Oil Shale, Vol. 14, No. 4 SPECIAL
pp. 476-487

ISSN 0208-189X


https://doi.org/10.3176/oil.1997.4S.05

# BATCH TRIALS TO SIMULATE BIOLOGICAL TREATMENT IN LAGOONS OF LEACHATE FROM OIL-SHALE ASH HEAPS

K. ORUPÕLD

Institute of Physical Chemistry,
University of Tartu
Tartu, Estonia

A. OHLSSON
T. HENRYSSON

Department of Biotechnology,
Center for Chemistry and Chemical Engineering,
Lund University
Lund, Sweden

*Lagoons can be used for the treatment of many kinds of waste-waters. This study is focused on the biological treatment of leachate from oil-shale ash heaps in lagoons. To be able to perform these studies in the laboratory in a reasonable time the lagooning process was simulated by a batch process. The influence of a number of parameters, such as temperature, nutrients, aeration and inoculation, on the treatment process was investigated. It was shown that the success of the treatment process, measured as removal of organic compounds, was dependent on nutrients and inoculum. It was fully possible to get a successful treatment also at a low temperature, even if the degradation was initially somewhat slower. The best treatment results were achieved with intermittent aeration (1 day aerobic, 6 days anaerobic). In this case the phenolic compounds (phenol, dimethylphenols and cresols) were degraded to below their detection limits (1 mg/l) and the overall degradation of organic compounds was 75 %.*

## Introduction

Lagoons have been widely used for waste-water treatment. They are usually ponds of large area, providing long retention times for the purification processes. Lagoons are known to be capable of dealing with the whole spectrum of different waste-waters containing biodegradable organic material [1, 2].

The advantage of ponds is that their construction cost is very much less, up to 50 % less, of other, more sophisticated waste-water treatment plants. A biological oxygen demand (BOD) reduction of 99 % is often possible and the long-term average concentrations of refractory materials in the effluents can be 50 % less from stabilization ponds than from an activated sludge process, for instance [3]. Although lagoons are fairly simple systems they represent a complex interaction of physical, chemical and biological processes which must be understood in order to be facilitated. Consequently, to ensure the efficient treatment of waste-water in large-scale, continuous-mode lagoons, studies on a laboratory scale should be carried out. One way to simulate a real lagooning system is to perform a number of batch trials. In batch mode the reactor is charged with the waste and the process is allowed to proceed to completion. This method has the advantage that the evaluation of the processes can be followed as a function of time and the decision as to when and under which conditions an acceptable level of degradation of pollutants has been achieved can be arrived at.

In this study a number of batch trials were carried out in order to find the optimum conditions for the treatment of leachate from oil-shale ash heaps in lagoons. It is proposed that engineered ponds will be used in the future to treat the runoff from ash heaps from the oil shale industry in the Kohtla-Järve district in Northeastern Estonia [4]. The ponds can be used either as pretreatment prior to conveying the water to the regional waste-water treatment plant or as a treatment system alone for the management of the ash heap leachate if the effluent can meet the requirements of the Helcom recommendations for treated effluents to the Gulf of Finland.

Since both aerobic and anaerobic conditions are likely to occur in the real lagooning system both conditions were tried. Intermittent aeration was tested to simulate a repeated alteration in the lagoons between aerobic and anaerobic conditions. As temperature is one important environmental parameter influencing the activity and growth rate of microorganisms and it varies widely during a year, trials were performed at two different temperatures. The impact of the other important components on the purification process, such as inoculum and nutrients, was also studied.

## Materials and Methods

### Leachate

The leachate studied was from the oil-shale, semicoke ash dumping area in Kohtla-Järve, Estonia. Under the influence of precipitation and drainage water pumped onto the hills to compact the ash, the organic components are leached. The leachate was collected on the 24th of September 1995, from the ditch that conveys the untreated leachate to the Kohtla River and finally to the Gulf of Finland. The results of the analysis of the leachate used in this study are shown in Table 1.

