Influence of Ozonation on Biodegradability of Refractory Organics in a Landfill Leachate*

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Received 18 April 2001

The effectiveness of ozone treatment for improvement of the biodegradability of biorefractory organic pollutants contained in a landfill leachate after biological pretreatment was studied. Contaminants transformation was monitored by means of overall parameters related to the concentration of organic compounds in the treated samples, *i.e.* chemical oxygen demand (COD) and biochemical oxygen demand (BOD). Approximately 60 % reduction of COD in biologically pretreated landfill leachate was observed after about 10 to 11.5 h lasting ozonation. Maximum observed BOD_5 value, measured by the respirometric method was 244 mg dm^{-3}. Biodegradability expressed as BOD_5/COD ratio increased from zero up to a maximum value of 0.21, corresponding to the ozone consumption of 0.7 mg per mg of reduced COD.

Many industrial wastewaters as well as landfill leachate contain high amounts of biologically resistant organics. Usually, a combination of biological and chemical oxidation processes is applied in order to diminish their content and fulfil the effluent standards. The chemical oxidation processes, including ozonation, can either lead to a total degradation of chemical compounds, or to transformation of resistant highly hydrophobic organics to more polar molecules. These processes can be preferably used to transform recalcitrant organic wastewater constituents to biodegradable organics [1]. Investment costs for biological treatment processes are about 5 to 20 times smaller in comparison with chemical processes such as ozone or hydrogen peroxide treatment. Likewise, operational costs for biological wastewater treatment processes are typically from 3 to 10 times smaller than for chemical processes [2].

Ozone possesses oxidizing properties desirable for its use in wastewater treatment. It is a powerful oxidant capable of oxidative degradation of many organic compounds, it is readily available, soluble in water, and leaves more biodegradable by-products [3].

The lower values of Monod half-saturation constant and higher values of the maximum specific oxygen uptake rate for pretreated textile wastewater by ozone compared to the untreated wastewater were measured [4]. This indicates the increased affinity of the modified substrates by ozonation to biological oxidation. The effectiveness of ozone treatment for improving the biodegradability of recalcitrant pollutants was proved by the ozonation of a bioresistant chemical intermediate, azo dye [5]. The inhibition effect of microbial growth during biodegradation of textile wastewater caused by previous ozonation combined with UV radiation and H_2O_2 addition was only about 10 %, while untreated wastewater exhibits 47 % of inhibitory action [6]. Partial oxidation of recalcitrant organics in the effluent of a plant for the oil reclaiming wastewater treatment by ozone and ozone/hydrogen peroxide was shown to increase significantly the biological degradability [7]. However, chemical oxidation of organic wastewater constituents with ozone or ozone/hydrogen peroxide will not always lead to an improved biodegradability. For example, the papermill wastewater and wastewaters resulting from soil remediation treated with ozone and ozone/hydrogen peroxide did not improve biological degradability of organic constituents [8].

The composition of landfill leachate is highly variable and depends on many factors such as refuse characteristics, hydrology of the site, climate, season, age of the site, height of refuse, and moisture routing through the refuse. However, three types of leachate can basically be distinguished, depending on the landfill age [9]. Volatile fatty acids (VFA) are the main contribution to the high COD value of young leachate. COD/BOD ratio values range from 3.3 to 10 and VFA represent 10 % to 30 % of the total organic matter contained in intermediate leachate [9]. Fulvic acids

*Presented at the 28th International Conference of the Slovak Society of Chemical Engineering, Tatranské Matliare, 21—25 May 2001.

and humic substances represent the nonbiodegradable COD and 76 % to 90 % of the total organic content in old leachate [10]. COD/BOD ratio values are usually greater than 10 for old landfill leachate [9].

Presently, biological treatment is preferably used for ammonia removal and/or as a first stage of readily biodegradable young leachate treatment. Procedures of biological treatment are simple, cheap, and efficient. Various chemical and physicochemical processes (precipitation, coagulation, oxidation, adsorption) are applied for nonbiodegradable organics removal. Combinations of biological and chemical processes are very promising because they improve the biodegradability of recalcitrant organics.

