



SUCCESSFUL LANDFILL LEACHATE WASTEWATER TREATMENT USING THE SEQUENCE OF OZONATION, ADSORPTION ON CHARCOAL AND PHOTO-OZONOLYSIS

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Landfill leachate derived from the landfilling practice of the municipal wastes is a problem affecting all countries and continents. Even after the shutdown of a landfill site, the leachate production continues for decades. In this work a solution for the landfill leachate treatment has been proposed based on three fundamental steps: the pre-ozonolysis of the leachate, the passage of the ozonized leachate through a fixed bed of activated carbon and the final step consisting in a photo-ozonolysis stage involving the simultaneous action of ozone and UV light. A distinction between the chemical structure and chemical behaviour of young and mature leachate was evidenced by thermal analysis of the soluble organic matter (SOM) obtained from these substrates. Furthermore, a distinction between young and mature leachate was also evidenced in terms of their different reactivity toward ozone as illustrated by the COD abatement and by FTIR spectroscopy on pristine and ozonized SOM. A modular pilot plant for the treatment of different landfill leachates was presented and proposed.

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Introduction

Landfilling of municipal wastes is a usual disposal practice common throughout the entire world¹⁻⁵. One of the main problems linked to the municipal waste landfilling is the production of landfill leachate, a problem which persists for several years even after the landfill site is shut down.¹⁻⁵ The landfill leachate derives from the fermentation of the organic matter present in the municipal wastes which lead to decomposition products which are washed out and diluted by the meteoric precipitations. The landfill leachate does not have a stable chemical composition but undergoes a gradual composition evolution also affected by the local environmental and weather circumstances.¹⁻⁵ The young leachate is characterized by a mixture of organic matter with low molecular weight, it is in large part biodegradable and it is the result of the initial rapid aerobic fermentation with the liberation of CO₂, H₂ and the production of free carboxylic acids so that all locally available oxygen is consumed.¹⁻⁵ The end of the aerobic fermentation can be evidenced by a peak in COD and BOD level and the accumulation of ammonia/ammonium ion and chlorides. Then the anaerobic fermentation prevails, a stage which is also called methanogenesis due to the production and release of methane accompanied by CO₂.¹⁻⁵ A slow gradual decline in COD and BOD level can be observed toward limiting values. Aged leachate is characterized by stabilized values of COD and by alkalinity in contrast with the acidic properties of the young leachate. The most interesting feature of aged or mature leachate is the fact that its soluble organic matter is

recalcitrant any to biological-based oxidation process and it is necessary to proceed with strong oxidation processes to get rid of it. On the other hand the young landfill leachate presents the advantage of being more easily degradable either by biological oxidation-based processes as well as by chemical processes.¹⁻⁵ The toxicity of landfill leachate is certainly due to the high ammonia level and chlorides but moreover by the richness of the dissolved transition metals whose origins derive from the corrosive nature of landfill leachate which slowly dissolves metals from the soil mixed with the wastes and from any metallic debris present in the landfilled wastes.⁶ Additional undesired components found in landfill leachate are the so-called xenobiotics, i.e. substances originating from household or industrial chemicals and present in relatively low concentrations. Despite the transition metals ions and the xenobiotics, the leachate is anyway toxic because it is a broth of bacteria and nutrients and of course any adventitious pathogen can survive and reproduce in such a medium.⁶ Thus, the basic idea of the pre-ozonation treatment presents many benefits. Among the solutions for the treatment of landfill leachate, the ozone treatment was proposed by numerous authors.⁷⁻¹⁸ Initially it was mainly proposed as the stabilizer of the leachate properties,¹³ but later it was recognized the benefits of ozonation (or other oxidation processes) to facilitate the biological treatment.⁸ The fact that landfill leachate is composed by refractory organic matter led the researchers to apply a series of advanced oxidation processes in its treatment.⁹ However the benefits of the ozone pre-treatment of the landfill leachate became evident already several years ago and in more recent years the efficiency of such pre-treatment process was brought to the highest level so that about 3 mg O₃ per mg of COD were necessary to reduce by 50% to starting COD level of a landfill leachate.⁹⁻¹² Concrete benefits were also obtained by landfill leachate pre-ozonation with a drastic cut of the COD, followed by

activated carbon adsorption.¹³ With this approach the adsorption efficiency of the activated carbon is considerably enhanced thanks to the pre-ozonation of the leachate.¹⁴ Furthermore, the leachate biodegradability is enhanced by the pre-ozonation and the perozonation¹⁴ but also the reverse approach was studied with the biological digestion of the leachate, followed by ozonation.¹⁶ The latest trends involve the use of catalytic ozonation of the leachate in the presence of suitable oxides.^{16,17,18} In this paper, after a brief review of the organic matter present in the landfill leachate with a clear distinction between young and old landfill leachate, and an analysis of certain properties, we will focus on the results regarding the landfill leachate treatment with ozone followed by activated carbon and completed by a photo-ozonolysis.^{19,20,21}

