact column. To do so, the ozonation pilot plant had two ozone analyzers. The first, which was installed where the gas flowed into the column, measured the quantity of ozone applied to the sample. The second analyzer, positioned at the gas outlet from the column, measured the quantity of ozone not consumed by the sample. The difference between the measurements indicated the quantity of ozone consumed by the sample. These measurements were performed throughout the experiment.

Initially, untreated leachate was ozonized, and then in the second stage, the leachate received a physicochemical pre-treatment before ozonation. During the tests, samples were drawn with pre-established ozone consumptions, so a subsequent evaluation could be made of the oxidation process. For the ozone treatment, the leachate was pre-treated with $\text{Al}_2(\text{SO}_4)_3$ and FeCl_3 together with cationic polyelectrolyte. The leachate was characterized before and after ozonation, through analyses of its COD, BOD_5 , color, turbidity, and DOC.

2.6. Biological treatability tests

Four reactors were used in the treatability tests, each with a 1000 mL capacity, and were batch operated and aerated, with the tests taking up 700 mL of the working volume. The biological sludge that came from a sewage treatment plant underwent an adaptation period of around 30 days, varying the proportion of effluent to domestic sewage being fed into the reactors. Nine treatability tests were held using leachate samples that had only been treated by the coagulation/flocculation process with $\text{Al}_2(\text{SO}_4)_3$, and using samples treated with $\text{Al}_2(\text{SO}_4)_3$ and ozonized with the following ozone consumptions: 0.5, 1.5, $3.0 \text{ g O}_3 \text{ L}^{-1}$. In all the treatability tests, a parallel experiment was run using a reactor with activated sludge and domestic sewage.

2.7. Microscopic observations

During the biological treatability tests, microscopic observations were made of the biological sludge. A drop of sample collected from the content of the reactors was placed on a slide and covered with a cover slip. The observations were made using a HUND WETZLAR H-500 optical microscope with phase contrast capacity. The samples were observed magnified to $100\times$, $400\times$ and $1000\times$. In the microscopic observations of the sludge, the following aspects were identified [17]: abundance of filaments in the flocs; the effect of the filaments in the floc structure; floc morphology, and the presence and types of protozoans or other organisms present.

3. Results and discussion

3.1. Characterization of the raw leachate

Some of the parameters used in characterizing the leachate from the Gramacho Landfill are presented in Table 1. This leachate has a high concentration of recalcitrant organic mat-

Table 1
Parameters used in characterizing the leachate from the Gramacho Landfill

Parameter	Average	Minimum	Maximum
pH	8.2	8.0	8.5
COD (mg L ⁻¹)	3096	2422	3945
BOD ₅ /COD	0.05	0.03	0.05
BOD ₅ (mg L ⁻¹)	130	106	195
DOC (mg L ⁻¹)	876	570	1254
Color (mg PtCo L ⁻¹)	5759	4680	9000
Turbidity (NTU)	144	72	178
N-NH ₄ ⁺ (mg L ⁻¹)	775	750	800
Chloride (mg L ⁻¹)	4635	4130	5140
Cd (mg L ⁻¹)	<0.01	<0.01	<0.01
Cu (mg L ⁻¹)	0.09	0.08	0.10
Cr (mg L ⁻¹)	0.15	0.1	0.2
Pb (mg L ⁻¹)	<0.1	<0.1	<0.1
Hg (mg L ⁻¹)	1.6	1.2	2
Mn (mg L ⁻¹)	0.13	0.05	0.2
Zn (mg L ⁻¹)	0.30	0.25	0.35
Ni (mg L ⁻¹)	0.18	0.10	0.25
Fe (mg L ⁻¹)	6.8	5.5	8.0
Al (mg L ⁻¹)	<1.0	<1.0	<1.0
Na (mg L ⁻¹)	2950	2700	3200
K (mg L ⁻¹)	1800	1700	1900
Ca (mg L ⁻¹)	280	240	320
Mg (mg L ⁻¹)	85	73	97

Range and average values correspond to 10 different samples, except metals determined twice.

ter, as indicated by its COD, and low biodegradability, the BOD₅/COD ratio around 0.05, as well as a moderate concentration of heavy metals.

