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Degradation efficiency and molecular size alteration during the aerobic microbial treatment of lignite pyrolysis deposit water

Abstract Investigations into aerobic biological degradation were carried out as part of an extensive programme designed to facilitate the cheap remediation of a pyrolysis waste-water deposit. Attention was focused on the processes of carbon conversion by different populations. The susceptibility of a body of lignite-processing deposit water to microbiological degradation was examined in batch investigations in a Sapromat system and in continuous bench-scale fermenter cultivations, with respect to nutrient supply, inoculation culture and molecular size distribution. It was found that degradation best occurs with an adapted mixed culture. The autochthonous culture removes 30% less dissolved organic carbon (DOC) and has a 40% higher specific oxygen demand. A shortage of phosphorus, investigated with a view to avoiding additional eutrophication problems in the open water in the case of in situ remediation, causes reduced DOC degradation and significantly higher specific oxygen demand. The biological process is overlapped by abiotic oxidation. During aerobic treatment, a concentration of colour-giving aromatic substances of between 0.5 kDa and 5 kDa was observed. This phenomenon is caused by the oxidation of low- and high-molecular-mass compounds. The removal of DOC is limited to 65% and mainly occurs in the range below 0.5 kDa (30%) and in the 0.5–1 kDa range (12%); the removal is negligible in the ranges 1–3 kDa (0.8%) and 3–5 kDa (2%) and a little higher in the ranges 5 kDa–0.3 µm (5%) and above 0.3 µm (6%). In the investigations it was discovered that DOC removal causes in the ranges below 0.5 kDa, 0.5–1 kDa and 5 kDa–0.3 µm mainly as a result of degradation, but the range above 0.3 µm is chiefly caused by bioadsorption. Aerobic microbiological treatment is able to remove most low-molecular-mass substances. In order to remove the macromolecular and colour-giving part of the deposit water, an additional treatment stage, e.g. flocculation, is required.

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Introduction

In eastern Germany, the pressure to utilise indigenous natural resources led between the 1920s and the 1960s to the development of an advanced chemical industry to refine the products obtained from lignite processing. This sector thrived until 1990, causing considerable environmental damage (TÜV Rheinland 1992).

Nearly a third of the mass of pyrolized lignite is water (reaction and inherent water), which is heavily loaded with volatile organic substances (mainly phenolic) and ammonia (Ringpfeil et al. 1988). Its composition differs from coal-processing waste-water in terms of load and compounds. Nevertheless, the biological treatment of lignite and coal pyrolysis water is basically comparable.

Many scientific publications consider both the aerobic and anaerobic degradation of the dissolved organic carbon (DOC) and nitrification and denitrification steps (Singer et al. 1978; Behrens et al. 1980; Fedorak et al. 1985; Koné and Behrens 1982; Pfeffer and Suidan 1985; Fedorak and Hrudey 1986; Martius et al. 1987; Nakhla and Suidan 1992). The specific features of the biological treatment of lignite waste waters are determined by: a lack of nutrients, abiotic oxygen demand approaching 10%, a strong foaming tendency, the formation of dark-coloured substances during aerobic treatment and a highly undegradable chemical oxygen demand (COD) residue (Franz 1975; Ringpfeil et al. 1988).

The technological developments include multistage plants to avoid toxicity effects during DOC degradation and nitrification (Ringpfeil et al. 1988; Martius and

Stottmeister 1993); however, the construction of treatment plants is limited by economic factors.

Nowadays, different types of contaminated sites exist dating back to the time before the application of any biological waste-water treatment methods, including: deposits of pyrolysis waters in former open-cast mines, contaminated plumes in groundwater born by waste-water injection into deeper geological formations and contaminated river sediments.

A pyrolysis water deposit with a volume of $2 \times 10^6 \, m^3$ (near Zeitz, Saxony-Anhalt) poses an ecological threat and remediation activities must be carried out immediately (Wießner et al. 1993, 1994; Kuschk et al. 1994). This site has been in existence for more than 40 years. The deposit water has changed over this time as a result of abiotic reactions, especially polymerisation connected with the formation of black, undegradable, toxic macromolecules. These substances affect the clean-up processes by interacting with many other contaminants and microorganisms (Stottmeister et al. 1994). These compounds can be compared to humic substances and exhibit the specific chemical reactions of this group (Kopinke et al. 1995).

With the ultimate goal of developing remediation strategies, the aims of this work are to investigate the possibility of the aerobic degradation of the deposit water by applying knowledge and experience from the treatment of freshly produced waste water (Ringpfeil et al. 1988), to optimise phosphate supply, to detect the possibility of activating the autochthonous (including long-term-adapted) microorganisms for DOC degradation and to study the influence of sorption effects in biomass–macromolecule interactions.