Experimental

Materials

Young and old landfill leachate were collected with the aid of the plant manager of the municipal landfill site located at about 70 km south of Rome. The young and old landfill leachate samples were analyzed immediately after transportation to the Actinium laboratory. Table 1 shows the analytical results.

Table 1. Analytical results on pristine samples of young and old landfill leachate samples.

	Young leachate	Old leachate 1	Old leachate 2
COD mg L ⁻¹	9200	1850	3135
Fe ²⁺ , mg L ⁻¹	11.7	13.3	9.79
NH ₄ ⁺ , mg L ⁻¹	132	214	171
Cl ⁻ , mg L ⁻¹	2140	2530	2400
pH	6.2	9.0	8.8

Methods

Isolation of the soluble organic matter (SOM) from young leachate and its TGA and FT-IR

Young leachate (500 ml) was distilled in a spherical flask under reduced pressure in a water bath kept at 95°C. The distillation residue is bituminous, sticky and viscous solid which stinks terribly. The distillation residue was sampled and submitted to a thermogravimetric analysis with simultaneous differential thermal analysis at a heating rate of 10°C/min under air flow in a Linseis apparatus model L81.

Another sample was analyzed at the FT-IR spectrometer Nicolet 6700 from Thermo-Fischer. The spectra were collected in reflectance mode on ZnSe plate and transformed in normal absorbance spectra through the spectrometer's Omnic software.

Isolation of the soluble organic matter (SOM) from young leachate and its TGA and FT-IR

The same procedures described in the above paragraph for the young leachate were also performed on old leachate 1 sample.

Ozonation of the young leachate

A series of experiments were performed by treating the young leachate batch-wise in a 2 L round-bottomed flask which was filled with 500 ml of the leachate, evacuated and filled with O₃/O₂ mixture to reach a ratio mg O₃/mg COD = 0.22. After shaking and suitable contact time the COD dropped from the initial value of 9200 mg L⁻¹ to 7830 mg L⁻¹. After the ozone treatment, all the water of the ozonized leachate was distilled off under reduced pressure in a water bath at 95°C leaving a dry residue which was collected for the FTIR analysis. In another experiment performed in conditions similar to those just described a mg O₃/mg COD = 0.35 ratio was reached after a suitable contact time and the COD dropped from the initial value of 9200 mg L⁻¹ to 4205 mg L⁻¹.

In another experiment, a tubular reactor with a fritted glass porous septum was loaded with 300 ml of young leachate acidified to pH = 5. Ozone produced at a rate of 5g/h was bubbled through the liquid at a flow rate of 4.5 L min⁻¹ for 19 min. This condition corresponds to mg O₃/mg COD = 0.58 and after this treatment the COD dropped to 1360 mg L⁻¹.

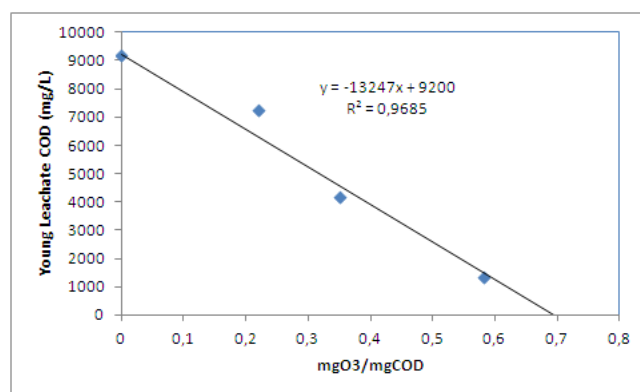


Figure 1. Pre-ozonation of young landfill leachate. The residual COD is a function of the ozone dose expressed as (Leachate COD) = -13247 (mg O₃/mg COD)+9200

The data in Fig. 1 are a summary of these results. From the graph of Fig. 1, it is possible to extrapolate that with mg O₃/mg COD ≥ 0.70 ratio one could get rid of the SOM in the young leachate.