The main objective of this work was to study the effectiveness of ozone treatment with regard to an enhancement of biological degradability of landfill leachate organic pollutants which are not removed during a biological treatment.

THEORETICAL

A number of methods used to determine biological degradability have been elaborated. The OxiTop® Control System was applied for respirometric measurements. If oxygen is consumed in a closed vessel at a constant temperature, an underpressure develops. If gas is released, an overpressure develops. If oxygen is converted to carbon dioxide by respiration, there is no direct change in pressure. Therefore sodium hydroxide is placed in the neck of the bottle. Sodium hydroxide and carbon dioxide react chemically to form sodium carbonate. This causes a removal of the carbon dioxide formed from the gas phase and results in a measurable negative pressure due to the respiration of oxygen. The OxiTop®-C measuring head measures and stores a pressure developed during the respirometric test. The pressure values from the measuring heads are collected and processed by the OxiTop® OC110 controller. The BOD values are calculated using the negative pressure values from the OxiTop®-C measuring head by the formula [11]

$$\mathrm{BOD} = \frac{M(\mathrm{O_2})}{RT_\mathrm{m}}\left(\frac{V_\mathrm{t}-V_\mathrm{l}}{V_\mathrm{l}}+\alpha\frac{T_\mathrm{m}}{T_0}\right)\Delta p(\mathrm{O_2})\ (\mathrm{mg\ dm^{-3}}) \qquad (1)$$

EXPERIMENTAL

The ozonation batch apparatus is composed of 0.04 m i.d. and 1.7 m long glass columns. Ozonized gas was produced from pure oxygen by a laboratory ozone generator (AZCO HTU, 500-DC, Canada) with the maximum capacity of 250 mg h^{-1}.

The experiment was done in the parallel semicontinuous reactors. 1.5 dm^{-3} of landfill leachate after biological pretreatment was introduced to the columns and ozonated by bubbling ozonized oxygen gas injected at the column bottom through porous gas diffusers. The leachate introduced to ozonation columns had the same properties and the experiments differed in the time of leachate exposition to the ozone. The oxygen-ozone gas stream was fed to the reactor with a constant flow rate of 30 dm^{-3} h^{-1}.

COD analysis was carried out according to a standard method [12]. BOD values were measured by the OxiTop® Control System [11].

Organic impurities content in a raw landfill leachate in terms of COD was about 5300 g m^{-3}, ammonium nitrogen content 470 mg dm^{-3}, and pH value 7.8. BOD_5 content in the raw landfill leachate was about 80 mg dm^{-3}. Thus COD/BOD_5 ratio value was significantly higher than 10. The landfill leachate was subjected to the biological treatment in a completely mixed intermittently aerated bioreactor. The effluent from the bioreactor contained about 20 mg dm^{-3} of ammonium nitrogen. The content of biologically resistant COD was about 3500 mg dm^{-3}. The effluent concentration value of COD allowed by the legislation [13] for the investigated landfill site varies from 85 mg dm^{-3} to 185 mg dm^{-3} according to leachate flow.

The effluent from the bioreactor, *i.e.* biologically pretreated landfill leachate was ozonated with the aim to increase a biodegradability of the residual COD. Biodegradability of ozonated leachate was determined *via* BOD_5 measurement during different time periods. A small amount of an effluent from a lab-scale model of activated sludge process fed with the landfill leachate was used as bacterial seed. Nitrification and denitrification activated sludge process took place in the bioreactor. It was fed with the same landfill leachate. No withdrawal of excess sludge was performed during the study.

The evolution of biodegradability through ozonation of refractory organic compounds contained in the biologically pretreated landfill leachate was evaluated also by means of COD/BOD_5 ratio values.

