NEW DEVELOPMENTS IN THE RADIOLYSIS AND OZONOLYSIS OF LANDFILL LEACHATE

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Old and young municipal landfill leachates samples were radiation processed with γ rays at a dose rate of 1 kGy h^{-1}. The fate of the soluble organic matter (humic substance) present in the leachates was followed by the chemical oxygen demand (COD) measurements. The radiolysis of old landfill leachate is a not an effective process in comparison to ozonolysis but can be enhanced significantly by the addition of H_2O_2 to the old leachate prior to radiolysis and by bringing the pH of the leachate to zero. Some radiolyzed sample were further ozonized to reduce to the minimum possible the COD level. Young landfill leachate results instead more prone to radiolysis and less sensitive to ozonolysis than the old landfill leachate.

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Introduction

Landfilling of the municipal wastes is still today one of the major way to get rid of garbages.[1] However, the landfilled wastes release for years a liquor due to the decomposition of the organic garbages and due to the rain waters which pass through the landfill washing away and extracting the soluble or solubilised matter.[1] The black liquor is known as landfill leachate. There is no standard landfill leachate since its properties in terms of type and concentration of soluble organic matter, inorganic components vary with atmospheric conditions and ageing of the landfill site.[2,3] In general, in the rainy seasons the landfill leachate presents lower concentration of soluble organic matter and inorganic components while in the dry seasons it occurs the opposite. Furthermore, the soluble organic matter present in a leachate is completely different if the leachate is coming out from a recent or an old landfill site.[2,3] In general, the old landfill leachate is characterized by relatively low content of soluble organic matter as measured by the COD (COD=Chemical Oxygen Demand) in comparison to the very high COD levels of a young leachate.[1-3] Additionally, the pH of an old leachate is typically weakly basic in contrast with the COD of a young leachate which is instead acidic.[1-3] The relatively low COD level of the old leachate is compensated by the fact that the soluble organic matter present in it under the form of humic substances (HS) is extremely refractory to oxidation even by powerful oxidizing agents like ozone.[4-6] It is also not biodegradable by microorganisms because it is already the result of methanogenic fermentation which has transformed the soluble organic matter present in the young leachate into methane and into a refractory HS.[1-3] In a previous work we have discussed about chemical structure of the HS of the old leachate.[7] The reason of its resistance to chemical and biochemical degradation must be attributed to its relatively high molecular weight and high degree of aromatic content.[2,3,6,7]

The purification of the water containing landfill leachate represents a real challenge. A number of different treatments have been proposed but does not exist "the dedicated treatment" for the landfill leachate.[1-8] The problem regards not only the degradation of the HS present in the leachate but also the elimination of certain transition metals which occur in the leachates[1-3,9] as well as the elimination of pathogens[1] which proliferate in a broth rich of nutrients as it is especially the young landfill leachate but also the old leachate. Therefore, the solution to the leachate problem should take into account these three problems all together: mineralization of the HS, elimination or reduction of transition metals and free ammonia (for old leachates) and sterilization of the leachate from the pathogens. In a previous work we have examined the combined action of activated carbon and ozone in the treatment of old leachate with encouraging results.[8] Indeed, the ozonolysis of old leachate leads to a reasonable, although unsatisfactory, reduction of the COD and to the sterilization of the liquor, while activated carbon is able to adsorb the oxidized HS and even large part of the transition metals.[6,8] In order to find more radical solutions, we have studied also the action of high energy radiation on old landfill leachate followed by ozonolysis.[7] Water radiolysis with γ radiation generates essentially •OH radicals which are the powerful oxidizing agents resulting also from advanced oxidation processes.[5,10-13] With surprise we have found that radiolysis of neat old leachate is completely not effective on the mineralization of HS.[7] The reason of this failure is certainly to be ascribed to the high concentration of carbonate, bicarbonate ions and free ammonia in the leachate which act as free radical scavengers especially against the •OH radicals hindering the effects. Furthermore, previous studies have recommended the combined action of an oxidizing agent with radiation to treat polluted waters and wastewater.[10-13]

In the present work, the radiolysis of old landfill leachate has been conducted in presence of H_2O_2 as oxidizing agent and also in acidic conditions to decompose the carbonates and bicarbonates and to transform the free ammonia in ammonium ion. The radiolyzed leachate samples were also ozonized wherever possible and in any case the radiolysis effects on COD were compared with the ozonolysis effects. Also a sample of young landfill leachate with high COD was radiolyzed.