Ozonation of the old leachate

Also for the old leachate, a series of experiments of pre-ozonation were performed either batchwise or through the tubular reactor in a continuous ozone flow, as described in

the above section for the young leachate. The ozone dose is expressed as in the previous section as $\text{mgO}_3/\text{mgCOD}$. The mg COD refers to the starting COD level. The refractory nature of the old leachate is immediately evident in Fig. 2: even with $\text{mg O}_3/\text{mg COD} > 1$ the COD abatement is unsatisfactory. It is also worth a comparison between the slope of Fig.1 with that of Fig. 2. The slope of the former is more than 12 times more steeply than that of the latter. Fig. 2 also shows the results of the old leachate ozonation in the presence of 10% by weight of neutral activated alumina, type 507C Brockmann-I having a particle size below 150 mesh and pore diameter of 5.8 nm.

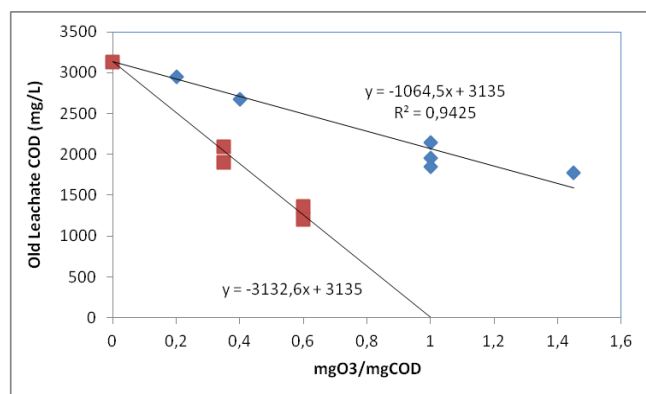


Figure 2. Pre-ozonation of old landfill leachate. The residual COD is a function of the ozone dose expressed as (leachate COD) = $-1064 (\text{mg O}_3/\text{mg COD}) + 3135$ (blue diamonds); The leachate ozonation in the presence of activated Al_2O_3 gives a threefold acceleration in the COD abatement (red squares).

The results are quite interesting, although it should be noted that even without ozonation alumina is able to reduce the COD of the old leachate from the initial 3135 mg L^{-1} to 2100 mg L^{-1} by simple adsorption process. Fig. 2 shows that 10% alumina with an ozone dose of $0.6 \text{ mg O}_3/\text{mg COD}$ gives a decisive advantage. As shown in Fig. 2, the extrapolation of these data suggests that at $\text{mg O}_3/\text{mg COD} \geq 1.0$ the total initial COD of the old leachate could be removed, although further work is needed to verify this extrapolation.

Adsorption through an activated carbon bed

Once pre-ozonized, especially the old leachate needs further treatments which cannot be limited only to the ozonation. As detailed in the patents,^{19,20,21} the pre-ozonized old leachate is passed through a fixed bed of granular activated carbon to reduce further the COD and make the leachate transparent to UV light and hence suitable for the photo-ozonolysis step of the final process.

Photo-ozonolysis

The photo-ozonolysis step is the final step process in the leachate treatment, when it is completely transparent to UV light. In this process complete sterilization is also achieved. Furthermore, the COD is further reduced within the desired

law limits for the discharge in the sewage or ponds or the surface waters. The detail of the process can be found in ref.^{19,20,21}

Results and Discussion

The key problem of the landfill leachate treatment is represented by the soluble organic matter which has been fractionated into three main components, i.e. humic and fulvic acids as well as the hydrophilic fraction.¹ The chemical structure of humic and fulvic acids from landfill leachate is rather complex and not univocal.^{22,23,24} It must be described by model structures because its complexity, exactly in the same way as for the humic and fulvic acids extracted from soils and lake sediments.^{25,26} In other words, it is completely reasonable to assume for the humic and fulvic matter from landfill leachate a structural analogy with that extracted from soil and other fluvial or lake sediments. This assumption is anyway substantiated by a series of experimental data.^{1-5,22-24,25,26}

