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Biological decomposition of dichloromethane from a chemical process effluent

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Abstract

The application of specialized microorganisms to treat dichloromethane (DM) containing process effluents was studied. An aerobic fluidized bed reactor with a working volume of 80 l filled with sand particles as carriers for the bacteria was used. Oxygen was introduced into the recycle stream by an injector device. DM was monitored semi-continuously. A processor controlled the feed volume according to the DM effluent concentration. Mineralization rates of 12 kg $DM/m^3_{bioreactor} \cdot d$ were reached within about three weeks using synthetic wastewater containing 2000 mg/l DM as single carbon compound. DM from process water of a pharmaceutical plant was reduced from about 2000 mg/l in the feed to below 1 mg/l in the effluent at volumetric loading rates of 3 to 4 kg $DM/m^3_{bioreactor} \cdot d$. Degradation of wastewater components like acetone and isopropanol were favoured, thus making the process less attractive for waste streams containing high amounts of DOC other than of DM. DM concentrations of up to 1000 mg/l were tolerated by the immobilized microorganisms and did not influence their DM degradation capacity. The ability to mineralize DM was lost when no DM was fed to the reactor for 10 days.

Introduction

Dichloromethane (DM, CH_2Cl_2) or methylene-chloride was widely used in pharmaceutical industries, in metal manufacturing plants, in paint industry and to a certain extent in the food industry. For a long time the man made compound was considered as a safe solvent with many advantages for chemical processes. However, safety studies with DM indicated that high concentrations could damage the nervous system and the respiratory organs of mammals. Like other halogenated chemicals, DM was classified as a potential carcinogen (Jongen et al. 1978). A detailed review of the current understanding of the biotic and abiotic chemistry of the halogenated aliphatics has been published by Vogel and co-workers (1987).

The apparent hazard to human health had prompted governments to introduce tougher laws to cut the release of chlorinated hydrocarbons to the environment. The strict regulations released on this class of chemicals will result in new processes, formulations etc., where the chlorinated solvents are replaced by nonchlorinated ones, in recycling of the chemicals, in stopping certain processes, or in closing down plants working with chlorinated compounds. As a result of such actions the annual production volume is likely to be reduced dramatically and thus the release of DM into the environment, since the produced quantities of DM roughly represented the environmental losses of DM which is typical for a compound mainly used as solvent (Pearson 1982). Nevertheless there still exist several production processes where DM is used

for different reasons and where it can not be replaced by other chemicals.

Disposal of used DM and DM contaminated waters from chemical processes can best be achieved by redox processes, by which the chemical is finally decomposed to hydrochloric acid and carbon dioxide. Using other technologies like dumping, stripping or activated carbon adsorption the ecological problems of DM are shifted from the water phase the another environment, thus requiring further treatment steps to clean up that environment as eg. soil, air, carbon, respectively, thus leading to higher disposal costs.

It was the purpose of this paper to show the applicability of specialized microorganisms in quantitatively disposing DM containing wastewater from a chemical plant. It has been reported previously that DM was mineralized by microbial strains, which were isolated from locations where the halogenated compound was present at non toxic concentrations for a long period of time and where the bacteria had naturally evolved (Brunner et al. 1980; Scholtz et al. 1988; Stucki et al. 1981). However, so far biotechnological application of these microorganisms with their unique degradation potential has been scarce (Gälli & Leisinger 1985; Stucki 1989). In this paper data are presented about the application and maintenance of DM degrading bacteria in a fluidized bed pilot reactor controlled by a semi-continuous DM monitoring system to efficiently treat DM containing chemical process water.

Materials and methods

Microorganisms and fluidized bed reactor

Microorganisms used in this study were described by Stucki et al. 1981. The bacteria were precultured in a MBR-laboratory fermenter on 2 to 10 g DM/l according to Gälli & Leisinger (1985), harvested by centrifugation and frozen at $-20°$ C until they were used as inoculum for the 145 l fluidized bed column. The total height of the glass column including its expansion unit of plastic material at the top was 4 m, the column diameter was 0.2 m and the working volume was 75 to 85 l (Fig. 1). Sand (30 to 36 l) with a diameter of 0.1 to 0.3 mm was used as carrier. It expanded up to 140% to its volume when the bed was fluidized by applying a high recycle stream (500 to 700 l/h). Temperature (30° C) and pH (7.2) were measured in the recycle stream and were controlled by a heater which was installed at the head of the column and by the addition of NaOH (7 M), respectively (Fig. 1). Wastewater (0 to 30 l/h) was added into the recycle stream.

