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Batch methanogenic fermentation experiments of wastewater from a brown coal low-temperature coke plant

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Abstract

Coke plant effluents with high contents of organic compounds are mainly treated by biological aerobic fermentation after physical pre-treatment. In this study, a brown coal condensate wastewater from a low temperature coking process was fermented under methanogenic conditions in discontinuous experiments. By this fermentation, acetate, propionate, and the main polyphenolic compounds (catechol, resorcinol and hydroquinone) were degraded to a level below the detection limit. The COD was reduced by 72% with a residual concentration of 2.1 g/L. This anaerobic fermented wastewater had a residual BOD_5 of 0.66 g/L and 2.2 L CH_4 were formed per litre of wastewater. An abiotic pre-treatment for this wastewater with air had a negative effect on the COD reduction and decrease of colour on the methanogenic fermentation due to the autoxidation of polyphenolic compounds to humic-like compounds. This study showed that methanogenic fermentations in the treatment sequence of brown coal coking wastewaters could reduce energy consumption for aeration in further treatment processes and had the potential for a better effluent quality due to a less formation of recalcitrant humic-like compounds.

Key words: brown coal coke processing; methanogenic fermentation; humic-like compounds

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Introduction

In comparison to products from bituminous coal, fine coke formed from lignite by contemporary pyrolysis processes shows special sorption and catalytic behaviour and is of interest for application in many fields such as metallurgy, chemistry and environmental technology (Kurtz, 1977; Hauffe, 1993; Runge, 1995). However, coking plants create environmental problems, particularly from highly loaded condensation waters as liquid effluents.

The high organic load of coke plant wastewaters with aromatics and short-chain fatty acids is usually reduced by an aerobic fermentation step (Ringpfeil et al., 1988; Zhang et al., 1997; Ghose, 2001). In general, the anaerobic methanogenic fermentation of wastewaters highly loaded with organic biodegradable compounds has some basic advantages in comparison to the aerobic fermentation. There is a lower energy consumption (no need for aeration), a lower amount of excessive biosludge production, etc. (Schink, 1988). Therefore, an anaerobic digestion step is usually applied for the treatment of wastewaters with high organic loads preferentially from agriculture, food industry, and in some cases even in chemical and other industries (Grasius et al., 1997).

First experiments on anaerobic fermentation of aromatic ingredients from coal processing wastewaters were carried out in the early 60ties (Chmielowski et al., 1965; Chmielowski and Kusznik, 1966). Meanwhile, for a wide range of organic ingredients (alcohols, fatty acids, phenolic compounds), the option for their methanogenic biodegradation is known (Fedorak and Hrudey, 1988). Consequently, more applied investigations of anaerobic treatment for complex coal processing wastewaters were conducted (Fox et al., 1990; Kindzierski et al., 1991). However, major problems arise from toxic compounds like cyanide, high concentrations of phenolic and recalcitrant compounds (Nakhla et al., 1990). In contrast to coal pyrolysis (coking) wastewaters, the wastewaters from brown coal (lignite) low temperature pyrolysis are characterized by high contents of polyphenolic compounds like catechol, resorcinol, hydroquinone and their alkylated derivatives. In dependence on the brown coal (lignite) quality and the technical process used, the content of polyphenolic compounds may range up to 13 g/L, particularly depending on the coking temperature. The ammonia-nitrogen concentration usually is in the range of 3 to 6 g/L and the content of cyanide and rhodanide can be neglected in the brown

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coal pyrolysis wastewaters (Ringpfeil et al., 1988).

Because of the high content of recoverable compounds like tar, oils, and phenols, the wastewater treatment procedure often starts with physical treatment like mechanical separation and extractive dephenolizing. However, after these recovery steps residual concentrations of phenolic compounds up to 1 g/L and of fatty acids up to 3 g/L were still observed (Ringpfeil et al., 1988). For further purification of the pretreated wastewaters, biological processes were developed (Jardinier et al., 2001; Li et al., 2003), whereas microbial methanogenic treatments for brown coal pyrolysis wastewaters have not been reported on an industrial scale.