*Table 1.* **A Presentation of Some Chemical Parameters of the Raw Leachate**

| | |
|---|---|
| pH | 9.5 |
| Alkalinity to pH 3.7 | 145 mg/l $CaCO_3$ |
| Total N | 12.59 mg/l |
| Total $PO_4^{3-}$-P | 0.14 mg/l |
| $SO_4^{2-}$ | 817 mg/l |
| COD | 900 mg/l |
| $BOD_7$ | 597 mg/l |
| Phenol | 18 mg/l |
| Cresols | 14 mg/l |
| Dimethylphenols | 2 mg/l |

The leachate contained several organic compounds from which only phenol, various cresols and dimethylphenols were identified and analyzed in this study. These phenolic compounds formed approximately 9-10 % of the chemical oxygen demand (COD) of the leachate.

## Experimental

The batch trials were performed in 1 liter Erlenmeyer flasks. Each flask was stirred magnetically. The aerobic flasks were equipped with an air diffuser and aerator. The flasks used in anaerobic trials were closed with rubber stoppers to ensure anaerobic conditions. Two glass tubes went through the rubber stopper, one for sampling (closed with a tubing clamp) and the other one to lead any gas out of the flask. Most of the experiments were performed at room temperature. Temperature in the batches rose to as much as 29 °C probably because of the stirrer and the aerator. Some trials were made in a cold room at approximately 10-12 °C.

The nutrients were added to the leachate as $NH_4Cl$ and $K_2HPO_4$. As inocula in the experiments activated sludge from the Kohtla-Järve regional waste-water treatment plant, sediment sludge from the bottom of the ditch where the leachate was collected, influent to the Lund municipal waste-water treatment plant and adapted sludge from the other batches after the end of the trials were used.

## Chemical Analysis

BOD was determined according to the Swedish standard (SS 02 81 43). The alkalinity of the leachate was measured with a titration to fixed pH end point [5]. The pH was measured by a bench-top pH meter. COD was used to monitor the biodegradation in batches and was determined by Dr. Lange cuvette-tests (Dr. Bruno Lange Gmbh, Berlin) on samples filtered through a 0.45 μm membrane filter (Minisart N, Sartorius). The concentrations of $SO_4^{2-}$, total $PO_4^{3-}$-P and total N were also determined by Dr. Lange cuvette-tests.

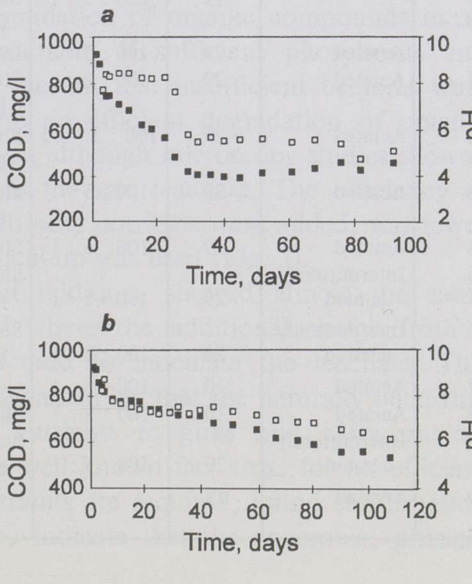
For the determination of phenol, cresols and dimethylphenols a Varian Star HPLC system with a variable-wavelength UV-Vis detector was applied. The wavelength used was 208 nm. This wavelength was chosen to detect the peaks of both phenolic and non-phenolic compounds and follow the counts under the total area of the peaks. The main column was an end-capped C18 column (150 × 4 mm, 5 mm particle size) and the guard-column a C18 column (20 × 4 mm, 40 mm particle size). The column was kept at 50 °C, the flow rate 1 ml/min and the injection volume 50.0 µl. The mobile phase consisted of HPLC grade methanol and phosphate buffer (pH 3). Water samples were prepared for HPLC analysis by adjusting the pH to 3 with sulfuric acid. The individual compounds of cresols and dimethylphenols could not be resolved with the available technique so that they were identified and determined as two groups of compounds. With the above-mentioned equipment at 208 nm the detection limit for phenol, the groups of cresols and dimethylphenols was approx. 1 mg/l.