Materials and methods

Characterisation of the water

The waste water used for the investigations is deposit water from a low-temperature carbonisation process, changed by storage for about 30 years. The water was taken from the anaerobic zone at a depth of 20 m and stored in a nitrogen atmosphere to avoid autoxidation processes. Table 1 contains an analysis of the water.

Inoculation cultures

For continuous fermentation, an activated sludge from a municipal waste-water treatment plant was adapted by draw and fill for 3 months. The inoculation of the batch experiments was carried out by means of different inoculation cultures: (a) a 3-month adapted mixed population from continuous cultivation at 15°C and 72 h retention time with about 400 mg/l dry weight; (b) an activated sludge from a synthetic waste-water pursuant to OECD guidelines (1:10 diluted) (OECD 1976) with about 400 mg/l dry weight; (c) the autochthonous culture of the deposit-water lake, taken from the surface layer.

Table 1 Analytical characterization of the lignite pyrolysis deposit waste-water (mean values of 15 samples)

Parameter	Concentration (mg/l)
Nitrogen (NH_3)	180
Total organic carbon	630
Chemical O_2 demand (COD)	2030
Dissolved organic carbon	555
COD, filtered	1710
Phenol (water steam volatile)	135

Analysis

The analytical evaluation of the processes was based on the measurement of DOC concentration with a total organic carbon (TOC) analyser, TOC 5000, from the filtered sample (0.45 µm), and TOC concentration with a TOC 5050 analyser from the stirred sample (both Shimadzu Corporation Kyoto, Japan), as well as on the measurement of light absorption in the ultraviolet and visible range with an spectrophotometer (DMS 100; Varian). The absorbance at $\lambda = 436$ nm measures the typical brown colouring of the water caused by humic substances (Abbt-Braun 1989). Light absorption at $\lambda = 270$ nm characterises a typical local maximum of the absorption curve of the water. Light absorption in this part of the spectrum is also typical of phenolic compounds and delocalised electron systems of the nucleus of humic matter (Abbt-Braun 1989). Specific parameters are defined by calculating the quotient of the absorption values and the DOC value for the further description of alterations in the proportions of fractions of different molecular mass.

Batch cultivations

The investigations into the nutrient supply required for aerobic degradation, the importance of inoculation and biological oxygen demand were carried out in batch cultivations at 25°C using the Sapromat system (Voith, Germany).

In this device, cultivation occurs in vessels stirred and kept at the required temperature fitted with a carbon dioxide absorber (soda lime pellets; Merck 6839.1000) and a gas-proof connection with a pressure switch and an electrochemical oxygen supply. The carbon dioxide formed is adsorbed and the resulting vacuum is compensated for by electrochemical oxygen production of the same volume. This enables the growth rate and growth inhibition to be recorded via the oxygen consumption curves.

Undiluted water (see Table 1) with the addition of 20 ml/l inoculation cultures a–c and various nutrients was used for the investigations. The experiments were ended when the oxygen uptake over 6 h was less than 2 mg/l (BOD_e, the end biological O_2 demand). The DOC and TOC of the original and the degraded samples and the biological O_2 demand after 5 days (BOD_5) and BOD_e were used for evaluation. To avoid the impact of nitrification processes, 2 mg/l N-allylthiourea (Merck, no. 808158) was added (Offhaus 1973).

The mean values of the lowest six experiments with a standard deviation lower than 5% of the arithmetic mean value of the BOD were used to interpret the results.

Aerobic fermentation

The experiments were carried out using a bench-scale fermenter with a 1.4-l reaction volume and controlled conditions of temperature, pH and dissolved oxygen (Biostat MD2, Braun-Biotech).

Untreated water from the anaerobic zone of an open-coal pyrolysis waste-water deposit was used (Wießner et al. 1993). The main contamination parameters are shown in Table 1. In order to create convenient degradation conditions 46 mg/l phosphorus (as PO_4) was added and activated sludge was used as inoculum; this came from a local waste-water treatment plant, which was continuously adapted for a period of 3 months to the pyrolysis waste-water. Continuous fermentation was carried out at a temperature of 15°C, an aeration rate of $15 l^{-1} h^{-1}$ and with a hydraulic retention time of 23 h.

The pH of the original water was 7.7. Because of the addition of H_3PO_4 it dropped to 6.9, whereas during the degradation process in the fermenter it increased to 8.2.

Evaluation was based on the average of stable results of four samples in the steady state at intervals of three retention times.

Bioadsorption

The experiments to analyse the bioadsorption processes were accomplished by using washed biomass adapted to the waste-water as well as that grown in synthetic domestic model waste-water, pursuant to OECD guidelines (OECD 1976). The washing procedure was carried out by centrifugation of the sludge from the waste-water at 12 000 rpm and by subsequent suspension of the sludge in a physiological sodium chloride solution and repeated centrifugation. Average values of five experiments were used for evaluation purposes. Bioadsorption was executed by shaking 250 ml waste water with a biomass concentration of 2 g/l for 0.5 h.