Therefore, the task of the present work was to investigate the option and effectiveness of the anaerobic fermentation of brown coal low-temperature coke plant wastewaters and the conversion of the organic ingredients into biogas. The limiting factors of the methanogenic fermentation of this complex wastewater were determined particularly regarding the high content of highly reactive polyphenols that may cause the formation of brown coloured persistent polymeric products. The formation of such persistent compounds during aerobic biological treatment processes is one of the reasons for the high residual DOC after the treatment. Hence, methanogenic fermentation as a part of a necessary sequence of treatment steps carries the potential of reducing the energy demand of this wastewater treatment process and of decreasing the residual DOC of the effluent.

1 Methods

1.1 Brown coal pyrolysis wastewater

For the experiments, a mixed condensate water consisting of brown coal coking and gasification was used. The main components and characteristics of the wastewater are listed in Tables 1 and 2. By gas chromatography/mass spectrometry more than 42 further aromatic and non-aromatic compounds were detected in lower concentrations (Kuschk, 1991). Due to the high affinity of the polyphenolic compounds to oxygen, storage and manipulations of the wastewater were carried out under nitrogen atmosphere.

Table 1 Composition of the mixed wastewater from the brown coal gasification and low temperature coking plant

Parameter/Compound	Concentration (g/L)
COD	9.1
Catechol equivalents	1.35
Volatile phenols	0.03
Acetate	1.9
Propionate	0.4
Methanol	0.94
Ammonia-nitrogen	0.8

Table 2 Polyphenolic components of the mixed wastewater from the brown coal gasification and low temperature coking plant.

Compound	Concentration (mg/L)
Catechol	700–800
Resorcinol	25–50
Hydroquinone	25–50
Pyrogallol	10–25
Phloroglucinol	10–25

1.2 Fermentation experiments

In all fermentation experiments with undiluted wastewater or wastewater diluted with distilled H_2O, the same amount of nutrients were added (NaCl 0.9 g/L, $MgCl_2 \cdot 6H_2O$ 0.1 g/L, $K_2HPO_4 \cdot 3H_2O$ 0.3 g/L and 10 mL/L trace mineral solution TMS3 as described by Kuschk (1991). In experiments with diluted wastewater, for equalizing effects of ammonium, NH_4Cl was added to the final ammonia-nitrogen concentration of 0.8 g/L (in accordance with the original wastewater composition, Table 1). Finally, the media were adjusted to pH 7.0. All experiments were conducted at 30°C in the dark.

1.2.1 Balancing the fermentation process

A long-term batch fermentation experiment of the undiluted wastewater was performed in a 10-L flask for estimation of COD removal kinetics and measuring of the biogas formation. About 10 vol.% of anaerobic river sediment (Saale-River near the city Halle, Germany) was used as inoculum. The experiment was realised under anaerobic conditions by purging the headspace of 10 L flask and tubes with N_2 at the beginning of the experiment.

1.2.2 Toxic effects

For the investigation of toxic effects in dependence of the wastewater dilution and the influence of abiotic air pretreatment batch-tests were conducted in 120 mL serum bottles. Anaerobic conditions were realized by purging the culture media (100 mL) approximately 5 min with N_2 at a flow rate of 0.5 L/min before inoculation with anaerobic sludge (Saale-River sediment which was already pre-exposed for 6 months to 50% diluted wastewater).

1.3 Analytical methods

COD was determined by a modified dichromate method (Martius and Hannes, 1985). BOD_5 determinations were performed according to standard method DIN-38412-T24. Because of the high reactivity of the water ingredients causing fast inactivation of adsorbents in HPLC columns, the analysis of the polyphenols in the effluent was done by thin layer chromatography (Thielemann, 1973). Methanol, acetate, and propionate were measured by gas chromatography (GCHF-18.3, Chromatron Berlin, Germany) (Böttcher, 1982). Water steam volatile phenols like phenol, cresols, and xylenols were extracted by steam distillation and measured after adding 4-aminoantipyrin colorimetrically (DIN 38409-H16-3). To simplify the analysis of the mixture of phenolic/polyphenolic compounds which were partly highly reactive with oxygen (Fig. 4), the sumparameter "catechol equivalents" was defined. Therefore, the overall content of aromatic compounds (catechol equivalents) in the complex effluent was measured by diluting a centrifuged fluid sample, measuring the absorbance at a wavelength of 270 nm and referring this absorbance to a

calibration curve of catechol concentrations. For assaying methanogenic activity, the gas produced in the 10 litre flask batch experiment and in the 120 mL serum bottles was analysed for methane by gas chromatography (Heyer and Suckow, 1995).