3.2. Coagulation/flocculation tests

The best conditions for coagulation/flocculation tests were evaluated considering COD and DOC removal. Table 2 shows the ranges of the best results for these tests. Fig. 2 presents the results of COD and DOC removal under the optimum conditions determined for each coagulant used.

The best conditions determined from the coagulation/flocculation process, as measured by COD and DOC removal, were obtained when Al₂(SO₄)₃ and FeCl₃ were applied as coagulants, together with cationic polyelectrolyte. It was observed that the coagulation/flocculation process presented excellent COD and DOC removal. COD removal for both Al₂(SO₄)₃ and FeCl₃ reached around 40%, while DOC removal was 25% for Al₂(SO₄)₃ and 31% for FeCl₃.

Table 2
Best conditions for coagulation/flocculation leachate treatment

Coagulant	Coagulant concentration (mg L ⁻¹)	Polyelectrolyte	Polyelectrolyte concentration (mg L ⁻¹)	pH
Al ₂ (SO ₄) ₃	650–700	Nalco 7128	3.0	4.5–5.0
FeCl ₃	700–950	Nalco 4684	3.0	4.0–5.0
Cationic tannin	500–750	Nalco 7128	3.0	4.0–5.0
Aluminum polychloride	850–950	Nalco 4684	3.0	4.0–5.0

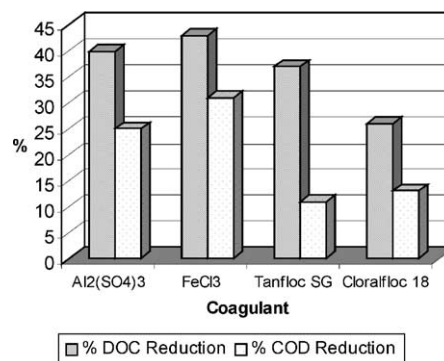


Fig. 2. Best coagulation/flocculation conditions for each coagulant tested.

As expected, it was observed in this study that the pH is the parameter that most influences the coagulation/flocculation process, since for high pH's, COD and DOC removal were around 15 and 10%, respectively. Since for high pH's, COD removal levels lower than 20% were achieved for all the coagulants tested.

The leachate's BOD₅/COD ratio with any tested coagulant did not change significantly after the coagulation/flocculation process. The BOD₅/COD ratio values before and after the coagulation/flocculation process remained around 0.05.

3.3. Ozonation tests

When the primary treatment was applied before the ozonation tests, Al₂(SO₄)₃ and FeCl₃ were used in conjunction with cationic polyelectrolytes, as they presented the best performances. The results of the ozonation tests with the leachate, without pre-treatment and using Al₂(SO₄)₃, are presented in Figs. 3 and 4. The leachate obtained after the primary treatment was ozonized up to 5.0 g O₃ L⁻¹ doses. After this point no further consumption of ozone was observed.

A slight increase in COD at the beginning of ozonation can be observed in Fig. 3(A). In the study by Nilsun [18], the author reports that this is due to a rapid change in the structure of the organic compounds as a consequence of reactions in the formation of short-term intermediates that are more easily oxidizable in the COD test.

Fig. 3(D) shows that the greater the ozone concentration consumed, the greater the degradation of organic matter, expressed by DOC reduction. In the ozonation tests, reductions in color and turbidity of the leachate were also observed, as can be seen in Fig. 3(B) and (C). This color reduction of the leachate due to ozonation has been previously reported in the literature [9].