## Results and Discussion

The different conditions for the batches are listed in Table 2.

Batch *20* was run as a blank test where all the biological activity was prevented by adding $CuSO_4$ and adjusting the pH to investigate the effect of aeration on the decomposition of the organic compounds. Phenol, cresols and dimethylphenols remained in this batch until the end of the experiment, up to 65 days. The maximum COD decrease during this time was 25 %.

The decrease in COD can probably be explained by the evaporation of some of the compounds. This means that the disappearance of phenolic compounds and the COD reduction of more than 25 % is certainly caused by biodegradation processes.




⟶

*Fig. 1.* Changes of the COD (■) and pH (□) values with time in aerobic batch *1* (*A*) and anaerobic batch *2* (*B*) when nothing was added to the leachate in batches

Nothing was added to the leachate in batch *1* and *2*. Batch *1* was aerated while batch *2* was not aerated so that anaerobic conditions could be established in the flask. These trials were carried out as a reference for the other batches in which the biodegradability of leachate at different conditions was assayed. The changes of pH and COD values in the batches with pure leachates are given in Fig. 1. In the aerobic batch *1* 25 % of COD removal was achieved within 8 days and the highest removal achieved was 58 %. In the anaerobic batch a 25 % removal was not seen until the 45th day and the highest COD removal achieved within 100 days was 40 %. The phenol, cresols and dimethylphenols disappeared from aerobic batch *1* in the first week, but remained in the anaerobic batch until the end of the trial. The results from batches *1* and *2* give general information of how much degradation will occur and

*Table 2.* **Conditions Used for the Different Batches**

| Batch | Aeration | Temp. °C | Nutrient addition COD : N : P | Inoculum | Explanations |
|---|---|---|---|---|---|
| 1 | Aerated | 29 | – | – | – |
| 2 | – | 29 | – | – | – |
| 3 | Aerated | 29 | 100 : 5 : 1 | – | – |
| 4 | – | 29 | 250 : 5 : 1 | – | – |
| 5 | Aerated | 29 | – | Sludge from Kohtla-Järve WWTP | – |
| 6 | Aerated | 12 | 100 : 5 : 1 | Sludge from Kohtla-Järve WWTP | – |
| 7 | – | 29 | – | Sludge from Kohtla-Järve WWTP | – |
| 8 | Aerated | 29 | – | Sludge from ditch | – |
| 9 | – | 12 | 250 : 5 : 1 | Sludge from Kohtla-Järve WWTP | – |
| 10 | Aerated | 29 | 100 : 5 : 1 | Influent to Lund WWTP | – |
| 11 | Aerated | 29 | 100 : 5 : 1 | Sludge from Kohtla-Järve WWTP | – |
| 12 | Aerated | 29 | 100 : 3 : 0.5 | Sludge from Kohtla-Järve WWTP | – |
| 13 | Aerated | 29 | 100 : 5 : 1 | Sludge from Kohtla-Järve WWTP | Manual pH regulation |
| 14 | Aerated | 29 | 100 : 5 : 1 | Sludge from batch 5 | |
| 15 | Intermittently aerated | 29 | 100 : 5 : 1 | Sludge from Kohtla-Järve WWTP | 1 day aerobic, 6 days anaerobic |
| 16 | Intermittently aerated | 29 | 100 : 5 : 1 | Sludge from Kohtla-Järve WWTP | 1 day aerobic, 6 days anaerobic |
| 17 | Aerated | 10 | 100 : 5 : 1 | – | |
| 18 | Aerated | 10 | 100 : 5 : 1 | Sludge from batch 6 | |
| 19 | Intermittently aerated | 29 | 100 : 5 : 1 | Sludge from Kohtla-Järve WWTP | 6 h aerobic, 7 days anaerobic |
| 20 | Aerated | 29 | – | – | Biological activity prevented |

on the change in pH when the ponds are used simply as equalization basins before other treatment methods are used.