Micro- and ultrafiltration

Separation according to molecular size was carried out in 10-ml and 250-ml pressure filtration cells (Amicon Ltd.) by means of flat membrane filters type YC 05 (Amicon) and flat membrane filters type Omega (modified PES) (Filtron) under nitrogen pressure. The following filtration steps were implemented: 0.3 μm, 5000 g/mol, 3000 g/mol, 1000 g/mol and 500 g/mol.

The molecular size ranges were calculated by means of the differences between the filtrate parameters.

Results

Characterisation of the oxygen-uptake curves

The water from the anaerobic zone was characterised by high autoxidation ability. The processes of autoxidation include different reactions, but in the BOD measurements only the fast oxidation processes in the first 1–2 h of aerobic conditions were measured. The oxygen-uptake curves show first a rapid rate of climb and then the typical microbial growth curve with a diauxic course but, in comparison to easily utilisable substrates, extremely prolonged oxygen consumption after the log phase (see Fig. 1A). The course of the uptake curves clearly permits the determination of oxygen demand caused by autoxidation (see Fig. 1B).

In order to verify the abiotic origin of the oxygen demand of about 40 mg/l in the first hour, the experiment was repeated – first without soda lime and then with sterile, filtered water without nutrients. The oxygen-uptake curves in the first 5 h of aerobic conditions
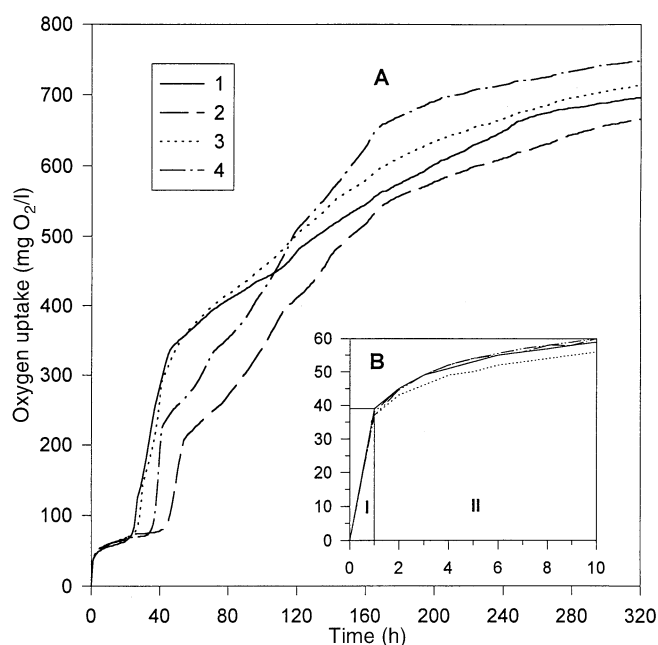

Fig. 1A, B Courses of the typical oxygen-uptake curves for various inoculation cultures (**A**) and the proportion of abiotic oxygen consumption (**B**). *1* Inoculum *a* with added phosphorus, *2* inoculum *c* with added phosphorus, *3* inoculum *a* with addition of a complex nutrient solution, *4* inoculum *b* with added phosphorus, *I* fast abiotic oxygen consumption, *II* lag phase

were confirmed in each experiment. Further considerations must thus take into account this amount of oxygen not caused by biological degradation processes.

Characterisation of the degradation behaviour of different mixed cultures

The aim of the investigation was to examine the degradation potential of the autochthonous microorganisms from the surface water. Comparison was carried out in a Sapromat device with the inoculation cultures a–c and the addition of excess phosphorus (46 mg/l). BOD_e corrected for the abiotic oxygen demand ($BOD_{e,corr.}$), the degraded DOC (DOC-d) and also the quotients BOD_e/BOD_5 and $BOD_{e,corr.}/DOC$-d were used to assess the degradation process. The ratio of the BOD values permits estimation of the velocity of the degradation process and the ratio of $BOD_{e,corr.}/DOC$-d represents the oxygen demand needed for the biological conversion of 1 g carbon, i.e. it reflects the ratio of assimilation to dissimilation.