In this context, it is particularly interesting a comparison of the soluble organic matter (SOM) derived from young landfill leachate against aged or mature leachate. Many authors have insisted on this specific point regarding the biodegradability of the former and the refractoriness toward oxidation of the latter as well as the H/C, O/C and N/C ratios and the BOD/COD ratios, showing that by passing from young to mature leachate it is increased the aromatic content, the molecular weight, the carbon content and $\text{BOD}/\text{COD} \rightarrow 0$. Indeed, the refractoriness toward oxidation of mature leachate is underlined by our studies on the radiolysis of the landfill leachate, which were surprisingly unsuccessful in terms of COD abatement.^{27,28}

We have had the opportunity to isolate the SOM of a young and old leachate samples in a landfill located at about 70 km south of Rome. Fig. 3 shows the thermogravimetric analysis (TGA) of these two SOM performed in air flow. The SOM from young landfill leachate when heated in air shows a linear weight loss up to 328°C (-10% by weight). Above that temperature the differential thermal analysis (DTA) performed simultaneously to the TGA shows a strong exothermal peak due to partial combustion of the SOM (compare Fig.3 with Fig.4). The DTA peak in Fig. 4, occurs at 416°C accompanied by a secondary feature at 428°C . At the end of the combustion process, i.e. above 600°C the total weight loss undergone by the SOM of the young leachate is -37.8% measured at 600°C . At 580°C the DTA registers an endothermic transition due to the melting or thermal decomposition of a mineral component.

As shown in Fig. 3 and 4, the thermal behavior of a SOM from mature, old leachate heated in the air is completely different than that of young leachate without any abrupt weight loss. In fact, the SOM from old leachate shows a general and gradual trend to weight loss with a total weight loss of -28.5% at 750°C . However, the corresponding DTA reported in Fig. 4 is richer in transitions than those observed in the case of the young leachate. In fact, the SOM from old leachate shows two endotherms already at 86°C and at 154°C partially associated with trapped water evaporation. Then two main exothermal peaks are observed at 253°C and at 524°C and two much smaller exothermal transitions are

detected at 280°C and at 334°C. However, these DTA exothermal transitions have a limited impact on the TGA curve. For example, to the exothermal peak at 253°C corresponds a weight loss on only 4.4% and to the other exothermal peak at 524°C, it corresponds a local weight loss of 3.2%. Thus, at these temperatures are volatilized or burned really small amounts of the SOM fractions from old leachate.

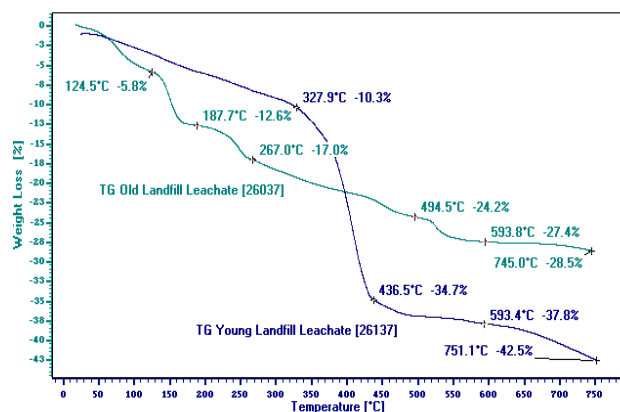


Figure 3. TGA in the airflow of the organic matter from young leachate (dark blue line) and from old leachate (light blue line).

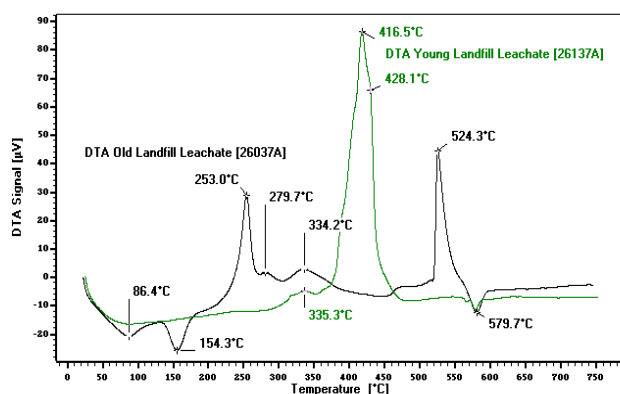


Figure 4. DTA in the airflow of the organic matter from young leachate (green line) and from old leachate (black line).