RESULTS AND DISCUSSION

The effectiveness of supplied ozone transfer was determined experimentally by the iodometric method [12]. Fig. 1 shows the time courses of accumulative amounts of supplied (theoretically produced) ozone and that transferred into fresh water at experimental conditions given above. As can be seen, both accumulative dependences were linear in time. It follows from this a rather constant efficiency of the ozone transfer in fresh water of about 71 % of the amount theoretically produced.

Fig. 2 presents the evolution of COD with the ozonation time. Prior to ozonation, the landfill leachate was treated by the process of biological nitrification and denitrification with the aim to reduce a high content of ammonium nitrogen and to remove a portion of biodegradable organics. For each ozonation experi-

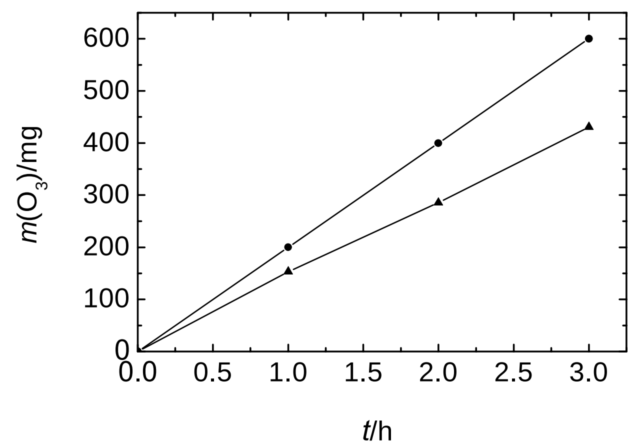

Fig. 1. Accumulative amount of generated (▲) and transferred (●) ozone *vs.* time dependence.

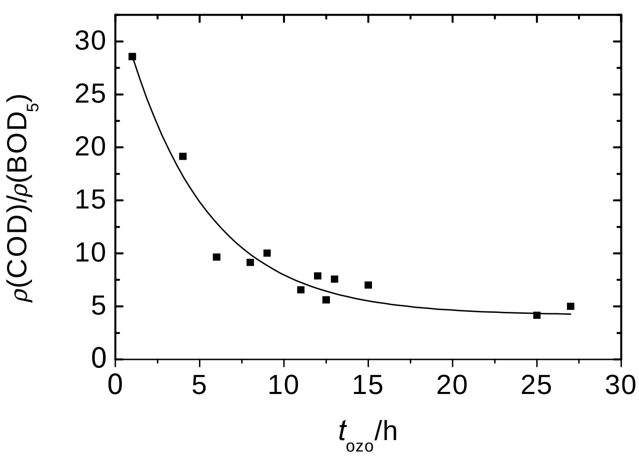

Fig. 4. Evolution of COD/BOD_5 ratio with ozonation time.

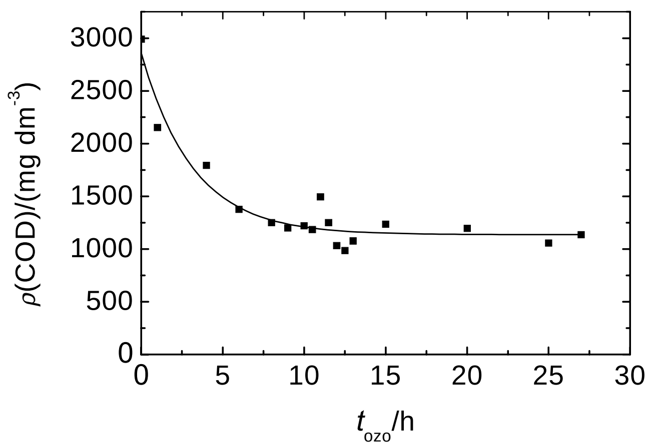

Fig. 2. COD variation *vs.* ozonation time.

