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Aerobic bio-oxidation combined with ozonation in the treatment of landfill leachates

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Abstract. The objective of the study was to improve an aerobic bio-oxidation process of landfill leachates. Two processes were studied: aerobic bio-oxidation combined with ozonation in a re-circulation system (repetitive sequential aerobic bio-oxidation–ozone treatment) and aerobic bio-oxidation combined with catalytic ozonation in a re-circulation system. It was shown that both processes are effective in landfill leachate purification even at small dosages of consumed ozone.

Key words: landfill leachate, aerobic bio-oxidation, ozonation, combined process.

INTRODUCTION

As more European Union regulations become standardized, landfill leachate treatment is expected to become an increasingly important issue for all European countries in the near future.

Typically, a common landfill leachate treatment process is aerobic bio-oxidation. However, for landfill leachate containing heavily biodegradable compounds it is impossible to achieve the needed purification degree using only biological treatment methods. Many recent developments and applications involve combined processes based on a combination of ozonation and biological purification. Ozonation of wastewater before biological treatment has been found to increase the removal of organic material by subsequent biological treatment [1]. For the same purpose post-ozonation can be applied together with directing the treated water to the subsequent biological treatment stage [2, 3]. It has been

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shown that introducing ozone directly into the activated sludge reactor can improve biological treatment of wastewater [4].

The results of our previous study [5] indicated that aerobic bio-oxidation is efficient in purifying young landfill leachate only under stable operational conditions and when a long residence time is used. In all the tests of aerobic bio-oxidation the ratio BOD/COD decreased. The tests showed also that post-ozonation of the biologically treated landfill leachate improves the bio-degradability of organic compounds. Ozonation in a re-circulation system should increase the efficiency of bio-oxidation. It has also been shown [6] that the use of small amounts of activated carbon can improve the perfomance of an ozonation process. Therefore, in the present work the following combined processes were studied: aerobic bio-oxidation combined with ozonation in a re-circulation system (repetitive sequential aerobic bio-oxidation–ozone treatment) and aerobic bio-oxidation combined with catalytic ozonation in a re-circulation system.

EXPERIMENTAL

As the present work was an extension of the study of purification processes of landfill leachates reported in [6] the same synthetic solution was used as the initial wastewater. The organic part of the synthetic solution had the following composition: acetic acid – 40 g/L, propionic acid – 15 g/L, butyric acid – 15 g/L, valeric acid – 5 g/L, acetone – 5 g/L, ethanol – 5 g/L, propanol – 5 g/L, carbohydrates – 3 g/L, toluene – 0.5 g/L, and phenol – 1 g/L. The main compounds in the inorganic part were Na, Ca, Mg, Fe, K, SO_4^{2-}, Cl^-, and Mn, and Zn, Cr, Co, Ni, and Cu as impurities. The synthetic leachate was made daily by dilution of concentrated solutions. The nutrients N (as NH_4) and P were added during dilution in proportion to the organic (destructable) part. The main parameters of the synthetic solutions used in experiments were: COD – 2800 mg/L, BOD – 1500 mg/L, pH = 6.

The experimental apparatus (Fig. 1) consisted basically of a laboratory bio-reactor and a re-circulation system. The apparatus was operated in a continuous flow mode and a long-lasting uninterrupted operation was guaranteed by an automatic control system based on a computer.

The biological reactor was an aerobic activated sludge reactor with aeration (volume 7.5 L) and settling (volume 2.5 L) chambers. Aerobic conditions and mixing in the reactor were assured through continuous aeration with submerged diffusers in the aeration unit. The activated sludge was developed up and acclimated to the synthetic landfill leachate in the reactor. The main part of the re-circulation system was an ozonation column (volume 2.3 L) that was filled with broken granite (particle size ~7 mm) when aerobic bio-oxidation combined with ozonation was studied and with carbon (particles of the same size) when aerobic bio-oxidation combined with catalytic ozonation was studied. The ozone–air mixture was generated in the corona discharge ozone generator (Clear Water Tech, model P-2000) fed by dry air.