In summary, in Fig. 3 is shown very clearly the differences between the SOM from a young and old leachate. The former indicates an abrupt weight loss above 327 °C and the total weight loss at 750 °C is -42.5 % against -28.5 % at the same temperature of the SOM from old leachate. From these results a clear difference in the thermal behaviour and oxidation, also emerges the radical chemical difference between SOM from young and old leachate, with the latter being much less volatile due to the higher molecular weight and much less oxidizable than the former.

It is also interesting to discuss shortly the changes in the FT-IR spectra observed in the SOM from a young and old leachate. The young leachate is much reactive with ozone than the old leachate. Fig. 5 shows that the ozonation removes almost completely the infrared band at 1563 cm^{-1} which is one of the most intense bands in the pristine spectrum of young leachate. In fact, after ozonation the original band at 1563 cm^{-1} is reduced to a small shoulder at 1550 cm^{-1} . The infrared absorption band at 1563 cm^{-1} could be due to aromatic rings, to carboxylic acid salts or to unsaturated diketones and similar structures which give rise to the keto-enol tautomerism, i.e. the $-\text{CO}-\text{CH}_2-\text{CO}-$ type of structures.²⁹

Because of the fast and effective reaction with ozone, in the young leachate the band at 1563 cm^{-1} can almost certainly assign to highly substituted aromatic rings and/or to unsaturated diketones, since neither ketones and aldehydes, nor the carboxylic acid salts show a so special reactivity toward ozone.

On the other hand, Fig. 6 shows the FTIR spectrum of SOM from old landfill leachate. The spectral difference with the young leachate, at least limited to the samples we have studied, are relatively small. However, the SOM from old leachate shows a prominent infrared band at 1570 cm^{-1} with two shoulders at 1589 and 1668 cm^{-1} . In the case of mature leachate the ozone treatment does not affect significantly the band at 1570 cm^{-1} . Consequently, in a mature leachate this infrared band belongs mainly to non-oxidizable aromatic rings. This time the results of ozonation is the growth of the bands at 1665 and 1715 cm^{-1} , a clear sign of the slow oxidation which leads to ketone and carboxylic groups. Furthermore, the band originally at 1570 cm^{-1} and relatively sharp, broadens and is shifted at 1583 cm^{-1} .

The results of the infrared study matches perfectly with the COD abatement by leachate pre-ozonation. More in detail, the young leachate responds very well to the pre-ozonolysis as shown in Fig. 1, even with a relatively small ozone dose it is possible to reduce drastically the COD content of a young leachate. Fig. 1 suggests also that an opportunely calibrated ozonation could remove completely the COD of a young leachate. It is only a matter of costs and practical convenience to decide to which level the pre-ozonation of a young leachate should be pushed and then followed eventually by activated carbon adsorption and finished by a short photo-ozonolysis step to reach the limiting COD level required by law to discharge the treated water.

The infrared study has shown that the old leachate is oxidized but not mineralized by the ozonation as it happens for a young leachate. Indeed, Fig. 2 shows that the pre-ozonolysis of the old leachate is at least more than 12 times less effective in COD abatement than the case of a young leachate. This is indeed due to the presence of refractory SOM in the old leachate. Some evident benefit is offered by the pre-ozonation of the old leachate in presence of activated alumina. Alumina is able to adsorb the SOM of old leachate, but the combined alumina and ozone action on old leachate presents clear merits as shown in Fig. 2 and deserves further investigations. Probably, ozone oxidizes the SOM adsorbed on the alumina surface with higher efficiency than the direct ozone treatment of the old leachate without alumina catalyst. It is plausible to think that on alumina surface in presence of water, ozone decomposes into OH free radicals and this may justify the observed higher efficiency of ozone in the degradation of the SOM from old leachate. Even in the hypothesis that the surface of alumina will be saturated at a certain stage by the SOM of the old leachate, the alumina regeneration could be achieved by heating the spent alumina in air at a suitably high temperature to burn the adsorbed deposit and re-utilize it without any special precaution. Precautions are instead needed by the regeneration of the spent activated carbon, to avoid an excessive consumption of it at each regeneration stage.

Especially for the old leachate, the pre-ozonation is desirable to reduce the COD level and to prolong the life of

the activated carbon. In other words, the direct passage of the raw old leachate through an activated carbon bed will accelerate its saturation much more than the case of a pre-ozonized leachate, which has already undergone a COD reduction by the ozone treatment.