Experimental

Landfill leachate sampling

Landfill leachate sample was obtained from a municipal landfill located in the central Italy. Three different samples of landfill leachate were taken from the site. One sample was taken in a site which is 6–7 years old and consists of an old landfill leachate with COD = 5165 mg L^{-1}. The second sample was taken in the oldest area of the landfill site which was about 10 years old and was characterized by a COD = 2376 mg L^{-1}. The third sample was taken in another area which has been recently land-filled and the resulting leachate is defined as young landfill leachate with a COD = 9200 mg L^{-1}.

COD (Chemical Oxygen Demand) measurements

The COD (Chemical Oxygen Demand) was measured with the bichromate methodology according to the ISO 15705 standard test.

Irradiation procedure

The landfill leachate samples in closed vials were irradiated in presence with a ^{60}Co γ-ray source at the CNR–IMC facility using a dose rate of 1 kGy h^{-1}.

Old and virgin landfill leachate radiolysis followed by ozonolysis

The virgin old landfill leachate having a starting COD value of 5165 mg L^{-1} was transferred in 7 different vials which were tighly closed with a screw cap. Each vial was filled with 20 ml of leachate. Only 1 vial was kept as reference and the other vials were irradiated at 12.5, 25, 50, 100, 200 and 400 kGy respectively. After the radiolysis the vials were opened and sampled for the COD analysis and for the pH measurements. Afterwards the radiolyzed sample were ozonized following a standard procedure reported in a previous work.[14] After the ozonolysis the COD of each sample was measured again.

Old landfill leachate radiolysis with H_2O_2 followed by ozonolysis

In this series of experiments the old and virgin leachate had a COD = 2376 mg L^{-1}. The addition of 1 ml of H_2O_2 to the leachate led the COD (after 14 days) at 1872 mg L^{-1} while the pH remained unchaged at about 8.4. The COD value of 1872 mg L^{-1} was taken as starting value for all the following experiments. A series of 6 vials were filled with 20 ml each of old landfill leachate and treated with 1 ml each of H_2O_2 36% solution. Only 1 vial was kept as reference and the other vials were irradiated at 12.5, 25, 50, 100, 200 and 400 kGy respectively. After the radiolysis the vials were opened and sampled for the COD analysis and for the pH measurements. Afterwards the radiolyzed sample were ozonized following a standard procedure reported in a previous work.[14] After the ozonolysis the COD of each sample was measured again. Also the reference, non-radiolyzed sample having a starting COD =1872 mg L^{-1} was ozonized and the COD was measured again after the ozonolysis.

Old landfill leachate radiolysis with H_2O_2 at pH = 0

In this series of experiments the old and virgin leachate had a COD = 2376 mg L^{-1}. The acidification of 20 ml of leachate with 1 ml of HCl 9% brings the pH from 8.4 to nearly zero. After the acidification the COD was found at 1990 mg L^{-1}. The addition of 1 ml of H_2O_2 to the leachate led the COD (after 14 days) at 1858 mg L^{-1} while the pH=0. The COD value of 1858 mg L^{-1} was taken as starting value for all the following experiments. A series of 6 vials were filled with 20 ml each of old landfill leachate and treated with 1 ml each of H_2O_2 36% solution. Only 1 vial was kept as reference and the other vials were irradiated at 12.5, 25, 50, 100, 200 and 400 kGy respectively. After the radiolysis the vials were opened and sampled for the COD analysis and for the pH measurements.

Young and virgin landfill leachate radiolysis

In this series of experiments the young and virgin leachate with a COD = 9200 mg L^{-1} was irradiated in a series of 3 vials filled with 20 ml each of the young leachate. The vials were irradiated at 100, 200 and 400 kGy respectively. After the radiolysis the vials were opened and sampled for the COD analysis and for the pH measurements. Only the reference sample was ozonized and the resulting COD measured.

Results and Discussion

Radiolysis and ozonolysis of old landfill leachate

As discussed in a previous work[7] the radiolysis of an old landfill leachate is completely unsuccessful since the COD of the leachate remains practically unaffected by the action of γ radiation at any dose level. Even at the very high dose of 400 kGy (Fig. 1, blue line and circles) the radiolysis of an old landfill leachate does not lead to any evident abatement of the COD level. The ozonolysis of radiolyzed landfill leachate leads to a reduction of the COD but not at the same level reached by direct ozonolysis of pristine and not radiolyzed leachate (Fig. 1).