COD data from different aerobic and anaerobic batches are shown in Figures 2 and 3, respectively.

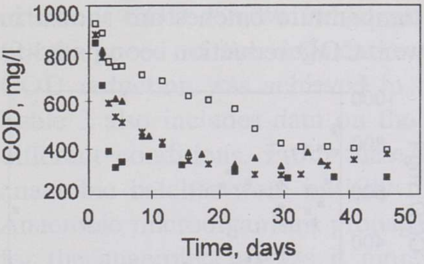



*Fig. 2.* The COD values for different aerobic batches at 29 °C. Batch *1* (□); batch *3*, nutrients (▲); batch *5*, inoculum (*); batch *11*, nutrients, inoculum (■)

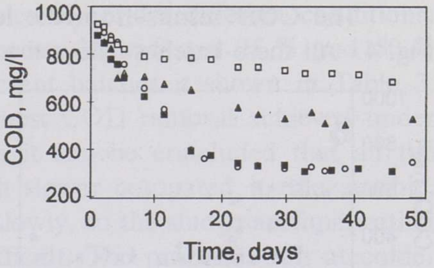



*Fig. 3.* The COD values for different anaerobic batches. Batch *2*, 29 °C (□); batch *4*, 29 °C, nutrients (▲); batch *7*, 29 °C, inoculum (■); batch *9*, 12 °C, nutrients, inoculum (○)

Nutrients were added according to the values suggested in the literature. The COD : N : P ratios 100 : 5 : 1 and 250 : 5 : 1 were used in the aerobic and in the anaerobic batches, respectively. As can be seen from Figures 2 and 3 the biodegradation of leachate was in principle achievable under both aerobic and anaerobic conditions. The removal of COD under anaerobic conditions was slower than in the aerobic batches which were otherwise kept under the same conditions.

Nutrients were added to batches *3* and *4*, but no inoculum was used. This was done to see whether the bacteria occurring naturally in leachate are able to reach a significant degradation of organic compounds in an aerobic and an anaerobic environment if sufficient phosphorus and nitrogen is available. The results showed that insufficient bacteria were present in the leachate to develop an efficient degradation of organic material under anaerobic conditions, although microscopy studies showed that some bacteria were present in the raw leachate. The efficiency of biodegradation in batch *4*, to which only nutrients were added, was lower compared to batch *7*, in which inoculum was used (Fig. 3).

Aerobic batch *3*, with nutrient addition, showed almost the same degradation efficiency as batch *5* where the additional sludge from a waste-water treatment plant was used to inoculate the leachate. This finding can perhaps be explained by assuming that the naturally occurring bacteria in the leachate lacked nutrients to grow and carry out an efficient aerobic degradation. The well known fact that, for an efficient biodegradation, inoculum and nutrients are required, found confirmation also in this work. The results also indicate that the anaerobic, phenoldegrading organisms may be obtained by culturing the aerobic sludge under anaerobic conditions, as shown in Fig. 3 (batches *7* and *9*). The successful degradation of the organic compounds in the leachate under anaerobic conditions is in contradiction to earlier studies, which got very low degradation in anaerobic batches [6].