The results of the investigations are shown in Fig. 2. The best degradation results were achieved with the 3-month-adapted mixed culture. The activated sludge showed approximately 10% less and the autochthonous culture about 30% less DOC removal (see Fig. 2A). The BOD_e/BOD_5 and BOD/DOC ratios (see Fig. 2B) indicate that the autochthonous culture is
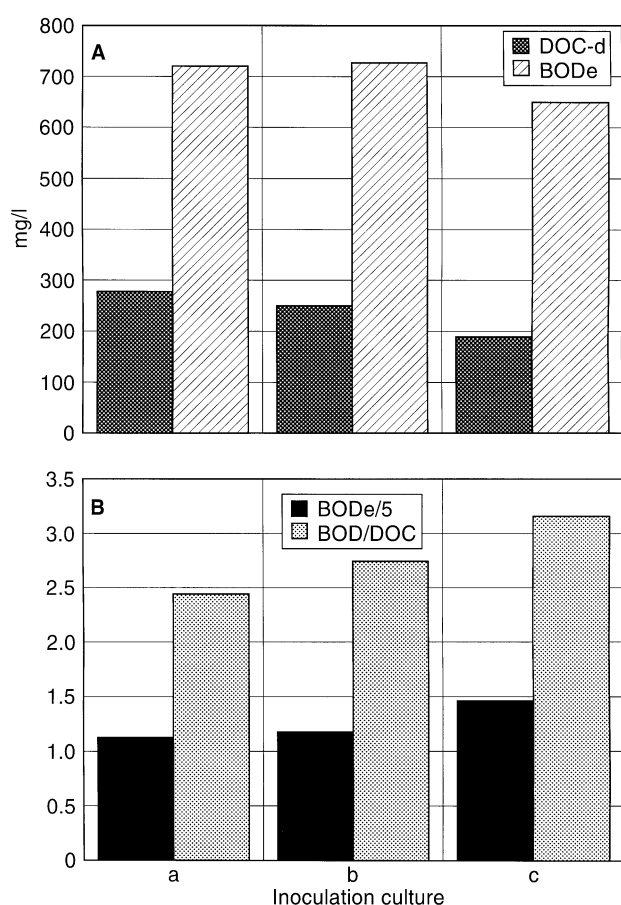
Fig. 2A, B Characterisation of the degradation process for different inoculation cultures by the degradation parameters (**A**) and by the ratios of the end biological O$_2$ demand to that after 5 days (BODe/5) and the ratio BOD/degraded dissolved organic carbon (BOD/DOC) (**B**)

not able to achieve fast degradation and needs about 40% higher respiration than the adapted culture.

Influence of the nutrient supply

From former investigations into fresh lignite-processing waste-waters (Ringpfeil et al. 1988) and the initial analysis of the deposit water, it is known that aerobic degradation is strongly influenced by nutrients.

In order to check the nutrient concentration required, a series of experiments was carried out with the Sapromat respirometric cultivation device. Formulations of the undiluted water were first compared with the inoculation cultures a and c with a complete nutrient solution (Offhaus 1973) and with the addition of just phosphorus. The aim was to ensure complete carbon conversion without nutrient or phosphorus limitation. A phosphorus concentration of 46 mg/l (corresponding to an amount about twice as high as that calculated) was therefore added and the correlation C:N:P = 30:5:1 was used for complete TOC conversion (cf. Table 1). The addition of phosphorus was carried out by dosing with 0.1 ml/l 85% phosphoric acid. The nitrogen content of the water was in excess (see Table 1).

None of the results showed significant differences in the oxygen-consumption curves following the addition of the complete nutrient solution or with phosphoric acid only. The DOC degradation of about 260 mg/l shows that only about 50% of the DOC is biodegradable under these conditions.

According to the theoretical C:N:P ratio (see above), 8.6 mg phosphorus (as PO$_4$) is needed for unlimited degradation in waste-water treatment. It is assumed that, during degradation lasting about 300 h, the phosphate demand is drastically reduced by the process of biomass lysis.

The results of the experiments with graduated phosphorus concentrations and different inoculation cultures are shown in Table 2. In the case of inoculation with the adapted mixed culture, clear limitation effects only occur at a phosphorus concentration of 0.92 mg/l, i.e. about ten times lower than the theoretical level.

Limitation is characterised by 22% lower DOC degradation. Small effects are to be noticed at a phosphorus concentration of 4.6 mg/l, i.e. half the amount theoretically needed, with DOC degradation reduced by 10% and higher dissimilation shown by an 18% higher BOC/DOC ratio. It is assumed that the effects of phosphorus limitation are compensated for by

Table 2 Comparison of biological O$_2$ demand (*BOD*) values and degraded dissolved organic C (*DOC-d*) for different levels of degraded phosphate dosing and inoculation cultures. *BOD$_e$* end BOD, *BOD$_{e,corr}$* BOD$_e$ without the abiotic O$_2$ demand, *BOD$_{e/5}$* ratio of BOD$_e$ to BOD at the end of 5 days, BOD/DOC ratio of BOD$_{e,corr}$ to DOC-d