The COD data can be elaborated as index values according to the following equation:

$$COD_{\text{Index Value}} = [(COD)_x/(COD)_0]100 \quad (1)$$

with $(COD)_0$ the chemical oxygen demand of the pristine, virgin leachate and $(COD)_x$ the chemical oxygen demand measured at any radiation dose level.

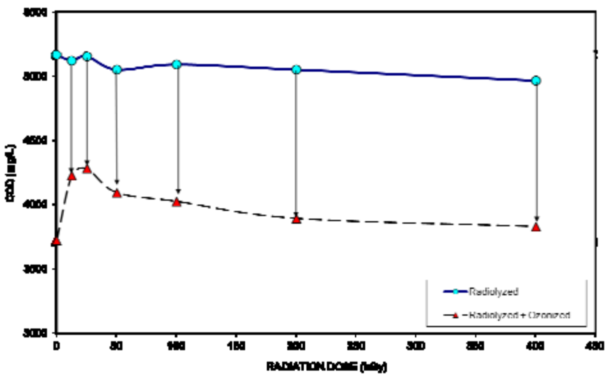

Figure 1. The radiolysis of an old landfill leachate has no effects on its COD and causes a resistance to ozonolysis

Of course, in the condition that $(COD)_x = (COD)_0$ then the $COD_{\text{Index Value}} = 100$. Then, from Fig. 2 it is possible to observe that that after the radiolysis of the landfill leachate up to 400 kGy the COD remained 96% of the starting value, a really negligible reduction. The subsequent ozonolysis reduces the COD to 74% of the original value but the direct ozonolysis of pristine leachate (without radiolysis) leads directly to a COD which is 72% of the starting value.

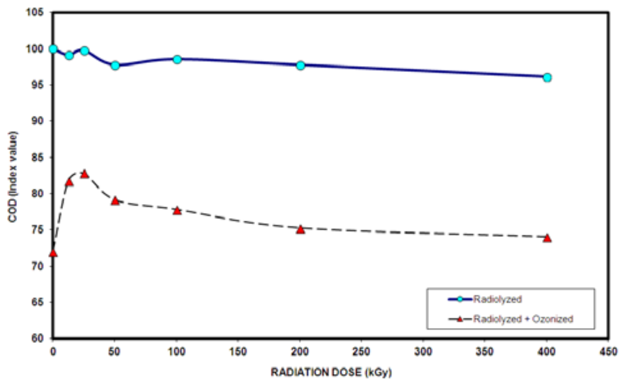

Figure 2. COD index values of radiolyzed (blue circles) and radiolyzed + ozonized (red triangles) landfill leachate

Thus, the conclusion is that high energy radiation is not able to degrade the organic soluble matter present in the leachate which is composed by humic substance and consequently such matter is considered highly refractory to degradation.[7] As discussed in the introduction, the water radiolysis generates the powerful hydroxyl radicals which are very effective on the degradation of simple aromatic substrates but cannot be as effective with humic acids because these molecules are already highly polyhydroxylated.[3,7] Another key hindering effect occurring during the radiolysis of a leachate is due to the presence of carbonate ions, ammonium ions and several transition metal ions which certainly scavenge the •OH species inhibiting the degradation reactions expected by the hydroxyl radicals. Only in this way it is explainable the failure of the old leachate radiolysis process.[10-13]

Furthermore, Fig. 2 shows an increased resistance of the landfill leachate to ozonolysis after the radiation processing. Such effect is particularly evident at the low radiation dose of 12,5 and 25 kGy and becomes less evident at higher doses.

For example, at 25 kGy the ozonolysis leads the COD to 83% of the pristine leachate while the direct ozonolysis without radiation processing leads to 72% of the starting value. This fact can be explained in terms of crosslinking reactions occurring in the humic substance especially at low radiation doses making the substrate less prone to react with ozone. After all, it is well known that the radiation processing of macromolecules has a double effect of causing crosslinking reactions and chain scission reactions.[10] For the humic substance present in the landfill leachate it appears that at low radiation dose in weakly alkaline conditions the crosslinking reaction is prevalent reducing the sites where ozone can exert its oxidative degradation action.