2 Results and discussion

2.1 Batch methanogenic fermentation process

The kinetics of COD-removal, the decrease of the absorbance at 270 nm, the cumulative formation of methane, the degradation kinetics of fatty acids (acetate and propionate), and the alteration of pH value during the fermentation of the wastewater are shown in Fig. 1.

The formation of biogas started after a short lag period of about 4 days (Fig. 1a). With this lag-phase the pH began to drop down to a minimum of 6.8 after 8 days (Fig. 1b). The acetate degradation started also 4 days after inoculation whereas a significant decrease of propionate was observed only after 75 days. At the end of the experiments, both compounds were degraded almost completely. Therefore, it can be assumed that the initial pH drop is mainly caused by the generation of carbon dioxide from the degradation of acetate and other readily degradable compounds. This effect, however, was compensated by the elimination of fatty acids leading to an increase of pH to about 7.2.

After 177 days of digestion, the COD value decreased from 7.55 to 2.10 g/L (Fig. 1a) which corresponds to a COD-removal of about 72%. Almost all of methanol (data not shown), propionate, and acetate were converted. It should be mentioned that the fermentation process had not yet completely ceased after 177 days. The concentration of aromatic compounds determined by UV-absorption decreased by 35.8% only (Fig. 1a). Thus, the remaining COD of 2.1 g/L after the fermentation is caused approximately to 65% by non-degradated aromatic compounds (calculated on the basis of catechol equivalents) and 35% by unknown substances.

As a result of the fermentation process, 2.1 L of methane were formed per litre of wastewater (Fig. 1a). The methane yield calculated from the batch fermentation experiment was 0.385 L CH_4/g COD and exceeded the theoretical value of 0.35 L CH_4/g COD by about 9.1%. However, this difference is hardly within the standard deviation for the COD estimation. In addition, the COD estimation excludes, for instance, some N-heterocyclic compounds like pyridine, which are also constituents of coal processing effluents (Leithe, 1972). The results of thin layer chromatography have shown that almost all polyhydroxybenzenes like catechol, resorcinol etc. were degraded to concentrations below the detection limit of < 2.5 mg/L. Surprisingly, hydroquinone remained unchanged during the period of 177 days. The recalcitrance of hydroquinone during the batch experiment is unclear because its methanogenic biodegradability is well known from literature (Szewzyk et al., 1985; Szewzyk and Schink, 1989). However, the remaining hydroquinone concentration of about 5 to 15 mg/L corresponds to a theoretical COD value of 9.5 to 28.5 mg/L, which is negligible on the overall COD mass balance.

The BOD_5 decreased by 93.5% from 7.1 to 0.66 g/L during the fermentation. Thereby, it is to be assumed that a combined anaerobic/aerobic treatment would still result in an effluent COD of about 1.4 g/L. This recalcitrant remaining COD most likely consists of yet unknown monomeric compounds and humic-like oligo- and polymers generated in the physical effluent pre-treatment steps where air contact was not absolutely excluded. Therefore, additional COD removal can only be achieved with physical or chemical treatment methods such as adsorption, chemical oxidation, ultrafiltration.

A decrease in the concentration of ammonia was not to be expected. Ammonia remained almost unchanged and was not significantly incorporated into the biomass after anaerobic treatment (data not shown). In addition, the biomass yield is about 90% lower than that by aerobic processes. Nevertheless, even with the commonly practicised aerobic processes, there is a need for further treatment with nitrification and denitrification (Ringpfeil et al., 1988; Zhang et al., 1998). Highly concentrated wastewater or the methane formed in the anaerobic treatment step could be used as a source in reducing equivalents for denitrification (Werner and Kayser, 1991). The partial nitrification (nitritification) in combination with the anaerobic ammonium oxidation (Fux and Siegrist, 2004) may be a promising strategy for nitrogen removal of such effluents pre-treated