The results obtained from the ozonation tests show that the primary treatment reduces the required ozone concentration consumption up to three times; i.e. for a given COD, DOC and BOD₅/COD ratio, the required amount of ozone to treat the raw leachate is three times larger than that necessary to oxidize the leachate which has been previously submitted to a coagulation/flocculation treatment. It can be seen from the

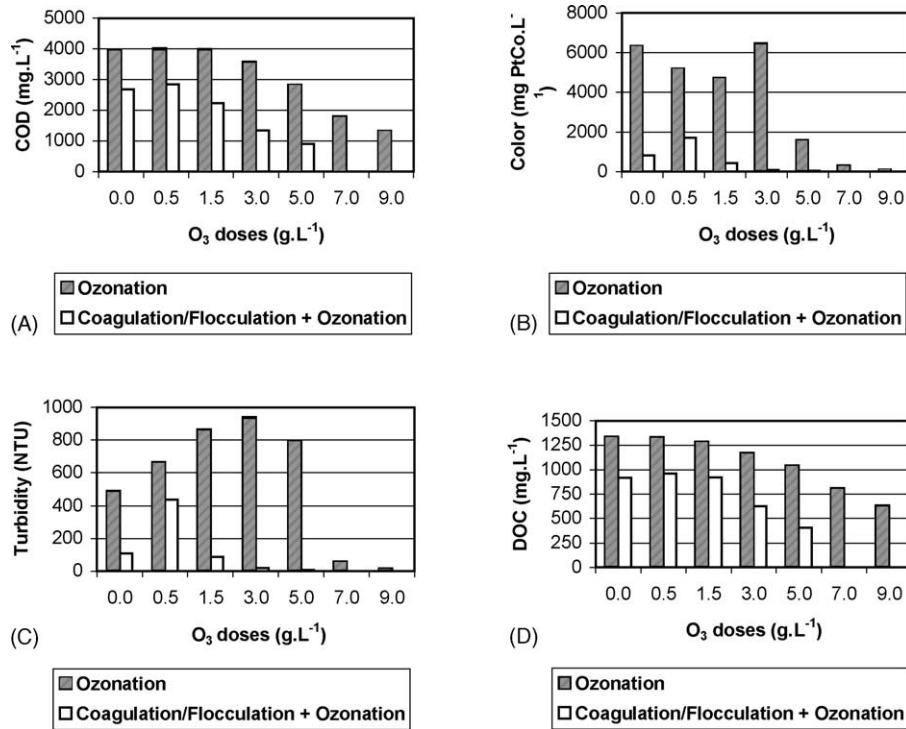


Fig. 3. Reduction of COD (A), color (B), turbidity (C) and DOC (D), with and without physical–chemical pre-treatment.

graphics presented in Fig. 3 that a dose of 3.0 g O₃ L⁻¹ for pre-treated leachate showed equivalent results to a dose of 9.0 g O₃ L⁻¹ for raw leachate. The same was also observed for color and turbidity removal.

In the case of more recalcitrant effluents, such as the leachate, the use of ozonation before a biological process aims to increase the biodegradability of the effluent, thereby making it easier for the organic matter to be assimilated subsequently by a biological process, which is a less costly process. For the Gramacho Landfill leachate, the change in the BOD₅/COD ratio according to the ozone consumption employed can be seen in Fig. 4.

It was found that the greater the ozone consumption, the greater the COD removal, and that with ozone doses of

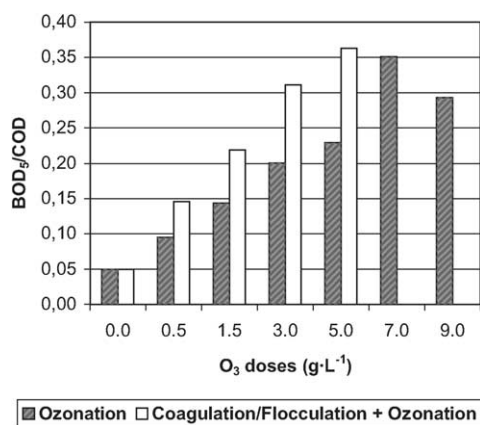


Fig. 4. BOD₅/COD ratio with and without physical–chemical pre-treatment.

1.5–3.0 g O₃ L⁻¹, there was a significant increasing in the BOD₅/COD ratio, which dropped from around 0.22 to 0.33, which suggests the leachate can be treated by a biological process.