Radiolysis and ozononolysis of old landfill leachate after H_2O_2 addition and pH adjustment

Because of the disappointing results from the straight radiolysis of the landfill leachate, it was thought to add an oxidant to the leachate prior to the radiolysis.[11] It was expected that the combined action of an oxidant with the radiation will improve the effects of the latter. As described in the experimental section, a new sample of old landfill leachate having lower COD value than that reported in the previous section, was treated with H_2O_2 and then submitted to radiolysis at the usual radiation doses. The starting COD value of the pristine sample was 2376 mg L^{-1} and the addition of H_2O_2 without radiation lowered the COD to 1872 mg L^{-1} which was taken as the real starting value for this series of experiments. The series of experiments on old landfill leachate have shown that the pH of the leachate is not affected by the radiation treatment. In fact, the pH of the leachate was 8.5 in the pristine sample and it was found at the same level also after 400 kGy. Instead, the leachate pre-treated with H_2O_2 and then radiolyzed shows a clear trend toward a reduction in the pH value (Fig.3).

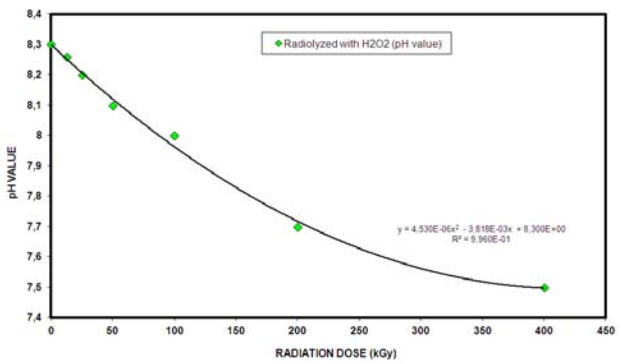

Figure 3. Reduction of the pH as function of the radiation dose: old landfill leachate with H_2O_2

Old landfill leachate is characterized by a weak alkaline pH usually comprised between 8 and 9. Basic pH is due to the presence of free ammonia in the leachate. As shown in Fig. 3, the leachate radiolysis in presence of H_2O_2 leads to a pH reduction from weak basicity toward neutrality. This trend could be explained in terms of reduction of the free ammonia concentration because of its reaction with •OH radicals with formation of hydroxylamine NH_2OH or other oxidation products like nitrite and nitrates.[10]

Even more interesting than the pH trend as function of the radiation dose is the COD trend in the leachate radiolyzed with H_2O_2. Fig. 4 shows clearly a trend to lower COD although an induction threshold is also evident till 50 kGy. In other words, the COD level of the H_2O_2 treated leachate remains practically unchanged till a threshold of 50 kGy, showing afterwards, at higher radiation doses, a clear trend to lower COD values never seen in the case of the radiolysis of the virgin leachate as shown in Fig. 1 and 2.

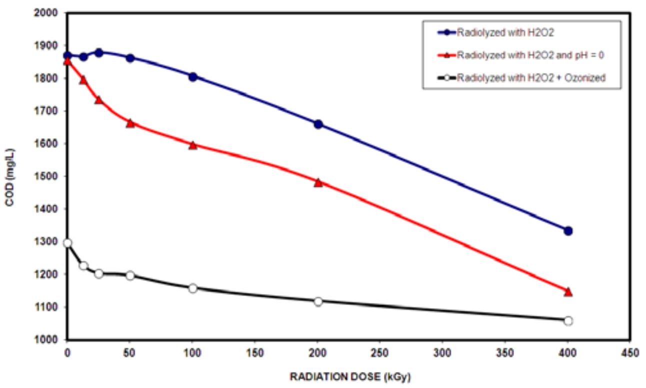

Figure 4. COD values of landfill leachate radiolyzed in presence or without H_2O_2; note the pH=0 effects

Therefore, it can be affirmed that the idea to add H_2O_2 to the leachate prior to the radiolysis was successful in the effectiveness of the partial mineralization of the soluble organic matter. In Fig. 5 the COD reduction occurred in Fig. 4 was indexed according to eq. 1 considering 100 the starting COD level of the leachate treated with H_2O_2.