The COD results from the low temperature batches are shown in Fig. 4. All these batches showed a slower COD reduction compared to

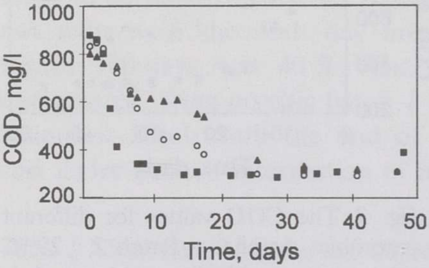



*Fig. 4.* The COD values for aerobic batches at 10-12 °C. Batch *6*, 12 °C, nutrients, inoculum (■); batch *17*, 10 °C, nutrients (▲); batch *18*, 10 °C, nutrients, inoculum (○)

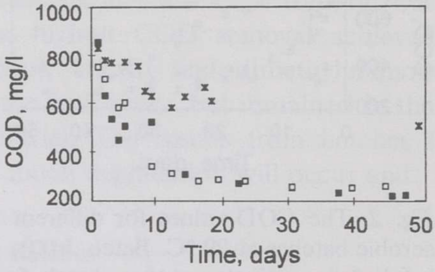



*Fig. 5.* The COD values for the intermittently aerated batches at 29 °C. Batch *15*, 1 day aerobic, 6 days anaerobic (■); batch *16*, 1 day aerobic, 6 days anaerobic (□); batch *19* 6 hours aerobic, 7 days anaerobic (✻)

*Table 3.* **A Presentation of the Time to Reach the Indicated Levels of Removal for the COD Content, the Time to Reach the Detection Limits of Phenol Content, and the Highest COD Removal Achieved**

| Batch | Time to reach 25 % removal, days | Time to reach 50 % removal, days | Time to reach detection limit for phenol, days | Highest COD removal achieved, % |
|---|---|---|---|---|
| 1 | 8 | 26 | 10 | 58 |
| 2 | 44 | > 90 | > 90 | 40 |
| 3 | 3 | 6 | n.a. | 65 |
| 4 | 9 | 50 | n.a | 46 |
| 5 | 2 | 11 | 3 | 67 |
| 6 | 3 | 5 | 4 | 68 |
| 7 | 5 | 13 | 5 | 70 |
| 8 | 6 | 19 | 15 | 52 |
| 9 | 7 | 10 | 7 | 65 |
| 10 | 1 | 3 | 2 | 74 |
| 11 | 1 | 3 | 2 | 69 |
| 12 | 2 | 4 | 2 | 69 |
| 13 | 1 | 3 | 2 | 71 |
| 14 | 2 | 3 | 2 | 64 |
| 15 | 1 | 4 | 2 | 75 |
| 16 | 3 | 6 | 3 | 75 |
| 17 | 6 | 20 | 7 | 66 |
| 18 | 6 | 16 | 6 | 66 |
| 19 | 7 | > 75 | > 75 | 45 |
| 20 | 55 | > 75 | > 75 | 25 |

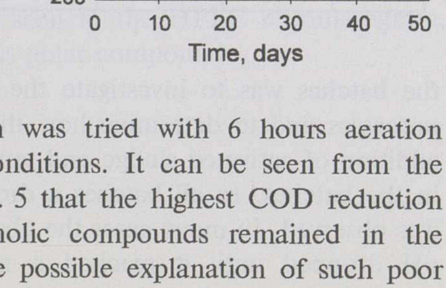
Note: n.a. - not analysed.

the high temperature batches that were otherwise run under the same conditions. However, the final COD values in the low and high temperatures batches were not significantly different.

By simulating the lagooning processes by batch trials two important factors can be investigated: (1) the efficiency of the degradation or the extent of COD removal which is achievable under different conditions, (2) the speed of the degradation process. How fast a 25 % and 50 % COD reduction was achieved in different batches is shown in Table 3. Table 3 also includes data on the highest COD removal achieved under different conditions. From these data it can be concluded that all the anaerobic batches were initially much slower compared to the aerobic. Anaerobic microorganisms propagate slowly, so the sludge acclimatization for the anaerobic process is more difficult. The processes run at colder temperatures were slower than the others performed at warmer temperatures, but did not show any significant differences in the highest COD removal achieved.