An improvement in the performance of the ozonation was observed when the coagulation/flocculation process using FeCl₃ was employed. However, in this case, the increase in the BOD₅/COD ratio was smaller than that obtained with Al₂(SO₄)₃.

3.4. Biological treatability tests

Biological treatability tests demonstrated that removal of both COD and DOC was moderate. It was observed that when the leachate was ozonized with 1.5 and 3.0 g O₃ L⁻¹ doses, the COD and DOC removal was more extensive than in samples with a dose of 0.5 g O₃ L⁻¹.

The biological treatment of the effluent from the coagulation/flocculation process did not promoted any removal of COD. Furthermore, microscopy revealed that the biological sludge flocs were poorly aggregated and protozoans were absent. The biological treatment of the ozonized effluent (ozone dose of 0.50 g O₃ L⁻¹) led to COD and DOC removals of 10%. This result is consistent with the low DBO₅/DQO ratio presented by this effluent. The effluent ozonized with a higher ozone dose (1.5 g O₃ L⁻¹) presented higher COD and DOC removals, 24 and 13%, respectively, in the biodegradation assay. When the effluent ozonized with the highest ozone dose (3.0 g O₃ L⁻¹) was submitted to biological treatment the removals of COD and DOC attained 22 and 20%, respectively.

Table 3
COD and DOC reductions obtained in each treatment step

	O ₃ (g L ⁻¹)	% COD reduction	% DOC reduction	BOD ₅ /COD
Coagulation/flocculation		30–40	25–35	0.02–0.04
Ozonation	0.5	0–8	0–2	0.1–0.14
	1.5	9–15	1–7	0.17–0.25
	3.0	25–50	18–40	0.2–0.3
Biological treatment	0.5	10	10	–
	1.5	24	13	–
	3.0	22	20	–

Even though the BOD₅/COD ratio of the leachate was raised by the ozonation. However, it can be observed that this effluent still contains compounds that are difficult to degrade biologically. The COD and DOC removals attained in these experiments are shown in Table 3.

3.5. COD and DOC reductions obtained in the combined treatment

The COD and DOC reductions obtained for the coagulation/flocculation process followed by the ozonation and biological treatments are presented in Table 3.

By observing the results in Table 3, it can be seen that although the ozonation led to an increase in the BOD₅/COD ratio, which would favor biological treatment, it only led to moderate COD and DOC removal. It could be suggested that the biological treatment was only able to consume part of the BOD₅, due to the remaining toxicity of the leachate which inhibits the activity of biological activated sludge.

The COD and DOC reductions attained in the combined treatment for ozone doses of 0.5, 1.5 and 3.0 g O₃ L⁻¹ are presented in Table 4.

Applying a coagulation/flocculation process as a physicochemical pre-treatment improved the performance of the ozonation, reducing the required amount of ozone. This improvement was more remarkable when Al₂(SO₄)₃ was used as the coagulating agent. However, the aim of the primary treatment was achieved, since the COD and suspended solids were reduced and ozone usage was optimized.

3.6. Microscopic observations of the sludge

The microscopic observations were performed on samples of activated sludge from the following treatments: domestic waste (control), samples treated only by coagulation/flocculation and samples treated with Al₂(SO₄)₃ and ozonized with 0.5, 1.5 and 3.0 g O₃ L⁻¹ doses. These ex-

periments were held to observe the quality of the activated sludge for the effluents used in the treatability tests. Thus, some parameters required for the good performance of the activated sludge process were identified: the amount of filaments in the flocs; the effect of filaments on floc structure; floc morphology and the presence and types of protozoans or other organisms that may be present.

The activated sludge that only underwent primary treatment with Al₂(SO₄)₃ gradually lost its good characteristics as the concentration of leachate in the reactor was raised. There were few flocs and few filaments connecting them together. No protozoan of any species was observed in the sludge, which shows the recalcitrance of this leachate. When the activated sludge was exposed only to leachate (without the addition of domestic sewage), its activity stopped completely. Thus, the biological process cannot treat the leachate treated only with the coagulation/flocculation process.