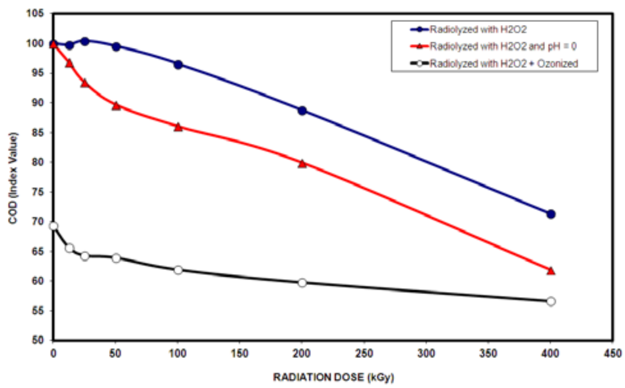

Figure 5. COD data in the ordinate of Fig. 4 are reported as index value by putting 100 the COD of the pristine landfill leachate.

At 200 kGy (Fig. 5) the COD was reduced to 89% of the starting value and at 400 kGy to 71% of the starting value. These results were never reached with the virgin leachate radiolyzed to these dose levels in the absence of H_2O_2 (compare Fig. 2 with Fig.5). The radiolyzed samples treated with H_2O_2 after radiolysis (at any dose used) did not show any residual level of unreacted H_2O_2 suggesting that it was consumed completely in the oxidation process of the soluble humic matter. To assess the complete consumption of H_2O_2, an assay of each radiolyzed sample was treated with a small amount of catalase, the enzyme which specifically decomposes hydrogen peroxide. There were no evidences of O_2 liberation after the addition of catalase, confirming the decomposition of all H_2O_2 originally added. The ozonolysis of the radiolyzed samples brought the COD level between 65% to 58% of the starting value respectively at the lowest and highest radiation dose employed (Fig. 5). These results are significantly better than the results obtained from the direct ozonolysis of the landfill leachate treated with H_2O_2 but not radiolyzed where the COD abatement was stopped to only 69% of the starting value. The ozonolysis results in the COD abatement of the H_2O_2-treated and radiolyzed leachate samples are even better than the ozonolysis results of the radiolyzed virgin leachate samples. In the former case (Fig. 5) the best result is the COD reduction to 58% of the starting value while in the latter case (Fig. 2) the COD reduction due to radiolysis + ozonolysis stopped at 75% of the starting value at 400 kGy for both cases. Furthermore, even at low radiation dose the leachate + H_2O_2 shows a good tendency to undergo the ozonolysis without showing the phenomenon of ozonolysis resistance observed and discussed for the virgin leachate in Fig. 1 and 2 attributable to a prevalent crosslinking reaction at low radiation doses. Thus, the addition of H_2O_2 is beneficial also in this regard.

Fig. 4 and 5 show also the COD reduction occurred to a landfill leachate sample treated with H_2O_2 and also treated with HCl to pH=0 prior to radiolysis. The acidification causes the release of CO_2 by the decomposition of carbonates and bicarbonates and the locking of free ammonia into the ammonium ion. As mentioned previously, the CO_3^{2-} and HCO_3^- ions are among the most effective inhibitors and scavengers of the •OH radicals.[2,4-6] Their elimination with the acidification of the leachate makes the combined effects of the H_2O_2 with the γ radiation more effective in the mineralization of the humic substances. Indeed the COD abatement as function of the radiation dose as shown in Fig. 4 and 5 is immediately measurable even at very low radiation doses, without the dose induction effect observed in the previous case (leachate + H_2O_2 without pH adjustement). At 50 kGy the COD is 90% of the starting value dropping to 80% at 200 kGy and to 62% the starting value at 400 kGy. These results are significantly better than those obtained at the same doses without the pH adjustments (see Fig. 4 and 5). Thus, it is confirmed that the elimination of CO_3^{2-} and HCO_3^- ions is a necessary operation to enhance the effect of hydroxyl ions.

Quantitative evaluation of the COD abatement efficiency

In order to quantify the radiolysis efficiency in the COD abatement in the various conditions adopted, we have used the eq.2:

$$\ln\frac{(COD)_x}{(COD)_0}D^{-1}=\eta \qquad (2)$$

where the meaning of $(COD)_x$ and $(COD)_0$ was already defined in the case of eq.1 and D is the radiation dose in kGy. Therefore η is expressed in kGy^{-1} and is a measurement of the efficiency in the COD abatement as function of the radiation dose. By plotting $\ln[(COD)_x/(COD)_0]$ against the dose D the graphs of Fig. 6 are obtained and the slopes of the experimental data fitted with a line gives η, the efficiency of a given treatment in the COD abatement in the leachate. All the results of such analysis are reported in Table 1.