The determination of the oxygen concentration was performed at the top of the recycle stream with a WTW oxygen electrode E/O 200. When its concentration fell below 1.6 mg/l pure oxygen was released from a pressurized storage flask via a magnetic valve to an injector device. This injector device was built into the recycle pipe, and was located in the very bottom of the recycle stream down stream the recycle pump and shortly before the entrance into the fluidized bed column (Fig. 1). The purified wastewater, which was semi-continuously monitored for DM, as well as the unused oxygen, which was estimated at about 70% of the total oxygen supplied, left the system through the outlet and the exhaust, respectively. All connections and vessels were gastight and constructed of glass, hard plastics, steel and viton (tubings) in order to avoid losses of DM.

Composition of wastewater

Two types of DM containing wastewaters were used in this study. One was a prepared solution or synthetic wastewater, and the other was a process stream. To start and build up a biofilm in the fluidized bed reactor, bacteria were grown on non-sterile synthetic mineral salt medium, which had the following composition: KH_2PO_4 1,36 g/l, $(NH_4)_2SO_4$ 0,2 g/l, $MgSO_4 \cdot 7\,H_2O$ 0,1 g/l, trace elements' solution (Stucki et al. 1981) 1 ml/l, DM 100 mg/l. The DM concentration in the feed solution was increased to 2 g/l. Wastewater from the production of an intermediate of an antibiotic substance was saturated with DM (7 to 25 g/l). In addition it contained different organic components, which were mainly isopropanol and acetone. The content of

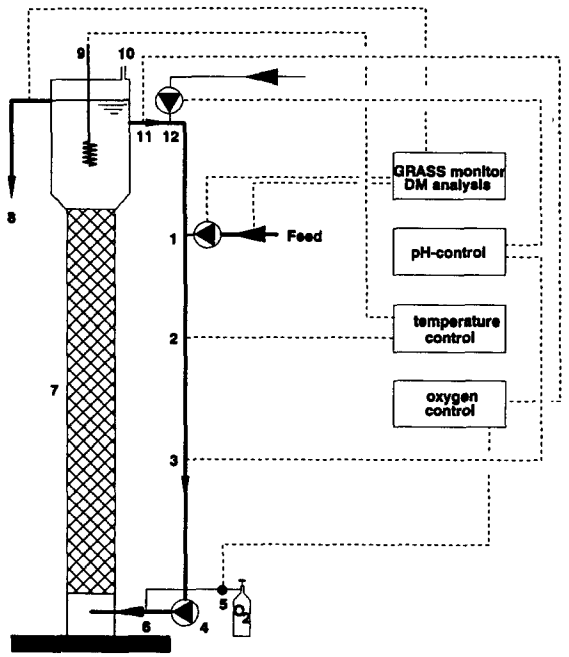

Fig. 1. Fluidized bed reactor. (*1*) Feed of wastewater to the recycle, (*2*) thermometer, (*3*) pH electrode, (*4*) recycle pump, (*5*) magnetic valve, (*6*) oxygen injector device, (*7*) fluidized bed (shadowed part of the reactor represents the volume of expanded sand bed), (*8*) effluent, (*9*) heater, (*10*) exhaust, (*11*) oxygen electrode, (*12*) NaOH feed. All parameters were analyzed continuously or semi-continuously, except DOC.