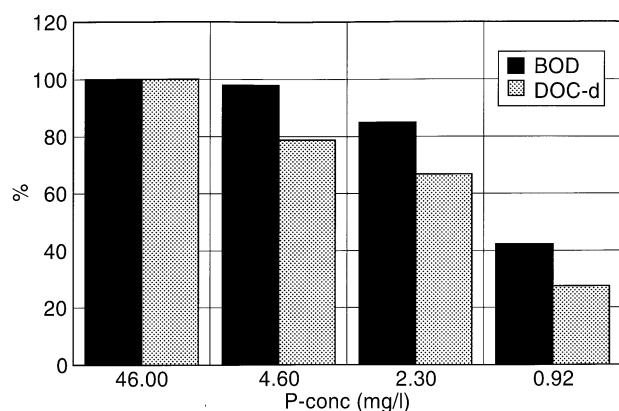| Inoculum	P (mg/l)	BOD$_e$ (mg/l)	BOD$_{e,corr}$ (mg/l)	DOC-d (mg/l)	BOD$_{e/5}$ (mg/l)	BOD/DOC (mg/l)
a	46.00	779	739	250	1.27	2.96
a	4.60	807	767	227	1.20	3.38
a	2.30	808	768	222	1.27	3.46
a	0.92	690	650	195	1.31	3.33
c	46.00	651	611	191	1.47	3.20
c	4.60	636	596	151	1.54	3.95
c	2.30	560	520	128	1.61	4.06
c	0.92	302	257	53	2.19	4.85

Fig. 3 Relative change of BOD and degraded DOC (*DOC-d*) depends on phosphorus concentration during degradation by the autochthonous culture (phosphorus excess = 100%)

Fig. 4 Molecular size distribution of the organic substances in the coal pyrolysis deposit water in the input and the output of the continuous aerobic fermentation process (15°C, 23 h retention time)

a phosphorus reserve in the cells grown with excess phosphorus.

The influence of phosphorus concentration in the cultivations with the autochthonous microorganisms grown under reduced phosphorus (cf. Table 2 and Fig. 3) is clearly apparent. It can be seen that degradation depends on the phosphorus supply.

Concentrations below that calculated lead to reduced (cf. DOC-d) and retarded (cf. BOD ratio) degradation, as shown in Fig. 3 and Table 2. Furthermore, an important higher specific respiration rate results (cf. BOD/DOC ratio).

Characterisation of microbiological degradation and bioadsorption by ultrafiltration

The characterisation of changes in the fractions of different molecular size was carried out on the basis of the ultrafiltration studies by Wilander (1972) and Buffle et al. (1978).

The soluble organic substances of the coal pyrolysis deposit water are differently distributed over the whole range of molecular masses as Fig. 4 shows. The investigations proved that the molecular mass range of 300–1000 kDa can be assigned to the 0.16–0.3 μm range of the spectrum of microfiltration. The highest relative DOC proportion of 67% is attributable to the fraction below 1 kDa. In the relatively wide range of 5 kDa to 0.3 μm the relative DOC proportion is as high as in the narrow range of 1–5 kDa. The relative proportion shown by microfiltration to be above 0.3 μm is 13%. Detailed investigations show that the high-molecular-mass organic compounds in the micrometer range are mainly distributed between the filtration limits of 0.45–0.8 μm.

Continuous aerobic microbiological treatment causes a decrease in the content of the soluble organic substances of 65%. Although it involves all fractions, the
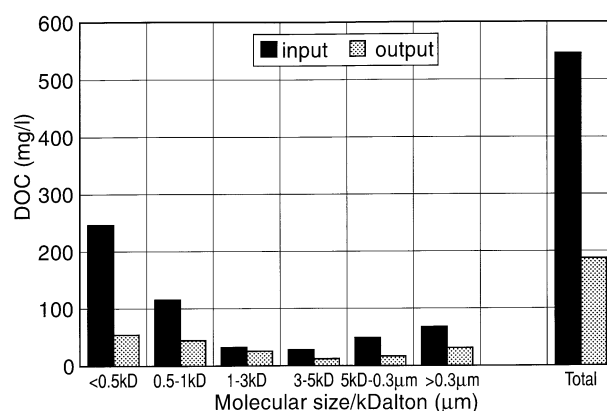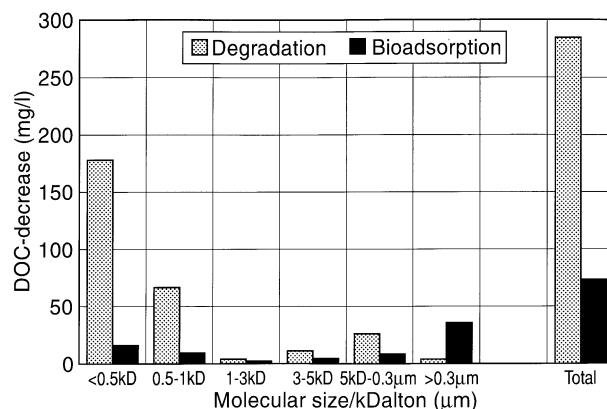

Fig. 5 Molecular size distribution of the absolute decrease of the organic substances by microbiological degradation and bioadsorption during the continuous aerobic fermentation process

highest effects are observed in the low-molecular-mass range below 1 kDa. The changes in the fractions of 1–5 kDa are comparatively low but unexpectedly high, in the molecular mass range larger than 0.3 μm (cf. Fig. 4).