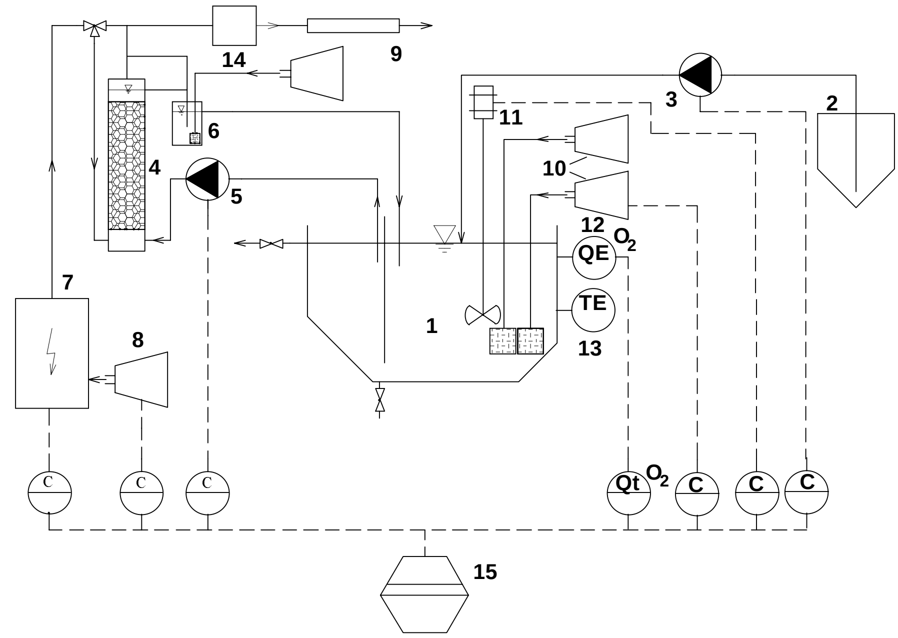

Fig. 1. Laboratory test equipment: 1 – aerobic activated sludge reactor; 2 – feed storage container; 3, 5 – pumps; 4 – ozonation column; 6 – ozone separation unit; 7 – ozone generator; 8, 10 – air compressors; 9 – residual ozone destruction unit; 11 – agitator; 12 – dissolved oxygen concentration sensors; 13 – temperature sensors; 14 – ozone analyser Anseros GM-6040; 15 – controlling PC.

In the experiments of the combined treatment, the re-cycling system was operated. Biologically treated TMP-water was pumped from the settling chamber of the bioreactor by a circulation pump to the bottom of the ozonation column and ozonized. Before the ozonated water was returned to the bioreactor, it passed through the ozone separation unit, where the residual ozone was purged by air. The residual ozone from the ozonation column and the ozone separation unit was destructed thermally.

The main operating conditions of the combined processes were as follows: retention time – 2 days; influent flow rate – 0.21 L/h; re-circulation flow rate – 0.88 L/h; ozone–air mixture flow-rate – 0.5 L/min; ozone concentration in the inlet gas to the ozonation column – 32 mg/L; ozone concentration in the outlet gas from the ozonation column – 5 mg/L; temperature – 20 °C; and dissolved oxygen concentration in the bioreactor – 2–3 mg/L.

Taking into account the productivity of the ozone generator and the small ozone dosages used in experiments (beginning from 10 mg/L of treated water), the wastewater in the column was ozonated in a cycle mode once an hour. The duration of a single ozonation $\Delta\tau$ was calculated using ozone balance:

$$\Delta\tau = \frac{V\,dn}{V_{\mathrm{O3}}(C_{\mathrm{O3IN}} - C_{\mathrm{O3OUT}})}, \qquad (1)$$

where V_{O3} – ozone–air mixture flow-rate

C_{O3IN}, C_{O3OUT} – average ozone concentrations in the inlet and outlet gas

V – influent flow rate

dn – consumed ozone dosage.