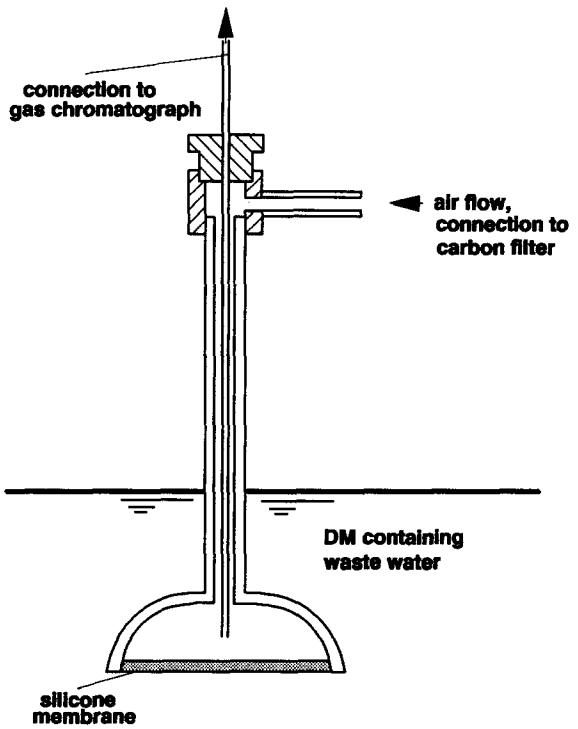

Fig. 2. Sniffer for DM analysis. A sintered glass filter was sealed off by a silicone membrane and dipped into the DM containing wastewater stream. The DM molecules, which diffused through the membrane, were taken up by a stream of filtered air and transported to the gas chromatograph.

dissolved organic carbon (DOC) varied between 8 and 50 g/l. The pH of the waste medium was between 9 and 10, and its salt concentration varied between 30 and 150 g/l. The mineral salts solution (15 ml per l wastewater) was added separately to the bioreactor and contained the following compounds: NH_4Cl 10 g/l, $MgSO_4 \cdot 7H_2O$ 2 g/l, KH_2PO_4 10 g/l, $CaCl_2$ 0,5 g/l. Additionally a trace elements' solution (3 ml per l wastewater) (Stucki et al. 1981) was fed separately to the recycle stream.

Analytical methods

Standard methods were used for the determination of chloride and dissolved organic carbon (DOC). Salt concentrations were measured as inorganic residues after sample incineration at 600° C. DM was analyzed by using a Grass monitor, which is a specially developed CIBA-GEIGY monitoring system (Grass & Widmer 1981; Widmer et al. 1984). Sniffers (Fig. 2) were introduced into influent and effluent of the treatment system to sample the highly volatile DM. The sniffers consisted of a sintered glass filter sealed off by a silicone membrane that was in contact with the liquid wastewater phase. The DM molecules, which diffused through the silicone membrane were carried to a trapping column by a flow of air purified by an activated carbon filter. The trapping column consisted of a glass capillary filled with suitable adsorbent material. The adsorption column was heated periodically following a specific temperature profile, which was dependent on the wastewater components. The desorbed DM was analyzed in a gas chromatograph equipped with a FID detector. The limit of quantitation for DM with the method used amounted to 1 mg/l.

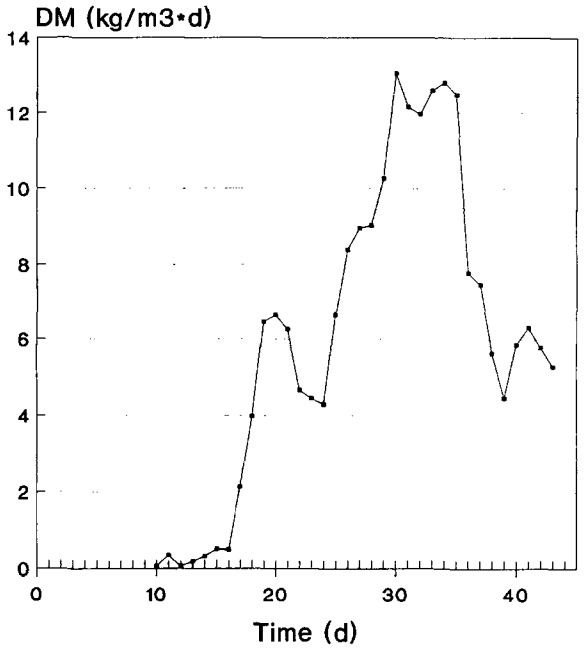

Fig. 3. Increase of DM volumetric load with synthetic wastewater.