Figure 5 documents bioadsorptive effects and biodegradation with respect to the fractions of different molecular size in the waste-water. It shows the distribution of the DOC decrease caused by the aerobic fermentation process. The bulk of the DOC decrease caused in metabolic reactions of the microorganisms and the bioadsorptive fixation of organic substances is evaluated as being 13% of the DOC content of the waste-water. Effects of bioadsorption can be observed in all fractions and the range of microfiltration larger than 0.3 μm shows the highest value; 92% of the total DOC decrease in this fraction is caused by bioadsorption. The relative proportions in the various ultrafiltration ranges are 8% below 0.5 kDa, 11% 0.5–1 kDa, 32% 1–3 kDa, 28% 3–5 kDa and 24% in the fraction from 5 kDa to 0.3 μm.
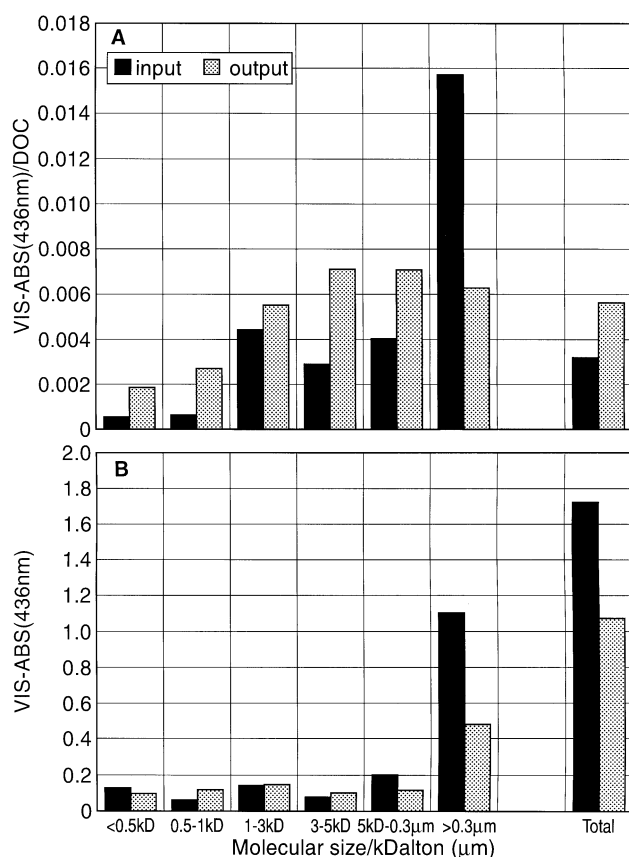
Fig. 6A, B DOC-specific absorption in the visible spectrum (436 nm) (**A**) and absolute adsorption at 436 nm (**B**) as a function of the molecular size distribution of organic substances in the input and output of the continuous aerobic fermentation process

Table 3 Relative decrease of UV and visible absorption in the fractions of different molecular size as a result of bioadsorption

Wavelength	Decrease in absorption (%)			
	0.5–1 kDa	1–3 kDa	3–5 kDa	>0.3 µm
Visible (436 nm)	0	37	28	50
UV (270 nm)	19	8	8	52

Table 4 Percentages of the total decrease of the UV and visible absorption as a result of bioadsorption by the fractions of different molecular size

Wavelength	Percentage of total decrease (%)			
	0.5–1 kDa	1–3 kDa	3–5 kDa	>0.3 µm
Visible (436 nm)	0	8	4	88
UV (270 nm)	13	3	2	82

formed aromatic substances seem to be very intense in their colouring effect.

Discussion

The results discussed represent part of an extensive programme studying the remediation of pyrolysis waste-water deposits. Investigations focusing on the aerobic biological degradation of the carbon source are a first step in microbiological investigations and are to be continued by examining nitrification and denitrification processes. The aim of the investigations was not to develop an optimum waste-water treatment technology but to examine the possibilities of a cheap in situ remediation process.

The results show that knowledge of the treatment technology of fresh lignite-processing waste-water can be only partly applied. The long lag phase, the small size of the first auxic step in the log phase and the protracted oxygen uptake are different from the stages in the degradation of fresh lignite-processing waste-water described by Martius et al. (1987). The differences between the fresh and the deposit water are caused by the various proportions of components of different molecular mass.