The actual ozone dosages consumed during a single ozonation were determined by the iodometric absorption method.

Samples from the initial and treated water were analysed for chemical oxygen demand (COD) and seven-day biochemical oxygen demand (BOD). Biomass concentrations in the bioreactor and settling chamber were also determined.

COD was analysed using Hach standard method and BOD was analysed with procedure 5210 of the Standard Methods for the Examination of Water and Wastewater.

RESULTS AND DISCUSSION

The following processes were under observation (the list is given in temporal order):

I. aerobic bio-oxidation with aeration in a re-circulation system;
II. aerobic bio-oxidation combined with ozonation in a re-circulation system; consumed ozone dosage $dn = 10$ mg/L;
III. aerobic bio-oxidation combined with ozonation in a re-circulation system; consumed ozone dosage $dn = 20$ mg/L;
IV. aerobic bio-oxidation combined with ozonation in a re-circulation system; consumed ozone dosage $dn = 30$ mg/L;
V. aerobic bio-oxidation with aeration in a re-circulation system;
VI. aerobic bio-oxidation with aeration in a re-circulation system (ozonation column was filled with carbon);
VII. aerobic bio-oxidation combined with catalytic ozonation on carbon in a re-circulation system; consumed ozone dosage $dn = 10$ mg/L;
VIII. aerobic bio-oxidation combined with catalytic ozonation on carbon in a re-circulation system; consumed ozone dosage $dn = 20$ mg/L;
IX. aerobic bio-oxidation combined with catalytic ozonation on carbon in a re-circulation system; consumed ozone dosage $dn = 30$ mg/L.

To maintain hydrodynamic conditions of the operation of the system the experiments were carried out as a test series. It should be mentioned that changes in the conditions caused disturbances in the operation of the bioreactor and therefore the duration of processes depended on the stabilization of the system.

Figure 2 presents the changes in the effluent COD and BOD, activated sludge concentration, and organics removal rate in the combined processes. The test series was started when the single aerobic bio-oxidation process had stabilized in the bioreactor at a residence time of 2 days. First of all the process flow configuration was expanded with a re-circulation system. The baseline for comparing the efficiencies of the processes was established by using air in the re-

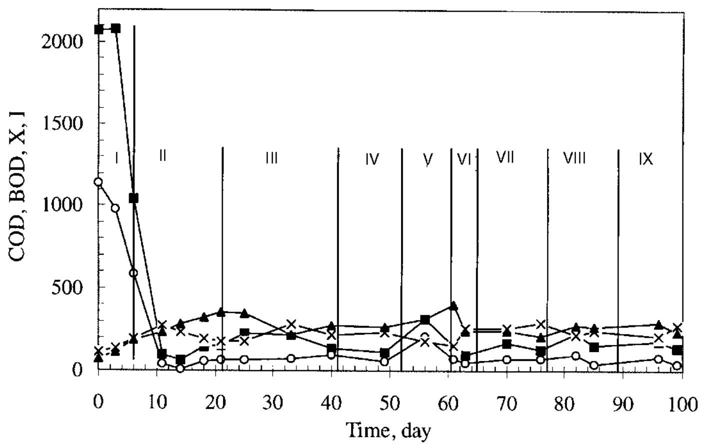

Fig. 2. Evolution of the effluent COD and BOD_7, biomass concentration X, and organics removal rate I in the combined processes of aerobic bio-oxidation with ozonation ($ABO + O_3$) and aerobic bio-oxidation with catalytic ozonation ($ABO + O_3 + C$). ■ – COD, mg/L; ○ – BOD, mg/L; × – X * 100, g/L; ▲ – I, mgBOD/(g day). I, II, III, IV, V – $ABO + O_3$ at ozone dosages of 0, 10, 20, 30, and 0 mg/L, respectively; VI, VII, VIII, IX – $ABO + O_3 + C$ at ozone dosages of 0, 10, 20, and 30 mg/L, respectively.

circulation system (process I). In this stage the efficiency in terms of COD increased from 23% up to 61% and in terms of BOD from 12% up to 55%. Also the activated sludge concentration and organics removal rate increased.