The batches that reached the lowest COD values were numbers *15* and *16* which were intermittently aerated, being aerated for 1 day and sealed with no aeration for 6 days (Fig. 5).

The reason for such relatively good COD reduction efficiency may be explained by the co-operation of aerobic and anaerobic bacteria. The experiment with intermittent aeration has much of importance for the simulation of processes in lagoons where aerobic as well as anaerobic conditions can occur. It has been shown in different applications that one possible alternative for the treatment of some compounds is their sequential exposure to specialized anaerobic and aerobic cultures [7, 8].




⟶

*Fig. 6.* The COD values for aerobic batches at 29 °C with nutrients and with different inocula. Batch *10*, influent to Lund WWTP (□); batch *11*, sludge from Kohtla-Järve WWTP (▲); batch *14*, sludge from batch *5* (■)

In batch *19* intermittent aeration was tried with 6 hours aeration followed by 7 days of anaerobic conditions. It can be seen from the results shown in Table 3 and in Fig. 5 that the highest COD reduction achieved was only 45 % and phenolic compounds remained in the leachate at the end of the trial. One possible explanation of such poor degradation may be that the 6 hours long aeration was too short for the development of the aerobic culture and at the same time it destroyed the growth of anaerobic bacteria.

Different inocula were used in the aerobic experiments to find out whether one is better than the others. Some of the results are shown in Fig. 6. As can be seen, there was no significant difference in the COD removal rates and the final values if either activated sludge from the waste-water treatment plant (batch *11*), municipal waste-water (batch *10*) or inocula from an old batch (batch *14*) were used for the inoculation. The idea behind the preparation of inoculum from the old batch at the end of the trial was to obtain the sludge adapted to a certain environment. In batch *8* the leachate was inoculated with sediment sludge from the bottom of the ditch from which the leachate was taken. The results showed no appreciable improvement in organic removal when compared with batch *1* (Table 3). It indicates that addition of sludge from the ditch did not supply the leachate with any additional viable microorganisms.

*Table 4.* **Some Characteristics of the pH Changes in the Different Batches**

| Batch | Lowest pH value | Final pH value | Time to reach pH < 6, days |
|---|---|---|---|
| 1 | 4.73 | 5.10 | 29 |
| 2 | 6.11 | 6.11 | > 100 |
| 3 | 4.42 | 5.30 | 7 |
| 4 | 5.55 | 5.55 | 34 |
| 5 | 5.29 | 5.39 | 14 |
| 6 | 3.99 | 4.30 | 8 |
| 7 | 4.90 | 5.10 | 13 |
| 8 | 7.69 | 7.69 | > 50 |
| 9 | 3.95 | 3.95 | 16 |
| 10 | 5.03 | 6.45 | 5 |
| 11 | 4.81 | 6.10 | 3 |
| 12 | 5.64 | 5.81 | 4 |
| 13 | 5.19 | pH regul. | 4 |
| 14 | 5.58 | 6.42 | 5 |
| 15 | 6.71 | 7.44 | > 72 |
| 16 | 5.30 | 5.31 | 39 |
| 17 | 3.47 | 3.55 | 33 |
| 18 | 3.96 | 3.98 | 26 |
| 19 | 6.55 | 6.55 | > 100 |

The same conditions were used in batches *11* and *12* except for the COD-to-nutrients ratio, in order to investigate how different nutrient additions effect the degradation. Considering the cost of treatment it is preferred to keep the nutrient addition as low as possible. The data in Table 3 do not show any significant difference in results due to the addition of different amounts of nitrogen and phosphorus to the leachate.

One important factor affecting the biological activity and growth rate of bacteria is pH. The purpose of the pH measurements in the batches was to investigate the pH changes due to the degradation processes and to determine how the different factors, such as nutrients, addition of activated sludge and temperature, affect the pH of the liquor in the batches. In all batches a drop in pH from its initial value of 8.5 was observed. In many cases the change in pH was not monotonous. The pH dropped until it reached a minimum value. In some batches it gradually increased again, but always remained below its initial value. Table 4 gives the minimum pH, final pH values and rates of fall in pH in various runs.