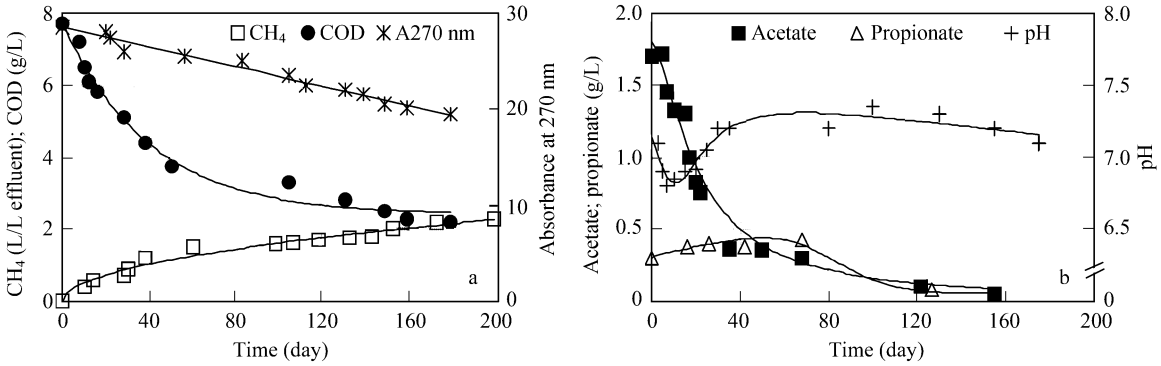

Fig. 1 Kinetics of COD-removal, absorbance at 270 nm (A270 nm), cumulative formation of methane (a) and the degradation kinetics of fatty acids related to the changes of pH (b).

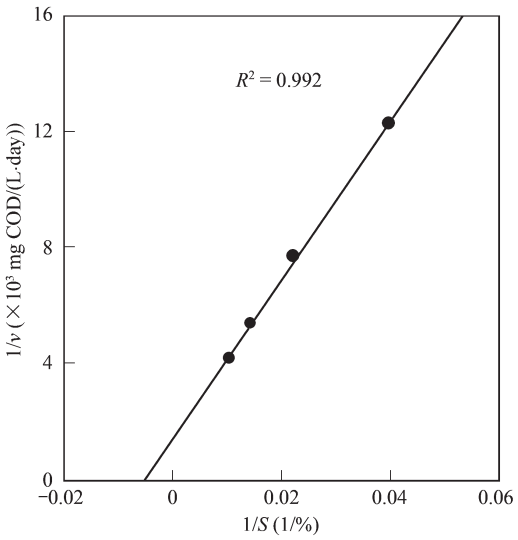

Fig. 2 Lineweaver-burk-plot of maximal COD-conversion rates against the wastewater concentration.

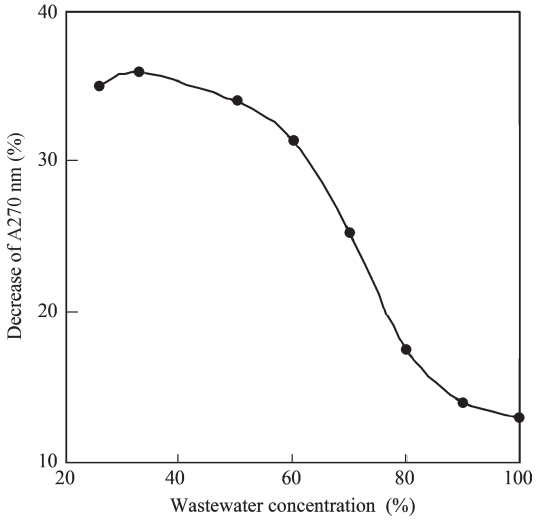

Fig. 3 Decrease of the absorbance at 270 nm (A270 nm) depending on the wastewater concentration after the methanogenic fermentation.

by anaerobic fermentation which still have a high ammonium concentration.