Table 1. Efficiency η in the COD abatement and residual COD levels

	η [eq.2]	η index	Residual COD at 400 kGy [eq.1]
Old Landfill Leachate Radiolysis	1.08×10^{-4}	100	96.1%
Old Landfill Leachate + H_2O_2 + Radiolysis	9.67×10^{-4}	895	71.4%
Old Landfill Leachate + pH =0 + H_2O_2 + Radiolysis	1.21×10^{-3}	1120	61.9%
Young Landfill Leachate Radiolysis	4.22×10^{-3}	3910	59.8%
Old Landfill Leachate Ozonolysis only	n.a.	n.a.	72.0% (*)
Old Landfill Leachate Radiolysis followed by ozonolysis	2.70×10^{-4}	350(**)	74.1%
Old Landfill Leachate + H_2O_2 + Ozonolysis only	n.a.	n.a.	69.3% (*)
Old Landfill Leachate + H_2O_2 + Radiolysis followed by ozonolysis	3.64×10^{-4}	1232(**)	56.7%
Young Landfill Leachate Ozonolysis only	n.a.	n.a.	85.1% (*)

n.a. = not applicable; (*) Residual COD after ozonolysis without radiolysis, thus not at 400 kGy; (**)Derived from the sum of η radiolysis with that of ozonolysis

The elaboration of the experimental data to obtain the η is shown in Fig. 6 as example.

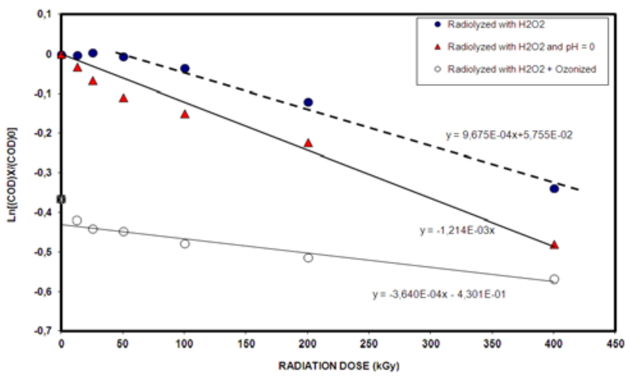

Figure 6. Evaluation of the efficiency η in the COD abatement evaluated according to Eq. 2

As already said, all the data concerning the efficiency of the COD abatement are reported in Table 1.

The radiolysis of old and virgin leachate gives η = 1.08 x 10^{-4} kGy^{-1}. The addition of H_2O_2 to the old landfill leachate gives η = 9.67 x 10^{-4} kGy^{-1}. In this case, the first three data points were not considered in the calculation of the slope because of the presence of a threshold effect: only above 50 kGy are evident the effects of radiation on the COD (see also Fig.6). The adjustement of the pH=0 in combination with H_2O_2 yields η = 1.21 x 10^{-3} kGy^{-1}. As summarized in Table 1, putting as 100 the η value in the COD abatement efficiency in the radiolysis of virgin leachate, the addition of H_2O_2 gives an improvement of a factor 8.95 in η, about one order of magnitude and the results are even above one order of magnitude when the leachate pH is brought to zero together with the addition of H_2O_2, the improvement factor becomes 1.12.

Radiolysis of young leachate

Young landfill leachate is an immature form of landfill leachate with very high COD levels, much higher than those of the old leachate as can be found in Fig. 7.[1-3] The young landfill leachate is one or two years old and it is characterized by an acid pH, its COD level although very high is not stabilized and can change with time. Furthermore, the young leachate is in a phase when the methanogenic fermentation has not yet been started, thus the soluble organic matter has not yet reached the complex polymeric chemical structure typical of the humic substances which are found in the old leachates. In the young leachate the soluble organic matter has lower molecular weight, it is more saturated and less aromatic than the humic substance of the old, mature leachate. Consequently, the young leachate is much less reactive with ozone than the old landfill leachate. In Table 1 it is shown that the COD abatement due to the ozonolysis of a virgin young leachate leads to 85.1% of the starting value while for old and mature leachate the ozonolysis reaches to 72% of the starting COD value. On the other hand the young leachate appears much more sensitive to the radiolysis since, as shown in Fig. 7 the COD undergoes a rapid drop as function of the radiation dose even without the addition of an oxidizing agent.