The rate of pH decrease was higher in the batches in which the COD reduction was faster. pH values lower than 4 were found only in cold temperature batches. As can be seen from the data in Table 4 the pH stabilized between 5 and 6 in most cases even if it had been lower for some time during the experiment. In general all batches, in which a considerable COD reduction occurred, showed a tendency to lower the pH from the starting value of 8.5 down to a level not very favorable for the bacteria. The decrease of pH during the biodegradation can be attributed to the production of organic acids, which are known to form in the degradation of phenolic compounds, for instance. Since the leachate itself had a relatively low buffering capacity, the acids that are produced can reach concentrations exceeding the buffer capacity of the leachate. In batch *13* an attempt was made to keep the pH to about 6-7 by pH regulation. No significant effect of the pH adjustment on the efficiency of COD removal could be seen (Table 3).

The HPLC chromatogram of the leachate is shown in Fig. 7. Besides the identified phenolic compounds three large peaks can be seen. Since these compounds eluted fast and their peaks appeared at the beginning of the chromatogram, they should be very polar compounds. According to the results of HPLC analysis it was possible to see which compounds disappeared first and which remained until the end of the trial. Due to the biodegradation, the phenol, cresol and dimethylphenols disappeared first. The data on phenol degradation are given in Table 3. After the disappearance of the phenolic compounds from the leachate the HPLC analysis showed a degradation of the peak with a retention time of about 5.4 minutes followed by the degradation of the other big peak at 3.8 minutes. As a result of the biodegradation only the peak of the most polar compound was still left at the end of the treatment. Fig. 8 shows a typical HPLC chromatogram obtained after treatment of the leachate in batch reactors. In some batches, such as *5*, *12*, *13*, *14*, *15* and *16*, there was an increase in the peak area of the most polar compound at the end of the experiment. Although the area of this peak increased, no big changes in the COD values of these samples were observed. We suggest that a degradation of polymers, not seen in the HPLC chromatogram, was responsible for the increase of this polar compound.

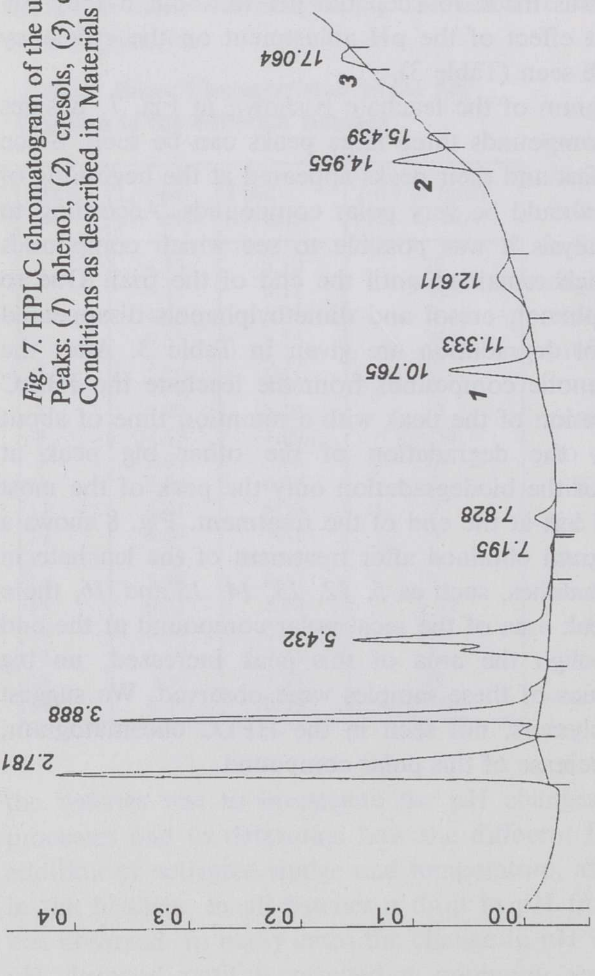



*Fig. 7.* HPLC chromatogram of the untreated oil-shale ash heaps leachate. Peaks: (*1*) phenol, (*2*) cresols, (*3*) dimethylphenols. Conditions as described in Materials and Methods