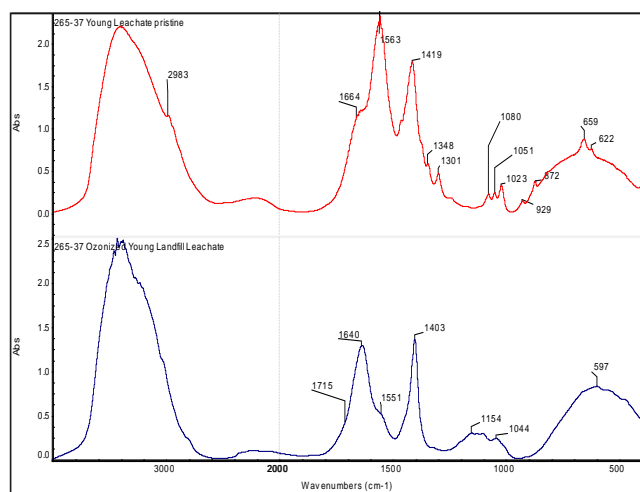


Figure 5. FTIR of pristine SOM from a young leachate (upper trace in red) and after ozonization of the same SOM (lower trace in dark blue).

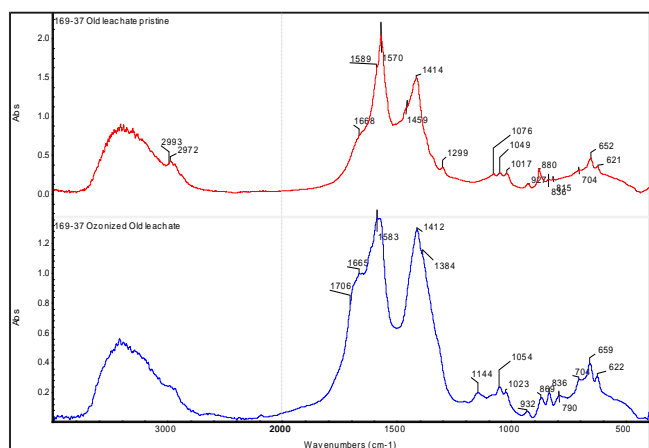


Figure 6. FTIR of pristine SOM from an old leachate (upper trace in red) and after ozonization of the same SOM (lower trace in blue).

Furthermore, the pre-ozonization of the old leachate leads to SOM oxidation as shown by FTIR spectroscopy (Fig.6) and this will be a further aid for the adsorption of the oxidized SOM on the surface oxygen-bearing functional groups present in the activated carbon. Indeed, the patented process¹⁹⁻²¹ proposes the passage of the pre-ozonized leachate through a granular activated carbon bed. Norit type activated charcoal was found as one of the activated carbons more effective in the absorption of the pre-ozonized leachate. It is thought that the simultaneous action of ozone and activated carbon on old leachate could further reduce the COD because the free radical mechanism is also activated by the carbon surface.

When a mature leachate having COD = 3135 mg L⁻¹ is passed through a column of activated charcoal, the COD drops to 650 mg L⁻¹ but the bacterial load remains very high. Furthermore, with such treatment the activated carbon saturates very quickly (see Fig.7). The proposed and patented process¹⁹⁻²¹ instead is based on a pre-ozonolysis

step which clarifies the leachate and reduces the COD to 2253 mg L⁻¹. The resulting oxidized leachate is easily adsorbed on activated carbon so that the COD drops to 270 mg L⁻¹. As final step, the removal of the residual refractory soluble organic matter and the water sterilization is achieved with a photo-ozonolysis treatment reaching a residual COD of 62 mg L⁻¹, a value well inside the Italian law limits for the discharge in surface waters, in the ground or in the sewage (see Fig. 7).

It is worth reminding here that until the leachate is dark in color the photo-ozonolysis is impossible since the UV light is adsorbed and scattered. It is absolutely necessary, before proceeding with the photo-ozonolysis to clarify the leachate. This task is accomplished by the pre-ozonolysis followed by the passage through an activated carbon bed. The residual COD is finally removed by the combined action of ozone and UV light (photo-ozonolysis). The final photo-ozonolysis stage is also a grant for the sterilization of the treated water.

There are other two main critical points in a landfill leachate: the need to remove the free ammonia content and the necessity to remove the transition metals. As already reported in literature,¹⁻⁵ large part of the ammonia can be removed by air bubbling through the leachate. This can be accomplished just before the pre-ozonolysis stage. The pH adjustment of a leachate, especially an old leachate is often necessary in order to achieve better results in the pre-ozonolysis stage. In our experience it is better to bring the old leachate pH below 7 and preferably between 5 and 6.