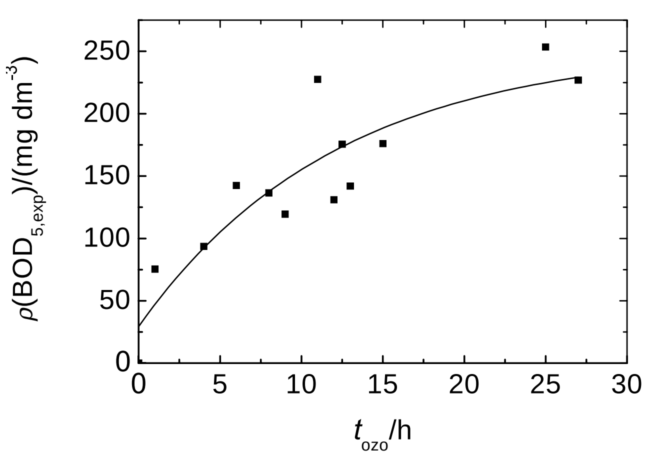

Fig. 3. BOD_5 changes with ozonation time.

ment, the initial COD value was the same. pH value of biologically pretreated leachate was about 8.2 and increased gradually up to 9.3 during ozonation. According to the results shown in Fig. 2, the highest COD decrease rate was observed during the first 4 to 6 h of ozonation, when the COD removal efficiency achieved about 54 %. When the ozonation was prolonged to 12.5 h, the COD removal efficiency ranged between 50 % and 67 % (last efficiency value corresponds to 12.5 h of ozonation). These relatively small conversions of COD observed after 10 h of ozonation can be related in general to very high reactivity of organic compounds with ozone. This is followed by the formation of various intermediates of smaller molecular mass as alcohols, acids, *etc.* which contribute also to the oxygen demand before their final degradation.

In Fig. 3, the evolution of BOD_5 values *vs.* ozonation time is depicted. Significant increase of BOD_5 values for samples ozonated for 10 to 11.5 h was observed. Fig. 4 shows the values of COD/BOD_5 ratio *vs.* ozonation time dependence. The highest increase of biodegradability was observed for the initial period of ozonation (10—11.5 h). The highest biodegradability was achieved after 25 h of ozonation. However, the additional slow decrease of the COD/BOD_5 ratio value observed for prolonged ozonation of samples more than 11.5 h is negligible from the process efficiency and economical point of view.

CONCLUSION

An experimental investigation has been carried out with the aim to evaluate the potential of ozone treatment for improving the biodegradability of recalcitrant pollutants contained in the biologically pretreated landfill leachate. The efficiency of initial COD removal was about 60 % to 70 %. The highest decrease of COD content was observed during the first 10 to 11.5 h of ozonation. The maximum observed BOD_5 value measured in ozonated biologically pretreated landfill leachate by the respirometric method was 244 mg dm^{-3}. Biodegradability expressed as BOD_5/COD ratio increased from zero up to a maximum value of

0.21, corresponding to 0.7 mg of ozone consumed per each mg of COD initially present in the leachate.

Acknowledgements. The study has been supported by the Slovak Grant Agency, Grant No. 1/7346/00, for chemical sciences. The authors wish to thank also R. Bezák (WTW Ltd., B. Bystrica) for the support with the OxiTop® Control System.

SYMBOLS

BOD	biochemical oxygen demand	mg dm^{-3}
BOD_5	5-day biochemical oxygen demand	mg dm^{-3}
COD	chemical oxygen demand	mg dm^{-3}
$M(O_2)$	molecular mass of oxygen	mg mol^{-1}
R	gas constant (83.144)	mbar dm^{-3} mol^{-1} K^{-1}
t	time	h
T_0	reference temperature (273.15)	K
T_m	measuring temperature	K
VFA	volatile fatty acids	
V_t	bottle nominal volume	dm^3
V_l	sample volume	dm^3

Greek Letters

α	Bunsen absorption coefficient (0.03103)	
$\Delta p(O_2)$	difference of the oxygen partial pressure	mbar

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