When the leachate was treated with the coagulation/flocculation process with Al₂(SO₄)₃ and ozonized with 0.5 g O₃ L⁻¹ dose, the microscopic observations revealed that as the leachate concentration in the reactor increased, the final quality of the activated sludge deteriorated, i.e. a small number of filaments in the flocs structure was observed. Therefore, when the leachate is ozonized with low ozone consumption, it is still aggressive to the biological sludge, which reduces its quality.

When the leachate was treated with the coagulation/flocculation process, using Al₂(SO₄)₃, and ozonized with 1.5 and 3.0 g O₃ L⁻¹ doses, it was observed that when the leachate concentration was increased in the reactor, the sludge did not lose its characteristics. After acclimatization, it presented filaments as the floc structure, which gave the flocs a good structure and consistency. Protozoans were observed when the activated sludge was exposed only to this leachate, and it did not lose its biological activity after three consecutive tests.

Table 4
Total COD and DOC reductions attained with combined treatments

Combined treatment	% COD reduction	% DOC reduction
Coagulation/flocculation + ozonation (0.5 g O ₃ L ⁻¹) + biological treatment	33–38	25–38
Coagulation/flocculation + ozonation (1.5 g O ₃ L ⁻¹) + biological treatment	54–74	38–55
Coagulation/flocculation + ozonation (3.0 g O ₃ L ⁻¹) + biological treatment	62–84	50–75

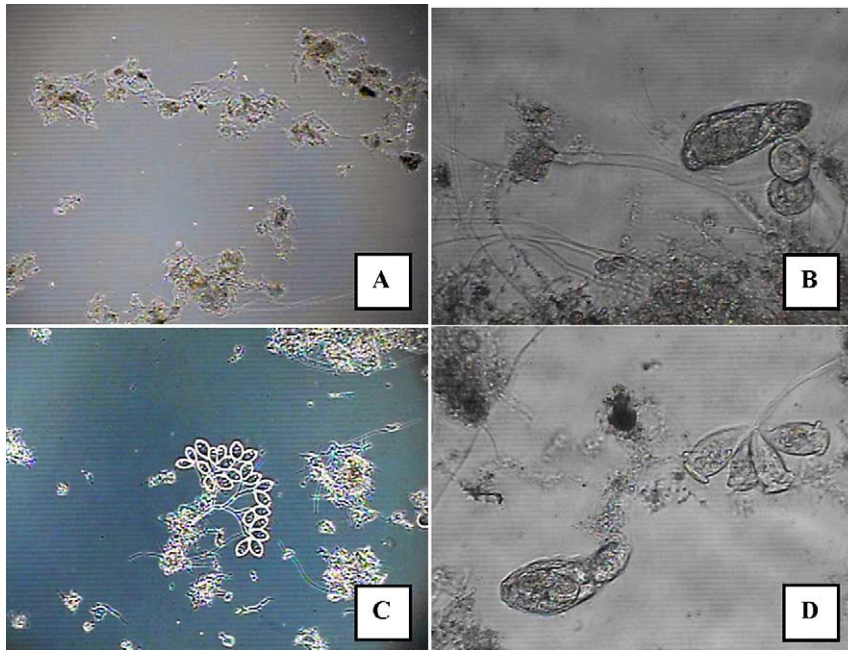


Fig. 5. Microscopy of biological sludge from the reactors operated at 25 °C, magnified to 100× (A, B and C) and 400× (C). (A) 60% of leachate and 40% of sewage; (B) 60% of ozonized leachate ($0.5 \text{ g O}_3 \text{ L}^{-1}$) and 40% of sewage; (C) 60% of ozonized leachate ($1.5 \text{ g O}_3 \text{ L}^{-1}$) and 40% of sewage; and (D) 60% of ozonized leachate ($3.0 \text{ g O}_3 \text{ L}^{-1}$) and 40% of sewage.

The ozonation stage is essential to the good performance of the biological process, since in the absence of this stage, the progressive death of the sludge was observed. Even for the ozonized leachate with a dose of $0.5 \text{ g O}_3 \text{ L}^{-1}$, the biological sludge was still affected.