Degradation of the organic carbon source is limited to 65% of the DOC in an adapted mixed culture. Unexpectedly, about 13% of the DOC, mainly from the molecular mass range larger than 0.3 µm, is removed by bioadsorption. In terms of microbiological degradation efficiency, the use of an adapted mixed culture is preferable but the advantages of in situ remediation must be seen in perspective. The fate of the DOC removed by bioadsorption in the case of in situ treatment has not yet been investigated. Both the formation of large macromolecular structures, including parts of

Figure 6A shows the change of the DOC-specific values of visible-light absorption by the aerobic microbiological processes. A clear increase in the value associated with colour-giving carbon compounds (absorption at $\lambda = 436$ nm) in the unfiltered water can be seen. This is caused by changes in the components of molecular size below 0.3 µm, especially in the range smaller than 5 kDa. In contrast to this, a clear decrease of the absorption values in the range above 0.3 µm occurs because of the bioadsorption effects described above. Tables 3 and 4 demonstrate these effects, showing that both colour-giving and aromatic substances are considerably fixed by bioadsorption. The effect of bioadsorption on colourless aromatic substances in the range 0.5–1 kDa is especially noticeable. It seems likely that, in some higher-molecular-mass waste-water components, especially in the range between 0.5 kDa and 0.3 µm, processes involving the formation of colour-giving aromatic compounds are occurring.

In reality there is an increase in the absolute colouring in the fractions between 0.5 kDa and 5 kDa due to the fermentation process shown in Fig. 6B. The newly

the dead biomass, and fixation in the sediments and/or the renewed dissolution of this part during the process of biomass lysis are possible.

In the case of re-dissolution of the adsorbed substances and biomass lysis products, the difference between the removal ability of the adapted activated sludge and that of the autochthonous microorganisms is clearly reduced. Moreover, the higher oxygen demand of the autochthonous flora caused by significantly lower biomass growth is balanced.

With respect to the eutrophication of an open body of water, the phosphorus supply must be very small in contrast with the optimum supply according to the waste-water treatment guidelines. The investigations show the possibilities and consequences of phosphorus shortage. With a lack of phosphorus, a significantly higher amount of oxygen is needed for the same DOC reduction. It is assumed that a lack of phosphorus affects bacterial growth by disrupting the energetic metabolism and leading to higher assimilation. Similar effects are described for phosphorus stress by Verstrate and Vissers (1980). The bioavailability of the phosphorus arising as a result of biomass lysis in such a complex aqueous mixture is not yet known.

The estimation of molecular size distribution during microbiological treatment shows that the main processes are (a) the microbiological degradation of low-molecular-mass organic compounds smaller than 1 kDa and (b) the immobilisation of high-molecular-mass substances larger than 0.3 μm by bioadsorption. This result corresponds to the experience of other authors, who have observed that biotreatment removed low-molecular-mass material more efficiently than high-molecular-mass material (Jokela et al. 1993).

One unexpected finding was the high total decrease of constituents in the range 5 kDa–0.3 μm and the relatively low proportion of bioadsorption. This can be explained by fluctuations in the fractions of different molecular mass caused by non-biological oxidative processes. Both biological degradation and bioadsorption show relatively small effects in the range 1–5 kDa.

The dissolved organic carbon content with a high molecular mass (about larger than 1 kDa) is hardly degradable. Moreover, the colour of the biologically treated water is somewhat lighter but the specific colour-giving part of the DOC in the fractions is not degradable to the same extent. One of the reasons for the intensive increase of colour in the fraction smaller than 0.3 μm is the preferential metabolism and the adsorption of colourless and non-aromatic carbon compounds by the microorganisms. From this it follows that additional treatment, especially with respect to high-molecular-mass and colour-giving substances, is required. The possibilities afforded by precipitation/flocculation with iron and aluminium salts are currently being investigated.

References

Abbt-Braun G (1989) Praktische Aspekte von Huminstoffen DVGW-Schriftenreihe Wasser Nr. 205:12, 1–22 Eschenborn

Behrens U, Bürger G, Stottmeister U, Hoh M, Franz B (1980) Gewinnung biokinetischer Daten von Abwässern mit dem Respirationsfermentor. Teil 1. Methodische Grundlagen und die Bestimmung der spezifischen Wachstums- und Sauerstoffaufnahmerate Acta Hydrochim Hydrobiol 8:443–454

Buffle J, Deladoey P, Haerdi W (1978) The use of ultrafiltration for the separation and fractionation of organic ligands in freshwaters. Anal Chim Acta 101:339–357

Fedorak PM, Hrudey SE (1986) Anaerobic treatment of phenolic coal conversion wastewater in semicontinuous cultures. Water Res 20:113–122