Regarding the transition metals present in the leachate, a complete analysis can be found elsewhere.⁶ In our studies on the transition metals removal from the leachate we have monitored essentially the iron and manganese content. Our studies have evidenced that the passage through the activated carbon bed is a very effective tool in the removal of the transition metals bringing their level within the law limits.¹⁹⁻²¹ Consequently, the leachate passage through an activated carbon bed after the pre-ozonolysis is a crucial step in this context.

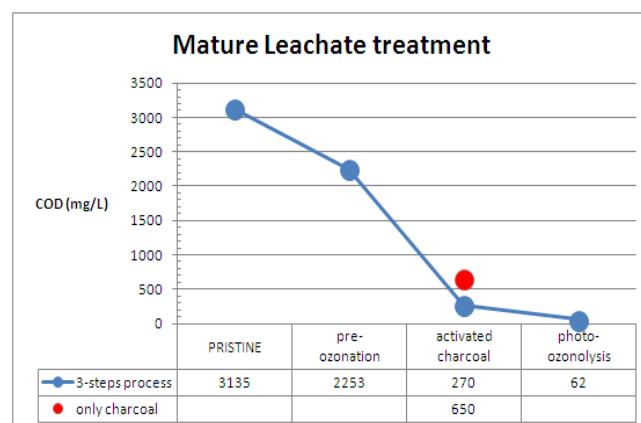


Figure 7. COD changes after the treatment of a mature (old) leachate with the treatment pre-ozonolysis adsorption on activated charcoal and photo-ozonolysis (blue traces). The red bullet shows the COD reduction produced by a straight absorption of the leachate on activated charcoal which however is swiftly saturated in contrast with the pre-ozonolysis leachate treatment which prolongs the life of the activated charcoal.

It is also worth reminding here that ozone is able to oxidize the transition metals to their highest oxidation stage. In general the transition metals at the highest oxidation stage present a much lower solubility in water with respect to their solubility at the lower oxidation stage. Thus, the pre-ozonolysis stage could be considered of key aid in the reduction of the transition metals content in the leachate.

Fig. 1 has shown that a young leachate could be treated with ozone only for the COD removal. However, in Fig. 8 are reported the typical results derived from the train pre-ozonation, passage through a fixed bed of activated carbon and photo-ozonolysis. The results in Fig. 8 are really impressive in the treatment of a young landfill leachate with a starting value of 9200 mg L⁻¹. The direct adsorption of raw young leachate on activated charcoal causes a COD reduction down to 5520 mg L⁻¹ and a saturation of the activated charcoal. Instead, the pre-ozonolysis is particularly effective on the young landfill leachate reducing the COD in a single step from 9100 to 1360 mg L⁻¹. The oxidized leachate is then passed through activated charcoal so that the COD is further brought down to 328 mg L⁻¹. The final COD abatement and sterilization is achieved by the photo-ozonolysis step reaching a COD of 107 mg L⁻¹, inside the limits of the Italian law for the discharge in surface waters (see Fig. 8).

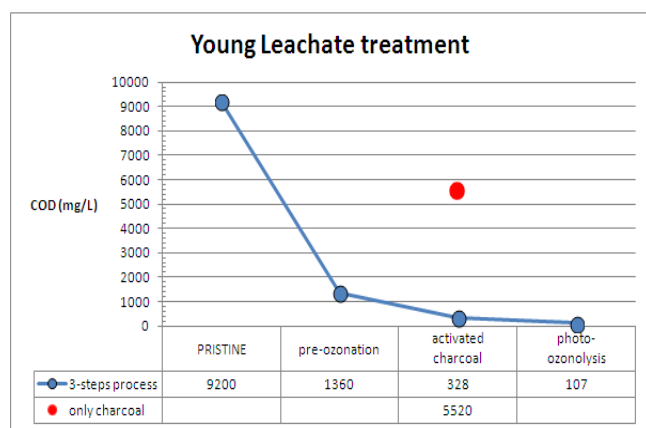


Figure 8. COD changes after the treatment of a young landfill leachate with the sequential treatment pre-ozonolysis adsorption on activated charcoal and photo-ozonolysis (blue traces). The red bullet shows the COD reduction produced by a straight absorption of the leachate on activated charcoal.