Fig. 5 shows the evolution of the biological sludge when the following composition was utilized: 60% of leachate and 40% of sewage. It can be clearly observed that the sludge quality improved when the ozonized leachate was treated together with sewage.

Microscopic observations showed that the sludge quality was improved when the effluent was submitted to moderate and high ozone doses (1.5 and $3.0 \text{ g O}_3 \text{ L}^{-1}$). This was probably caused by the oxidation of organic substances and ammonia removal, which may cause detrimental effect to the microbial community. When the highest ozone dose was applied, the removal of ammonia reached 25%. It is well known that high levels of ammonia affect the performance of the biological process [19].

3.7. Toxicity tests

The average results for LC50-96h for the three tests performed on the two species are summarized in Table 5.

The results in Table 5 show that the raw leachate was highly toxic both to *B. rerio* and to *P. vivipara*, and that though the successive treatments reduced toxicity, the leachate still remained toxic. The toxicity was probably not related to the high chloride concentration present in the leachate, since *P. vivipara* is a marine organism. These results are in complete agreement with those obtained in the biological treatment, i.e. even though the BOD₅/COD ratio obtained with the combined treatment was adequate for biological treatment, the biological process did not have a good performance, probably due to the high toxicity. Since the concentration of ammonia is very high and was only partially removed by the combined treatment (20%, ozone dose of $3.0 \text{ g O}_3 \text{ L}^{-1}$), it is probably responsible for the observed toxicity and the poor performance of the biological process. These observations

Table 5

Average LC50-96h in the tests on *B. rerio* and *P. vivipara*, for raw and treated leachate collected during the dry period (2001, May) and the rainy period (2001, October)

	<i>B. rerio</i> acute toxicity CL50-48h		<i>P. vivipara</i> acute toxicity CL50-96h		<i>B. rerio</i> acute toxicity CL50-96h	
	May	October	May	October	May	October
Raw leachate	<5%	2.24	2.24	2.24	4.97	6.22
Pre-treated leachate by coagulation/flocculation	7.07	9.25	7.07	7.07	5.23	6.67
Ozonized leachate ($0.1 \text{ g O}_3 \text{ L}^{-1}$)	7.07	14.54	9.25	13.24	8.89	7.07
Ozonized leachate ($0.5 \text{ g O}_3 \text{ L}^{-1}$)	11.06	16.29	11.07	10.79	10.62	11.67
Ozonized leachate ($1.5 \text{ g O}_3 \text{ L}^{-1}$)	9.25	15.16	11.07	14.48	12.39	17.65
Ozonized leachate ($3.0 \text{ g O}_3 \text{ L}^{-1}$)	14.48	17.32	15.87	14.48	11.79	12.07

have been confirmed in another recently published work [20], which demonstrated that the toxicity of this leachate is associated to the high ammonia concentration.

4. Conclusions

The ozonation stage produced excellent results, increasing the biodegradability of the leachate. The experiments showed that the original BOD₅/COD ratio of 0.05 was raised to approximately 0.3 after ozonation. It was further observed that the greater the ozone concentration, the greater the COD removal from the leachate and the better the performance of the biological process.

The treatability tests showed clearly that ozonation is an important stage in treating this leachate. During biological treatment, the activated sludge showed good characteristics when ozonized with 1.0 g O₃ L⁻¹, and most importantly, no reduction in its activity was observed.

The biological treatment led to moderate COD and DOC reductions, which demonstrated how very recalcitrant this leachate is, and how great an impact it could have if discharged as it stands into the environment.

The toxicity test results showed that this leachate is highly toxic, even after undergoing a series of treatments, which justifies the low efficiency rate of the biological process. Toxicity test and microscopy observation of sludge were essential to explain the low efficiency of the biological treatment.

The studied combination of processes led to a good reduction in the COD and DOC of this leachate, considering its resistance to treatment. However, the efficiency of the biological treatment must be improved to further reduce its recalcitrance.

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