Significant changes occurred when ozonation with the consumed ozone dosage $dn = 10$ mg/L was applied (see Fig. 2, II). Properties of the activated sludge (sludge volume index, structure, and growth rate) improved. The efficiency of the process increased rapidly and achieved 95% in terms of both COD and BOD. To maintain activated sludge concentration in the bioreactor in the range 2–4 g/L, part of the activated sludge was removed periodically.

Our previous experiments of post-ozonation of biologically treated synthetic landfill leachate [5] indicated that the ratio $\Delta COD/dn$ (removal of COD in mg/L per 1 mg/L of consumed ozone) ranged from 0.5 to 2, and the increase in the biodegradability was not high at the ozone dosage of 10 mg/L. Thus, the improved efficiency in the combined process could not be explained only by destructive properties of ozone or improved biodegradability of treated water in the ozonation column. In addition, the residual ozone must have had promoting or catalysing effect on the microbial activity in the bioreactor. In the combined process, the biomass growth rate (one of the characteristics of biomass activity) increased even at low ozone dosages. Microbial growth consists of a complex network of metabolic reactions and in all probability the ozone affects as catalyst the exponential growth phase of microorganisms' metabolism.

Subsequent increases of the ozone dosage to 20 mg/L and thereafter to 30 mg/L (processes III and IV) were followed by disturbances in activated sludge and decreased efficiency. The performance of the bioreactor stabilized swiftly.

The efficiency became high, but would not exceed significantly the values attained in process II. After ozonation was finished, the efficiency fell to 88% (process V).

Thereafter the ozonation column was filled with carbon and water was aerated (process VI). The adsorption on carbon led to an increase in the efficiency up to 96%. However, after the saturation of the carbon the efficiency began to decrease. In the catalytic ozonation at different ozone dosages (VII, VIII, IX) the efficiency ranged between 94% and 96%. The performance of the bioreactor was less stable than in the process where ozonation was combined with aerobic bio-oxidation.

In Fig. 3 the combined processes are compared in terms of effluent COD. There was practically no difference in the efficiency of the studied combined processes at the same consumed ozone dosages. This means that the expected catalytic effect of carbon on the ozonation process was not verified in this case. This can be explained by the fact that the biomass withdrawn from the bioreactor with re-circulating water covered the surface of the carbon particles and prevented the contact of ozone and carbon necessary in the catalytic process. The differences between the values of effluent COD at the outset were caused by different process conditions – catalytic ozonation was started when the ozonation column was aerated and filled with carbon, and probably adsorption on carbon occurred.

To ascertain optimum ozone dosages in the process of aerobic bio-oxidation combined with ozonation supplementary experiments were carried out. A purification efficiency of 96–97% was achieved both in terms of COD and BOD at consumed ozone dosages of 30–50 mgO_3/L (Fig. 4). The efficiency of the process was not improved with increasing the ozone dosage. The ozone dosage as high as 90 mg/L actually reduced the overall efficiency of the treatment process somewhat due to disturbances in the performance of the bioreactor.

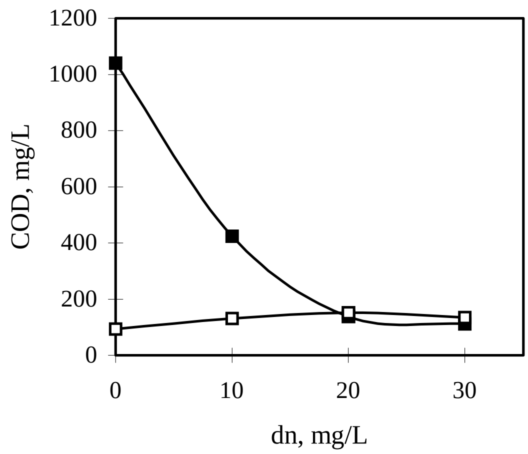

Fig. 3. Dependence of effluent COD on ozone dosage in combined processes. ■ – aerobic bio-oxidation with ozonation in a re-circulation system; □ – aerobic bio-oxidation with catalytic ozonation in a re-circulation system.