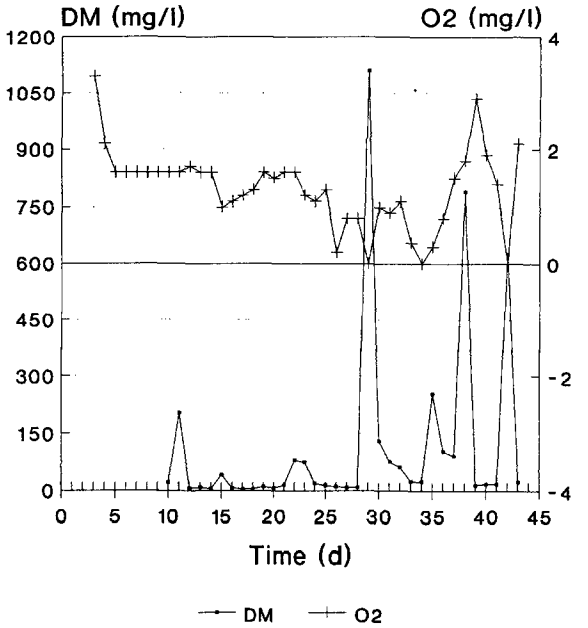

Fig. 4. DM and oxygen concentration in the effluent of the fluidized bed column.

Results

Degradation studies with synthetic wastewater

The pilot plant was started by adding 20 ml of concentrated frozen cells to the fluidized bed column filled with synthetic medium supplemented with 100 mg DM/l. Additional medium containing 2000 mg DM/l was added to the system at short intervals. DM degradation could easily be followed by observing the consumption of oxygen and sodium hydroxide, which was used for neutralizing the biological HCl production. After 10 days the addition of the medium was automatically controlled by increasing the feed volume if the DM concentration in the effluent fell below 100 mg/l. Thus it was possible to increase the DM volumetric load permanently. After one month volumetric loading rates of 12 to 13 kg DM/m^3 · d were reached (Fig. 3). The concentration of DM in the effluent, representing the DM concentration at the top of the bioreactor, was usually below 100 mg/l during that experimental period (Fig. 4, exception day 11: 200 mg/l).

An extraordinary high DM content in the bioreactor was found at day 29. Since the oxygen reservoir had run empty the DM concentration in the bioreactor reached nearly that of the incoming wastewater. The pump had not been programmed to stop the addition of fresh medium at too high DM concentrations. As soon as the failure was noticed, the feed pump was stopped and the bioreactor was supplied with oxygen again. The concentration of DM fell linearly and reached levels below 50 mg/l after 5 h (Fig. 5). The rate of DM disappearance during this part of experiment was 10 kg DM/m^3 · d and was near the maximal rate of 12 to 13 kg DM/m^3 · d, which was determined shortly afterwards between days 31 to 35 (Figs 3 and 4). Two effects were observed when slightly higher loading rates during days 31 and 34 were tried to be applied (data not shown, since these experiments were carried out during 2–4 h and data given in Fig. 4 show steady state performance).

- DM in the effluent increased dramatically indicating an overcharging of the system and
- oxygen concentration fell instantly.