Fedorak PM, Knettig E, Hrudey SE (1985) The effects of activated carbon on the methanogenic degradation of phenolics in H-coal wastewater. Environ Technol Lett 6:181–188

Franz B (1975) Reinigung von Gaswässern aus der thermischen Kohleveredlung. In: Strodzka K (ed) Hydrotechnik im Bergbau und Bauwesen. VEB Deutscher Verlag für Grundstoffindustrie, Leipzig, pp 336–358

Jokela JK, Laine M, Ef M, Salkinoja-Salonen, M (1993) Effect of biological treatment on halogenated organics in bleached kraft pulp mill effluents studied by molecular weight distribution analysis. Environ Sci Technol 27:547–557

Koné S, Behrens U (1982) Zur Kinetik der Denitrifikation. Teil 2. Mischpopulation und Gaswasser als Kohlenstoffquelle. Acta Hydrochim hydrobiol 10:243–250

Kopinke FD, Pörschmann J, Stottmeister U (1995) Sorption of organic pollutants on anthropogenic humic matter. Environ Sci Technol 29:941

Kuschk P, Wießner A, Martius G, Weißbrodt E, Stottmeister U (1994) Untersuchungen zur Sanierung wäßriger Altlasten der Braunkohlepyrolyseindustrie. Energieanwendung, Energie- und Umwelttechnik 43:309–312

Martius G, Stottmeister U (1993) Mikrobielle Reinigung von Abwässern der Braunkohlen-Carbochemie. Teil 1. Technologischer Entwicklungsstand awt Abwassertechnik 44:32–35

Martius G, Behrens U, Franz B (1987) Gewinnung biokinetischer Daten von Abwässern mit dem Respirationsfermentor. Teil 2. Einfluß des Sauerstoffpartialdruckes auf die spezifische Wachstumsrate beim aeroben biologischen Abbau von Prozeßwasser der Braunkohlenvergasung im mesophilen und thermophilen Temperaturbereich Acta Hydrochim Hydrobiol 15:389–400

Nakhla GF, Suidan MT (1992) Modelling of toxic wastewater treatment by expanded-bed anaerobic GAC reactors J Environ Eng 118:495–512

OECD (1976) OECD Technical Report 11.6.1976

Offhaus K (1973) Beurteilung der Abwasserreinigung durch analytische Verfahren Münch Beitr zur Abwasser Fisch Flußbiol 24:169–196

Pfeffer JT, Suidan MT (1985) Anaerobic-aerobic processes for treating coal gasification wastewater. In: Proceedings of the Industrial Waste Symposium, 58th Annual WPCF Conference

Ringpfeil M, Stottmeister U, Behrens U, Martius G, Bürger G, Wenige L (1988) Aerobic treatment of sewage from lignite (brown coal) processing. In: Wise DL (ed) Biotreatment systems, vol. I. CRC, Boca Raton, Fl, pp 1–61

Singer PC, Pfaender FK, Chinchilli J, Maciorowski AF, Lamb JC, Goodman R (1978) Assessment of coal conversion wastewaters: characterization and preliminary biotreatability. EPA Report 600/7-78-181

Stottmeister U, Martius G, Pörschmann J, Weißbrodt E, Kuschk P, Seidel H and Hofmann H (1994) Bioremediation of contamination in soil, sediments and water resulting from lignite pyrolysis. In: Institution of Chemical Engineers (ed) Second International Symposium on Environmental Biotechnology ISEB 2. I Chemistry. Rugby, pp 79–82

TÜV Rheinland (1992) Ecological recovery and development concept for the Leipzig/Bitterfeld/Halle/Merseburg area, vol. A1 (Environmental fields). Report 10402803, Umweltbundesamt Berlin UBA-FB 92-030/2, pp 51–92

Verstrate W, Vissers W (1980) Relationship between phosphate stress, effluent quality, and observed cell yield in a pure – oxygen activated – sludge plant. Biotechnol Bioeng 22:2591–2606

Wießner A, Kuschk P, Weißbrodt E, Stottmeister U, Pörschmann J, Kopinke F-D (1993) Charakterisierung des Wassers und des Sedimentes einer Braunkohle-Schwelwasserdeponie. WAP Wasser Abwasser Praxis 6/93:375–379

Wießner A, Kuschk P, Martius G, Eismann F, Zehnsdorf A, Weißbrodt E, Stottmeister U (1994) Abbaubarkeit von Schadstoffen im Braunkohlepyrolyse-Altwasser. WAP Wasser Abwasser Praxis 4/94:44–47

Wilander A (1972) A study on the fractionation of organic matter in natural water by ultrafiltration techniques. Schweiz Z Hydrol 34:190–200

.