2.2 Toxicity effects

The intensity of the anaerobic fermentation process was considerably dependent on wastewater dilution. In Fig. 2 the reciprocal values are plotted for the COD-removal rates during the first ten days of anaerobic fermentation against the wastewater concentration according to Lineweaver and Burk (1934). Assuming the validity of the Michaelis-Menten-model (Michaelis and Menten, 1913), the plot results a K_s-value, the half-velocity concentration which corresponds to a theoretical effluent concentration of 116%. For the aceticlastic methanogen *Methanosarcina*, a K_s-value of 5 mmol/L acetate was determined (Mah et al., 1978) whereas the K_s-value for *Methanothrix* species is considerably lower by about 0.5 to 0.7 mmol/L (Zehnder et al., 1980; Patel, 1984). Therefore, the values of aceticlastic methanogens are much lower than the acetate concentration in the effluent with 1.9 g/L. The reasons for the relatively high theoretical K_s-value estimated in the experiments with the lignite coking wastewater could be that, for the resulting K_s, further factors and compounds other than acetate could be responsible; furthermore, the wastewater could also contain inhibitors which are responsible for an apparently higher K_s-value for acetate.

The decrease of the absorbance at 270 nm was too low to contribute to the COD-conversion during the first ten days of fermentation (Fig. 1a). Thus, the degradation of aromatic compounds was of minor importance for the conversion kinetics, according to the Michaelis-Menten-model (Michaelis and Menten, 1913). From the batch-experiments with the different dilution ratios, the decrease of absorbance after 147 days of incubation was plotted over the wastewater concentrations as shown in Fig. 3.

The results show that higher wastewater dilutions would improve the degradation of UV-absorbing compounds. The maximum decrease of A270 nm was in the concentration range of 25% to 50% of the COD of the original wastewater and was about 20% higher than that with the non-diluted wastewater. The lower conversion of aromatic compounds (measured as A270 nm) of undiluted wastewater in comparison to higher dilutions are indications of toxic wastewater ingredients. However, the nature of these compounds is still unknown. It is most likely that high concentrations of phenolic compounds are responsible. Fedorak and Hrudey (1988) have shown that the phenol degrading bacteria are more sensitive to phenol itself than other members of the anaerobic sludge population such as fatty-acid degraders. Thereby, at phenol concentration of 1.2 g/L, the phenol degradation was almost completely inhibited, whereas the methanogenesis from fatty acids was unaffected.

2.3 Influence of abiotic air pre-treatment

In general, polyphenolic compounds have high affinity to oxidation. Originating from the high content of even these polyphenols, lignite coking wastewater ingredients are oxidized by air contact and form brown coloured compounds. Changes in the wastewater (which was previously stored under anaerobic conditions) regarding colour and COD, were already observed just after a half-hour of air exposure (Fig. 4). Within 24 hr, the absorbance at 490 nm rose up to over 455% (Fig. 4a). During this time the wastewater colour altered from yellow-pink to dark brown. Fewer alterations were observed at 270 nm. The COD decreased within 24 hr of air exposition by about 7.9% (Fig. 4b).

The abiotic reactions caused by air pre-treatment were found to have an influence on the subsequent anaerobic fermentation process. After 143 days, the residual COD of the pre-treated wastewater was about 36% higher than that in the fermented wastewater without contact to air (Fig. 5a). This detrimental influence is also obvious in the change at A270 nm (Fig. 5b). The value of the pre-treated wastewater was 33% higher in comparison to effluent without air contact, after 143 days.

Due to this autoxidation, polyphenols react with quinoid radicals to oligo- and polymeric "artificial"