It was concluded that higher concentrations of

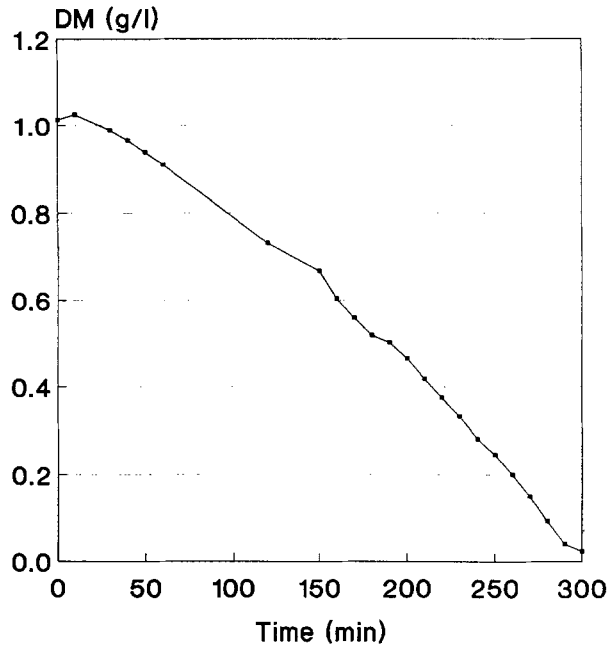

Fig. 5. Degradation of DM after insufficient oxygen supply. The degradation rate during the 5 h recovery period was about 10 kg/$m^3 \cdot$ d and was similar to the maximal degradation rate of 12 to 13 kg/$m^3 \cdot$ d determined during continuous operation of the fluidized bed reactor.

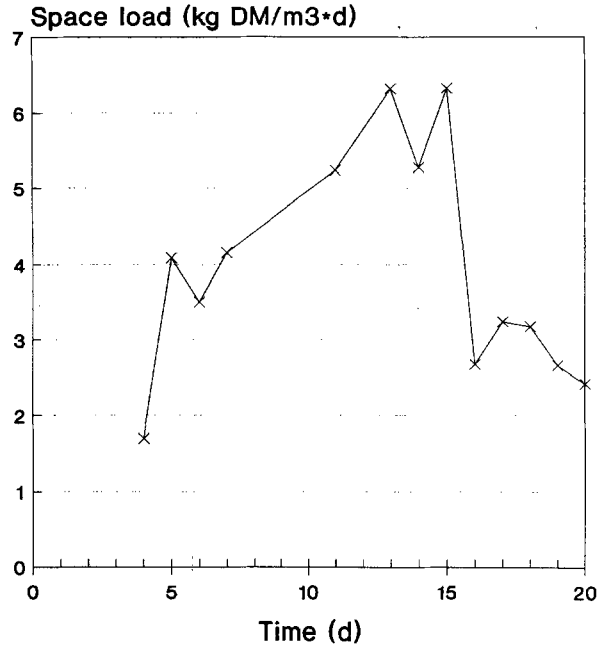

Fig. 6. DM volumetric load with chemical wastewater.

oxygen than 0.3–0.5 mg/l (measured at the top of the bioreactor) were necessary to degrade DM to below 1 mg/l. With the high DM loading rates applied the magnetic valve for the oxygen delivery remained open for most of the time, since the set oxygen level of 1.6 mg was rarely met. The input of oxygen could be increased by increasing the pressure at the storage flask. This, however, resulted in improper function of the injector device, producing large oxygen gas bubbles which disrupted the fluidized bed structure. It was therefore concluded that the maximal degradation rate of 12 to 13 kg DM/$m^3 \cdot$ d reflected rather a value limited by the maximum oxygen imput of the system used than the volumetric loading applied. Maximal DM degradation rates between days 31 to 34 corresponded to an oxygen uptake rate of about 4 kg $O_2/m^3 \cdot$ d with an oxygen supply rate of 13 kg $O_2/m^3 \cdot$ d.

Degradation studies with wastewater from a chemical production plant

After 35 days synthetic wastewater was replaced by chemical process water. This stream was 10 times diluted with clean water since the amount of salts was too high. DM volumetric loading rate was reduced to 4.5 to 7.5 kg DM/$m^3 \cdot$ d (Fig. 3) since the wastewater contained other degradable compounds than DM in varying concentrations. Under these conditions and under the DM space load applied, it was not always possible to meet the needed DM effluent qualities of below 1 mg/l or to supply the nessessary oxygen requirements for complete degradation of the wastewater components (Fig. 4, days 38 and 42, respectively). On these two days 360 l of diluted wastewater containing extraordinary high levels of DOC (final concentration 5 g/l) were fed into the system. Since the mineralization of the easy degradable compounds like isopropanol and acetone were favored, the decomposition of DM became incomplete and DM appeared at higher levels in the plant effluent. After these initial experiments in the pilot laboratory, the pilot plant was moved to the chemical plant,