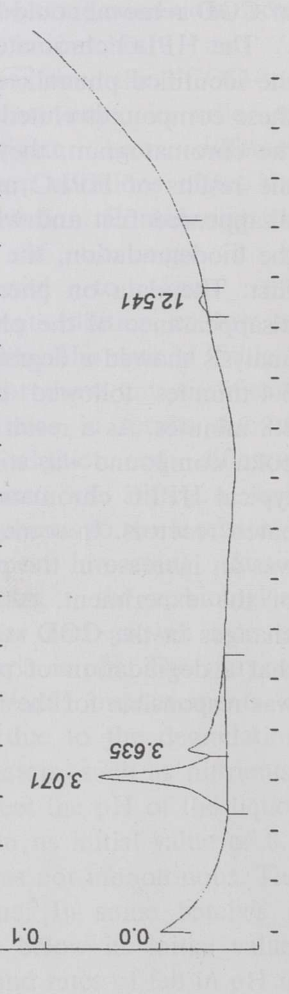



*Fig. 8.* Typical HPLC chromatogram after treatment of the leachate in batch reactors. This specific sample was from batch *10.* Conditions as in Fig. 7

## Conclusions

It can be concluded from the results that it was possible to treat the ash heaps leachate with biological methods. In this treatment it was possible to degrade the phenolic compounds to below their detection limits and the overall content of organic compounds by 75 %. Furthermore, it was found that both aerobic and anaerobic treatment is possible but that a combination is the most successful. It can also be concluded that the treatment can take place at a low temperature and that nutrients and inoculum were prerequisites for a successful treatment.

## Acknowledgment

The authors wishes to acknowledge the grants received from the Swedish Institute and from the Technical Faculty of Lund University (Lund Institute of Technology).

## REFERENCES

1. *Mara D. D.* and *Pearson H.* Artificial Freshwater Environment: Waste Stabilization Ponds // Biotechnology. (Rehm H.-J. and Reed G. eds.) VCH, Germany, 1986. P. 177-204.
2. *Horan N. J.* Biological Wastewate Treatment Systems. Theory and Operation // John-Wiley & Sons, Chichester. 1991.
3. *Ellis K. V.* Stabilization Ponds: Design and Operation // Crit. Rev. Environ. Control. 1983. V. 13. P. 69-102.
4. *Castaldi F. J.* An Evaluation of Technical options for Improvment of the Wastewater Treatment System in the Kohtla-Järve Region of Estonia // Environmental Health Project, Washington. 1996.
5. American Public Health Association Standard methods for the examination of water and wastewater // American Public Health Association, Washington, D.C. 1975.
6. *Kettunen R. H., Pulkkinen E. M., Rintala J. A.* Biological Treatment at Low Temperatures of Sulfur-Rich Phenols Containing Oil Shale Ash Leachate // Wat. Res. 1996. V. 30. P. 1395-1402.
7. *Armenante P. M.* Bioreactors // Biotreatment of Industrial and Hazardous Waste. (Levin M. A. and Gealt M. A. eds.) McGraw-Hill, New York. 1993. P. 65-112.
8. *Kettunen R. H.* and *Rintala A. J.* Sequential Anaerobic-Aerobic Treatment of Sulphur Rich Phenolic Leachates // J. Chem. Tech. Biotechnol. 1995. V. 62. P. 177-184.

*Presented by J. Kann*
Received November 21, 1996