Pilot Plant Description

The above (and other) experimental results were translated into patents¹⁹⁻²¹ and a pilot plant for the landfill leachate treatment was built. The layout of the pilot plant is shown in Fig. 9. The pilot plant was designed in a modular way so that it is possible to proceed directly and exclusively with the pre-ozonation of the leachate keeping excluded the activated carbon bed and the UV lamps. Afterwards the valves can be arranged in a way that the pre-ozonized leachate passes through the activated carbon bed. It is also possible to ozonize the leachate and inject it directly into the activated carbon column. Finally, the activated carbon column can be excluded and the treated leachate is sent through the UV lamps and continuously charged with the ozone to accomplish the photo-ozonolysis conditions. The

installed lamps have a total power of 440 W and the ozone generator is able to produce 50 g O₃ per hour at a flow rate of 16-20 L min⁻¹. The corona discharge ozone generator is coupled with an oxygen generator starting from air and using pressure swing adsorption (PSA) process through a dedicated zeolite bed.

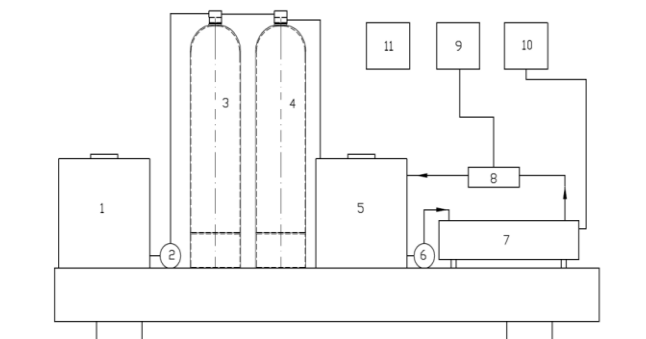


Figure 9. Photo-ozonolysis pilot plant layout. (1) Tank for the pristine leachate, (2) pump, (3) sand filter, (4) activated charcoal column, (5) batch with recirculation reactor, (6) pump, (7) horizontal UV lamps total power 440W, (8) venture injector, (9) ozone generator 50 g/h, water-cooled corona discharge coupled with PSA oxygen generator working at 16-20 L min⁻¹ (10) electrical controls for ozonizer and lamps, (11) electrical controls for pumps

Conclusions

The young and old or mature leachate are two completely different wastes not only in terms of COD level, pH, BOD/COD ratio and other analytical chemical parameters but especially on the chemical structure of the soluble organic matter (SOM) present in the leachate. In fact, the SOM isolated from a young leachate is more volatile and oxidizable at the TGA in air than the SOM isolated from an old leachate. This is due not only to significant differences in molecular weight between the two SOM but also to a different degree of chemical structural evolution. In fact, the SOM from young leachate is easily oxidizable and responds well the ozonation with impressive drop in the very high initial COD even with moderate ozone doses. The FT-IR analysis of ozonized SOM from a young leachate versus a reference pristine SOM shows that the ozone attack is directed toward unsaturated ketones and specifically to unsaturated diketones and triketones which present the keto-enol tautomerism phenomenon. Aromatic sites are probably highly alkyl substituted and hence easily degradable by the ozone attack.

On the other hand the old leachate is less sensitive to direct ozonation and the SOM from the old leachate after ozonation shows only limited evidences of oxidation. It was shown that the ozonation of old leachate could be enhanced in terms of COD abatement if conducted in presence of activated alumina. However, the refractory nature toward oxidation by an old leachate becomes immediately evident also in a simple ozonation stage.

Following the patents,¹⁹⁻²¹ an effective approach to get rid of the old leachate and to reduce its COD within the law limits involves a pre-ozonation of the leachate followed by a passage through a bed of activated carbon followed in its

turn by a final stage of photo-ozonolysis when the leachate is a clear transparent solution suitable to be irradiated in presence of dissolved ozone. It was shown that with these three stages treatment the law limits for the discharge in sewage or even in surface waters can be achieved.

Since the young leachate is so sensitive to oxidation it is recommended to oxidize it for example by ozone and then treat it with activated charcoal and eventually with photo-ozonolysis in the final stage, at a considerably lower costs than and old, mature leachate.

A pilot plant was designed and build to demonstrate the effectiveness of the proposed process in a larger scale. The pilot plant layout has been disclosed in this paper.

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