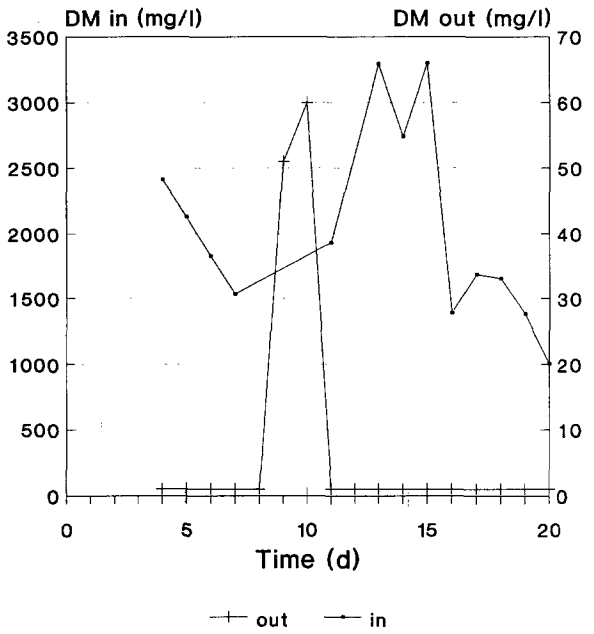

Fig. 7. DM degradation from chemical wastewater. DM concentration of the influent lay between 1.5 and 3.3 g/l. The effluent concentrations were mainly below detection limit (1 mg/l), except at days 9 and 10, when the system was overcharged with wastewater containing high amounts of DOC.

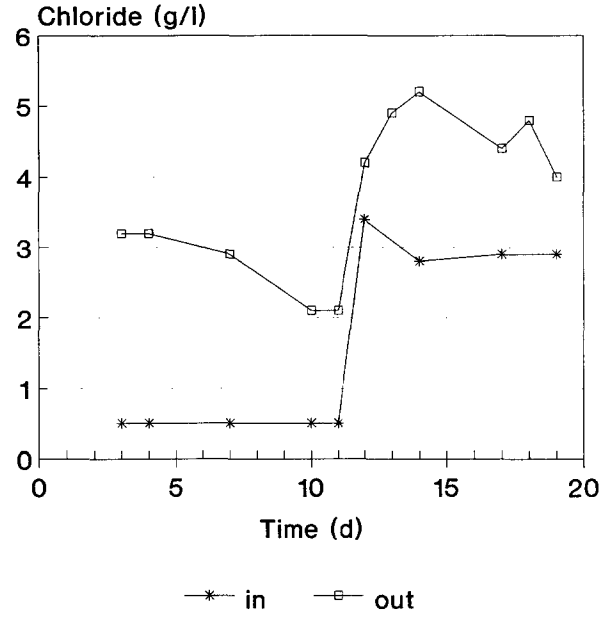

Fig. 8. Chloride production by biological treatment of DM containing wastewater.

where process water was permanently available. After this movement, for which the biological system was shut down for 30 h, the fluidized bed reactor was again fed with wastewater. The immediate consumption of NaOH and oxygen indicated, that DM degrading activity was still present. The analytical system (Grass monitor) was reconnected 4 days later. To gain DM effluent concentrations of < 1 mg/l low DOC volumetric loading rates were applied. During the first 4 days the DM volumetric load amounted to about 2 kg DM/m^3 · d and was later risen to about 4 to 6 kg DM/m^3 · d (Fig. 6). DM concentration in the effluent was below 1 mg (Fig. 7) except at day 9 and 10 due to high amounts of DOC other than DM in the influent.

For the final experimental period at the production site the feed volume was based on a constant DOC volumetric loading rate of 1,2 to 1,5 kg DOC/m^3 · d. Such maintenance resulted in a varying DM volumetric load (Fig. 6). DM concentrations in the effluent remained below 1 mg/l (Fig. 7). The production of chloride during the biological treatment of process water corresponded to the loss of DM indicating complete DM mineralization (Fig. 8). Losses of DM by evaporation were negligible since its concentration within the reactor was in the range of 1 mg/l and since oxygen was added only when its level fell below 1.6 mg/l.