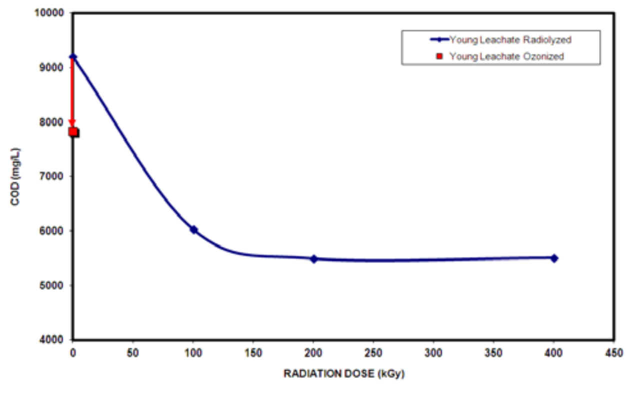

Figure 7. Radiolysis of a young, acidic landfill leachate having an high COD value.

The drop in COD is immediate already at low doses and largely overcomes the COD abatement reachable by simple ozonolysis. In fact, as shown in Table 1, with radiolysis the COD is reduced to 59.8% of the starting value against the 85.1% reachable by using ozonolysis only. Another distinguishable feature of the young landfill leachate regards the fact the maximum of COD abatement is achieved with about 100 kGy. Further radiolysis does not lead to any improvements in the COD even at 400 kGy (see Fig. 7). On the other hand the old landfill leachate with H_2O_2 and even better at pH=0 tends to have a linear response in the COD abatement as function of the radiation dose in the entire dose range explored, i.e. up to 400 kGy.

Using equation 2 and limiting the evaluation in the COD abatement efficiency up to 100 kGy, the young landfill leachate yields $\eta = 4.22x\ 10^{-3}\ kGy^{-1}$ which, as shown in Table 1 corresponds to 3.91 times the η value measured in the radiolysis of virgin and old landfill leachate.

Conclusions

The data in Table 1 clearly show that the radiolysis of virgin old landfill leachate cannot compete with direct ozonolysis since the maximum COD abatement with radiolysis is 96.1% against 72,0% of the original value achieved with ozonolysis.

It was shown that the radiolysis of the landfill leachate in presence of an oxidizing agent like H_2O_2 greatly improves the COD abatement and the response to the radiation dose. With H_2O_2 and radiolysis the COD abatement is reduced to 71.4% of the starting value and hence is comparable to the COD abatement obtained by the combined action of H_2O_2 and ozone without radiolysis: 69.3%. The ozonolysis of the radiolyzed leachate additionated with H_2O_2 leads to a residual COD 56.7% the starting value.

The water radiolysis generates •OH radicals which are scavenged by a series of ions and chemical species present in the leachate. Old landfill leachate is naturally weakly basic and contains free ammonia, carbonate and hydrogencarbonate anions. All these species are known to be excellent scavengers of the •OH radicals. This is the reason why the radiolysis of old and pristine landfill leachate is an unsuccessful process and becomes satisfactory only when an oxidant like H_2O_2 is added as a further source of •OH radicals. The present work as demonstrated that the acidification to pH=0 of an old landfill leachate combined with the H_2O_2 addition and with radiolysis leads to further improvements in the mineralization of the soluble organic matter as suggested by a residual COD at 400 kGy of 61.9% in comparison to 71.4% when the radiolysis of the leachate is conducted with H_2O_2 but in weakly alkaline medium and against 96.1% reached in weakly alkaline medium and in the absence of H_2O_2.

Young landfill leachate is naturally acidic and the soluble organic matter present in it has not reached the degree of complexity and aromaticity of that present in the old, mature landfill leachate. Thanks to the acidic ambient and to a less “refractory” soluble organic matter, the young landfill leachate is radiolyzed more easily than the old type yielding satisfactory results in the COD reduction already at relatively low dose. For example, the COD level is reduced to 59.8% with only 100 kGy whereas for the old landfill leachate we have reported previously the results achieved at 400 kGy. Radiolysis is more effective than ozonolysis in the case of virgin young landfill leachate since the radiolysis leads to a residual COD 59.8% of the starting value while the ozonolysis stops at 85.1%. This result is opposite to that with virgin and old landfill leachate which instead is more responsive to ozonolysis (72% residual COD vs starting value) than radiolysis (96.1% residual COD vs starting value).

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