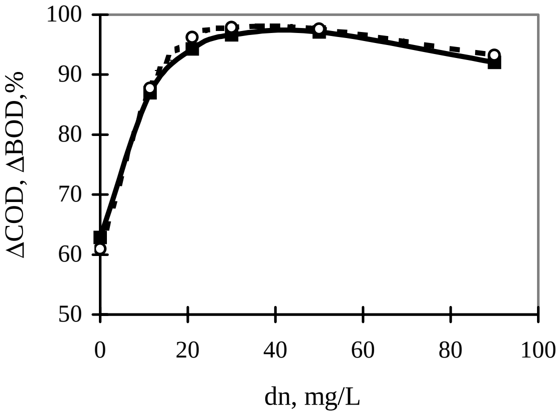

Fig. 4. The effect of ozone dosage on the efficiency of the combined process of aerobic bio-oxidation with ozonation in a re-circulation system. ■ – ΔCOD, %; ○ – ΔBOD, %.

CONCLUSIONS

Two combined processes of purification of landfill leachates were experimentally studied: aerobic bio-oxidation combined with ozonation in a re-circulation system and aerobic bio-oxidation combined with catalytic ozonation on carbon.

The results of experiments indicated that compared to simple aerobic bio-oxidation the process of aerobic bio-oxidation combined with ozonation in a re-circulation system enables to increase the efficiency of purification up to 96% in terms of COD at relatively low ozone dosages (30–50 mgO_3/L). The stability of the biomass was also improved: better settling properties of the sludge were achieved. This indicates that ozone does not act only as an oxidant but also as a catalyst of the biological process. The efficiency of the process was not improved with further increase in the ozone dosage.

It was established that in the case of aerobic bio-oxidation combined with catalytic ozonation on carbon the efficiency of the process was at the same level as in combination with ozonation only – the carbon used in experiments did not act as catalyst. Catalytic ozonation needs more detailed investigation using different types of granulated carbon and different ozone contactors.

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Prügilavete puhastamine kombineeritud protsessiga – aeroobne biooksüdatsioon koos osoonimisega

Inna Kamenev, Lui Pikkov ja Juha Kallas

Töö eesmärk oli leida bioloogilise ja keemilise oksüdatsiooni kombineeritud meetod, mis võimaldaks efektiivselt puhastada prügilavett. Uuriti kahte kombineeritud protsessi: aeroobset biooksüdatsiooni koos retsirkuleeritava vee osoonimisega ning aeroobset biooksüdatsiooni koos retsirkuleeritava vee katalüütilise osoonimisega.

Katsetes kasutati sünteetilist prügilavett, mille koostis vastas noorte prügilate nõrgvete omale. Katsed tehti laboratoorses katseseadmes, mille põhiosad olid aeroobne bioreaktor ning kontaktaparaat, milles toimus retsirkuleeritava vee osoonimine. Seadme pideva töö tagas arvutil baseeruv automaatne juhtimissüsteem.

Selgus, et puhastatava sünteetilise prügilavee töötlemine retsirkulatsioonisüsteemis väikeste osooni doosidega (30–50 mg/l) võimaldab suurendada puhastusprotsessi efektiivsust kuni 96% keemilise hapnikutarbe eraldamise järgi ning ühtlasi soodustab biomassi stabiilsuse paranemist. On tõenäoline, et osoon ei toimi mitte üksnes kui oksüdeerija, vaid ka kui bioloogilise protsessi katalüsaator. Osooni dooside suurendamisel kombineeritud protsessi efektiivsus ei tõusnud. Katalüütilise osoonimise puhul osutus protsessi efektiivsus samaks, kuid bioreaktori töö oli vähem stabiilne.