Finally, possible wastewater shortage during production stops, holidays etc. were simulated. When the fluidized bed reactor was fed at only a tenth of the rate of the usual DM load, the biological system kept its DM degradation capacity. Thus the requirement to keep the biological system active would amount to only about 300 g DM/m^3 · d. After a phase of 20 days with such reduced feed the bacteria regained a ten fold higher activity within 2 days. However, if DM in the feed was omitted or replaced by other carbon sources, the DM degradation ability was completely lost within 10 days, thus requiring new inoculum and a period of about 2 weeks for full recovery of DM degradation capacity.

Discussion

Biodegradation of synthetic chemicals has inten-

sively been studied during the last 10 to 20 years and a lot of different microorganisms with special degradation abilities have been isolated and identified (Müller & Lingens 1986; Nörtemann et al. 1986). So far the biotechnological application of such bacteria to purify polluted groundwaters or wastewaters has been rare despite of the big expectations held in the biological detoxification potential. A first step to make use of dichloromethane degrading bacteria in practice was made by Gälli & Leisinger (1985) who showed that the DM conversion rate in a 4.3 l reactor could be increased to 38 kg DM/m^3 · d using immobilized cells on sand particles. These authors pointed to the importance of immobilizing the slowly growing bacterial cultures leading to high enough DM mineralizing capacity with reasonable reactor volumes. Further steps towards the practical application of specialized microorganisms for wastewater purification were now reported in this study. Bacteria were immobilized on sand particles in a fluidized bed reactor. Such reactors and their characteristic performance in wastewater purification (biofilm development, sludge production, sludge removal, oxygen input systems etc.) were well described and full scale reactors have been erected all over the world (Sutton 1981; Ryhiner et al. 1988; Sutton & Mishra 1989). Maximal DM degradation rates of 12 kg DM/m^3 · d were reached in the 80 l fluidized bed reactor, using a synthetic wastewater containing DM as single carbon and energy source. In contrast to Brunner et al. (1981) who found considerable inhibition of the growth rate at 12 mM DM (corresponding to 960 mg/l) with a continuous culture the immobilized microorganisms were not affected by high DM concentrations, showing a linear degradation rate over a wide range of concentration (Fig. 5). The fact that immobilized bacteria were very resistant to suboptimal environmental conditions has recently be published elsewhere (Diekmann et al. 1990).

Although the wastewater originated from an antibiotics production process, there was no indication that components of the process water inhibited the degradation of DM as it was observed by Kohler et al. (1986) with water of a dumping site. The maximal degradation rate based on DOC was 1.7 kg/m^3 · d with synthetic wastewater (corresponding to 12 kg DM/m^3 · d. In order to meet low DM effluent concentrations (< 1 mg DM/l) with process water the DOC loading rate was set to between 1.2 to 1.5 kg DOC/m^3 · d. Thus the DM space time yield with low DM effluent concentrations was the higher the less DOC other than DM was present in the wastewater.

Winkelbauer & Kohler (1989) reported about efficient stripping of DM when treating trickling water polluted with DM by an aerated rotating disc reactor. In order to avoid stripping problems they suggested an oxygen controlled aeration with pure oxygen. The fluidized bed reactor used in this study was maintained at a constant oxygen level of 1.6 mg/l. Oxygen was added automatically and only if required. Thus its consumption during the start up phase was linearly dependent on the DM degradation capacity. Losses of DM by stripping at concentrations above 100 mg DM/l were estimated to 1 to 3%. However, at DM concentration of below 1 mg/l (Fig. 7), hardly any DM was lost through the offgas.

The study showed that wastewater polluted with DM could be efficiently treated by using specialized microorganisms. Apart from controlling the process parameters used in conventional wastewater treatment, it was nessessary to determine some other important parameters like DM, and salt concentrations etc. to control the ambitious process and to get good purification efficiency. However, with more and improved on line analytical methods available more biological end of process treatments will likely be realized in future.

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