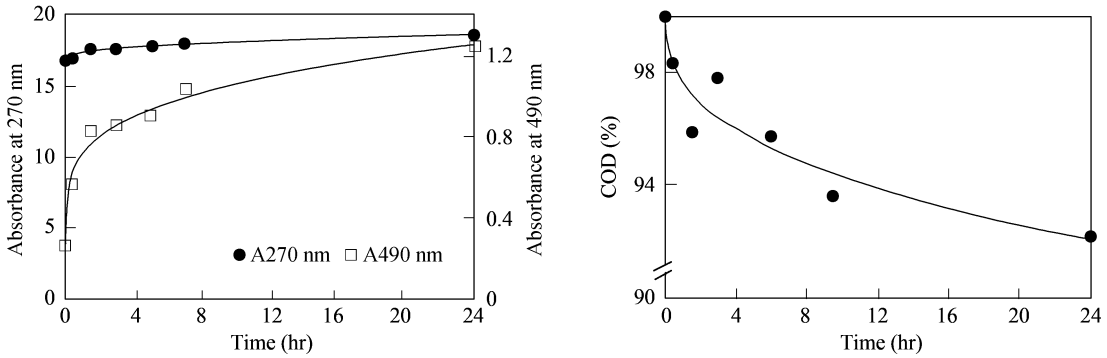

Fig. 4 Changes of the absorbance at 270 and 490 nm (a) and COD (b) of the wastewater depending on the duration of air exposition.

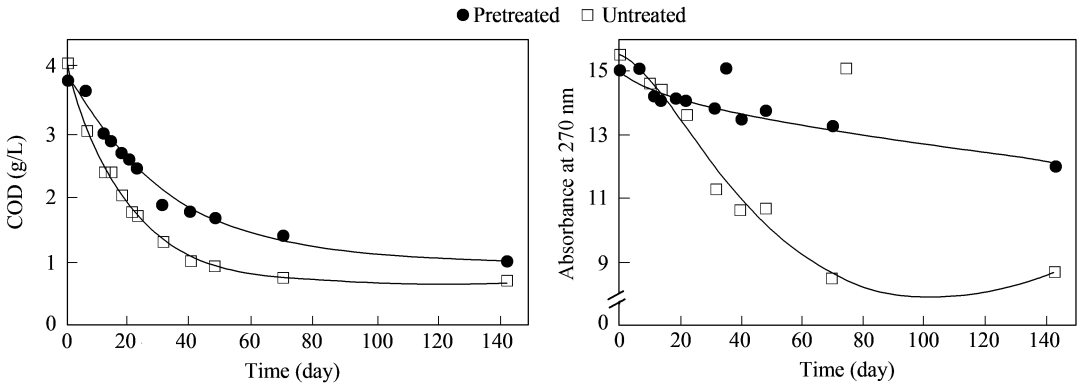

Fig. 5 Influence of wastewater pre-treatment by air on the COD-conversion (a) and the decrease of absorbance at 270 nm (b) during the subsequent methanogenic fermentation.

humic-like compounds (Müller-Wegener, 1976). The formed oligomeric autoxidation products cause considerably higher toxic effects than their monomeric compounds. However, further polymerization of these oligomeric compounds forms high molecular humic-like compounds of less toxicity. These products cause the brownish colour of the effluents and are biologically persistent (Field et al., 1989a, 1989b; Field and Lettinga, 1989).

The results show that the abiotic air pre-treatment of the brown coal pyrolysis wastewater containing polyphenolic compounds had an inhibitory effect on its further methanogenic fermentation. The autoxidation of polyphenols to humic-like compounds generates the brownish colour and the high non-biodegradable residual COD in biological aerobic treatment plants for coke plant effluents (Kim and Lee, 2004). Due to this and further problems such as foaming and high energy requirement for aeration of the aerobic fermentation of such effluents, an anaerobic digestion step would not only improve the effluent quality but would also save energy costs and generate usable biogas.

3 Conclusions

From the results of this study, the following conclusions can be derived:

The main portion of COD of effluent was reduced after methanogenic fermentation. The residual COD was mainly caused by UV absorbing (aromatic) compounds. The wastewater contained unknown toxic ingredients. While the methanogenic fermentation of acetic acid was not influenced, the removal of UV absorbing compounds was inhibited in the case of higher effluent concentrations.

Short term abiotic air treatment of the effluent resulted in a brownish colouration due to the formation of recalcitrant humic-like compounds by autoxidation of polyphenols. This may result in a detrimental effect on COD reduction.

In general, for the treatment of such brown coal coke plant effluents, a preliminary methanogenic fermentation step can be recommended. The potential for a better effluent quality by limiting polyphenol autoxidation to recalcitrant humic-like compounds may save energy consumption needed for aeration in further aerobic treatment steps.

New concepts for ammonia removal by partial nitrification and anaerobic ammonium oxidation would allow a more efficient nitrogen removal step to be realized at the end of the treatment sequence for such industrial wastewater.

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